

## Microelements Migration from Industrial-Household Sewage Deposits Applied as Organic Fertilizers in Forestry

N. N. KULIKOVA, L. F. PARADINA, A. N. SUTURIN, I. V. TANICHEVA, S. M. BOIKO, E. I. KOZYREVA and E. V. SAIBATALOVA

*Limnological Institute, Siberian Branch of the Russian Academy of Sciences,  
Ul. Ulan-Batorskaya 3, Irkutsk 664033 (Russia)*

*E-mail: kulikova@lin.irk.ru*

(Received November 30, 2004)

### Abstract

Effect of the deposits from the industrial-household sewage on the macro- and microelemental composition of a forest grass stand and of a young growth of pine and larch has been studied when the deposits are applied as an organic fertilizer. It was found that upon addition of deposits, the content of some chemical elements in soil is increased. Concentration of some elements (V, Mn, Ni, Cr, Zn) is as great as MPC. Plants of herbage react most actively to an increase in the concentration of chemical elements in soil with the deposit. The maximum changes have been registered in the elemental composition of roots of herbaceous plants.

### INTRODUCTION

Applying the deposits of industrial-household sewage water (DSW) to fertilize soils in tree-planting culture, in municipal and working settlement forestry, during reforestation on the cuttings down, on barrens, on blanks, in the forests of recreation function, when creating the stable and long-term forest ecosystems on the technogenically disturbed ground is considered to be one of the efficient ways of their salvage [1]. Application of wastes from sewage treatment in this field is caused by a shortage of traditional manures. However, almost all of DSW were discarded at dumps until the recent times and so were useful for afforestation, reforestation and greenery planting components: organic matter, compounds containing nitrogen, phosphorus and potassium; biophylic macro- and microelements. Thus, dangerous foci of the environment pollution were formed.

The major impeding factor for DSW application in forestry and agriculture is the presence

of heavy metals in the deposits. Unlike the organic contaminants, which are gradually reclaimed upon their ingress in soil during the biological circulation, these compounds are capable of preserving their toxicity for decades [2].

### OBJECTS AND TECHNIQUE OF INVESTIGATION

Sewage disposal plants of the Angarsk petrochemical company (APCC) have accumulated about 60 000 m<sup>3</sup> of DSW, which contain mixed products of sewage treatment from the APCC and commercial manufacturers of the city of Angarsk and of its domestic sewage. DSW storage time in the sludge beds ranges from 4 to 8 years.

Determination of standard characteristics of deposits, specifically, water content, pH<sub>KCl</sub>, content of organic matter, nitrogen, phosphorus, potassium and microelements (Pb, As, Hg, Ni, Cr, Mn, Zn, Cu), colititre, presence of helminths eggs, pathogen enterobacteria, BCGP, had been made at the certified labora-

tory of the Irkutsk centre of agrochemical service, parasitologic department and at bacteriological laboratory of the Centre of the State Sanitary and Health Service (Gossanepidnadzor) of Irkutsk Region by the procedures specified in Sanitary Regulations and Standards 2.1.7.573–96.

To study the possibility to use DSW from APCC as fertilizers, an experimental microfield has been arranged on the alluvial sod medium-loamy soil in the central bottom land of Goloustnaya River (the Pribaikalia South Taiga Soil District). A homogeneous district of the mixed forbs forest with a mature grass stand and with a young growth of Scotch pine (*Pinus sylvestris* L.) and Siberian larch (*Larix sibirica* Ledeb.)

was used to make an experiment. Upon removing a herb layer (10 cm) on the test forest allotments  $2 \times 2$  m in size,  $10 \text{ kg/m}^2$  DSW with the water content of 60 % were added to each of the allotments in the top part of the root zone of pine and larch young growth and then the removed herb layer was put back. Forest allotments that were set off within the limits of the trial area and were not treated with DSW served as a reference. An experiment was repeated four times. Samples of soil, of a grass stand and of needles of a young growth were taken in August during six years.

