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Research into heavy metal concentrations in agricultural soils

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This paper describes soil pollution in a pig farm while fertilizing soil by organic fertilizers. The farm needs to get IPPC permit, so it is essential to determine pollution impact on the environment. The paper analyses the distribution of heavy metals concentrations in the polluted soil and their dependence on the depth and time after slurry land spreading. Comparison with maximal available values (MAC) and distribution of pollutants concentrations at different seasons is also given. Since heavy metals are added to pigs fodder as additives and the amount of organic fertilizers applied exceeds the allowable norms determined in Directive 91/676/EEB, it was decided to investigate soil pollution by metals, which are the most common in pigs manure: Cu, Zn, Ni, Cr and Pb. Another reason for choosing to investigate these pollutants is that soil pollution by heavy metals in agricultural fields fertilized by organic fertilizers is very poorly investigated.

Key words: pollution with heavy metals, soil pollution, agricultural sector, liquid swine waste

INTRODUCTION

Presently, large swine-breeding farms are gaining in popularity, as well as poultry farms are expanding in Lithuania. The seasonality of production and crop rotation have influence on the formation of plant cultivation waste. In addition, the plant cultivation waste boasts a wider application and is mainly used as fodder. It is less harmful and does not cause greater environmental problems, therefore, under our country's conditions, when evaluating the real potential of biogas production, it is recommended to focus major attention to animal breeding farms, first of all, swine-breeding complexes (Duris, 1997). However, there emerges a very complicated situation when fields, being in close proximity to swine-breeding farms, are fertilized by various mineral fertilizers, while liquid swine waste from these farms is used for additional fertilization of these fields, which at the same time increases pollution with heavy metals. Large amounts of sewage having unpleasant smell accumulate. The application of liquid animal waste onto the soil results in the formation of excess nutrients, part of the sewage might reach underground waters, higher pollution has a significant effect on ecosystems and via them on humans (Ebadi et al., 2005).

With Lithuania's integration into the European Union, environmental requirements to activity objects change. Since 1 January 2004, Procedure of Issuing Permits for Natural Resource Use and Setting the Limits of Natural Resource Use and Norms of Permissible Emissions was replaced by the implemented System of Integrated Pollution Prevention and Control Permits (IPPC). The aim of this system is to pass over from the unified environmental requirements applied by an enterprise to the setting of individual requirements for particular equipment. According to IPPC rules, the conditions of permits for Appendix 1. Facilities must be based on the concept of "the best available techniques", therefore, it is necessary to analyze the best available techniques of large objects that are potentially the biggest polluters in the animal husbandry sector (Ure, 1996).

The swine breeding sector, to be more widely analyzed in this paper, is characterized by big environmental pollution (emissions into the atmosphere, water, soil) (Voronkienė et al., 2001). Many swine breeding farms in Lithuania dilute accumulated liquid animal waste with water and outpour it onto the soil. Therefore, it is necessary to analyze the impact of this pollutant on the environment and determine which technologies are most suitable for this sector to reach a high level of environmental quality.

There are many land plots which are polluted with heavy metals one way or another. This pollution might cause significant adverse effects such as damage to eco-systems, change in soil quality and respective reduction of its use for farming, pollution of underground water layers, and harm to both human and animal health.

Agriculture is one of the main sources of pollution with heavy metals. Soil fertilization with manure is still one of the most frequently used technical means in Lithuania. Manure is considered to be a good fertilizer but when used in big amounts to enhance soil fertility it becomes one of the main sources of pollution with heavy metals in agriculture (Hutchinson, 2003).

The Balčiūnai farm, in compliance with the JSC System requirements, was selected for the experimental research. Its design production volume amounts to 48,000 pigs per year. The complex is located near Pilviškiai town, Vilkaviškis district.

After signing contracts with local farmers, the liquid swine waste is outpoured onto the fields from April through November.

