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## Change of the Groundwater Chemical Composition in a Pig Breeding Enterprise

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### Abstract

This paper presents data on the groundwater chemical composition in the boreholes installed in moraine loam, sandy loam and sand fields, watered with slurry from a pig breeding enterprise (annual watering rate - 460 m<sup>3</sup> ha<sup>-1</sup>).

The investigations aim to determine the influence of the fields, watered with slurry from a pig breeding enterprise, on the groundwater quality.

In the observed boreholes samples of the groundwater were taken and water level was measured twice a year: in spring, before the fertilization, and in autumn, at the end of the fertilization period. The following indices were determined in the water samples: NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>. The unified water quality investigation methods, approved by the ministry of Environment, were used to conduct chemical analysis of the water samples.

As the groundwater was mowing towards southeast, south and southwest from the fertilized field, the boreholes in the lowest place of relief (borehole 1 and borehole 4) had the highest water mineralization and irregularly distributed concentration of the most important anions: HCO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup>. Besides, the highest groundwater mineralization was determined in the borehole 4, which was installed in the soil with a peat layer.

No influence of water level fluctuations and the amount of the nutrients coming with slurry on the concentrations of chemical elements was determined, as the obtained results of correlation analysis were not statistically significant.

At the increasing total water hardness, mineralization also increased, while the increasing mineralization gave rise to the amount of chlorides and sulphates in the water.

According to the investigation data, in the period of observation the areas watered with slurry had an insignificant influence on the groundwater quality: formation of hydrocarbonate, slightly mineralized and hard water.

*Key words: groundwater quality, pig breeding enterprise, slurry*

### Introduction

Members of Pig-Breeders' Association have plans to increase the number of pigs up to 2.5 mln. by the year 2015. Pig-breeding is known to be a highly polluting production activity. Big concentration of animals significantly increases environmental pollution.

Sources of agricultural pollution are spread over a huge territory and, therefore, hardly visible. For this reason agricultural activity is sometimes supposed to have little influence on the quality of the environment. However, research shows that about 60–70 % of nitrogen and 10–20 % of phosphorus in the Lithuanian rivers are of agricultural origin (Šileika..., 2007).

The in force legislation of Environmental Monitoring provides obligatory observation of groundwater quality in the territories of animal-breeding complexes and in the fields, where the slurry is spread. Water often contains high concentrations of nitrogen compounds, which exceed the estimated standard of nitrates, and especially - the value of 75 %, which is critical to take measures for reduction of significant and constant increase tendencies (Direktyvos..., 2005).

In Lithuania groundwater is used for drinking, which makes its quality very important. When change of the chemical composition of water is caused by natural reasons, which are independent of human activity, the quality of water usually meets the drinking water requirements. However, often are the cases when the groundwater quality decrease is caused by farming activity. Rubbish dumps, sewerage water reservoirs, pesticide application equipment washing grounds, ect. impair the water quality. Big and small animal-breeding enterprises, which accumulate big amounts of manure, are considered sources of pollution (Tumas, 2003). Large amounts of manure accumulate in big animal husbandry enterprises.

The most recent data on chemical composition and quality of groundwater, received from the Environmental Protection Agency, states that concentration of nitrates in the groundwater directly depends on the intensity of anthropogenic load. In 2009, average concentration of nitrates in urbanized environment was 21 mg l<sup>-1</sup>, in agricultural land – 9.8 mg l<sup>-1</sup>, in meadows and pastures – 1.3 mg l<sup>-1</sup>, and that of natural background – 0.7 mg l<sup>-1</sup>. The concentration of nitrates, exceeding the highest permissible concentration (50 mg l<sup>-1</sup>) was determined only in 1 of 81 places of observation; in 3 places of observation this concentration was close to the limit (>38 mg l<sup>-1</sup>) (Aplinkos būklė..., 2009).