Elemental composition of the samples taken during the microfield experiment was determined by atomic emission (with the MAES-10

TABLE 1

Macro- and microelemental composition of the deposits from sewage (DSW) of APCC ( $n = 14$ ,  $P_{0.95}$ )

Element	Content			Element	Content				
	DSW of APCC	Standards*			DSW of APCC	Standards*			
		1	2	3		1	2	3	
<i>Macronutrient elements, mass %</i>									
Na	$0.53 \pm 0.17$	–	–	0.63	P	$1.92 \pm 0.52$	–	–	0.08
Mg	$0.75 \pm 0.18$	–	–	0.63	K	$0.51 \pm 0.14$	–	–	1.36
Al	$3.7 \pm 0.9$	–	–	7.13	Ca	$1.83 \pm 0.43$	–	–	1.37
Si	$7.9 \pm 0.4$	–	–	33.0	Fe	$4.03 \pm 0.83$	–	–	3.8
<i>Micronutrient elements, mg/kg of dry mass</i>									
Li	$18.5 \pm 4.4$	–	–	30	Zr	$100 \pm 20$	–	–	300
Be	$1.8 \pm 0.4$	–	–	6	Nb	$4.1 \pm 0.8$	–	–	0.01
B	$26.9 \pm 6.3$	–	–	10	Mo	$8.2 \pm 1.7$	–	–	2
Sc	$5.7 \pm 1.0$	–	–	1	Pd	$0.30 \pm 0.07$	–	–	0.001
Ti	$1530 \pm 270$	–	–	4600	Ag	$15.6 \pm 3.6$	–	–	0.1
V	$35.5 \pm 6.9$	–	–	100	Cd	$5.7 \pm 1.5$	30	10	0.5
Cr	$819 \pm 80$	–	–	500 200	Sn	$51.6 \pm 10.3$	–	–	10
Mn	$480 \pm 40$	2000	1500	850	Sb	$7.1 \pm 1.3$	–	–	0.5
Co	$62.4 \pm 17.3$	–	–	50 10	Ba	$1160 \pm 270$	–	–	500
Ni	$53.3 \pm 15.3$	400	100	40	La	$15.7 \pm 2.7$	–	–	29–40
Cu	$250 \pm 50$	1500	500	20	Yb	$1.2 \pm 0.2$	–	–	3
Zn	$1100 \pm 260$	4000	1200	50	W	$10.5 \pm 2.3$	–	–	1
Ga	$11.0 \pm 2.6$	–	–	15	Hg	$0.9 \pm 0.2$	15	5	0.01
Ge	$4.1 \pm 1.2$	–	–	5	Tl	$2.5 \pm 0.8$	–	–	0.1
As	$1.9 \pm 0.5$	20	–	1	Pb	$131 \pm 30$	1000	200	10
Sr	$240 \pm 50$	–	–	300	Bi	$12.9 \pm 2.7$	–	–	0.8
Y	$7.4 \pm 1.3$	–	–	15					

Notes. 1. Content of Au, Pt, Te, In, Hf, Ta, U and Th is  $< 0.1 \text{ mg/kg}$ . 2.  $P_{0.95}$  is 95 % probability level,  $n$  is the replication index.

\*1 – standard requirements to DSW according to Sanitary Regulations and Standards 2.1.7.573–96 [3], 2 – ecological standards [4], 3 – average soil content [5].

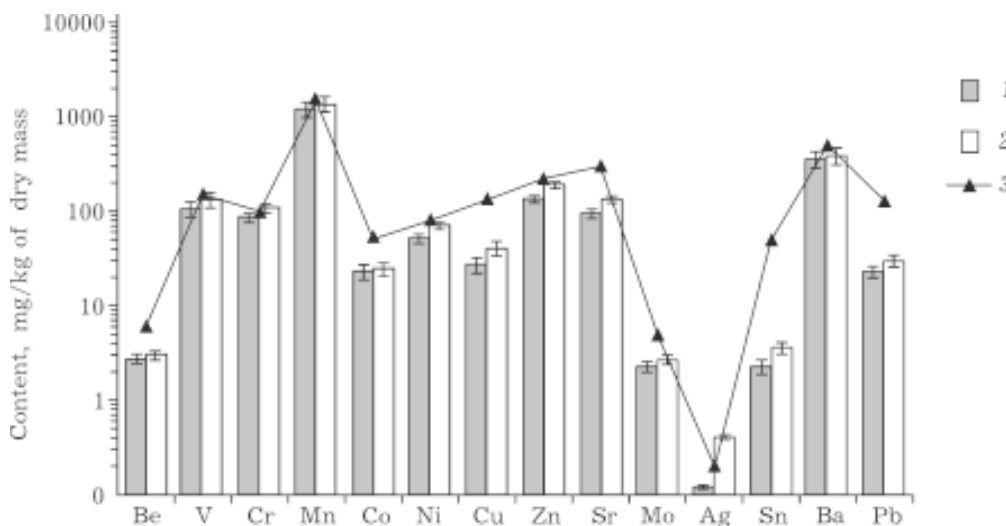


Fig. 1. Microelemental composition of humus-accumulative horizon A1 of the alluvial sod soil: 1 - the reference (soil without fertilizer), 2 - A1 + DSW (10 kg/m<sup>2</sup>), 3 - MPC or average soil content (Be, Ag, Ba) [5, 6].

device) and mass-spectral methods with an inductively coupled plasma (ILP-MS) (with quadrupole mass spectrometer PlasmaQuad PQ2<sup>+</sup>).