Prior to outpouring it onto the soil the waste is diluted with water, mixed well by supplying air to the accumulated liquid, the amount of sewage in this liquid accounts to about 5–7%.

The liquid fertilizer is applied on the soil surface every fortnight, approximately. In our case the liquid animal waste is applied on the area of roughly 2,000 ha. The main portion of the fertilized land is comprised of meadows, while the remaining part is used for growing agricultural cultures.

Since it is common knowledge that swine fodder additives contain a lot of heavy metals, and the use of liquid animal waste for fertilizing results in the excess concentrations of heavy metals in the soil, while the rates of these concentrations are set pursuant to the Directive 91/676/EEC, it was decided to examine the soil pollution with heavy metals that are most often discovered in the liquid swine waste, namely, Cu, Zn, Ni, Cr and Pb. Another reason of research into pollution with heavy metals is that research seeking to determine this pollution of land used for agricultural purpose is very scarce (Ebadi et al., 2005).

The main aims of the paper are: to determine the distribution of heavy metals concentrations in the soil fertilized with the liquid swine waste; dependence of metal concentrations on different depths of the soil; dependence of metal concentration on the time elapsed from the waste application on soil surface; dependence of changes in metal concentration on the season of the year; to evaluate how the company complies with the pollution criteria for IPPC permits.

MATERIALS AND METHODS

The experimental research of heavy metals was performed on the land plot of 30 ha area, used as a pasture, having even surface, covered with low grass, the prevailing type of the soil being middle size loam. The field is not far from the Vilkaviškis-Pilviškiai road, from another side borders a forest and a land reclamation ditch. This area was selected for the research because due to the land reclamation ditch located on the edge of the area the excess humidity (precipitation, spilt liquid swine waste etc.) seeps towards the ditch, which might precondition the change of heavy metal concentrations, and the road going nearby the area may serve as a secondary source of heavy metals in this field.

The researched field was divided into 9 parts of 3.3 ha area each, and samples were taken from 16 points. The researched field has a square form, distance among researched points is 180 meters.

Samples were taken by stainless steel scoops, put into plastic bags and delivered to the laboratory. The mass of the samples amounted to 0.6–0.8 kg. Prevalent soil was rich loam.

At all the 16 selected points samples were taken at two soil depths: 0–10 cm and 10–20 cm. Each sample was taken using the envelope principle. Fig. 1 shows the layout of sampling points. Samples were taken at different times elapsed from the liquid swine waste outpouring onto the soil: 1 day after, 7 days after and 14 days after, prior to repeating waste application (Fig. 1).

Soil samples were taken during different seasons of the year when the liquid swine waste was outpoured onto the fields: in spring (1–14 April), summer (1–14 June), autumn (1–14 October) (Lapinskienė et al., 2003). The experimental research was carried out at the Lithuanian University of Agriculture, Laboratory of Agrochemical Research.

Determination of heavy metals concentration. Analysis of heavy metals was performed by the atomic absorptive spectroscopy (AAS) method. 10 grams of soil were dried at 105 °C temperature for 2 hours. After drying the sample was sieved through the sieve of 1 mm diameter meshes, afterwards dried at 105 °C temperature for 30 minutes. Then the weighted sample was put into a plastic package, later 0.5–1.0 ml. of distilled water and 21 ml of concentrated HCl and 7 ml HNO_3 acid solution were added to it. The samples were mineralized following the methods setting the required temperature and time, which are approved by the European Union and applicable in Lithuania. Upon completion of mineralization, the sample was taken out and cooled to 50–70 °C temperature. Then solution from the vessel was filtered through a glass strainer to vessels of 50 ml each. The vessel was washed by 5 ml of diluted HNO_3 (1 : 1), and afterwards by 5 ml of distilled water. These liquids used for washing were also filtered through the glass strainer. Upon completion of the filtering the vessel was supplemented by distilled water up to the mark. Next, the concentrations of metals were determined using Buck Scientific 210 VGP spectrometer with an air-acetylene flame. If the organic part in the sample content is big, 10–20 grams of the sample have to be put into a porcelain vessel and burnt at 450 °C temperature for 12 hours. Afterwards 1.0–1.5 g of the soil undergo mineralization with "royal live water" according to the previously described methods (Sabienė et al., 2004).

