ENVIRONMENTAL ENGINEERING
The 8th International Conference
May 19–20, 2011, Vilnius, Lithuania
Selected papers

ISSN 2029-7106 print / ISSN 2029-7092 online
ISBN 978-9955-28-828-2 (2 Volume)
ISBN 978-9955-28-827-5 (3 Volume)
http://enviro.vgtu.lt

INFLUENCE OF SLURRY ON ORGANIC MATTER FLUCTUATION IN GROUNDWATER

Stefanija Miseviciene

Department of Land Reclamation, Faculty of Water and Land Management, Lithuanian University of Agriculture. Parko 6, Vilainiai LT-58102, Kedainiai district, Lithuania. E-mail: Stefanija.Miseviciene@lzuu.lt

Abstract. The paper analyses the data on the change of the groundwater organic matter content in the observed boreholes, equiped in light soils fertilized with the slurry from pig-breeding enterprise. The investigations aimed to determine the influence of the fields fertilized with the slurry from pig-breeding enterprise on the migration of organic matter in the groundwater. The work involved natural investigations, analysis of the water samples was carried out following the Unified Water Quality Research methods, approved by ministry of Environment.

The investigations established that meteorological conditions and groundwater level had some influence on water level fluctuation in the boreholes. The higher the air temperature and the lower the precipitation, the lower is the groundwater level in the boreholes. The fluctuations of the groundwater level in the boreholes 2 and 3 were bigger, because the groundwater level in these boreholes is closer to the soil surface.

Fluctuation of water levels influenced concentrations of organic matter: the closer water level is to the soil surface, the higher COD and TOD concentrations were observed.

The groundwater flow direction had the influence on the higher hard oxidised organic matter content in the boreholes 1 and 4, because in these boreholes the groundwater lies deeper than in the boreholes 2 and 3.

The investigations established that the fields fertilized with slurry had insignificant influence on the groundwater quality: the dominant sectional water composition stayed the same as in the water that is naturally emerging in the nature.

Keywords: Pig-breeding enterprise, groundwater, organic matter.

1. Introduction

Due to the occurrence close to the soil surface, the groundwater is higly sensitive to pollution. This water consists mainly of the absorbed atmospheric and surface waters, thus, the main factor for the formation of chemical and microbiological composition of groundwater is composition of surface water. Quite a lot of organic matter is oxidized during the infiltration process – mean values of permanganate oxidation and bichromate oxidation in the groundwater are two and more times lower than those in the surface water. Slight changes of the mean values of permanganate oxidation are observed in the groundwater, while those of bichromate oxidation decrease at the increasing distance from the infiltration basin. In the course of surface water filtration into the ground a non-intensive further oxidation of stable organic substances takes place (Diliūnas *et al*. 2003).

When change of water chemical composition is caused by natural reasons, independent of human activity, water quality normally meets the drinking water requirements. The investigations have established a slightly increased permanganate oxidation, however, this phenomenon is characteristic to the entire territory of the country (maximum value of permanganate oxidation is – 22.24, minimal – 0.16, mean – 5.01 mg l^{-1} O_2) (Domaševičius *et al*. 1996).

Sources of non-point pollution are the most real polluters of groundwater. In Lithuania pig-breeding has always been a very important branch of animal husbandry. Rural and Agricultural Development Strategy gives priority to meat (bacon) pig-breeding. By the year 2015 the production of pork is likely to have reached 230 thous tones (Vasiliauskienė ir *et al*. 2005).

The Institute of Geology has investigated the influence of the utilization of slurry from animal husbandry complexes on the chemical composition of groundwater. Results of the investigations, which were carried out in the period of 1977–1980, show that despite high watering rates – 300 m^3 ha^{-1}, groundwater is not polluted in the complexes, which have irrigation fields overgrown with perrenial grasses. Dense grass roots‘ system accumulates dispersive substance of the dilluted slurry during every watering, therefore, a higher sorption capacity bio-film forms, which reduces slurry infiltration to deeper soil layers. This impact is particularly strong in moraine loam soils (Diliūnas *et al.* 1996).

Having spread animal slurry in the pastures at the rate of 230 m^3 ha^{-1}, the concentrations of pollutants in the groundwater at all depts are established to be by 95% lower than those in the slurry. Mechanical retention is the main factor reducing the amount of microorganizms and chemical oxygen demand (Lopez Periago *et al.* 2002).

