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The effect of ZeoVit sorptive features on nitrogen compounds, heavy metals and biological activity changes in sewage sludge

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Problems of utilization of sewage sludge faced by cities, different industrial companies, agricultural farms are related to its agrochemical, chemical, toxic and organoleptic properties. Often the use of sludge as a fertilizer is impeded not by its chemical properties, but also by organoleptic properties, namely smell. The intensity of smells is related to the concentration of ammonia nitrogen in the sludge. Therefore, the objective of our work was to evaluate the influence of the natural sorbent ZeoVit on organic and mineral nitrogen forms, biological activity alterations in sewage and to study the concentration of heavy metals in the substratum.

The research was carried out in field and laboratory conditions for the following variants: sludge mulched with zeolite mixed with the sorbent and mulched with the sorbent and only mixed with the sorbent.

The amounts of common nitrogen in the sludge substratum decreased most significantly in the variant where the sorbent was mixed with sludge and also mulched. In this case, a stable tendency of the reduction of nitrogen concentration was established. However, it requires a large input of the sorbent (120–130 kg per ton of sludge). When sludge is only mixed with the sorbent (50 kg/t sludge), the level of nitrogen in the substratum decreases to 65.5% within 4 weeks. Zeolite is an effective measure for suspension of ammonia nitrogen emissions. The sorbent not only decreases emissions of ammonia nitrogen into the atmosphere, but also suspends a significant part thereof in the deep layers of sludge.

At lower temperatures (close to 0 °C), the adsorption of common and ammonia nitrogen from the sludge processed with the sorbent is more dependent on the level of humidity and pH than in the summer season, because in the warm environment not only physical and chemical processes become more active, but also activity of pedobionts increases and strongly influences common and ammonia nitrogen adsorption alterations in the substratum.

It was established that the superfluity of bacteria dissolving organic nitrogen and micromycetes remains at the level typical of sludge substratum, however, the sorbent slightly suppresses the hyperactive reproduction of bacteria dissolving organic nitrogen. Biotests and zoocenosis show that zeolite has no negative influence on the coprophagous biota of the soil.

By mixing and mulching the sludge with zeolite, the strongest influence of it on reducing the concentration of heavy metals was obtained. Copper, chromium, nickel, cadmium are accumulated best, and lead is accumulated worst.

To reduce emissions of ammonia nitrogen from the surface of sludge, the sludge should be mulched, and to increase the immobilization of ammonia nitrogen and heavy metals in the deep layer of sludge it would be purposeful to mix the sorbent with sludge.

Key words: sewage sludge, zeolite, nitrogen, heavy metals, microorganisms, pedobionts

INTRODUCTION

Sewage sludge is a huge concern when talking about cities, industrial companies and animal breeding facilities which produce a great amount of sludge, especially when it accumulates in vast amounts. Many countries' experience and long-term work of Lithuanian scientists show that sludge may be re-used not only for re-cultivation of spoiled grounds and dumps, but also for fertilizing fields, growing crops and other plants (Bekintienė, Šleinys, 1992; Gasiūnas, 1997; Lašinskienė, 1997; Bandzaitienė, 1997; Labokas, 1997; Eitminavičiūtė et al., 1997).

Usage of sludge as a fertilizer faces several problems such as too high amounts of heavy metals in sludge, excess of nitrogen compounds, sharp and unpleasant smell. This smell is very hard to suppress and, what is most important, it may affect people's health. The smell from sludge is caused by the decomposition of proteins, which results in ammonia spread in the air. This is extremely dangerous as part of ammonia nitrogen turns into nitrates which may get into groundwater.

Unpleasant smell is the main reason why sludge is not very popular as a fertilizer. This is not a trivial task to solve as the toxicity of smell is hard to compare with the effect on human health in terms of economic value. Substances that cause the unpleasant smell are counted over 30 (Baerlocher et al., 2007). The most important of them are ammonia, sulphur compounds, mercaptans. There are several known techniques that may be applied to remove the smell: gas collection, burning, bio-filters, chemical substances, absorption systems, etc. All of these measures should be evaluated by two main factors: environmental friendliness and minimal expenses. Bio-filters and organic gas adsorption systems meet these requirements.

One of the adsorption systems is zeolite. Zeolite is a natural aluminous silicate with a crystal structure. There are over 100 types of natural zeolite, and only some of them (mordenite, chabazite, clinoptiloliteare) are used in industry, agriculture, hygiene and ecology after special processing. Zeolite can easily absorb and lose water and exchange lots of cations without changing its inner structure. Huge amounts of bags and canals pass water molecules which then form a hydration sphere for the exchange-enabled cations. Zeolite can absorb and adsorb various materials from liquids and gas-mixes very efficiently.

Zeolite's feature to absorb smell is vastly used for reducing gas emissions such as ammonia, methane, sulphur hydrogen, and other. This means that zeolite can be also applied in dumps, sewage cleaning systems, agriculture, compost plants, etc.

Soil organisms play an important role in the process of mineralization and utilization of the sludge as an organic fertilizer. The sorbent's effect on their activity is also very important.

That is why we chose natural zeolite for our research to reduce sludge smell dispersion. The purpose of our work was to evaluate organic and mineral nitrogen and biologic activity alterations in sludge processed by mineral zeolite and to study transformations of heavy metals in the substratum.

MATERIALS AND METHODS

Laboratory research. In the 2004 research, we used crude and superficial sludge from Vilnius sewage. The purpose of the research was to study changes of biological activity in the sludge depending on the drainage technique and the way zeolite was used. The research was carried out in the following four variants: 1) the surface of crude sludge covered with the sorbent, 2) crude sludge mixed with the sorbent, 3) superficial sludge covered with the sorbent, 4) superficial sludge mixed with the sorbent. The substratum was placed in plastic vessels with three recurrences for each method. Each vessel contained 2 kg of natural damp sludge and 100 g of the sorbent. The surface layer or the sorbent was about 5 cm thick. The measures were calculated according to manufacturing standards: 1 ton of sludge / 50 kg of sorbent.

The tests were started on 9 July 2004 and finished after four weeks – on 17 August 2004.

Samples of the first and third variants were taken from the surface (mulch) and depth (sludge) layers. Samples from the second and fourth variants were taken only form the sludge. Samples from the substratum were taken 2 and 4 weeks after the start of the research (Table 1).

