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Investigation of Water Quality in the Agricultural Area of Lithuanian Karst Region

Aurelija Rudzianskaitė

Additional information is available at the end of the chapter

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Abstract

In North Lithuania, karst processes are developing in the formations of the Upper Devonian represented by fissured gypsum-dolomite. The result of these processes on surface is the formation of sinkhole. The precipitation infiltrates into the karst aquifer not only through Quaternary sediments but also through karst sinkholes. The groundwater is extremely vulnerable to pollution in karst region. Agricultural practise is prevailing in this region. The objective of chapter is present of the results from various investigations on drainage, rivers, sinkholes and ground water quality in the agricultural area of Lithuanian karst region. This study was prepared on the basis of scientific publication analysis and the generalization methods were used. Based on this result, chemical composition of research water is mostly depended on the type of soil, meteorological conditions and land used. Higher amount of nitrogen and phosphorus are leached out in winter and spring periods.

Keywords: agriculture area, nitrogen compounds, total phosphorus, sinkhole, water quality

1. Introduction

The karst phenomena occur in different countries (Central America, North and South China, Slovenia, Estonia, Latvia etc.). The water in a karst aquifer is a major water resource in many regions of some countries [1].

The karst region is located in North Lithuania. Karst processes occur in carbonate rocks (gypsum-dolomite) forming different surface and underground karst features such as sinkholes, caves and caverns. Gypsum is soluble and hence its layers can dissolve and the protective cover strata of karst rock become unstable and may subside. In region, gypsum
occurs in contact with water and this causes subsidence problems. In agriculture land, these phenomena are inconvenient, but in urban area, they constitute a geological hazard that can seriously affect development and human safety [2].

The rate of chemical denudation of soluble rocks is one of the main factors determining the intensity of karst process. Gypsum denudation is mainly predetermined by water balance, which depends on meteorological conditions (precipitation and evaporation). The highest intensity of gypsum denudation is during the spring flood and the lowest in the dry period. Since 1978, the intensity of karst denudation has been increased by 30% [2, 3].

The main human activities influencing karst development are groundwater extraction and agriculture [4, 5].

Karst region is densely populated. The two districts (Biržai and Pasvalys) with more than 53,000 of inhabitants [6] are located in it. Soils are fertile; agriculture has been a traditional activity on these soils. Precipitation water dissolves not only natural salts from soils but also nutrient surplus from agriculture areas where unbalanced fertilisation rate was applied. Problems are caused by filtration of the water which is rich in salts and which pollutes groundwater. The major amount of precipitation infiltrates into the karst aquifer through Quaternary sediments, however, infiltration takes place through karst sinkholes as well [3, 7]. Karst groundwater becomes polluted frequently and in shorter time periods than water in non-karstic aquifers [1].

The purpose of this chapter is to present a short review of the research finding on water (drainage, stream, groundwater and sinkhole) quality in agricultural area of North Lithuanian karst region.

2. Geology of the North Lithuanian karst region

The total area of Lithuania is 65,300 km² and is situated along the south-eastern shore of the Baltic Sea [8]. The karst region is located in North Lithuania (mainly in Biržai and Pasvalys administrative districts) and borders with the karst territories of the neighbouring South Latvia (Figure 1).

The karst processes highly active are related to Upper Devonian gypsum and dolomites that occur beneath the Quaternary cover (Table 1). Mainly of Quaternary deposits consist of loam and sandy loam, sand, gravelly sand, gravel clay and silt; in some places, karstified rocks are overlain by the Pamūšis Formation (dolomitic marl, clay and other) and the Istras Formation (dolomite) of Upper Devonian [4, 7, 9].

Karst in the North Lithuania is matured not only at the land surface (sinkholes, karst shafts and dolines) but also in the subsurface (cavities and caves). In the region of active gypsum, karst (the area of 400 km²) is counted more than 8500 different size and shape sinkholes [4, 7, 9].