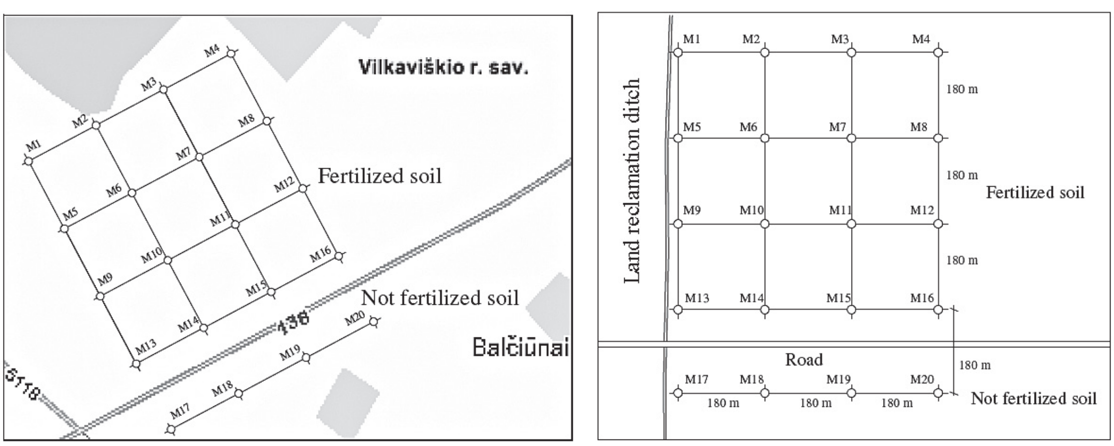

Fig. 1. Layout of sampling points

Concentration is calculated according to the following formula:

$$W(Me) = (C_{Me} \cdot f \cdot V) \,/\, W, \qquad (1)$$

where $W(Me)$ is metal concentration, mg/kg; C_{Me} is metal concentration in solution, mg/l; f is dilution factor; V is volume, l (0.05 l taken for research); W is sample mass, kg, recalculated for the mass of a dry sample.

RESULTS

The maximum permissible concentrations of heavy metals are set in the hygiene standard HN 60 : 2004. This standard (HN 60 : 2004) sets the maximum permissible concentrations for the metals Cu, Cr and Pb, which is 100 mg/kg for each, Zn – 300 mg/kg and Ni – 75 mg/kg.

Figures 2–4 show the dependences of Cu, Cr and Pb concentrations for the season of the year, at 0–10 cm soil depths, at different times of applying the liquid swine waste onto the soil (Fig. 2).

One day after the waste application, Cu amount exceeds the standard by 1.1–1.7 times. Cu concentration is 1.4 times higher in autumn than in spring. Cr and Pb concentrations do not exceed the values established by the standard, but in autumn the concentrations of these metals are higher by 1.3 and 1.6 times, respectively.

7 days after applying the liquid swine waste onto the soil surface, Cu amount at the depth of 10–20 cm does not exceed the set standards, while at the depth of 0–10 cm it reaches the norm only in autumn. Cu shows 1.8 times higher concentration in autumn than in spring. Cr and Pb concentrations are lower than the values established by the standard but, like in the first case, the concentrations of these metals are higher by 1.3 and 1.6 times, respectively, in autumn than in spring.

14 days after the outpouring, none of the metals show concentrations reaching permissible standard values. During the autumn season copper concentration is 3.7 times higher than in spring. The dependence of Cr and Pb concentrations on the season of the year remains the same and is 1.3 and 1.6 times higher, respectively (Fig. 3).

Figs. 2–4 show that in spring Cu, Cr and Pb concentrations are the lowest, while in autumn the highest. This can lead us to the conclusion that metals are accumulating in soil.