Table 1. **Concentration of heavy metals (mg/kg) in Vilnius city sewage sludge**

Metal	Fluctuation limits		Category of sludge	Highest allowed level in the soil
	1992–1996	2004		
Cd	1.2–3.9	2.4–2.6	II	0.8–1.4
Cr	110–261	33–50	I	40–60
Ni	120–150	28–36	I	35–45
Pb	18–31	26–31	I	40–60
Cu	211–277	108–124	II	40–60
Zn	656–949	360–456	II	120–200
Hg		0.100	I	

Common nitrogen (N_{comm}) and humidity were analysed two times: after two and four weeks. Microbiological tests were carried out after two weeks. Zoocenotic and substratum toxicity (viability of radish seeds) tests were carried out at the end of the research.

Field tests. In October–November, the 2004 test at a sewage farm of Vilnius was carried out by mixing crude and superficial sludge with zeolite according to the technological requirements of the sewage farm. It was expected that due to the porous structure of zeolite, the sorption and ionic exchange features of the sorbent will reduce nitrogenous matters in the sludge and impact the heavy metals, pH, humidity alterations and fauna of the soil.

Sludge was taken to a special concrete facility which had four separate sections. Each of them had about 4.5 tons (1 dumper) of sludge (6 m long, 3 m wide and 0.8–0.9 m high). In the first section (1.), standard sludge was placed (without the sorbent). In the second section (2.), the surface of sludge was covered with a 4–6 cm layer of sorbent (0–3 mm granules). In the third section (3.), sludge was mixed with the sorbent at the following rate: 50 kg of sorbent per 1 ton of sludge or 5% sorbent / 1 cubic meter of sludge. The surface of the sorbent was also covered with a 4–6 cm layer of sorbent. In the fourth section (4.), sludge was mixed with the sorbent in the proportion indicated above.

The research was set up on 5 October 2004. Samples of the substratum were taken every week from the surface and depth layers (sludge) on the following dates: October 12, October 19, October 28 and November 4.

During the field test, the following indicators were analysed: common nitrate and ammonia nitrogen, heavy metals (cadmium, chromium, nickel, lead, copper, zinc and mercury), humidity (%), temperature (t °C), pH and zoocenotic activity.

Common nitrogen was tested by Kjeldal's method, nitrate and ammonia nitrogen by the spectrometric method, and pH was tested by the potentiometric method. Humidity was tested by heating the substratum for 48 hours at a constant temperature of 105 °C, Heavy metals were tested by the atomic adsorption and mineralization methods.

For bio-tests, the radish viability and *Eisenia fetida* worm survival tests in the substratum were carried out. For the radish viability test, separately superficial and crude sludge were used. A suspense of sludge was filtered and then used to moisten filter paper. Five radish seeds were placed on the paper and germinated for 3 days (the experiment was repeated 5 times).

For the worm survival test, two types of sludge were used as well. Superficial and crude sludge was mixed with the sorbent, and the test was repeated 3 times. Ten mature worms (with saddles) were placed in the bucket and covered with moistened cardboard. The microfauna (zoocenosis) of the soil was analysed by the modified Tulgren's extractor (Криволуцкий, 1995).

Microbiological analysis was carried out by the attenuation method, placing samples of the substratum on a solid environment. For the tests to determine the amount of bacteria that dissolve organic nitrogen, we used the beef-peptone-agar environment. For micromycetes, acidulated (to 4 pH) Chapek's environment was applied (Сэги, 1983).

The data were processed by MS Excel to provide statistics.

RESULTS

Due to quite a high content of Cd, Cu and Zn metals, Vilnius sewage sludge is classified to the 2nd category (Sewage sludge usage standards, LAND 20-2001) (Table 1).

Agrochemical and agrophysical features indicate that sludge is a fertilizer rich in biogenic elements. Comparing our research with the previous studies, sludge in the year 2004 showed an increase of phosphorus, nitrogenous compounds and organic matter. Sludge was damper because the crude sludge was mixed with the superficial sludge on the sewage farm (Table 2).

According to a sanitarian-hygienic evaluation, the sludge was determined to be "clean". Heavy alkalinity has a positive impact on the sanitarian-hygienic features of sludge. According to indicators listed in Table 2, sludge contained quite high amounts of common and ammonia nitrogen. These parameters are not declining and, on the contrary, have a tendency to rise. Therefore, it was interesting to observe these alterations in both laboratory and field researches.

Field tests

Common nitrogen test. In the field tests where sludge was processed by several different methods, the largest amounts of common nitrogen (6–7%) were found in the first variant – sludge with no sorbent. The content of N_{comm} in the surface and depth of sludge was almost the same. The second variant, which was covered with the sorbent, showed quite clear differences between the surface and deeper layers. The depth showed the level of N_{comm} close to the first variant, whereas the surface layer had only 0.5% after one week and was increasing gradually up to the fourth week when it reached 5% (Fig. 1). Quite the same tendencies were noted in the third variant where the substratum was mixed and covered with the sorbent. Only in this case the content of common nitrogen in the deeper layers was much lower than in the first variant – 4.5% versus 6–7%. The surface of the third variant had more of N_{comm} than the second one: 2.5% after one week, which then gradually grew up to 3% (or 30 g/kg dry matter). The fourth variant, which was mixed with the sorbent, indicated equal levels of common nitrogen in both layers: 4–5% (or 40–50 g/kg dry matter) (Fig. 1).

Ammonia nitrogen tests. In the field tests, sludge specimens indicated quite a high content of ammonia nitrogen. In the surface layer of the substratum, this level ranged from 2.58 (the third variant – sludge mixed and covered with the sorbent) to 5.8 g/kg (the first variant without the sorbent), while the deeper layers showed the levels from 3.26 to 6.68 g/kg. Such a huge content of ammonia nitrogen is the main reason why sludge has an unpleasant smell.