The investigations have established that application of pig slurry at the rates bigger than those used by plants causes accumulation of nitrates in the surface soil layer. This is particularly obvious in the warm season, when NO_3 – N in the soil water reaches 300 mg l^{-1}. In the rainy period the nitrates are washed down to the depth of at least 4 m even in clay soils (Mantovani *et al.* 2006).

The comparative investigations have established that spread of pig slurry up to 150 m^3 ha^{-1} and application of mineral fertilizers in grain crops increase the amount of nitrate nitrogen in the soil water at the depth of 0.9 – 1.2 m: mineral fertilizers – up to 44.7, slurry – from 19.9 to 28.0 mg l^{-1} (Dauden *et al.* 2003).

The recent data of the Environmental Protection Agency indicates 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^{-1}, in agricultural land– 9.8 mg l^{-1}, in meadows and pastures – 1.3 mg l^{-1}, and that of natural background – 0.7 mg l^{-1}. The concentration of nitrates, exceeding the highest permissible concentration (50 mg l^{-1}) 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^{-1}) (Aplinkos būklė…, 2009).

The natural water, next to mineral substances, contains various organic materials, which form in the water as a result of vital activity and disintegration products of water organizms and, also, come from the basin surface with wastewater and precipitation (Unifikuoti...; 1994).

Groundwaters and their chemical characteristics are closely related with the soil and vegetation cover and appear to be an important indicator of physical-geographical conditions of the environment. Chemical composition of these waters depends of the regional physical-geographical conditions, climate being the main of them as it determines not only direction of hydrochemical process but also the character of vegetation, soil formation and weathering processes, intensity of microorganizms‘ activity, etc (Ignatavičius, 1960).

The groundwater quality most depends on lithology and anthropogenic load of the aquifer sediment. The groundwater of sandy, clay, organic matter and gypsum rich sediments differs in its hydrochemical composition. In sandy sediments the mean values of the organic matter permanganate and bichromate number (1.75 and 5.04 mg l^{-1} O_2) are lower than those in clay sediments (1.98 – 6.65 mg l^{-1} O_2) or naturally organic matter rich sediments (11.05 – 31.44 mg l^{-1} O_2) and are very similar to the values of gypsum sediments (1.12 – 5.09 mg l^{-1} O_2) (Arustienė *et al.* 2003; Pocienė *et al.* 2005).

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. 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.

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 the work – to determine the influence of the fields, irrigated with slurry from a pig-breeding enterprise, on the migration of organic matter in the groundwater. To achieve this goal the following activities have been fulfilled: investigation of soil composition in the fields irrigated with slurry, observation of meteorological conditions, measurement of the groundwater level in bireholes and determination of chemical composition of the groundwater.

2. Location and methods

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 appatarus DD-30. These apparatus are connected to the hydrants of the underground pipeline network. Water discharge of the irrigation apparatus is 30 l s^{-1}. Perennial weeds grow in the watered fields. Structure of the enterprise territory is presented in Figure 1.

Analysis of the local hydrographical network brings to the assumption that groundwater aquifer occupies quite a big area in the intervalley of the Minija and its tributaries: the Agluona and the Rokupis. The production territory of the enterprise and the irrigation fields occupy central and south-eastern parts of this area, thus, the groundwater that forms in this territory as a result of infiltration of precipitation and the polluted water, spread in the fields, flows to south-east, south and south-west. In the east, the filtered water gets into the Agluona and its tributaries, while from the west part of the watered fields it moves to west and north-west directions to the Rokupis and its tributaries (Fig 1).

Fig 1. Scheme of the investigation object: 1 - 4 goundwater observation boreholes and their soil profiles; 5 – fields, watered with slurry; 6 – slurry reservoires; 7 – pig-houses; 8 – plant layer of the soil; 9 – sandy loam; 10 – priemolis; 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^3 of thick manure fraction and 29 500 m^3 of slurry per year. Besides, the neighbouring settlement annualy contributes on average 30 500 m^3 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^{-3}, in 2002 – 0.75, 0.03 and 1.36 kg m^{-3}, in 2003 – 0.67, 0.02 and 0.98 kg m^{-3}, in 2004 – 1.21, 0.03 and 0.71 kg m^{-3}, in 2005 – 0.97, 0.15 and 0.52 kg m^{-3}. The average concentration of nitrogen in slurry has been determined to be 0.87 kg t^{-1}, that of phosphorus – 0.05 kg t^{-1}, that of potassium – 0.96 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 m^3 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. Tape-measure is used to determine the water level at 0.1 m accuracy before water is pumped out of the boreholes. The water samples are analyzed for the following indices: COD and TOD.