The thickness of the cover of the karst rocks in the area varies from parts of the first metre up to 70 m and has a common tendency to increase southwards and especially westwards.
Figure 1. Location of Lithuanian karst area: (1) Pre-quaternary carbonates; (2) area of intensive karst in North Lithuania (according to literature [2, 3]).

<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Formation</th>
<th>Index</th>
<th>Thickness, m</th>
<th>Description of sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
<td></td>
<td>Q</td>
<td>0–20</td>
<td></td>
<td>Moraine loam</td>
</tr>
<tr>
<td>Devonian</td>
<td>Upper</td>
<td>Pamusis</td>
<td>D,&lt;sub&gt;pm&lt;/sub&gt;</td>
<td>15</td>
<td>Clayey marl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Istras</td>
<td>D,&lt;sub&gt;ys&lt;/sub&gt;</td>
<td>3–9</td>
<td>Dolomite fissured</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tatula</td>
<td>D,&lt;sub&gt;tt&lt;/sub&gt;</td>
<td>11–15</td>
<td>Gypsum interlayers with marl and dolomite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pliavinia</td>
<td>D,&lt;sub&gt;kp&lt;/sub&gt;</td>
<td>6–12</td>
<td>Dolomite fissured</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D,&lt;sub&gt;js&lt;/sub&gt;</td>
<td>13–18</td>
<td>Dolomite clayey</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D,&lt;sub&gt;j&lt;/sub&gt;</td>
<td>2.0–9.9</td>
<td>Dolomite, marl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sventoji</td>
<td>D,&lt;sub&gt;sv&lt;/sub&gt;</td>
<td>90</td>
<td>Sand interlayer with siltstone and sandstone</td>
</tr>
<tr>
<td>Middle</td>
<td></td>
<td>Upninkai</td>
<td>D,&lt;sub&gt;up&lt;/sub&gt;</td>
<td>70–110</td>
<td>Sand clayey and clay</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Narva</td>
<td>D,&lt;sub&gt;nr&lt;/sub&gt;</td>
<td>~100</td>
<td>Clayey-carbonate deposits</td>
</tr>
</tbody>
</table>

Table 1. Stratigraphy of the Middle-Upper Devonian sediments in the North Lithuania [4].
Sinkholes are located in the areas with the cover thickness less than 25 m. In the areas where the cover thickness is up to 5 m, new sinkholes are forming intensively [9, 10].

3. Hydrogeology and hydrology of the North Lithuanian karst region

The North Lithuania karst region is located in the eastern part of the Baltic Artesian Basin. The active water change zone is up to 270 m thick and includes aquifers in the Quaternary and in the Upper Devonian (the Istras-Tatula, Kupiskis-Suosa and Sventoji-Upninkai) formations. This series of aquifers is underlain by the 60–100 m thick regional aquitard of the Narva Formation. The main source for recharge of the Istras-Tatula and Kupiskis-Suosa aquifers is shallow groundwater and surface water. All aquifers are being exploited to a different extent for drinking and domestic purposes and for industrial needs in this region [4, 11]. The infiltration rate of precipitation influences variations in level and chemical composition of groundwater. Ground collapse affects the Quaternary cover and permits ready recharge of surface water into the Upper Devonian aquifers. The intensive karst zone is referred to the areas with intensive water circulation in open gypsum systems [4, 11, 12]. Water of the aeration zone mostly infiltrates through vertical fissures until it reaches either horizontal channels or impermeable soil layer. A large amount of precipitation is collected in the bottom of the sinkholes, which are open holes or filled with permeable deposits [7].

In the karst region, most of the sinkholes are dry. Only during spring floods, they collect and temporarily retain atmospheric water or groundwater. In the course of time, the newly occurring sinkhole becomes shallow as a result of sedimentation processes and transforms into small bogs. As a result of a very good hydraulic link between the surface and groundwater, part of sediments is eliminated with the ground run-off [3]. Karst lakes and dry sinkholes make natural drainage systems through which precipitation, snow melting and overland flow access gypsum strata of the Lower Devonian [2, 12].