In the second specimen (covered with the sorbent), the content of ammonia nitrogen in the surface layer was almost the

Table 2. **Agrochemical properties of Vilnius city sewage sludge**

Indicator	1992–1994		2004	
	Average	Fluctuation limits	Average	Fluctuation limits
Total P %	0.75	0.64–1.0	1.5	0.8–2.7
Total N %	1.63	1.4–3.2	5.35	4.9–6.6
$N\text{-}NH_4$ mg/kg	368	360–384	5320	4550–5850
$N\text{-}NO_3$ mg/kg	367	328–407	2.27	2.1–4.0
Amount of organic substances %	46.3	4.0–50	67.2	31.6–83.2
pH	11.5	10.6–13.0	11.8	11.5–12.0
Humidity %	66.4	64.8–68.5	79.4	64.6–83.3

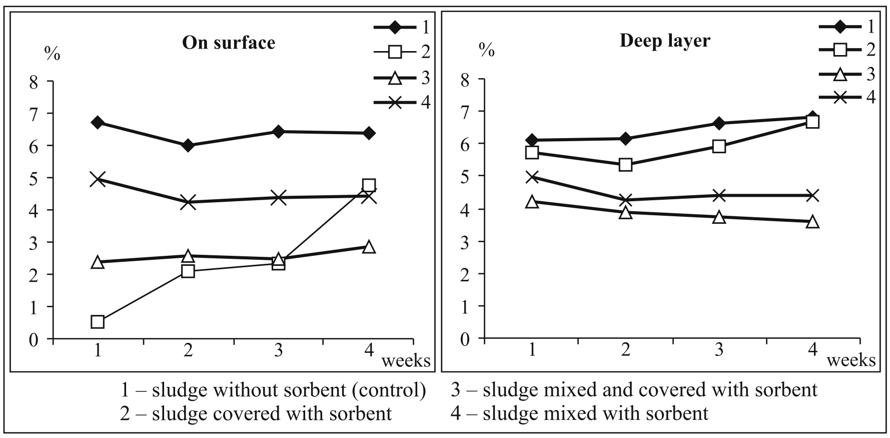


Fig. 1. Common nitrogen ($N_{comm.}$) changes in sludge covered with sorbent

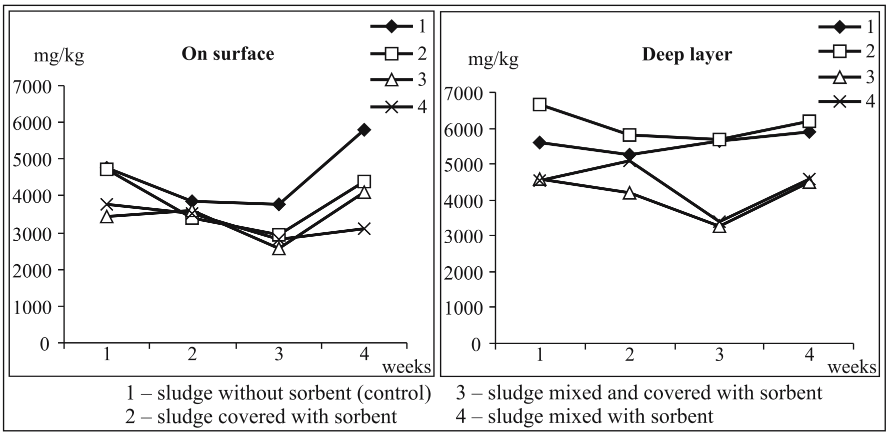


Fig. 2. Ammoniac nitrogen (N-NH_4) changes in sludge processed with zeolite

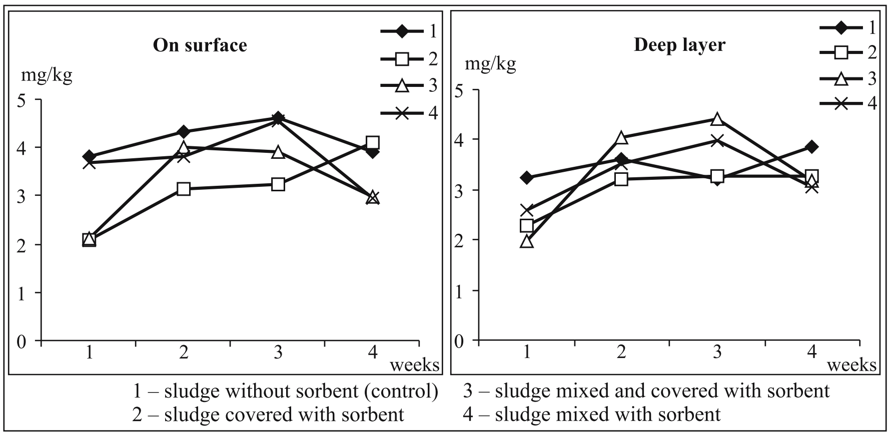


Fig. 3. Nitrate nitrogen (N-NO_3) changes in sludge processed with sorbent

same as in the initial (control) sludge after one week, which then started to decrease continuously: in the second week it was by 11.5% lower than in the initial (control) sludge, in the third week by 21.7% and in the fourth by 24.5% lower (Fig. 2).

All the specimens contained less N-NH_4 in the surface layer than in the depth of sludge. The latter was highest in the first (initial) and in the second (covered with the sorbent) variants. The graphs of ammonia nitrogen changes in the depth of sludge were very similar in the third (sludge mixed and covered with the sorbent) and fourth (sludge mixed with the sorbent) variants. It displayed a decrease of ammonia nitrogen: the first week in the third and fourth variants there was 72.2% and 79.7% of N-NH_4, respectively, the second week it was 93.8% and 92.2%, the third week results showed 68.3% and 74.1%, and in the fourth week it was 70.3% and 53.4% in comparison with the initial (control) sludge.

We noted that in the second specimen the coverage of the sorbent in the depth of sludge had not decreased the level of ammonia nitrogen; on the contrary, its concentration slightly rose. In the first week of the testing it was by 19.3% higher than in the initial (control) sludge. The further analysis didn't show such sharp differences, although in all cases it was higher than in the initial (control) sludge (Fig. 2).

Combined preparation of sludge (covering and mixing with the sorbent in the third variant) and only mixing (the fourth variant) had a similar effect. After three weeks, the content of ammonia nitrogen was 57.8% and 60.3% respectively. As the results are quite similar and the amount of the sorbent used in those two variants is very unequal, it is clear that to decrease the content of ammonia nitrogen in sludge it is enough to mix it with the sorbent.

Nitrate nitrogen test. The content of nitro nitrogen in all of the specimens was minor and ranged from 1.98 to 4.4 mg/kg, thus showing no severe threat to the environment. The highest level of nitro nitrogen throughout all the testing was detected in the first variant (without the sorbent) surface layer, and in the depth the amount of N-NO_3 was much lower. In the specimens that had been processed with the sorbent, the content of N-NO_3 in the surface and depth of sludge was almost the same. All these variants showed a similar tendency: on the first week the amount of nitro nitrogen was small, then it gradually rose and finally (in the fourth week) decreased (Fig. 3).