Analysis of the experiment findings shows that metal concentrations distribute nearly equally within the entire researched area, except for the left side of the field where the land reclamation ditch is situated. Research findings vary from 158.5 to 179.4 mg/kg. The decrease in Cu concentration by the land reclamation ditch is around 10%, measuring point section M1–M13. It can be assumed that the decrease in heavy metal concentration by the land reclamation ditch was recorded due to the fact that when collecting excess humidity from the researched field the amount of flowing water increases and at the same time large amounts of metals are washed out of the soil.

All the experimental findings confirm that the highest concentrations are during the first days after the liquid swine waste application onto the soil surface, and later they are decreasing.

Depending on the time of application, from 1 to 14 days, the copper concentration decreases, on average, by 7.1 times at the soil depth of 0–10 cm, and around 8.5 times when the sampling is made at the depth of 10–20 cm, by 5.5 and 6.4 times in summer and 2.7 and 2.9 times in autumn, respectively. Depending on the time of outpouring, from 1 to 14 days, Cr concentration decreases, on average, 1.2 times at both researched soil depths in spring and summer, and 1.3 times at both researched depths in autumn. Depending on the time of outpouring, from 1 to 14 days, lead concentration decreases, on average, 1.6 times at the depth of 0–10 cm and around 1.5 times at the depth of 10–20 cm in spring, 1.5 times in summer and 1.7 times autumn at both depths (Fig. 4).

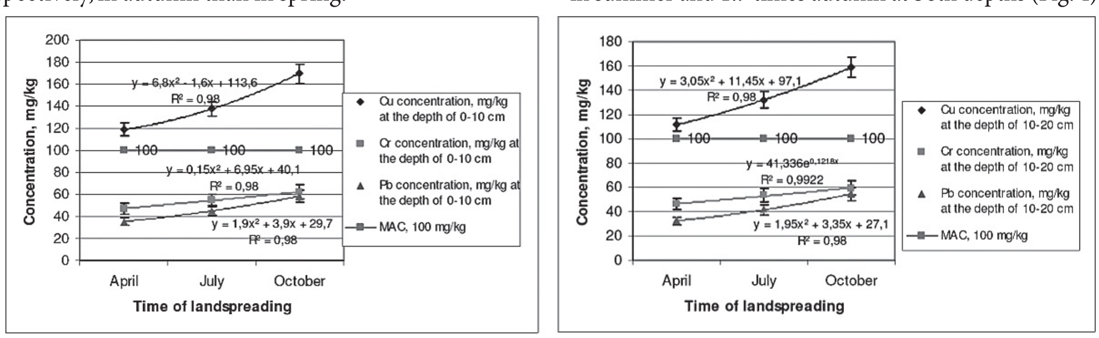

Fig. 2. Dependences of Cu, Cr and Pb concentrations on the season of the year 1 day after the waste application (a: at the depth of 0–10 cm, b: at the depth of 10–20 cm, section M3–M15)

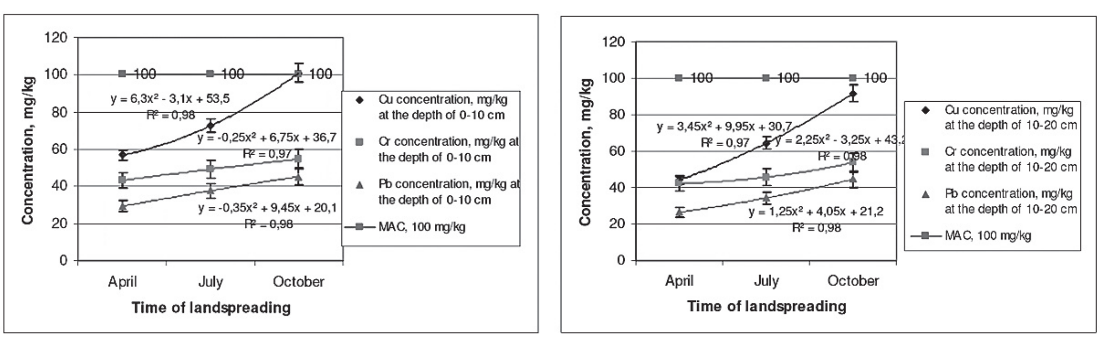

Fig. 3. Dependences of Cu, Cr and Pb concentrations on the season of the year 7 day after the waste application (a: at the depth of 0–10 cm, b: at the depth of 10–20 cm, section M3–M15)