The investigation results have established that chemical composition of groundwater mostly depends on the ground in the horizon of its accumulation. The amount of humus and clay particles in the soil influences the nitrogen concentration in the groundwater. Here, the impact of humus is related to the crops produced, while the increasing number of clay particles reduces the leaching of nitrogen (Pocienė, Pocius, 2005).

Spreading of slurry from animal husbandry enterprises in fields results in different levels of groundwater pollution: solid areal of polluted groundwater does not form in loamy formations of these fields, but it does form in sandy formations. In the latter case the formation covers both the focus of pollution and the section of approximately 100 – 150 m in the groundwater flow direction (Žemaitis, 1993).

The Lithuanian law on the Environmental Monitoring (Lietuvos..., 1999) provides that the entities, which

in the course of activity create the environmentally dangerous materials are obliged to conduct monitoring of natural environment condition. In order to establish general requirements for the analysis and monitoring of the impact of animal husbandry territories and agricultural irrigation fields on groundwater composition, the LR order, presenting the procedure of ecogeological investigation and monitoring of animal husbandry complexes' impact on groundwater, was confirmed on June 22nd, 2010 (suspended until January 1st, 2011). The document determines the requirements for ecogeological investigations in the territories of animal husbandry complexes and agricultural irrigated fields, general groundwater monitoring principles and limit concentrations of the main polluting materials in groundwater (Lietuvos..., 2010).

The pig-breeding enterprise is attributable to the group of entities, which increase technological load on the environment but do not constitute direct threat to the environmental objects. Aim of this work is to determine the influence of the fields, watered with slurry from a pig-breeding enterprise, on the groundwater quality.

### The place and methods of research

The research was carried out in a pig-breeding enterprise, located in the south-eastern part of Klaipėda region. Production territory – 23.96 ha (area of 10 ha is built up with production buildings, area of 12.96 ha – slurry storage tanks). This compact territory can be divided into 3 parts: northern, central and south-eastern. The south-eastern part has the Administrative Building, pig-houses and other buildings, the central part of the territory – liquid manure storage tanks (slurry reservoirs), the northern part (130 ha) – watered fields with irrigation system since 1984. From the accumulation reservoirs the slurry is pumped via underground pipelines to the irrigated fields and is spread there with irrigation apparatus DD-30. These apparatus are connected to the hydrants of the underground pipeline network. Perennial weeds grow in the watered fields. Structure of the enterprise territory is presented in Figure 1.



Figure 1. **Scheme of the investigation object:** 1 - 4 groundwater observation boreholes and their soil profiles; 5 – fields, watered with slurry; 6 – slurry reservoirs; 7 – pig-houses; 8 – plant layer of the soil; 9 – sandy loam; 10 – loam; 11 – sand; 12 – peat; 13 – direction of the groundwater flow; 14 – aquifer level

To determine the groundwater chemical composition 4 boreholes have been installed in moraine loam, sandy loam and sand fields. The borehole 1 (depth - 4 m) enables to observe the groundwater in the western part, the borehole 2 (depth – 4.5 m) – in the central part of irrigated fields, and observation in the borehole 3 (depth - 6 m) gives information about groundwater in the eastern part of irrigated fields. The borehole 4 (depth - 6 m) has similar purpose – the information obtained here tells about the hydrochemical condition of the water flowing out of the irrigated fields and moving under the slurry reservoirs.

The enterprise, which has 1600 sows and 7900 fattening pigs, accumulates on average 1500 m<sup>3</sup> of thick manure fraction and 29 500 m<sup>3</sup> of slurry per year. Besides, the neighbouring settlement annually contributes on average 30 500 m<sup>3</sup> of household wastewater of low fertilization value. The following amounts of nitrogen, phosphorus and potassium have been determined in the slurry to be spread, respectively: in 2001 – 0.77, 0.04 and 1.21 kg m<sup>-3</sup>, in 2002 – 0.75, 0.03 and 1.36 kg m<sup>-3</sup>, in 2003 – 0.67, 0.02 and 0.98 kg m<sup>-3</sup>, in 2004 – 1.21, 0.03 and 0.71 kg m<sup>-3</sup>, in 2005 – 0.97, 0.15 and 0.52 kg

$\text{m}^{-3}$ . The average concentration of nitrogen in slurry has been determined to be  $0.87 \text{ kg t}^{-1}$ , that of phosphorus –  $0.05 \text{ kg t}^{-1}$ , that of potassium –  $0.96 \text{ kg t}^{-1}$ .