Heavy metals. Tests of heavy metal concentration were carried out twice: at the beginning of the research (05 10 2004) and at the end – after four weeks. Even the first tests showed 10% to 30% lower levels of almost all heavy metals except lead (Fig. 4).

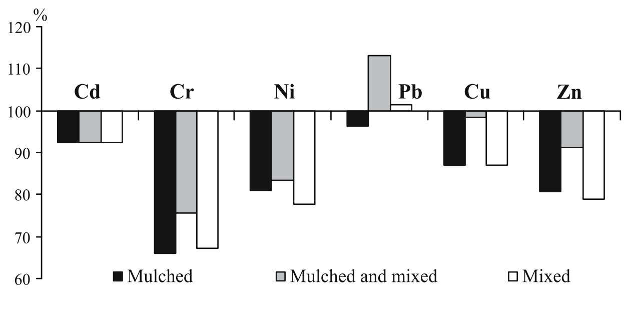


Fig. 4. The level of heavy metals in the beginning of the research in the sludge processed with the sorbent (100% – level of metals in the control sample)

After four weeks, the analysis showed even a greater drop of heavy metals in the substratum with the sorbent (Fig. 5). The most efficient heavy metal absorber was the third specimen where sludge was covered and mixed with the sorbent. The heavy metal levels were reduced in comparison with the initial (control) sludge: 44.71% less of copper, 43.93% less of chromium, 39.7% of nickel, 37.5% of cadmium, 37.3% of zinc; lead showed a decrease of about 19% and mercury about 15%.

The process of heavy metal collection from sludge to the pores is quite difficult. In the specimen where sludge was covered and mixed with the sorbent, chromium and copper decreased almost two times, while the least impact was noted on lead (Fig. 5).

Tests showed that zeolite might me used as a heavy metal absorber (Erdem et al., 2004). Molecules of heavy metals such as copper, chromium, nickel, cadmium, zinc, lead, mercury get into the pores of the sorbent where they get immobilized and thus their chance to spread into the environment decreases (Abollino et al., 2003). Although the sorption of various metals and their ionic exchange speed is different, four weeks are enough for the sorbent to acquire a significant amount of heavy metals, even though some of the heavy metals' concentrations were not very high.

pH level tests. The specimen with no sorbent indicated a 0.4 higher pH concentration in the surface of the substratum than in the sludge. The second specimen, which had been covered with the sorbent, showed the same results in the deep layers of sludge as in the initial (control) specimen, while the surface of sludge showed profound differences. After the first week the pH was the same in both layers, but later it started to diverge and reached 6.2 in sludge and 7.2 in the surface.

In the third variant (covered and mixed with the sorbent), the pH value in the depth of sludge kept rising to the surface pH value which was 7.6 throughout the whole study and varied only slightly.

The fourth specimen (sludge mixed with the sorbent) showed similar values of pH in both layers, which were close to the initial (control) specimen's surface pH values (Fig. 6).

Humidity variation tests. Tests indicated that the substratum with no sorbent had similar humidity levels in all layers, while specimens with the sorbent had a tendency to have a deeper level of the substratum damper than the surface layer, except for the fourth variant (sludge mixed with the sorbent) where no clear difference in layer humidity was noted. All variants processed by the sorbent were less humid in the surface and depth of sludge as compared with the initial sludge (Fig. 7).

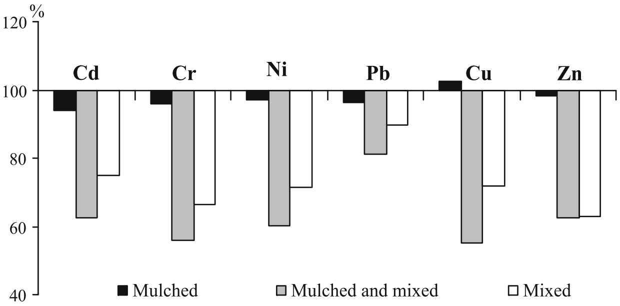


Fig. 5. The level of heavy metals in the sludge processed with sorbent after 4 weeks from the beginning of the research (100% – level of metals in the control sample)