Karst rivers are recharged mainly through the precipitation. A low part of run-off is formed by the karst groundwater. Many rivers in the region cut upper part of the karst rocks and aquifers [4]. The groundwater discharge into the karst rivers of the region makes up from 25 to 40%, whereas in non-karst rivers it comprises only 8–16% of the annual run-off. The run-off of karst rivers in drought periods always exceeds the run-off of non-karst rivers [11].

4. Meteorological condition

The climate of the karst region as everywhere in Lithuania is intermediate between the maritime and continental climates. The annual infiltration of precipitation exceeds evaporation [8]. Air temperature observations in the active karst zone were started only in 1924 [12].

According to the data of Biržai Meteorological Station, the long-term annual averages of the main climatic characteristics are as follows: air temperature 6.6°C; precipitation 661 mm. The
mean temperature for July, the warmest month of the year, is 18°C, and for January, the coldest month, it is 3.6°C below zero. The rainfall during a warm season, from April to October, makes up 80% of precipitation. Long-term mean monthly amount of precipitation is varying from 36 to 81 mm.

Snow appears at the end of November and melts at the end of March. Thickness of snow cover reaches 6–44 cm. The mean depth of freezing is varying 17–99 cm.

During the last decades of the twentieth century, winter season temperature particularly near ground surface has increased significantly [12]. A distinct increase in air temperature has been observed since 1960. In karst region, the average temperature of January and February increased in the period 1961–1990 compared with the period 1931–1960 by 0.5°C [13].

The researchers [12] state that mean temperature in summer decreased until 1980 and then started to increase. Significant increases in annual, winter and summer temperatures were observed in 1994–2004. Increases in air temperature, during both cold and warm seasons, influenced other hydrometeorological characteristics and the solubility of gypsum.

5. Water quality

5.1. Agricultural drainage

Agriculture has been a traditional activity on soils of North Lithuania karst zone, whereas these soil are comparatively fertile. Agricultural areas in mainly administrative district Biržai make up 69% and in Pasvalys it is 79.9%, whereas in Lithuania it makes average 61.3% [14].

Lithuania is in the zone of surplus humidity, therefore, agricultural areas need soil drainage. The total drained land area occupies 47% of the Lithuanian land area and 86% of the agricultural land area, of which 87% is tile-drainage [8]. The leaching of nutrients from agricultural fields is one of surface and groundwater pollution sources. The most chemical matter contained in the soil is water-soluble; therefore, hydrological regime changes in the ecosystem are closely related to changes in nutritive leaching. By means of drain, much nitrate (NO₃⁻) and other elements contaminating the stream (drainage receivers) water are leached out. The study results [15, 16] in moraine sandy loam and glacial-lacustrine clay soil show that the drainage water influenced on water quality of streams via drained agricultural areas. As a matter of fact, the nitrogen amount leached via drainage, which has impacts on the concentration quantity in stream water (Figure 2). NO₃⁻ amount leached out by the drain water (determination coefficient 0.28–0.89), influence concentration fluctuations of the same compound in the stream. In view to phosphorus amount in the stream water, it was the result of other sources and factors. It was established [15] that stream water mineralization was greater, and its chemical composition depended on soil texture, fertilizers application and intensive land use in the drained areas. Mostly higher nitrate concentration was under the conditions of run-off formation after the dry period of the year; higher total phosphorus concentrations occurred when higher precipitation amount fall, particularly in summer.
It is known that the water quality depended on cultivated crops in this area. The highest concentration of nitrate nitrogen (NO$_3$-N) was found when growing potatoes and lower one was found when growing perennial grasses (Figure 3). However, concentration of total phosphorus (TP) increases in drainage water when growing perennial grasses [17, 18].