Chemical analyses of the water samples are conducted at the Chemical Analythical laboratory of the Water Research Institute, the Lithuanian University of Agriculture following the application of unified methods (Unifikuoti nuotekų…, 1994).

3. Results and discussion

Data of Klaipėda Meteorological station provides that precipitation norm of many years is 708 mm, average air temperature of many years – 7.0 °C; that of vegetation period – respectively 451 mm and 12.2 °C; of cold period – respectively 257 mm and – 0.26 °C (Table 1).

Table 1. Meteorological conditions during the period of investigation

Indices	2001	2002	2003	2004	2005
Precipitation, mm	855	647	729	661	756
% of the average perennial rate	120	91	103	93	107
Average air temperature, ^{o}C	8.0	8.6	7.7	7.8	7.9
Deviation from the average perennial rate, ^{o}C	+1	+1.6	+0.7	+0.8	+0.9

During the period of investigations the yearly amount of precipitation changed from 661 mm in 2004 (this was by 7% lower than the average of many years) to 855 mm in 2001 (this by 20% exceeded the average of many years); the highest average air temperature was 8.6 ^{o}C in 2002 and this by 1.6 ^{o}C exceeded that of many years.

In respect of yearly precipitation the driest year was 2002 (647 mm) and 2004 (661 mm), when the corresponding index was lower than the multi-rate by 9 and 7 % respectively.

The correlation analysis established that temperature and precipitation influenced the fluctuation of water levels in the boreholes: the higher temperature and less precipitation, the lower was water level in the boreholes.

$$z = 1.84011 - 0.001718x_1 + 0.0143x_2, \quad (1)$$

here: z – the groundwater level in the boreholes m; x_1 – precipitation mm; x_2 – average year temperature^{o}C; n = 34, r = 0.58, $F_{theor.} = 3.3 < F_{total.} = 8.18$.

According to the scientific literature, the groundwater level fluctuations stronly depend on the depth of the aquifer. If the groundwater is close to the soil surface, the level fluctuation is more sensitive to the air temperature than precipitation (Chen *et al.* 2004). The groundwater level fluctuation is particularly obvious in the relatively not deep aquifers. At the increasing depth of the groundwater aquifer, this difference decreases (Giedraitienė, 2004).

When the groundwater occurs in a very deep soil layer (down to 10 m depth), the influence of meteorological conditions on the fluctuation of levels is late by up to a year and follows the laws of independent mode (Baužienė, 2003; Giedraitienė, 1996).

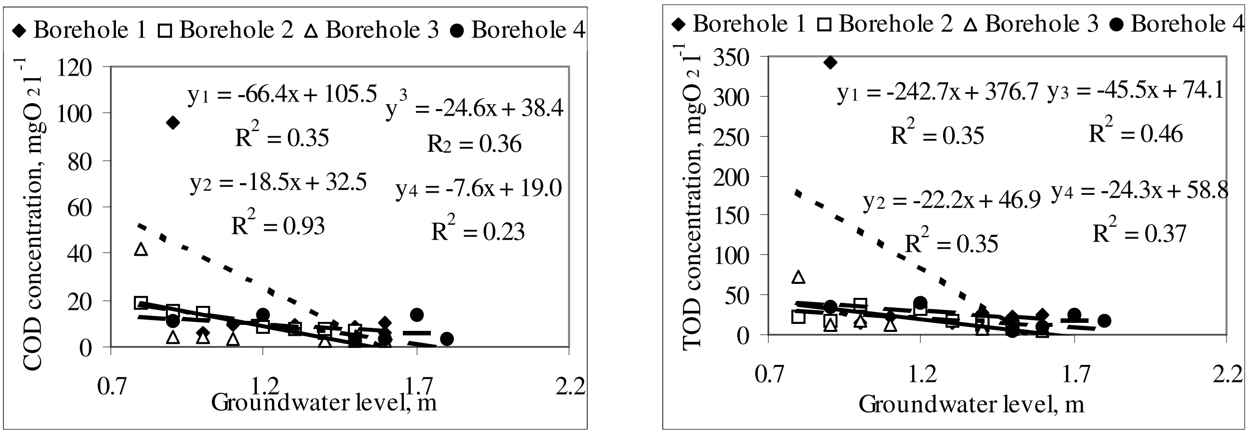
In the boreholes 2 and 3 of the investigated object the groundwater occurence is the closest to the soil surface, thus, the variation coefficients indicate the strongest fluctuation of the water levels here as the precipitation infiltration quickly reaches the groundwater and raises its level. This fluctuation is also under the influence of soil composition: sand makes soil profile in the borehole 3, thus fluctuations here are stronger than those in the borehole 2 – variation coefficient 23 % (Table 2).