The slurry, diluted with household wastewater from the settlement, is spread in the area of 130 ha twice per year – in autumn and in spring. The onetime spreading load –  $230 \text{ m}^3 \text{ ha}^{-1}$ .

In the observed boreholes samples of the groundwater are taken twice a year: in spring, before the fertilization, and in autumn, at the end of the fertilization period after the last spread of the slurry. The following indices have been determined in the water samples:  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ . At the time of sampling the water level is measured with the tape-measure 0.1 m accuracy before the water is pumped out of the boreholes. The groundwater mineralization, determined by the dissolved non-organic materials, is calculated for each borehole.

Chemical analyses of the water samples are conducted at the Chemical Analytical laboratory of the Water Research Institute, the Aleksandras Stulginskis University following the application of unified methods (Unifikuoti nuotekų..., 1994).

## Results and discussion

Following the purpose of implementation of the European Parliament and Council directive 2000/60/EB, which determines the guidelines for the Community actions in the field of Water Policy, the director of the Lithuanian Geology Service at the LR Ministry of Environment issued the decree No. 1-06, on February 3rd, 2003, providing the list of toxic materials, the input of which into the groundwater must be stopped or significantly reduced (Lietuvos..., 2003). This list provides the following highest permissible concentrations (HPC) in the groundwater from the territories of animal and poultry farms when in the neighbouring areas this groundwater is not used for drinking and household purposes: nitrites ( $\text{NO}_2^-$ ) – 1, nitrates ( $\text{NO}_3^-$ ) – 50, ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) – 10, phosphates ( $\text{PO}_4^{2-}$ ) – 3.3, chlorides ( $\text{Cl}^-$ ) – 500, sulphates ( $\text{SO}_4^{2-}$ ) –  $1000 \text{ mg l}^{-1}$ .

The main elements, determining the groundwater quality in the fertilized fields and production territories of pig-breeding enterprises, are biogenic elements – nitrogen and phosphorus.

The nitrogen concentration totally depends on the intensity of biochemical and biological processes, which take place in the water. In natural environment nitrogen forms various non-organic and organic compounds. Ammonium  $\text{NH}_4^+$ , nitrites  $\text{NO}_2^-$  and nitrates  $\text{NO}_3^-$  ions are attributed to non-organic compounds. The nitrogen compounds are very easy to transform. These compounds show if the water is polluted and, also, they are toxic. The change of ammonium nitrogen in the water of boreholes in the five-year period of investigations is shown in Figure 2.

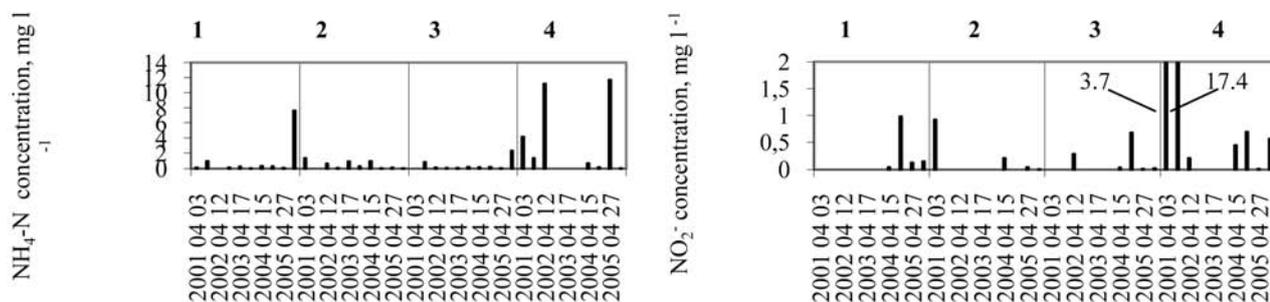


Figure 2. Change of ammonium nitrogen and nitrites concentrations in the groundwater

The ammonium nitrogen concentrations, determined in the samples from the borehole 4 in spring of 2002 and 2005 –  $11.2 \text{ mg l}^{-1}$  and  $11.7 \text{ mg l}^{-1}$ , respectively, exceeded the highest permissible concentration.