The studies [19] were carried out in spring crop fields (barley with perennial grass under crop) in sandy light loam and clay concluded that leaching of nitrate nitrogen and chlorine is mostly determined by fertilization rates; the effect of fertilization on leaching of potassium is less significant.

For Lithuanian conditions, the potential impact of climate change is associated with alterations in the precipitation pattern turning from snowfall to rainfall [20]. As a result, tile-drainage run-off volume tends to increase in the winter months.

The study [21] of clay and clay loam in the Lithuanian karst zone demonstrated that the average air temperature and precipitation from the period 1988 to 1999 exceeded the corresponding data from the period 1976 to 1987 by 1.3°C and 34 mm, respectively. A significant increase in the air temperature was observed in January and February (4.8°C). For this reason, a 3.3

Figure 2. Dependence of nitrate concentration in the stream water on the drainage function.

Figure 3. Nitrate nitrogen concentration (a) and total phosphorus concentration (b) in sandy soil water.
times higher drainage run-off volume was observed in the winter (January–February) and 1.6 times lower drainage run-off volume was identified in the spring (March–May) during the period 1988–1999 compared with the period 1976–1987. Concerning the changes of drainage hydrological regime in the cold period, the new environmental problems related to the increase of the leaching of nutrients were found.

Higher amount of nitrogen and phosphorus are leached out in winter and spring periods [18]. The peak concentrations of nitrate nitrogen occurred in winter and spring (due to the higher run-off) and at the onset of run-off after a dry period (due to the leaching of nitrogen that was not used during the dry period) [22].

5.2. River

The convection is mainly affected by transport processes of nutrients in karst region. In the first, nutrients with precipitation infiltrate via the aeration zone into the shallow aquifer and ending with surface or subsurface flow into the rivers [23].

Run-off and water quality of rivers are determined by a number of factors such as physical geographical conditions of the catchment climatic factors, human economic activity [24–26]. Inertia is a characteristic to the inflow of biogenic materials into the rivers. It is determined by forestless of the catchment, chemical properties of the soils and humus content [27]. In the last decade, the Mūša River catchment (karst region river) has received about 87% of the total nitrogen from arable land, waste water treatment, households and urban territories—10% and from wooded territories and pastures—3% [28]. Although agricultural production, use of mineral fertilizers and pesticides has decreased, concentration of nitrogen compounds in the rivers of agricultural influence has increased 2.5–3 times due to incorrect handling of manure, changes in the structure of agricultural lands and agrotechnics [29]. The researchers [30] stated that the stream pollution associated with agricultural activity, significantly water purified already at a 1.5 km stretch when stream flowing through forest-covered area. The average nitrogen concentration decreases about 3.0 times a day during the vegetation period and about 2.6 times a day during cold season of the year.

The highest total nitrogen amounts (about 36%) got to the rivers during the winter period (January–December), when there is no vegetation processes. In spring (March–April), in the period of snow melting, one third or 31% was scoured because of a higher run-off to the researched subcatchment and in the summer (May–August) and autumn seasons (September–November), 16 and 17% of all nitrogen falling to the subcatchment, respectively [31].

North Lithuania karst zone has specific geomorphological conditions. Here, the sinkholes that formed in the course of karst processes create favourable conditions for the interaction of surface and ground water. For example, direct zone of ground water nutrition is in the watershed of the Tatula and Apaščia Rivers. There exist more internal run-off zones of this kind, where most of the surface run-off gets to the horizons of soluble rocks [32]. Karst phenomena have the strongest impact on chemical composition of water in the middle reaches of the Tatula River and the lower reaches of the Lėvuo River [33].
Analysis of investigation results of small rivers of agricultural influence and big rivers of state monitored agricultural influence has established that bigger rivers have more intensive agitation processes in the flow and receive run-off from greater areas, while quality of small streams is under immediate impact of local factors and distinguished impact of particular factors in the catchments [34].