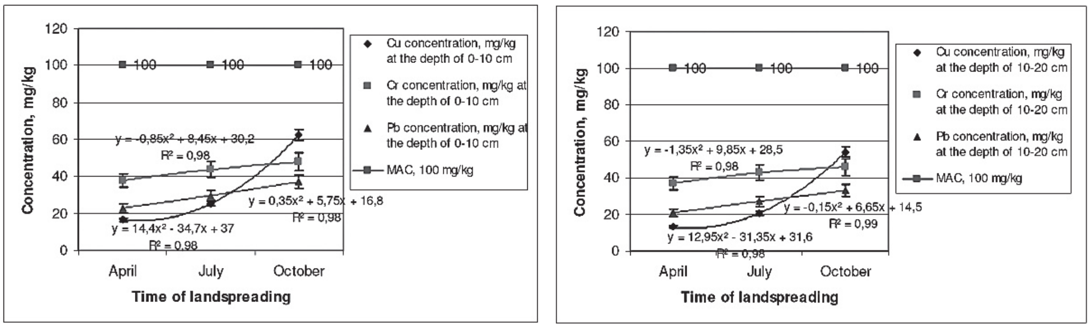

Fig. 4. Dependences of Cu, Cr and Pb concentrations on the season of the year 14 day after the waste application (a: at the depth of 0–10 cm, b: at the depth of 10–20 cm, section M3–M15)

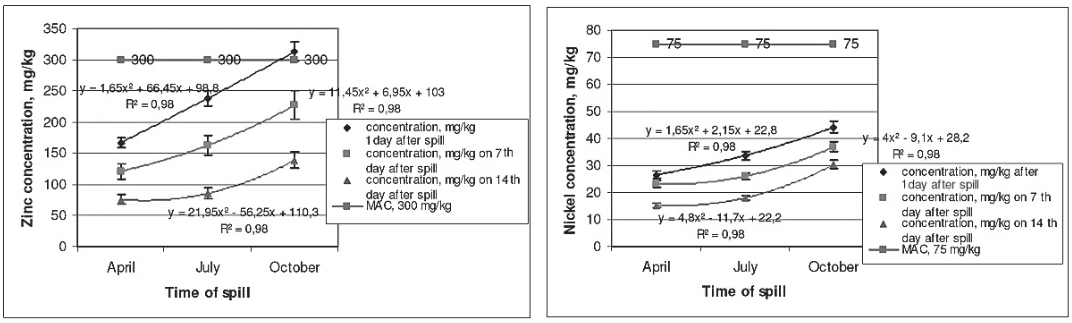

Fig. 5. Change in zinc and nickel concentrations during different seasons of the year at the soil depth of 0–10 cm (section M3–M15)