Table 2. Statistic data of groudwater levels

Statistika/Statistics	Borehole 1	Borehole 2	Borehole 3	Borehole 4
Number of members	9	9	10	6
Average, m	1.3	1.2	1.3	1.5
Standard deviation, m	0.26	0.25	0.30	0.32
Confidence interval, m	0.17	0.16	0.19	0.24
Minimum, m	0.9	0.8	0.8	0.9
Maximum, m	1.6	1.5	1.6	1.8
Coefficient of variation %	20	21	23	21

Sandy loam soil in the borehole 2 impedes the precipitation water filtration to the aquifer, therefore, the established variation coefficient is lower – 21%. The change of groundwater level in deep aquifers (boreholes 1 and 4) is not so strong as it takes more time for the precipita tion water to reach the aquifer, thus, the variation coefficients here are 20 and 21%, respectively.

Correlation analysis evaluates the significance of the interrelation between the fluctuations of water level and concentrations of organic matter (Fig 2).



Note: y – COD or TOD concentration in groundwater; x –level of groundwater in the boreholes

Fig 2. The dependence of organic matter concentrations in the boreholes water on the water level in the boreholes

Concentrations of permanganate and bichromate oxidations in water of the observed boreholes significantly increase when water is closer to the soil surface: medium strong and strong correlations are established, except in the borehole 4.

Mathematical statistical analysis of the five-year investigation data is done. The indices that describe the groundwater pollution with organic materials are presented in Table 3.

Table 3. Statistics of groundwater hydrochemical parameters

Indice	COD	TOD
Average	10.8	28.7
Moda	2.4	23.0
Median	6.5	15.85
Min	2.4	4.56
Max	96	342
Number of analysis	34	34

Significant change of hydrochemical data is observed in the period of investigations (e.g. the lowest and the highest values of TOD differ 75 times, those of permanganate oxidation – 40 times). Although arithmetical averages are higher than median values, the data is the most scattered in the sphere of lower than the medial values. In mathematical statistics, median is the random variable value, which divides the variation line into two equal parts. Half of the values are lower or equal, the other half – higher or equal to the median. The relative suggestion is that the values lower than the median reflect normal, those that are higher – increased pollution condition. Then the obtained data estimates COD lower than 6.5 $mgO_2\ l^{-1}$, TOD lower than 15.85 $mgO_2\ l^{-1}$ as normal values. Higher values are attributable to the category of increased values. According to permanganate oxidation during the five-year period of investigations and based on the comparison with the median, the cleanest water is in the borehole 3 (Fig 3).

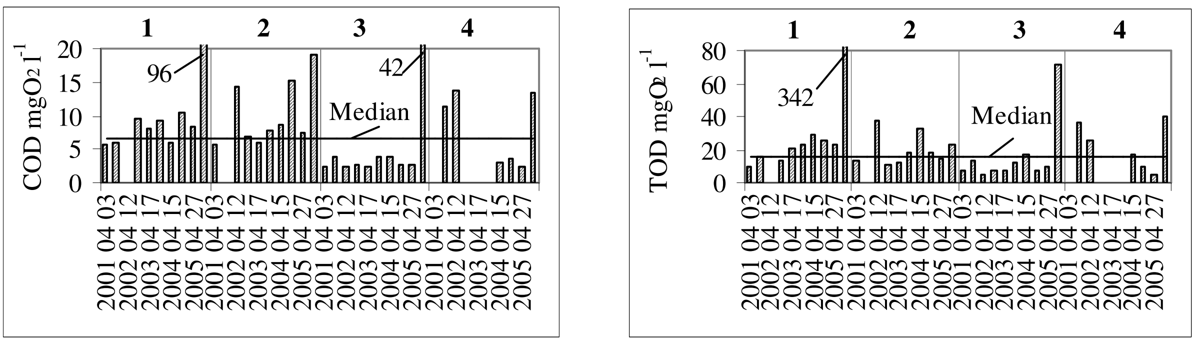


Fig 3. Permanganate and bichromate oxidation values in groundwater

In the sample, taken from this borehole in autumn of 2005 the permanganate oxidation was significantly higher than the median (6.1 times). According to permanganate oxidation, in the water sample, taken from the borehole 1 in autumn of 2005, the established value of this element was 13.9 times higher than the median. This had been influenced by increased amount of precipitation – 107% of multi-rate per year.