The peculiarities of hydrological regime and pollution were observed in an analysis of data from 1996 to 2005 in the rivers (Lėvuo, Tatula and Nemunėlis) of the karst region. Comparative analysis of water quality in rivers and stream (the Bėrė, tributary of the Mūša and the G-1, tributary of the Apaščia) is completed [35]. Only agricultural activity is developed in the catchments of these streams, there are no big settlements or concentrated pollution sources (Table 2).

In the period of investigations, concentration of nitrate nitrogen is up to 2.1 times smaller in the rivers than it is in the stream (Table 3). In streams of agricultural influence (the Bėrė and the G-1), cases of good ecological condition (NO₃₋N = 1.3–2.3 mg L⁻¹ [36]) make 33–38% of total number of measurements. Concentration of ammonium nitrogen (NH₄⁺-N) was similar and low in all the investigated rivers. During the period of investigations, the percentage of cases of good ecological condition (NH₄⁺-N = 0.10–0.20 mg L⁻¹) varied from 48 to 66.

<table>
<thead>
<tr>
<th>River/stream</th>
<th>Catchment area (km)</th>
<th>Forest (%)</th>
<th>Arable land (%)</th>
<th>Pasture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lėvuo*</td>
<td>1629</td>
<td>29</td>
<td>56</td>
<td>11</td>
</tr>
<tr>
<td>Tatula</td>
<td>453</td>
<td>14</td>
<td>73</td>
<td>10</td>
</tr>
<tr>
<td>Nemunėlis*</td>
<td>1892</td>
<td>15</td>
<td>51</td>
<td>30.6</td>
</tr>
<tr>
<td>Bėrė**</td>
<td>2.02</td>
<td>24</td>
<td>66</td>
<td>8</td>
</tr>
<tr>
<td>G-1**</td>
<td>1.63</td>
<td>14</td>
<td>46</td>
<td>35</td>
</tr>
</tbody>
</table>

*Catchment area in Lithuania country.
*Catchment area to the water quality study site.

Table 2. Description of study catchment of rivers and stream.

<table>
<thead>
<tr>
<th>NO₃₋N</th>
<th>Levuo</th>
<th>Tatula</th>
<th>Nemunėlis</th>
<th>Bėrė</th>
<th>G-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>Maximum</td>
<td>11.0</td>
<td>11.9</td>
<td>13.0</td>
<td>63.0</td>
<td>10.5</td>
</tr>
<tr>
<td>Average</td>
<td>3.08</td>
<td>3.25</td>
<td>2.82</td>
<td>6.01</td>
<td>3.67</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NH₄⁺-N</th>
<th>Levuo</th>
<th>Tatula</th>
<th>Nemunėlis</th>
<th>Bėrė</th>
<th>G-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0.004</td>
<td>0.007</td>
<td>0.007</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>Maximum</td>
<td>4.9</td>
<td>11.0</td>
<td>4.6</td>
<td>4.12</td>
<td>2.93</td>
</tr>
<tr>
<td>Average</td>
<td>0.518</td>
<td>0.485</td>
<td>0.364</td>
<td>0.401</td>
<td>0.306</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TP</th>
<th>Levuo</th>
<th>Tatula</th>
<th>Nemunėlis</th>
<th>Bėrė</th>
<th>G-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0.025</td>
<td>0.01</td>
<td>0.024</td>
<td>0.016</td>
<td>0.004-</td>
</tr>
<tr>
<td>Maximum</td>
<td>8.25</td>
<td>1.16</td>
<td>5.33</td>
<td>2.1</td>
<td>0.19</td>
</tr>
<tr>
<td>Average</td>
<td>1.139</td>
<td>0.144</td>
<td>0.232</td>
<td>0.122</td>
<td>0.045</td>
</tr>
</tbody>
</table>

Table 3. Nitrate nitrogen (NO₃₋-N), ammonium nitrogen (NH₄⁺-N) and total phosphorus (TP) concentrations in the river and stream water (mg L⁻¹).
Higher concentrations of total phosphorus are established in the Lėvuo and the Nemunėlis Rivers. Catchments of these rivers have more built-up territories, which may discharge various wastewaters. In the Bėrė stream, higher concentrations of total phosphorus might be determined by phosphorus content in the soil and rich fertilization.