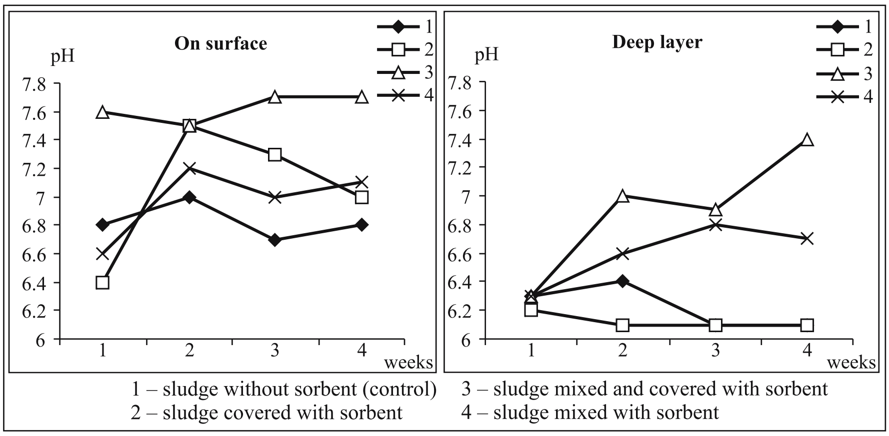


Fig. 6. Change of pH level in sludge processed with zeolite

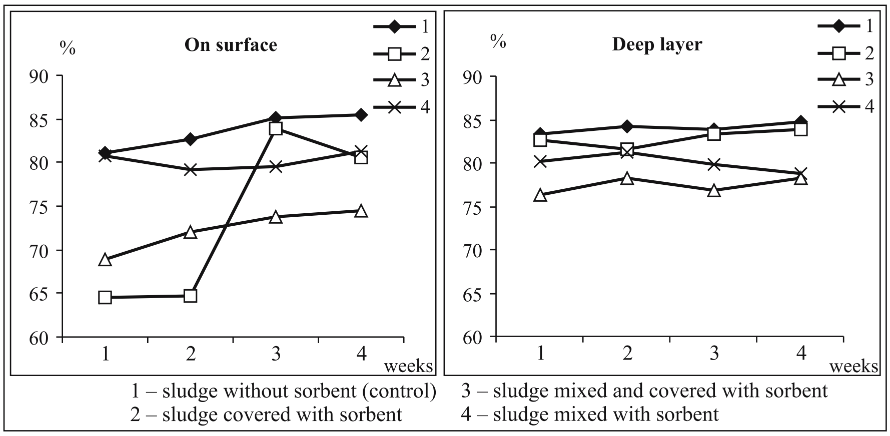


Fig. 7. Change of humidity level in sludge processed with zeolite

Laboratory tests

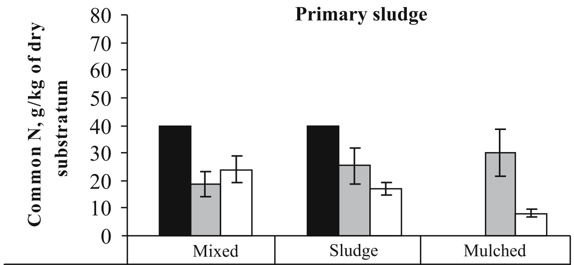
Common nitrogen test. From the organoleptic point of view, zeolite had a minor impact during the four-week period on the superficial sludge deeper layers because sludge when stirred still had a sharp smell, while the crude sludge was already quite dry after two weeks and its smell was weak. In laboratory conditions, two types of sludge were tested: crude and superficial which had different damp and common nitrogen amounts (68.5%, 83.3% and 39.8 g/kg, 77.6 g/kg dry matter respectively) (Figs. 8, 9).

In the substratum in which crude sludge was mixed with the sorbent, N_{comm} decreased by half after 2 weeks in comparison with the substratum which had no sorbent. The variant which involved superficial sludge showed even a greater decrease of N_{comm} – it was 5 times less than in the substratum with no sorbent. After four weeks, N_{comm} increased in both variants, but it didn't reach the initial level (Fig. 8).

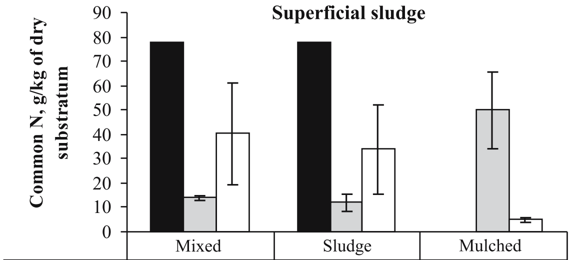
In the variants where the surface of sludge was covered with the sorbent, N_{comm} in the superficial sludge was the same as in sludge with no sorbent, while the crude sludge showed a gradual decrease of N_{comm}.

After two weeks, the surface of both crude and superficial sludge had a higher content of N_{comm} than the depth. This was especially obvious in the substratum with superficial sludge where N_{comm} in the surface layer comprised 80.7% of total N_{comm} (in the surface and depth of sludge). After four weeks everything changed. The content of N_{comm} in the depth of superficial and crude sludge was 5–6 times larger than in the surface, but its total amount decreased almost two times in comparison with the initial state.

After four weeks, in the substratum in which sludge was mixed with sorbent, the amount of N_{comm} in the deeper layers was similar to the total amount of N_{comm} in the substratum that was covered with the sorbent (Fig. 10). The variants where superficial sludge was covered and where it was mixed with the sorbent had a higher content of N_{comm} than the initial (control) sludge.

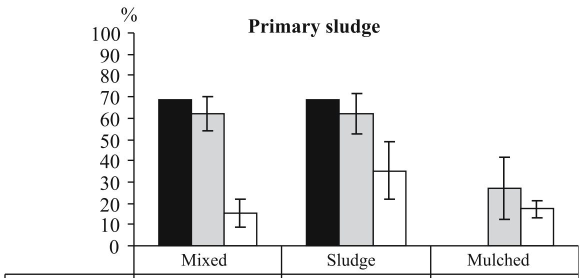


	Mixed	Sludge	Mulched
First week	39.8	39.8	
After 2 weeks	18.58	25.26	30.18
After 4 weeks	24.01	17.02	8.1

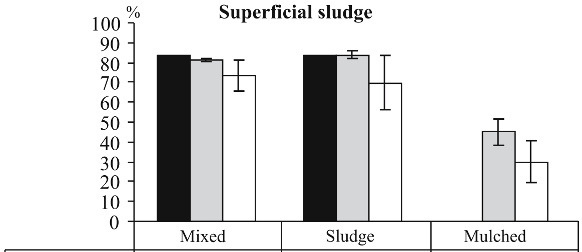


	Mixed	Sludge	Mulched
First week	77.6	77.6	
After 2 weeks	13.9	11.9	50.0
After 4 weeks	40.3	33.76	4.9

Fig. 8. Common nitrogen (N_{comm}) chnages in superflous and primary sludge covered with zeolite



	Mixed	Sludge	Mulched
First week	68.5	68.5	
After 2 weeks	61.87	62.37	27.3
After 4 weeks	15.2	35.4	17.3



	Mixed	Sludge	Mulched
First week	83.3	83.3	
After 2 weeks	81.3	84.0	45.0
After 4 weeks	73.5	69.77	30.0

Fig. 9. Change of a level of humidity of superflous and primary sludge, covered with zeolite

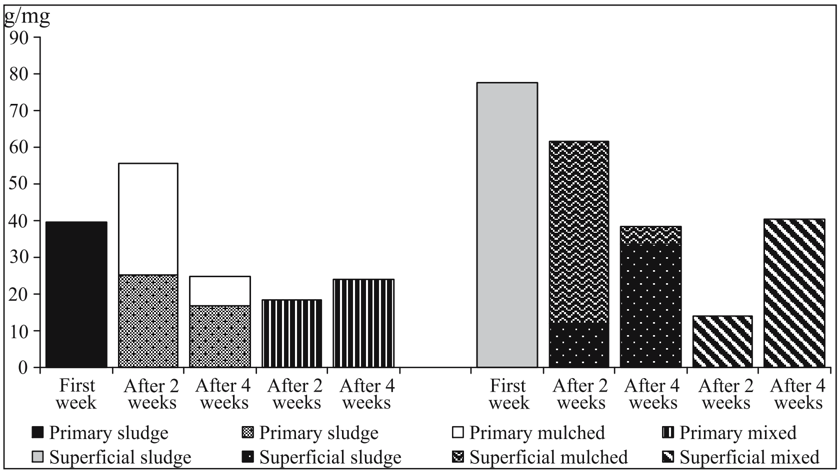


Fig. 10. Change of the total amount of common nitrogen (N_{comm}) in sludge and in the sorbent in primary and superficial sludge processed with the sorbent

Humidity variation tests. The superficial sludge was considerably more humid than the crude sludge. In the beginning of the research, the humidity was 83.3% and 68.5% respectively, but after two weeks the humidity of the crude sludge decreased and was very insignificant and statistically unreliable. The dampness of the superficial sludge did not change during the research (Fig. 9).