**RESULTS AND DISCUSSION**

DSW under study represent a black mass with the water content of 60–80 % and with the high content (50–60 %) of organic matter. DSW from APCC are characterized by significant percentage of biophylic elements (%): N 2.1–3.5, P 2.6–3.5, K 0.20–0.50; by higher than usual content of ammoniac (900–1600 mg/kg) and nitrate (≈290 mg/kg) nitrogen and by slightly acidic or nearly neutral reaction of a salt extract (pH<sub>KCl</sub> 5.5–6.8).

Mineral composition of DSW is dominated by Si, Al and Fe. Ca, Mg and Na are present tlevel close to average soil content. Extremely wide spectrum of microelements in the deposits is determined by a variety of industrial and household sewage sources of Angarsk. The content of Pb, As, Hg, Cd, Ni, Cr, Mn, Zn and Cu is several times less than their standard indices [3] and is at a level or somewhat more than ecological standards suggested by the authors of [4] for DSW. Concentrations of some elements that are not standardized in their content (Ba, B, W, Mo, Sn, Sc, Ag, Pd, Sb, Tl, Bi, Nb) in DSW were over their average soil content (Table 1).

Characteristics of bacteriological and parasitological contamination of DSW is of particular importance. No viable eggs of helminths and protozoa cysts have been detected in DSW samples that were taken from the bulk (0–20, 50–60, 110–150 cm) of deposits from various sludge beds and from the field area, where the deposits were collected upon clearing of sludge beds. No pathogen germs and bacteria from coliform bacillus group have been found in any of the samples.

On the addition of the deposit at a rate of 10 kg/m<sup>2</sup> in the alluvial sod medium-loamy soil, where the microfield experiment has been arranged, its Ni, Cu, Zn, Sr, Ag, Sn and Pb content increased. The upper limit of the concentration of V, Mn, Ni, Cr, Zn reached

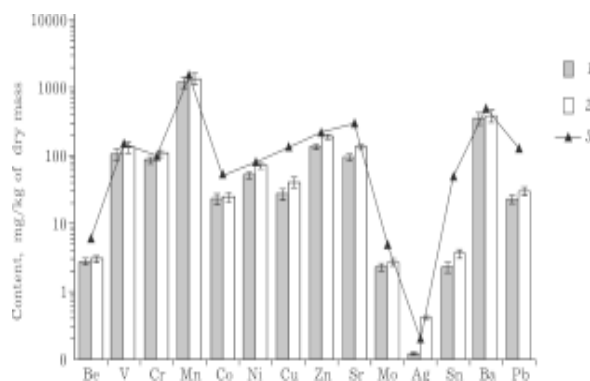


Fig. 2. Average accretion (n = 9) in height of pine (1) and larch (2) on the forest allotments of the microfield experiment for a period from 03.07.1997 to 03.09.1997.

TABLE 2

Content of macro- and micronutrient elements in the herbage samples of the mixed forest ( $n = 4$ ,  $P_{0.95}$ )