Nitrites are highly unstable compounds, therefore, they are found in very low quantities. Increased concentration of this element indicates high level of pollution. Figure 2 presents the graphs, which show the most significant changes of nitrites and ammonium nitrogen concentrations to take place in the borehole 4, where the samples taken in spring and autumn of 2001 had the concentrations exceeding the HPC 3.7 and 17.4 times, respectively.

According to scientific literature, a number of factors, such as lithological composition of rocks in the aquifer, activity of organisms, climate and surface relief determine the variety of ionic composition of groundwater (Ignatavičius, 1960). Analysis of the borehole profiles shows that in the borehole 4 peat makes 0.4 m thick soil layer. This is determined by nitrification and denitrification conditions as water in the peat layer contains much organic material, the disintegration of which requires a lot of oxygen. Therefore, in the process of oxidation the microorganisms use both free oxygen and that of nitrates and nitrites (Никаноров, 1989). Concentrations of this element in other boreholes are lower than the HPC, which brings to the statement that water is clean there as concentrations of nitrites do not exceed the standard.

Nitrates are the most stable ones of all non-organic nitrogen compounds. Increased concentration of nitrates indicates that water is polluted. In the five-year period of investigations concentrations of nitrates in the boreholes exceeded the HPC only two times (in boreholes 1 and 3) (Fig.3).

The most significant change of this compound is observed in the borehole 3, however, the concentrations do not exceed the HPC. The exception is spring of 2005, when the concentration exceeded the HPC by 1,1 times, and autumn of 2004, when in the borehole 1 the concentration of  $\text{NO}_3^-$  exceeded the HPC by 2.9 times.

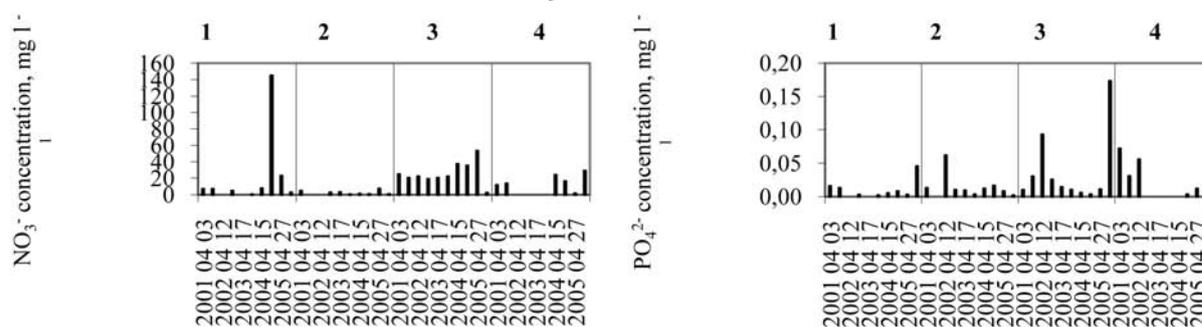


Figure 3. Change of nitrates and phosphates concentrations in the groundwater

Natural water contains very small amounts of phosphorus. Increased concentration of phosphorus means that the water is polluted as presence of phosphorus compounds indicates the process of disintegration of complex organic materials.

In the five-year period of investigations the amount of phosphates in all boreholes was very low (Fig. 3); the highest value of phosphates ( $1.6 \text{ mg l}^{-1}$ ) was two times lower than the HPC. According to the amount of phosphates in the groundwater, water was clean in all the observed boreholes.