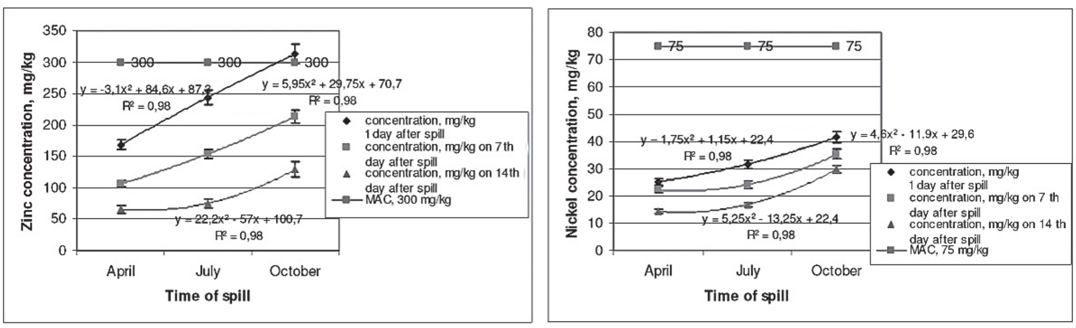

Fig. 6. Change in zinc and nickel concentrations during different seasons of the year at the soil depth of 10–10 cm (section M3–M15)

Since the concentrations of heavy metals depend on the soil depth, the obtained results show that copper concentration in the upper sampling layer is 13.4–23.5% higher than that determined in the second layer, the concentration of chromium is 5–7.1% and that of lead is 8.4–11.7%.

The research shows that lead concentration in the researched area has higher values by the neighbouring road. At the measuring points (in the section) M13–M16 lead concentrations by the road Vilkaviškis-Marijampolė increase, on average, by 9%. This shows that intensive traffic flows cause pollution.

Figures 5, 6 display the dependence of zinc and nickel concentrations on the season of the year at the soil sampling depth of 0–10 cm and on different time from outpouring the liquid swine waste onto the soil surface (Fig. 5).

At the soil depth of 0–10 cm zinc concentrations exceed the permissible norms only in autumn and this makes up 1.1 times after 1 day of outpouring. In autumn zinc concentration is 1.9 times bigger than in spring. The determined concentrations on nickel were regularly below the permissible limit and increased 1.7 times compared to those in spring.

At the soil depth of 10–20 cm zinc concentrations exceed the permissible norms only in autumn one day after outpouring the liquid swine waste onto the field showing the increase of 1.1 times. In autumn zinc concentration is 1.9 times bigger than in spring. In all the researched cases nickel concentrations are lower than the permissible ones, and an increase in concentration is 1.6 times comparing the autumn and spring seasons.

Like in previous cases, it was determined that zinc concentrations are the lowest in spring and afterwards gradually increase showing the highest concentrations of heavy metals in autumn. This once again proves the fact that a regular application of the liquid animal waste onto the soil results in the accumulation of metals in the soil (Fig. 6).

Change in nickel concentration preserves the same tendencies, and the maximum concentrations at both researched depths of the soil do not exceed the maximum standard rates applicable in Lithuania.

The experimental research determined maximum values of zinc concentration during the autumn season of liquid animal waste application, which change from 290 to 332.5 mg/kg. the estimated value is 10–15% higher than the one in research results by others foreign scientists (Chen, Lee 1997; Liu *et al.*, 1998). The analysis of research findings shows that zinc concentrations by the land reclamation ditch fall, on average, by 8%.

The research findings once again prove that the maximum concentrations of heavy metals are recorded during the first days after the liquid animal waste outpouring onto the soil and they are gradually decreasing until the next outpouring, however, due to intensive application of the waste, every 14 days, the accumulation of these metals has been observed in the soil.

Depending on the time elapsed from the liquid animal waste application, in the period from 1 to 14 days, zinc concentration, on average, decreases 2.2 times at the depth of 2–10 cm and around 2.6 times at the soil depth of 10–20 cm, by 2.8 and 3.2 times in summer, and 2.3 and 2.4 times in autumn, respectively. In the period from 1 to 14 days after the waste application, nickel concentrations decrease, on average, 1.7 times at the soil depth of 0–10 cm, and 1.8 times at the soil depth of 10–20 in the spring season, and 1.9 times in summer and 1.5 times in autumn at both researched soil depths.

Analysis of the heavy metals in question shows that the tendency of changes of heavy metal concentrations depends on the soil sampling depth. It is obtained that zinc concentration is 2–3.6% lower in the lower level of the researched soil 1 day after the waste application. When more days pass from the waste application this tendency becomes even more obvious and, on average, accounts for 1–19%. In the case of nickel the tendency is similar, and the concentrations recorded in the upper researched soil layer are higher by 5.7–11.8%.