Correlative analysis has established stronger correlation between concentrations of nitrate nitrogen in rivers and concentrations of ammonium nitrogen in streams, which assumes that change of these elements has common regularities. Concentrations of total phosphorus have very weak correlations, thus the reasons of their occurrence in water of the rivers should be different.

5.3. Sinkholes

Sinkhole water quality may worsen due to accumulation of organic materials (increasing peat content) or natural changes of environment (abrasion of slopes, overgrowth, etc.), while anthropogenic impact is minimal [37]. Sinkholes create favourable conditions for interaction of surface and groundwater. Identification of possible sources of sinkholes pollution is very important in the solution of groundwater safety problems.

The studies of water quality in sinkholes were carried out in the active karst zone in 2008–2012 (Figure 4) [38].

The research sinkholes were of different ages and have differently overgrown slopes (Table 4).

In most cases, nitrate nitrogen (0–0.97 mg L\(^{-1}\)) and total phosphorus (0.017–0.042 mg L\(^{-1}\)) concentrations in water of sinkholes were similar to this concentration in precipitation.

Figure 4. Scheme of location of studied sinkholes: (1) studied sinkholes; (2) river; (3) Biržai town; (4) Širvena Lake; (5–8) land group (5—first, 6—second, 7—third, 8—fourth).
Water quality of sinkholes depend on age sinkholes and slopes ground. The higher amounts of nitrate nitrogen (0–32.2 mg L\(^{-1}\)), total phosphorus (0.36–1.32 mg L\(^{-1}\)), sulphate (2.7–172.0 mg L\(^{-1}\)) and the amount of organic matter according to biochemical oxygen demand (1.91–76.0 mg O\(_2\) L\(^{-1}\)) were in water of peat-filled sinkholes than in water of sinkholes with mineral ground slope (young sinkholes) (Table 5). Water of sinkhole that is overgrown with trees and shrubs has the highest nitrate nitrogen (up to 32.2 mg L\(^{-1}\)) and sulphate (up to 172 mg L\(^{-1}\)) concentration.

### Table 4. Description of the research sinkhole.

<table>
<thead>
<tr>
<th>Sinkhole No</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The sinkhole (area is 0.105 ha) was old age (emerged 100–1000 years ago [39]) and peat-filled, covered with marsh vegetation, it was usually dry in the summer. The sinkhole was surrounded by meadows, at 25 m distance from the stream G-1</td>
</tr>
<tr>
<td>2</td>
<td>The sinkhole (few merged sinkholes) was old and peat-filled, overgrown with trees and shrubs, it is dry in the summer. The trees and shrubs covered area was 0.572 ha</td>
</tr>
<tr>
<td>3</td>
<td>The sinkhole (area is 0.021 ha) was a new one (emerged in the last 20 years). Water regularly filled it about 2 m from the ground surface. Slopes were mineral ground, mostly overgrown with grass vegetation, but fast growing shrubs, abrasion going on the slopes. The sinkhole was surrounded by meadows</td>
</tr>
<tr>
<td>4</td>
<td>The sinkhole (area is 0.057 ha) was young (emerged 20–100 year ago), water filled about 0.5 m above the ground surface, the coast was covered with wetland vegetation. In this environment, there were many dry and old sinkholes covered with grasses</td>
</tr>
</tbody>
</table>

Water quality of sinkholes depend on age sinkholes and slopes ground. The higher amounts of nitrate nitrogen (0–32.2 mg L\(^{-1}\)), total phosphorus (0.36–1.32 mg L\(^{-1}\)), sulphate (2.7–172.0 mg L\(^{-1}\)) and the amount of organic matter according to biochemical oxygen demand (1.91–76.0 mg O\(_2\) L\(^{-1}\)) were in water of peat-filled sinkholes than in water of sinkholes with mineral ground slope (young sinkholes) (Table 5). Water of sinkhole that is overgrown with trees and shrubs has the highest nitrate nitrogen (up to 32.2 mg L\(^{-1}\)) and sulphate (up to 172 mg L\(^{-1}\)) concentration.