After four weeks, the humidity of the crude sludge in the deeper layers decreased quite significantly, especially where the sorbent was mixed with sludge; here, the humidity decreased five times and reached 15.2%. The humidity in the depth of the superficial sludge covered with the sorbent and the humidity of sludge mixed with the sorbent showed only a 10–13% decrease of humidity, which was considered statistically unreliable (Fig. 9).

After two weeks, the surface of the superficial sludge was already much more humid than of the crude sludge. After four weeks, humidity sharply decreased in both cases, although at the top of the superficial sludge surface it was higher than in the crude sludge (Fig. 9).

Zeolite had a noticeable influence on the humidity of crude sludge. After four weeks, humidity in the depth of sludge decreased by half when sludge was covered with the sorbent and almost five times when the sorbent was mixed with sludge.

Toxicity expertise of the substratum. The crude sludge processed with the sorbent impeded the viability of the radish seeds only during the first day after which the viability was the same as in the control sludge. The superficial sludge still had a minor inhibitory effect on radish seeds even after three days (Table 3).

Zeocenitic tests. After four weeks, in all of the specimens many coprophagous paedobionts outspread (*Acaridiae, Collembola, Insecta* juv., *Nematoda*) which might have caused the increase of nitrogen because of their biomass. (Table 4).

Table 3. **Results of radish seed viability test**

Sludge	Repetition	After 24 hours	After 48 hours	After 72 hours
Superficial	1	3	5	5
	2	5	5	5
	3	2	3	3
	Average	3.3	4.3	4.3
Primary	1	4	5	5
	2	4	5	5
	3	3	5	5
	Average	3.7	5.0	5.0
Control (water)	1	5	5	5
	2	5	5	5
	3	5	5	5
	Average	5.0	5.0	5.0

Microbiological tests. As long-term experiments indicate (Bagdanavičienė, Ramanauskienė, 1997; Eitminavičiūtė ir kt., 2001), Vilnius sewage sludge is rich in saprophytic microflorae.

The superfluity of bacteria that dissolve organic nitrogen may vary within quite a large amplitude depending on the sludge drainage method and storage time. The amplitude may range from several millions CFU (colony forming units) on 1 g dry substratum (in fresh sludge) up to several thousand millions CFU in superficial sludge which had been kept in a pile for a while.

The content of micromicetes (microscopic mushrooms) also varies in huge amplitudes – from a few hundreds to a few millions CFU.

Keeping in mind the fact that these two microorganism groups actively participate in the decomposition of organic matter, especially protein nitrogen, we tried to analyse whether zeolite has a negative effect on these microorganism groups. Tests were carried out in the laboratory after two weeks.

The results indicated that the amount of bacteria and micromicetes that participate in decomposition of organic nitrogen in all of the specimens remained at the level common for the substratum of sludge (Fig. 11).

In the variations of the amount of bacteria, the level of humidity played the key role. The biggest amount of bacteria was detected underneath the surface of the superficial sludge, where humidity was close to the initial level (84%).

In the other variants, the results were similar. In the surface of the superficial and crude sludge, the abundance was also very similar (884.9 and 700.8 mill. CFU, respectively) (Fig. 11).

The substratum where the sorbent was mixed with sludge (superficial and crude) also showed similar results: 1465.5 and 1494.9 mill. CFU respectively (Fig. 11) in the depth of sludge. In the superficial sludge, under the surface there was 3 times more bacteria, indicating a very intensive process of ammonification. In the variant where the sorbent was mixed with sludge, the activity of bacteria was reduced. In the surface of the substratum there were two times less bacteria than in the deeper levels.

Zeolite had no strong impact on the spawning activity of micromicetes. In the substrata where sludge was mixed or not mixed with the sorbent, the abundance of micromicetes was the same. In the surface of superficial sludge, there was less micromicetes, although their abundance was two times higher than in the surface of the crude sludge (Fig. 11).

Table 4. **Superfluity of coprophagous zoocenosis in crude and superficial sludge after 4 weeks of processing with ZeoVit sorbent (laboratory research)**

Group	Mulched				Mixed			
	Primary		Superficial		Primary		Superficial	
	$\frac{\text{Thou ind./m}^2}{\text{mg/m}^2}$	Number of species	$\frac{\text{Thou ind./m}^2}{\text{mg/m}^2}$	Number of species	$\frac{\text{Thou ind./m}^2}{\text{mg/m}^2}$	Number of species	$\frac{\text{Thou ind./m}^2}{\text{mg/m}^2}$	Number of species
Acaridiae	$\frac{3710.8}{3.0}$		$\frac{163.7}{0.005}$		$\frac{5135.0}{5.0}$		$\frac{73.5}{0.003}$	
Collembola			$\frac{0.3}{0.0002}$	1			$\frac{0.3}{0.0002}$	1
Insecta juv.	$\frac{2.33}{0.6}$	2	$\frac{6.0}{16.67}$	5	$\frac{0.67}{0.18}$	1	$\frac{3.2}{0.87}$	2
Σ	$\frac{3713.3}{3.6}$		$\frac{170.0}{16.68}$		$\frac{5135.7}{5.18}$		$\frac{77.0}{0.873}$	