Analysis of moisture and pollutants' migration in the aeration zone has established the danger to pollute the groundwater horizon in big areas of sandy sections as the dominating lateral runoff transports the pollutants in the horizontal direction. The horizontal spread of pollutants is not strong where non-permeable moraine loams dominate. It locally concentrates in the focus of pollution and spreads in the vertical direction mostly. Then, the pollution puts the lower laying aquifers at a risk (Žemaitis, 1993).

The correlation analysis is done to determine the influence of the spread slurry on the groundwater. Weak and medium strong relations have been established between the amount of the nutrients that come with slurry and concentrations of these materials in the water of the observed boreholes. The borehole 1 is an exception, where concentrations of nitrates, nitrites and phosphates increase alongside with high amounts of nitrogen and phosphorus coming to the irrigation fields. The corresponding correlation coefficients are as follows:  $r = 0.62$ ,  $n = 9$ ,  $t_{\text{theor.95\%}} = 2.4 < t_{\text{fact.}} = 2.64$ ;  $r = 0.64$ ,  $n = 9$ ,  $t_{\text{theor.95\%}} = 2.4 < t_{\text{fact.}} = 2.89$ ;  $r = 0.60$ ,  $n = 9$ ,  $t_{\text{theor.95\%}} = 2.4 < t_{\text{fact.}} = 2.44$ . An uneven relief of the irrigated area also plays an important role here: this borehole is in the lowland, where big amount of slurry accumulates in the time of watering.

Correlation analysis shows that the nutrients, spread together with slurry, have no significant influence on the groundwater concentrations in other boreholes, as no statistically important relations have been established.

Correlation analysis of the influence of the water level fluctuations in the boreholes on the concentrations of nutrients reveals that rising water level increases concentrations of ammonium nitrogen in the boreholes 1 ( $r = 0.64$ ,  $n = 9$ ,  $t_{\text{theor.95\%}} = 2.4 < t_{\text{fact.}} = 2.84$ ) and 3 ( $r = 0.67$ ,  $n = 10$ ,  $t_{\text{theor.95\%}} = 2.3 < t_{\text{fact.}} = 3.42$ ), concentration of nitrates nitrogen in the borehole 2 ( $r = 0.65$ ,  $n = 9$ ,  $t_{\text{theor.95\%}} = 2.4 < t_{\text{fact.}} = 2.94$ ) and concentration of potassium in the borehole 1 ( $r = 0.64$ ,  $n = 9$ ,  $t_{\text{theor.95\%}} = 2.4 < t_{\text{fact.}} = 2.92$ ). No influence of the water level fluctuations on the concentrations of other chemical elements has been established as the obtained correlative relations are not statistically important. Increase of the latter concentrations is under the influence of the groundwater flow direction. As the groundwater moves towards south-east, south and south-west from the area, fertilized with slurry, water mineralization in the boreholes 1 and 4 is the highest one -  $699$  and  $728 \text{ mg l}^{-1}$ , respectively.

Analysis of the chemical composition of the groundwater states that the borehole 4 has the highest level of dissolved mineral materials (Table 1).

Table 1. Chemical composition of the groundwater (means  $\text{mg l}^{-1}$ )

Borehole No.	$\text{NH}_4^+$	$\text{K}^+$	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{NO}_2^-$	Sum of ions
1	1.4	23.4	36.8	109.0	15.1	382.0	47.3	60.7	21.9	0.14	698
2	0.6	12.2	13.3	82.1	12.2	262.0	51.9	16.8	2.2	0.13	453
3	0.6	18.6	26.6	47.4	10.9	196.0	29.6	25.2	25.8	0.11	381
4	5.4	27.5	103.2	86.2	15.5	373.0	66.4	94.3	13.6	3,3	788

Here, the total mineralization reaches  $788 \text{ mg l}^{-1}$ . In the water of the boreholes hydrocarbonates make from 43 to 58, and calcium ions - from 12 to 18 % of the total amount of ions.