CONCLUSIONS

1. The experimental research findings show the increase in heavy metal concentrations when the soil is fertilized with the liquid animal waste. Copper concentration changes from 10.5 to 179.4 mg/kg at the soil depth of 10 cm and from 9.0 to 167.8 mg/kg at the soil depth of 10–20 cm. One day after the waste application, copper concentrations exceed the permissible norms by 1.1–1.8 times, 7 days after, these values become equal to the permissible ones, and 14 days after they fall below the permissible ones.

2. Zinc concentration changes from 51.9 to 332.5 mg/kg at the soil depth of 0–10 cm and from 41.1 to 331.7 mg/kg at the soil depth of 10–20 cm. The set values at both depths were exceeded only in the autumn season and only 1 day after the waste application by 1.1 times. The increase in concentrations of both copper and zinc are related to the nutrient additives that are used at the farm. Cr, Ni and Pb concentrations in the researched samples did not exceed the permissible quantities.

3. The concentrations of heavy metals depend on the time elapsed from the waste application onto the soil. After the solution is outpoured onto the soil, the concentrations rapidly increase and afterward start gradually decreasing. In 14 days copper concentrations decrease 2.9–8.5 times, those of chromium – 1.2–1.3 times, lead – 1.5–1.7 times, zinc – 2.2–3.2 times, and nickel – 1.5–1.9 times.

4. Depending on the time elapsed from the liquid animal waste application, in 14 days zinc concentration decreases in spring, on average, 2.2 times at the soil depth of 0–10 cm and around 2.6 times at the soil depth of 10–20 cm, in summer it falls by 2.8 and 3.2 times, in autumn 2.3 and 2.4 times, respectively. In 14 days from the waste application, in spring nickel concentration, on average, decreases by 1.7 times at the soil depth of 0–10 cm and 1.8 times at the soil depth of 10–20 cm, in summer – 1.9 times, in autumn – 1.5 times at both researched soil depths.

5. The concentrations of heavy metals depend on the soil sampling depth. The findings show that the concentration of zinc is by 2–3.6% lower at the second depth one day after the waste application. After several days, the concentrations of heavy metals in the second depth are by 7–19% higher than in the first one. In the case of nickel this tendency remains similar, and the concentrations obtained in the upper researched layer are by 5.7–11.8% lower than those in the lower level.

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SUNKIŲJŲ METALŲ KONCENTRACIJŲ ŽEMĖS ŪKIO PASKIRTIES DIRVOŽEMYJE TYRIMAI

S a n t r a u k a

Žemės ūkis – vienas pagrindinių taršos sunkiaisiais metalais šaltinių. Dirvos tręšimas mėšlu vis dar lieka vienas dažniausiai naudojamų techninių priemonių Lietuvoje. Mėšlas yra laikomas gera trąša, bet, naudojamas jį dideliais kiekiais, kad padidintų dirvos derlingumą, yra vienas pagrindinių taršos sunkiaisiais metalais šaltinių žemės ūkyje.

Žinoma, kad naudojamuose kiaulių maisto papilduose yra nemažai sunkiųjų metalų, tai tręšiant srutomis viršijamos sunkiųjų metalų koncentracijos dirvožemyje. Jų kiekiai yra normuojami pagal 91/676/EEB direktyvą, todėl buvo nuspręsta ištirti dirvožemio taršą sunkiaisiais metalais, kurių dažniausiai aptinkama kiaulių srutose: Cu, Zn, Ni, Cr ir Pb. Be to, tyrimų, nustatant šią taršą žemės ūkio reikmėms naudojamoje žemėje, yra atlikta labai mažai.

Raktažodžiai: tarša sunkiaisiais metalais, žemės ūkis, skystasis, kiaulių mėšlas