Element	Variation of the experiment	Content *, mg/kg of dry mass	
		Roots	Aerial material
Na	Check	270 ± 20/280 ± 23	520 ± 40/360 ± 30
	A1 + DSW	390 ± 30/270 ± 23	350 ± 30/250 ± 20
K	Check	1600 ± 190/-	2900 ± 340/-
	A1 + DSW	1720 ± 200/-	3140 ± 370/-
Mg	Check	1020 ± 90/1010 ± 90	2560 ± 230/3130 ± 280
	A1 + DSW	1270 ± 110/1870 ± 160	2980 ± 270/3080 ± 280
Ca	Check	3310 ± 160/2630 ± 120	5420 ± 260/5460 ± 250
	A1 + DSW	3110 ± 150/2490 ± 120	6580 ± 310/6040 ± 300
Fe	Check	590 ± 30/590 ± 30	190 ± 10/120 ± 7
	A1 + DSW	470 ± 25/420 ± 20	195 ± 11/125 ± 6
Al	Check	580 ± 20/375 ± 15	300 ± 10/195 ± 6
	A1 + DSW	560 ± 20/240 ± 10	270 ± 10/190 ± 6
P	Check	690 ± 50/710 ± 50	1530 ± 110/1490 ± 110
	A1 + DSW	720 ± 70/680 ± 50	1350 ± 100/1230 ± 90
Cd	Check	0.25 ± 0.02/0.39 ± 0.03	0.26 ± 0.03/0.31 ± 0.03
	A1 + DSW	2.10 ± 0.20/3.90 ± 0.3	0.90 ± 0.10/0.90 ± 0.10
Pb	Check	1.68 ± 0.15/0.28 ± 0.03	0.35 ± 0.03/0.15 ± 0.03
	A1 + DSW	1.56 ± 0.14/0.68 ± 0.07	0.61 ± 0.05/0.20 ± 0.02
Zn	Check	44 ± 4/59 ± 6	29 ± 3/49 ± 5
	A1 + DSW	165 ± 17/190 ± 18	103 ± 10/100 ± 9
Co	Check	0.37 ± 0.03/0.18 ± 0.02	0.22 ± 0.02/0.19 ± 0.02
	A1 + DSW	1.05 ± 0.08/0.80 ± 0.06	0.43 ± 0.04/0.31 ± 0.03
Ni	Check	4.5 ± 0.7/6.0 ± 0.9	3.1 ± 0.5/4.9 ± 0.8
	A1 + DSW	8.9 ± 1.4/5.3 ± 0.9	6.0 ± 1.0/4.0 ± 0.7
Cr	Check	1.6 ± 0.2/1.1 ± 0.1	1.3 ± 0.2/1.9 ± 0.2
	A1 + DSW	6.9 ± 0.7/7.1 ± 0.9	1.9 ± 0.2/3.3 ± 0.4
Cu	Check	20.0 ± 2.3/38.9 ± 4.1	22.8 ± 2.5/43.0 ± 4.9
	A1 + DSW	25.1 ± 2.7/41.3 ± 4.5	29.0 ± 3.0/38.0 ± 4.3
Mn	Check	90 ± 14/160 ± 25	120 ± 20/130 ± 20
	A1 + DSW	160 ± 25/180 ± 30	140 ± 22/150 ± 25
Ag	Check	0.15 ± 0.02/0.15 ± 0.02	0.14 ± 0.02/0.15 ± 0.02
	A1 + DSW	0.26 ± 0.03/0.25 ± 0.03	0.17 ± 0.02/0.16 ± 0.02
Sn	Check	5.1 ± 0.5/3.6 ± 0.4	4.5 ± 0.4/1.5 ± 0.2
	A1 + DSW	10.2 ± 1.0/4.9 ± 0.5	6.3 ± 0.5/2.2 ± 0.2
Rb	Check	3.7 ± 0.3/3.6 ± 0.3	5.3 ± 0.5/8.7 ± 0.7
	A1 + DSW	4.7 ± 0.4/4.0 ± 0.3	10.1 ± 0.8/12.2 ± 1.0
Sr	Check	21.1 ± 2.0/20.9 ± 2.3	28.2 ± 2.7/21.8 ± 2.3
	A1 + DSW	24.2 ± 2.0/21.4 ± 2.1	31.3 ± 3.0/23.5 ± 2.0
Mo	Check	0.86 ± 0.05/0.37 ± 0.02	0.60 ± 0.04/0.79 ± 0.05
	A1 + DSW	0.81 ± 0.04/0.42 ± 0.02	0.75 ± 0.04/1.15 ± 0.07

Note. Dash means the content was not determined.

\*The first value is content on the second year after addition of DSW, the second value – on the sixth year.

the MPC level (Fig. 1). No negative response of plants to the DSW presence in soil was observed. On the contrary, soil fertilizing stimulated development of a young growth: the mean annual accretion in height for the period in point for pines and larches of A1 + DSW variation exceeded the reference one (Fig. 2).