Data presented in the Table 1 shows that in the borehole 4, which is in the peat soil layer, the amount of nitrites is by 33 times bigger than that in other boreholes, and the amount of ammonium exceeds that in the boreholes, equipped in sandy soils by 4 to 9 times. Scientific literature (Rudzianskaite et al., 2008) states that the reductive background of peat has the strongest impact on nitrogen and the less harmful nitric form ( $\text{NO}_3^-$ ) is turned to the very harmful nitric form ( $\text{NO}_2^-$ ).

Analysis of the chemical composition of the groundwater has established an abnormal increase of the most important anions in the boreholes 1 and 4:  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ .

Increased amounts of chlorides and sulphates in the groundwater are of secondary origin, and they mainly come from human activity. Use of chlorides in human household and their mobility are much higher than those of sulphates, therefore, chlorides determine the abnormal character of groundwater chemical composition formation (Ignatavičius..., 1960).

Concentrations of sulphates are lower than those of chlorides but they also have the highest values in the borehole 4. As water in this borehole has the highest mineralization level, concentrations of chlorides and sulphates are also the highest ones (mean concentrations 94.3 and 66.4  $\text{mg l}^{-1}$ , respectively), however, they are very low in comparison with the HPC. Scientific literature (Nikanorov, 1989) states that concentrations of chlorides and sulphates increase together with the increasing water mineralization (Table 2).

Table 2. Dependence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations in the groundwater on the degree of mineralization

Borehole No	Equation	r	Number of members	Student's criterion	
				$t_{\text{theor}95\%}$	$t_{\text{actual}}$
<b><math>\text{Cl}^-</math></b>					
1	$y = 0.1681x - 56.575$	0.99	9	2.4	261.9
2	$y = 0.0957x - 26.878$	0.91	9	2.4	14.2
3	$y = 0.1318x - 25.377$	0.99	10	2.3	280.0
4	$y = 0.221x - 79.899$	0.94	7	2.6	17.5
<b><math>\text{SO}_4^{2-}</math></b>					
1	$y = -0.0148x + 57.669$	0.35	9	2.4	1.1
2	$y = 0.2684x - 70.72$	0.83	9	2.4	7.1
3	$y = 0.0912x - 3.2727$	0.92	10	2.3	17.3
4	$y = 0.1196x - 27.888$	0.93	7	2.6	16.0

Note: The relation is significant when  $t_{\text{fact.}} > t_{\text{theor}95\%}$ ; y – concentrations of chemical elements  $\text{mg l}^{-1}$ ; x – mineralization of groundwater.

Water hardness is one of the components characterizing water quality. Total hardness of the water from the water supply system has been established not to exceed 7  $\text{mg-equiv. l}^{-1}$ , and that from the well – not higher than 10  $\text{mg-equiv. l}^{-1}$ .

The investigations show the existing direct dependence between the groundwater hardness and mineralization (Fig. 4).