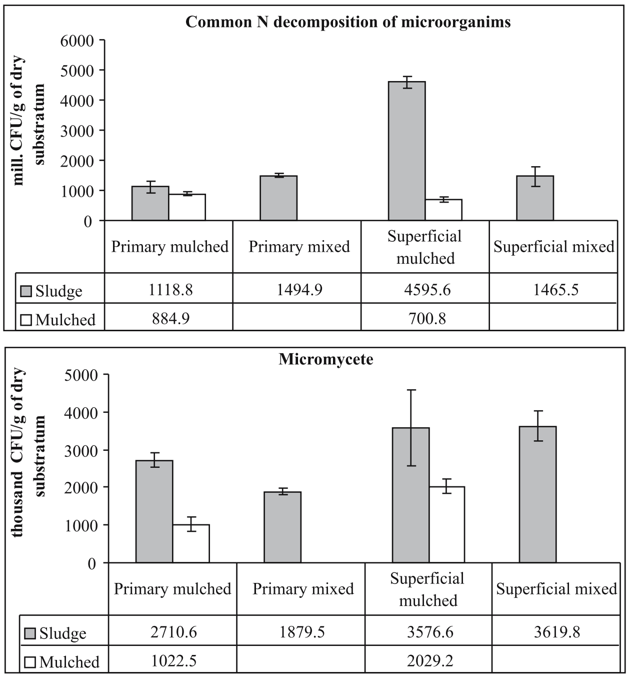


Fig. 11. Microorganism groups active after two weeks in substratum after sludge mulching with sorbent ZeoVit (laboratory test)
CFU – colony forming units

In all specimens, micromicetes were found in large diversity: most common where fungi ammonifiers and fungi that dissolve cellulose; they are the biggest ammonia users.

DISCUSSION

The peculiarities of changes of common and ammonia nitrogen in the sludge processed with the zeolite sorbent are very closely related to humidity and pH changes in the substratum. The sorbent being an active absorber of water and gaseous ammonia (NH_3) influences the distribution of N_{comm} and N-NH_4 among layers in the substratum. Figures 1 and 7 show that the curves of changes of N_{comm} and humidity are almost identical. Obviously dry sorbent poured over the sludge in variant 2 gradually absorbed water, and together with it organic nitrogen particles gradually penetrated the layer of sorbent. After four weeks, the level of N_{comm} in the upper layer of the sorbent approaches the level in the deep layer.

In variant 3 (mixed and mulched), the upper layer of sorbent also fills up with water and at the same time with organic particles of nitrogen. Besides intensive absorption of humidity into zeolite pores takes place also in the deep layer. Therefore, the deep layer mixed with sorbent becomes by 10% dryer than the control sample without sorbent, and the upper layer becomes dryer by 15%. The amount of N_{comm}, on the contrary, in the deep layer is higher than in the upper layer.

In sludge mixed with sorbent, differences in neither humidity nor common nitrogen between the upper and the deep layers were noted in variant 4. However, their amount in this variant was lower than in the control variant without sorbent.

Our data show that the sorbent can absorb humidity into its pores together with particles of organic nitrogen and in this way temporarily eliminate them from the substratum.

In field tests, N_{comm} gradually decreased in the deep (up to 0.5 m) sludge layer in the samples where the sludge was processed in a combined manner – by mixing the sorbent into the mass of sludge and mulching the surface of the pile of sludge. This method decreases effectively the level of common nitrogen in the sludge, but requires much sorbent – 120–130 kg per 1 ton of sludge. In this case, a stable tendency of a reduction of nitrogen concentration was established. Every week a gradual decrease of N_{comm} level was recorded: during the first week it amounted to 68.9%, during the second week to 62.9%, during the third week to 53.8% and during the fourth week to 52.9% of the total amount of nitrogen as compared with the control sample.

Quite good results were also obtained in the case when sludge was only mixed with the sorbent. Here the level of N_{comm} was by about 25–30% lower than in the control sample, and only 50 kg of sorbent per 1 ton of sludge was used. During the first week, the level of N_{comm} amounted to 78.0%, during the second week to 73.2%, during the third week to 63.3%, and during the fourth week to 65.5% versus the control sample.

Ammonia nitrogen, being very volatile, penetrates the upper layer equally rapidly in the aqueous (NH_{4+}) and gaseous (NH_3) form. Already in 1967–1970, the efficiency of zeolite in removing ammonia nitrogen from municipal and agricultural sewage was demonstrated (Ames, 1967; Mercer et al., 1970). Later, the amonia adsorption mechanism was analysed (Datka, Gil, 2001).

In our research, the content of N-NH_4 in the upper layer in comparison with the deepth in all variants with sorbent was the lowest and the pH levels were the highest (Fig. 2, 6). Evidently the ammonia accumulated in the upper layer accounts for a relatively large part of total nitrogen and determines the alkaline level of the substratum.

The zeolite sorbent is quite an effective measure for suppressing ammonia nitrogen emissions. The sorbent not only decreases ammonia nitrogen emissions into the atmosphere, but also suspends a significant part thereof in the deep layers of sludge. Mulching of the surface of sludge does not allow free and easy evaporation of ammonia nitrogen into the atmosphere and retains it inside the sludge, and insertion of the sorbent into the mass of the sludge decreases the level of ammonia nitrogen both on the surface of sludge and in its deep layers.

The effect of the sorbent differed in the sludge drained using different techniques. During the summer season, in laboratory research with small amounts of the test substratum (2 kg of humid sludge in a vessel) humidity evaporated from primary sludge, including mulch, more rapidly than from superficial sludge. The content of N_{comm} also decreased (Figs. 8, 9). In superficial sludge variants, in the deep layer humidity changed but little during the first two weeks, however, it penetrated the mulch layer quite intensively. After two weeks it reached 45%, almost half the level of humidity found in sludge substratum (83%). Obviously, the humidity could absorb a large part of common nitrogen particles into the mulch layer (Fig. 10). However, after four weeks of drying the upper layer of the sorbent, the content of N_{comm} in the lower layer increased again.

Changes of N_{comm} here were influenced not only by humidity, but also by the soil fauna and microorganisms, their abundance and thus the biomass being considerable (Table 4, Fig. 11).

Our earlier research of sludge has shown that the superfluity of microarthropods in the primary sludge in the period of 1–6 months amounts to 40, in the superficial to 34, and in the mix of these two types of sludge to 355 thou ind./m^2 (Eitminavičiūtė et al., 2001). The abundance of insect larvae in primary sludge may vary from 2.4 to 2.5 and in superficial sludge to 20.7 thou ind./m^2 in separate sludge degradation periods (Strazdienė, 1997).