The response of the grass stand to a change in elemental chemical composition of soil turned

out to be rather active. The content of the majority of microelements in the roots and aerial material of herbaceous plants on the next year upon addition of the deposit increased in comparison with the reference. Only Fe accumulation by roots and P accumulation in the green material reduced. The plants from the forest allotments with DSW absorbed Cd, Zn, Mn, Ni, Cu, Co, Pb, Sn, Ag, Rb and Cr more actively

TABLE 3

Content of macronutrient and micronutrient elements in the samples of needles of pine and larch ( $n = 4$ ,  $P_{0.95}$ )

Element	Variation of the experiment	Content*, mg/kg of dry mass	
		Pine	Larch
Na	Check	190 ± 20/170 ± 20	140 ± 10/160 ± 10
	A1 ± DSW	160 ± 20/160 ± 20	130 ± 10/165 ± 15
K	Check	2090 ± 110/2900 ± 150	2080 ± 110/2060 ± 120
	A1 ± DSW	2240 ± 120/2770 ± 150	2390 ± 130/2060 ± 110
Mg	Check	1120 ± 70/2770 ± 180	1160 ± 80/2720 ± 180
	A1 ± DSW	1220 ± 80/2960 ± 190	1200 ± 80/3090 ± 200
Ca	Check	3320 ± 310/6280 ± 610	3210 ± 320/5750 ± 560
	A1 ± DSW	3680 ± 360/5390 ± 520	3620 ± 350/5310 ± 510
Fe	Check	273 ± 15/169 ± 16	212 ± 22/148 ± 38
	A1 ± DSW	283 ± 14/159 ± 15	224 ± 14/138 ± 20
Al	Check	57 ± 3/370 ± 17	48 ± 2/390 ± 20
	A1 ± DSW	95 ± 5/360 ± 15	107 ± 5/340 ± 15
P	Check	550 ± 30/460 ± 20	650 ± 30/1870 ± 90
	A1 ± DSW	640 ± 30/790 ± 40	650 ± 30/1970 ± 95
S	Check	83 ± 4/85 ± 3	105 ± 5/85 ± 4
	A1 ± DSW	103 ± 4/109 ± 4	113 ± 5/100 ± 4
Cd	Check	0.25 ± 0.02/0.36 ± 0.03	0.12 ± 0.01/0.13 ± 0.01
	A1 ± DSW	0.27 ± 0.03/0.32 ± 0.03	0.28 ± 0.03/0.19 ± 0.02
Pb	Check	1.79 ± 0.07/1.09 ± 0.05	0.94 ± 0.04/0.79 ± 0.03
	A1 ± DSW	1.00 ± 0.04/1.26 ± 0.05	1.08 ± 0.05/0.81 ± 0.03
Co	Check	0.84 ± 0.04/0.66 ± 0.03	0.95 ± 0.05/0.59 ± 0.03
	A1 ± DSW	0.31 ± 0.02/0.43 ± 0.02	0.83 ± 0.04/0.46 ± 0.02
Ni	Check	1.8 ± 0.1/2.0 ± 0.1	1.6 ± 0.1/2.3 ± 0.2
	A1 ± DSW	3.4 ± 0.2/2.8 ± 0.2	4.0 ± 0.3/2.3 ± 0.2
Cu	Check	35.8 ± 1.7/29.2 ± 1.4	24.8 ± 1.2/124.0 ± 6.0
	A1 ± DSW	71.7 ± 3.4/57.7 ± 2.6	24.3 ± 1.2/135.0 ± 6.5
Mn	Check	180 ± 15/240 ± 19	135 ± 10/660 ± 50
	A1 ± DSW	290 ± 20/320 ± 20	310 ± 20/950 ± 70
Ag	Check	0.24 ± 0.03/0.19 ± 0.02	0.29 ± 0.03/0.14 ± 0.01
	A1 ± DSW	0.17 ± 0.02/0.21 ± 0.01	0.29 ± 0.03/0.16 ± 0.01
Sn	Check	2.8 ± 0.2/1.6 ± 0.1	35.1 ± 3.0/13.6 ± 1.1
	A1 ± DSW	2.8 ± 0.2/1.5 ± 0.1	35.2 ± 3.0/15.4 ± 1.3
Rb	Check	4.5 ± 0.2/8.0 ± 0.4	-/9.1 ± 0.4
	A1 ± DSW	7.9 ± 0.4/11.1 ± 0.5	-/11.6 ± 0.5
Sr	Check	62 ± 2/138 ± 5	-/132 ± 5
	A1 ± DSW	82 ± 3/147 ± 6	-/123 ± 4
Mo	Check	0.30 ± 0.05/0.30 ± 0.05	0.24 ± 0.04/0.23 ± 0.02
	A1 ± DSW	0.32 ± 0.05/0.28 ± 0.03	not found/not found

Note. Dash means the content was not determined.