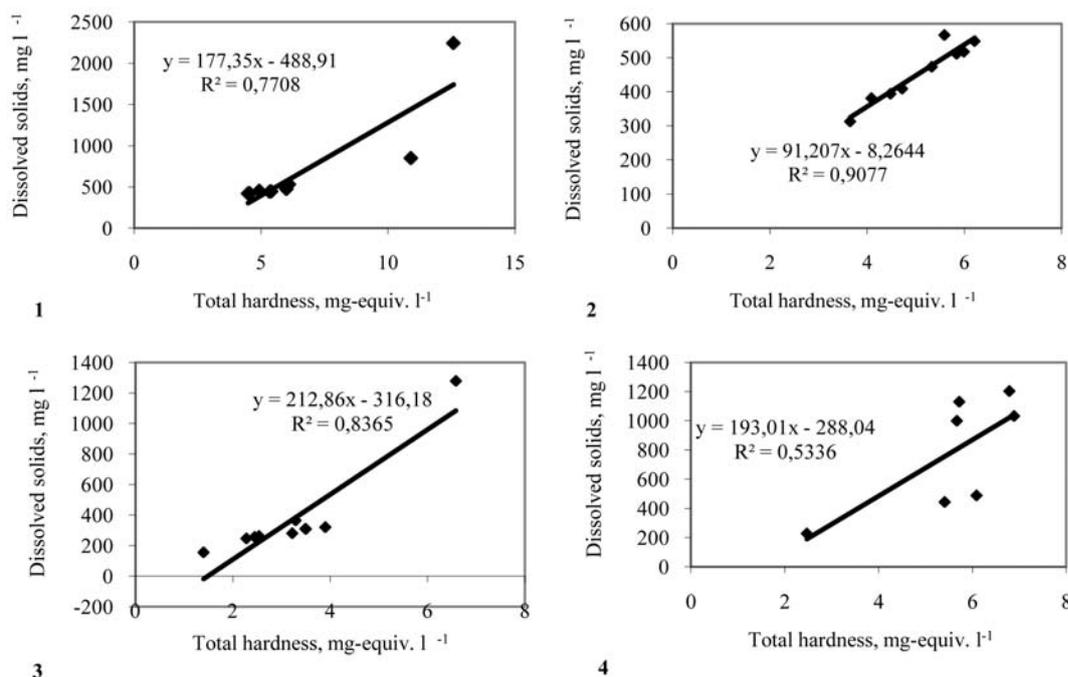


Figure 4. Dependence between total hardness and mineralization of the groundwater

The higher total hardness of the groundwater, the higher mineralization value is established: in the borehole 1 water is very hard – 12.6 mg-equiv. l<sup>-1</sup>, the established mineralization is 2244 mg l<sup>-1</sup>, in the borehole 3 a very soft water has formed – 1.4 mg-equiv. l<sup>-1</sup>, the established mineralization is 156 mg l<sup>-1</sup>.

Results of the investigations show that the area, where slurry is spread, has some but not very significant influence on the groundwater quality: the water that forms is hydrocarbonatic, weak mineralization, medium hard and hard.

## Conclusions

1. The groundwater quality most depends on the sediments, where it has accumulated. The highest groundwater mineralization has been established in the borehole 4, which has a peat layer.
2. Chemical composition of the groundwater depends on the direction of the groundwater movement. As the groundwater moves to south-east, south and south-west from the fertilized area, the highest mineralization is observed in the boreholes 1 and 4 – 699 and 728 mg l<sup>-1</sup>, respectively.
3. Statistically not important, weak and medium strong relations have been established between the amounts of the nutrients that come with slurry and concentrations of these materials in the groundwater of the observed boreholes. The borehole 1 is an exception, where the concentrations of nitrates, nitrites and phosphates increase. This is under the influence of the relief of the irrigated area: the borehole is in the depression, where much slurry accumulates in the time of watering.
4. As water in the boreholes rises to the soil surface, ammonium nitrogen concentrations in the boreholes 1 and 3 increase as well as those of nitrate nitrogen in the borehole 2 and potassium in the borehole 1. The water level fluctuations have been established to have no influence on the concentrations of other chemical elements as the obtained correlation is not statistically important.
5. In the boreholes 1 and 4 abnormal formation of the groundwater chemical composition:  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ , is due to the significant increase of chlorides and sulphates.
6. The degree of mineralization determines the increase of chlorides and sulphates in the groundwater: the correlation coefficients fluctuate Cl<sup>-</sup> from 0.83 to 0.99; SO<sub>4</sub><sup>2-</sup> from 0.69 to 0.87.
7. Nitrogen has the strongest influence on the groundwater quality: in the five-year period of investigations the ammonium nitrogen and nitrites concentrations, exceeding the HPC, have been established two times in the borehole 4, those of nitrates in the boreholes 1 and 3 – 1 time and water hardness in the borehole 1 – 2 times.
8. Concentrations of other investigated chemical elements do not exceed the HPC.
9. The area, where slurry is spread, has weak influence on the groundwater quality: the water that forms is hydrocarbonatic, weak mineralization, medium hard and hard.

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