Microfauna also propagates very actively in the sludge substratum alongside microorganisms. In the variants analysed by us, quite many nematodes were found feeding on bacteria cells. Few nematodes were found in the mulch layer. Few nematodes were also found in superficial sludge below the mulch layer, however, very many nematodes were found in the superficial and primary sludge mixed with zeolite. It is known that nematodes feeding on bacteria cells also regulate the abundance of bacteria ammonifiers in the substratum (Elliott, 1997; Gupta, Yeates, 1997; Стриганова, 1980).

In field tests when the temperature was low (late autumn), only separate pedobiont individuals were found. Therefore, in these tests, humidity and pH alterations were more significant for the distribution of organic particles.

The results of our study showed that the abundance of bacteria dissolving organic N and of micromycetes in all variants with zeolite in the sludge substratum remained at the same level typical of sludge substratum (Fig. 11). However, zeolite slightly suppressed the hyperactive reproduction of bacteria dissolving organic nitrogen. It is not bad because a slower disintegration of albumen determines lower emissions of ammonia and thus creates more favourable conditions to consume ammonia more completely with other organisms, non-organic sorbents and to intensify the processes of nitrification and to reduce the emissions of free ammonia.

The toxicity of sludge processed with the ZeoVit sorbent was analysed in two biotests – radish viability test and the survival of *Eisenia fetida* earthworms in the period of four weeks. Both tests have shown that sludge is not toxic. Besides, the fauna of sludge in the laboratory test showed that zeolite had no negative influence on the coprophagous biota of the soil.

The concentration of heavy metals decreases most effectively when the sorbent is mixed and mulched with sludge. This most probably can be explained by the fact that heavy metals get into the pores of the sorbent only in case the sorbent is close to the molecules of metals. When only the surface of sludge is mulched, immobilization of heavy metals in the pores of the sorbent is much slower. Copper, chromium, nickel, cadmium are accumulated best, and lead is accumulated worst. Erdem, Karapinar and Donat (2004) show that natural zeolites have a great potential to remove cationic heavy metal species from industrial wastewater.

CONCLUSIONS

1. According to laboratory and field tests, at a temperature close to 0 °C, the adsorption of common and ammonia nitrogen from the sludge processed with the sorbent was more dependent on the level of humidity and pH than on the summer season. It is known that in a warm environment not only physical and chemical processes become more active, but also activity of pedobionts increases and greatly influences common and ammonia nitrogen adsorption in the substratum.

2. In order to decrease the emission of ammonia nitrogen from the surface of sludge it should be mulched, and to increase the immobilization of ammonia nitrogen and heavy metals in the deep layer of sludge it is purposeful to mix sludge with a sorbent.

3. The concentration of heavy metals is most effectively reduced when sludge is mixed with a sorbent and mulched.

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SORBENTO ZeoVit SORBCINIŲ SAVYBIŲ POVEIKIS AZOTO JUNGINIŲ, SUNKIŲJŲ METALŲ IR BIOLOGINIO AKTYVUMO POKYČIAMS NUOTEKŲ DUMBLE

Santrauka

Miestų, įvairių pramonės įmonių, gyvulininkystės fermų nuotekų dumblo utilizavimo problemos susijusios su jo agrocheminėmis, cheminėmis, toksinėmis ir organoleptinėmis savybėmis. Dažnai dumblo kaip trąšos panaudojimą stabdo ne jo cheminės, bet organoleptinės savybės – būtent kvapas. Kvapų intensyvumas susijęs su amoniakinio azoto koncentracija dumble. Todėl mūsų darbo tikslas buvo įvertinti organinio ir mineralinio azoto formų ir biologinio aktyvumo pokyčius nuotekų dumble, apdorotame mineraliniu ceolitu, taip pat stebėti sunkiųjų metalų kiekių pokyčius substrate.

Tyrimai buvo atlikti lauko ir laboratorinėmis sąlygomis šiais variantais: dumblą mulčiuojant ceolitu, sumaišant su sorbentu ir mulčiuojant juo bei tik sumaišant su sorbentu.

Bendrojo azoto kiekiai dumblo substrate ryškiausiai sumažėjo variante, kuriame sorbentas buvo sumaišomas su dumblu ir dar mulčiuotas. Šiuo atveju buvo nustatyta stabili azoto koncentracijos mažėjimo tendencija. Tačiau tam reikia didelių sorbento sąnaudų (120–130 kg tonai dumblo). Dumblą tik sumaišius su sorbentu (50 kg/t dumblo) azoto lygis substrate per 4 savaites sumažėjo iki 65,5%.

Ceolitas yra efektyvi priemonė amoniakinio azoto emisijai sulaikyti. Sorbentas ne tik sumažina amoniakinio azoto emisiją į atmosferą, bet ir daug jo sulaiko gilesniuose dumblo sluoksniuose.

Žemoje (artimoje 0°C) temperatūroje bendrojo ir amoniakinio azoto adsorbcija iš dumblo, apdoroto ceolitu, labiau susieta su drėgme ir pH nei šiltuoju vasaros laikotarpiu. Šiltoje aplinkoje, be fizikinių cheminių procesų, dumble suaktyvėja pedobiontų, kurie turi ženklią įtaką bendrojo ir amoniakinio azoto adsorbcijos pakyčiams substrate, veikla.

Nustatyta, kad organinį azotą skaidančių bakterijų ir mikromicetų gausumas išlieka tokio lygio, kuris būdingas dumblo substratams, tačiau sorbentas šiek tiek stabdo per didelį organinį azotą skaidančių bakterijų dauginimosi aktyvumą. Biotestai ir zoocenozės rodo, kad ceolitas nedaro neigiamo poveikio dirvožemio kaprofaginei biotai.

Sumaišytame ir ceolitu mulčiuotame dumble pastebėtas sunkiųjų metalų koncentracijos sumažėjimas. Geriausiai yra akumuliuojamas varis, chromas, nikelis, kadmis, o blogiausiai – švinas.

Norint sumažinti amoniakinio azoto emisiją iš dumblo paviršiaus, reikėtų dumblą mulčiuoti, o siekiant padidinti amoniakinio azoto ir sunkiųjų metalų imobilizaciją giluminiame dumblo sluoksnyje būtų tikslinga sorbentą sumaišyti su dumblu.

Raktažodžiai: nuotekų dumblas, ceolitas, azotas, sunkieji metalai, mikroorganizmai, pedobiontai