In the boreholes 2 and 4 the dynamic change of permanganate oxidation was significant: more than twice higher concentrations were established 3 times during five-year investigation period, other values were close to the median or lower.

According to CODS, which shows the oxygen deficit for the oxidation of chemical substances, the highest pollution level was in the western part of the irrigation fields, where the borehole 1 is located. The cleanest water was in the borehole 3, except one case in autumn of 2005, when TOD concentrations in water samples 4,5 times exceeded the median.

In the groundwater the permanganate oxidation shows the content of easily oxidized, bichromate oxidation – hardly oxidized organic material.

The organic material content as well as the values of these indices depends on the amount of organic material in the sediment, on its availability (from natural and anthropogenic sources) and decomposition posibilities. Under the Lithuanian conditions the background values of the permanganate number are not high – from 1.2 to 4.8 mg l^{-1} O_2, those of bichromate number – from 4 to 14 mg l^{-1} O_2. This is determined by the conditions, predominating in the groundwater, which are favourable for the oxidation of organic materials (Arustienė, 2006).

Under natural conditions, the groundwater of marshy and marine sediments and of wet soils is characterized by the highest content of organic matter. Usually, these sediments are rich in organic matter, which is not disintegrated due to the oxygen deficit. Values of the permanganate number reach 10, and those of bichromate number – 30 mg l^{-1} O_2 (Arustienė, 2006).

At the increasing ratio between bichromate and permanganate oxidations the amount of the organic matter, which is not permanganate oxidated, i.e. is hardly oxidated, also increases in the subsurface water. The bigger content of humus materials in the groundwater, the less permanganate oxidated organic material, or at the increasing absolute values of bichromate oxidation, the amount of hardly oxidated organic material also increases (Arustienė *et al.* 2001).

Based on the ratio of bichromate and permanganate oxidations the samples can be divided into separate groups, where the groundwater is characterized by certain conditions of the organic matter formation. The ratio values are grouped by the amount of the permanganate oxidated organic matter. The following groups have been distinguished: when bichromate and permanganate oxidation ratio is less than 1.3 – more than 75% of organic matter is permanganate oxidated; when bichromate and permanganate oxidation ratio changes from 1.3 to 2.0 (75 – 50 %); when bichromate and permanganate oxidation ratio changes from 2.0 to 4.0 (50 –25 %); when bichromate and permanganate oxidation ratio <4,0 (>25 %) (Table 4).

Table 4. The groups of groudwater, distinguished by the proportion of permanganate and bichromate oxidation

Proportion group by TOD and COD	TOD/COD	Part of the organic matter oxidized by permanganate %	TOD average mg O_2 l^{-1}	$C_{org.}$ average mg l^{-1}	COD average mg O_2 l^{-1}	Number of samples	% of total number of samples
Borehole 1							
1	<1.3	>75	-	-	-	-	-
2	1.3-2.0	50-75	12.1	4.5	7.5	2	22
3	2.0-4.0	25-50	74.9	28.1	23.0	6	67
4	>4.0	<25	28.5	10.7	6.1	1	11
Borehole 2							
1	<1.3	>75	20.6	7.7	17.1	2	22
2	1.3-2.0	50-75	12.5	4.7	7.3	2	22
3	2.0-4.0	25-50	22.8	8.6	8.4	5	56
4	>4.0	<25	-	-	-	-	-
Borehole 3							
1	<1.3	>75	-	-	-	-	
2	1.3-2.0	50-75	38.3	14.4	22.2	2	20
3	2.0-4.0	25-50	9.3	3.5	3.0	7	70
4	>4.0	<25	17.1	6.4	3.96	1	10
Borehole 4							
1	<1.3	>75	-	-	-	-	-
2	1.3-2.0	50-75	25.8	9.7	13.6	1	17
3	2.0-4.0	25-50	22.9	8.6	7.7	4	67
4	>4.0	<25	16.4	6.2	3.1	1	17

The presented data shows that values of bichromate oxidation are higher than those of permanganate oxidation and their fluctuations in different boreholes vary: in the borehole 1 – from 1.6 to 4.7, in the borehole 2 – from 1.2 to 2.7, in the borehole 3 – from 1.7 to 4.3, in the borehole 4 – from 1.9 to 5.4 times. This means that the organic matter, contained in the water, has not been decomposed to more simple forms, which brings to the statement the this matter reached the boreholes not long ago and is related with fresh pollution or high activity of microorganisms (Klimas, 2002).