\*First value is the data from 1997; second – from 2002.

than in the reference, with their maximum level being detected in roots. On the sixth year after DSW addition, P content of the green material and Fe content in the roots of the grass stand is still reduced (Table 2).

An increase in the content of chemical elements upon DSW addition into soil has been revealed not only for the roots of the herbaceous plants that are quite often characterized by virtually unrestricted type of absorption [7], but also for the needles of the young growth of pine and larch. In this case, the difference in the chemical composition of the samples of needles from the woody plants, which were taken from the reference and experimental forest allotments, is less clear. On the second year after addition of deposits into soil, a higher concentration of P and S as compared to the reference has been found in the needles of the young growth of pine and larch, which are featured for a maximum accumulation of chemical elements [8]. DSW addition into soil did not lead to a decreased absorption of macronutrient elements, in particular Mg, P, S, K and Ca, by the young growth. Only a decrease of Na concentration in pine needles (Table 3) has been registered. On the second and sixth year after soil fertilizing with the deposit, an increase in the Mn content of the needles of the young growth has been found. A little bit higher concentration of Ni, Cu, Rb, Sr, Pb in the needles of pine and larch from the forest allotments fertilized by the deposit has decreased down to the reference level by the sixth year after the addition. Cd content on the second year after DSW addition was identical for the needles of the young growth both in the reference and in the experimental variation (see Table 3). It should be noted that the concentration of microelements in the needles of pine and larch that were growing on the forest allotments with DSW did not reach an excessive phytotoxic level [8].

## CONCLUSIONS

Thus, content of microelements in the soil fertilized with DSW from the sewage disposal plants of APCC was not over the MPC. Upon addition of the deposits, the quantity of

compounds with microelements available for plants in the soil increased, which was reflected in a change of the elemental chemical composition of plants. The maximum accumulation of microelements was registered in the roots of herbaceous plants. Under the effect of the deposits added into the soil, a certain increase occurred in the concentration of cadmium and zinc in the roots and green material of the grass stand of the mixed forest, together with some decrease of iron absorption by roots and phosphorus ingress in grass. It has been found that the effect of the deposit added into the soil upon the elemental chemical composition of shoots is weaker. By the sixth year of the experiment, content of chemical elements in pine and larch needles (major biosynthesis sites) [9], reached reference level, the young growth of pine and larch from the fertilized forest allotments being distinguished by a more active development.

Results of the experiment have demonstrated that the safest way to salvage the deposits of industrial-household sewage is their using in a tree-planting culture, during implementation of reforestation projects, in an amenity planting, during revegetation (for example, that of ash dumps with the subsequent meadow formation and wood planting culture). In this case, biogeocenoses, similar to natural ones, are gradually formed. These developments are characterized by a minimal egress of chemical elements beyond the limits of the ecosystem.

By virtue of the fact that the experiment in question involves an example of accumulation of heavy metals in plants, the deposits from APCC sewage, despite their qualification to standard requirements, cannot be recommended for fodder and food production.

## REFERENCES

- 1 D. H. Marx, C. E. Berry, P. P. Kormanik, *Amer. Soc. Agron. Ann. Meet.*, Cincinnati, 1993, p. 322.
- 2 A. I. Obukhov, I. O. Plekhanova, *Atomno-absorbtsionnyy analiz v pochvenno-biologicheskikh issledovaniyakh*, Izd-vo MGU, Moscow, 1991, p. 98.
- 3 *Gigienicheskiye trebovaniya k ispolzovaniyu stochnykh vod i ikh osadkov dlya orosheniya i udobreniya. sanitarnye pravila i normy SanPiN 2.1.7.573-96*, Minzdrav Rossii, Moscow, 1997.
- 4 D. S. Orlov, L. K. Sadovnikova, *Pochvovedeniye*, 4 (1996) 517.

- 5 G. V. Voitkevich, A. V. Kokin, A. E. Miroshnikov *et al.* (Reference book), Nedra, Moscow, 1990.
- 6 G. P. Bespamyatnov, Yu. A. Krotov, *Predelno dopustimye kontsentratsii khimicheskikh veshchestv v okruzhayushcheiy srede* (Reference book), Khimiya, Leningrad, 1985.
- 7 A. L. Kovalevskiy, *Biogeochemiya rasteniy*, Nauka, Novosibirsk, 1991.
- 8 A. Kabata-Pendias, *Trace Elements in Soils and Plants*, 3rd Edition, CRC, 2000.
- 9 I. S. Melekhov, *Lesovedeniye*, Lesn. prom-st, Moscow, 1980.