According to the investigation results, the water that has formed in the borehole 2, located in the field, irrigated with slurry from the investigated object, belongs to the first group. In this water easily oxidated organic matter dominates – the established concentration of bichromate oxidation is 20.6, the mean of permanganate oxidation is 17.1 mg O_2 l^{-1}, the total amount of organic matter ($C_{org.}$ average – 7.7 mg l^{-1}). 22% of all samples from this borehole are permanganate oxidated, water of this group is not found in other boreholes. Thus, water of the borehole 2 contains easily oxidated materials.

All boreholes have nearly equal amounts of the second group water: the biggest amount of easily oxidated materials is established in the boreholes 1 and 2 – 22, in the borehole 3 – 20, in the borehole 4 – 17 % of the total number of samples. Higher average concentrations of permanganate oxidation are established in the boreholes 3 and 4 –22.2 and 13.6 mg O_2 l^{-1}, respectively. Thus, an easily oxidated organic matter dominates in water of these boreholes.

The highest concentrations of bichromate oxidation are established in water of the third group: 74.9 and 22.9 mg O_2 l^{-1}, respectively, total amount of organic matter ($C_{org.}$) also increases – in the boreholes 1 and 4 – 28.1 and 8.6 mg l^{-1}, respectively. Comparison with other two boreholes shows that here the process of organic pollution has been going on for a long time already. This is influenced by the uneven relief of the irrigated area – the borehole 1 is equiped in the lowland, where the surface wastewater, influencing the groundwater quality, accumulates during watering. In the borehole 4 the increased content of humus materials is under the influence of peat soil layer.

In the water of the fourth group a hardly oxidated material dominates as less that 25% of organic matter is permanganate oxidated. According to the values of bichromate oxidation, the highest concentration is established in the borehole 1 – 28.5 mg O_2 l^{-1}, the increased one - in the borehole 3 – 17.1 and in the borehole 4 – 16.4 mg O_2 l^{-1}. No hardly oxidated materials are established in the borehole 2, which brings to the statement that organic materials do not stay in water of this borehole. As permanganate oxidation values 6.1, 3.96, and 3.05 O_2 l^{-1} in the boreholes 1, 3 and 4, respectively, are lower than total amount of organic material (mean values of $C_{org.}$ are 10.7, 6.4 ir 6.2 mg l^{-1}, respectively, these boreholes receive organic materials from the environment. The biggest amount of hardly oxidated organic matter is established in the boreholes 1 and 4 - 11 and 17 % of the total number of samples, respectively. This is influenced by the groundwater flow direction, as the groundwater level is significantly lower in the boreholes 1 and 4 (1.67 and 1.77 m, respectively) than that in the boreholes 2 and 3 (1.09 and 1.28 m).

The data presented in the Table 4 shows that water of the groups 2 and 3 dominates in the groundwater of the investigated object. Thus, the fields irrigated with slurry have no influence on the groundwater as, according to scientific literature, water of the groups 2 and 3 dominates in the nature (Arustienė *et al.* 2001).

4. Conclusions

1. In all boreholes fluctuations of organic compounds are not significant with exception of one case in autumn of 2005, when due to increased precipitation concentrations of COD and TOD were exceptionally high. Stronger fluctuations of organic matter concentrations are established in the boreholes 1 and 4.
2. Fluctuation of water level in the boreholes is under the influence of meteorological conditions (r = 0.58) and the depth of the groundwater occurence: the closer to the soil surface, the stronger fluctuations of groundwater level (variation coefficients are 23 and 21 %).
3. Fluctuation of water level in the observed boreholes influences concentrations of organic materials: the closer water level is to the soil surface, the higher are COD and TOD concentrations.
4. The groundwater flow direction influences the increased amount of hardly oxidated organic materials in the groundwater of the boreholes 1 and 4 as here the groundwater occurs deeper than the boreholes 2 and 3.
5. The investigations show that the areas irrigated with slurry have negligible influence on the groundwater quality as the dominating water group composition is the same as that of the naturally formed water.

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