### Table 5. Sinkholes and precipitation water quality (mg L\(^{-1}\)).

<table>
<thead>
<tr>
<th>Sinkhole No</th>
<th>Precipitation [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_3)-N</td>
<td>Minimum 0 0 0 0 0.04</td>
</tr>
<tr>
<td></td>
<td>Maximum 0.97 32.2 0.189 0.059 2.21</td>
</tr>
<tr>
<td></td>
<td>Average 0.10 11.39 0.02 0.01 0.73</td>
</tr>
<tr>
<td>TP</td>
<td>Minimum 0.042 0.036 0.017 0.013 0.021</td>
</tr>
<tr>
<td></td>
<td>Maximum 1.32 1.03 0.132 0.118 0.301</td>
</tr>
<tr>
<td></td>
<td>Average 0.42 0.35 0.05 0.05 0.111</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>Minimum 2.7 2.0 1.4 1.2 -</td>
</tr>
<tr>
<td></td>
<td>Maximum 50.0 172.0 42.0 31.0</td>
</tr>
<tr>
<td></td>
<td>Average 15.4 82.7 16.4 9.4</td>
</tr>
<tr>
<td>BOD</td>
<td>Minimum 2.13 1.91 1.56 1.41 -</td>
</tr>
<tr>
<td></td>
<td>Maximum 32.0 16.90 14.20 11.0</td>
</tr>
<tr>
<td></td>
<td>Average 12.61 8.45 4.0 1.41</td>
</tr>
</tbody>
</table>

SO\(_4\) – sulphate.
BOD – biochemical oxygen demand.

Table 5. Sinkholes and precipitation water quality (mg L\(^{-1}\)).
Analysing [40] the regime of water in four peat-covered sinkholes and groundwater of their vicinity, it was determined that during the periods of snow thaw and heavy rains the sinkholes receive subsurface and ground water from the vicinity, while during the dry period water accumulated in peat media of the sinkholes flows into the vicinity. The water in sinkholes gets abated and the sinkholes were draining groundwater intensively during dry period. The investigation [41] in the dry period shows that water level of peat-filled sinkholes was higher and nitrate nitrogen, chlorine and sulphate concentration were smaller. In this period, the sinkhole water percolating into a stream, it refills and at the same time attenuates stream water and makes its quality better, although a larger concentration of ammonium, nitrate and total phosphorus makes it worse.

5.4. Groundwater

Problems are caused by filtration of the water rich in salts, which pollute groundwater. Polluted drinking groundwater is dangerous for people’s health. The salt-saturated water becomes more aggressive and intensifies karst process of the rocks lying below, which definitely causes a risk to people’s property or event life [42].

The rural dwellers (53% of all rural population in Birzai and 70% in Pasvalys districts) are mainly using the ground water from individual dug wells. There are over 19,000 dug wells in Birzai district. They can be characterized as wells in which the admissible water pollution rates are exceeded two or more times. In 2004, microbiological analyses were carried out in 77 town and 278 village wells. The analyses showed that drinking water did not correspond to the hygienic standard in 28.5% of town and 20.5% of village wells. Town wells had increased chemical pollution and village wells had increased microbiological pollution of water [43]. The nitrate concentration in wells in the moraine sandy loam was higher than in the glacial lacustrine clay and it exceeded the highest allowed value (HAC 50 mg L$^{-1}$) from 1 to 33 times (Figure 5). The highest quantity of organic substances (according to permanganate oxidation) were found in the wells of glacial lacustrine clay and shallow wells (moraine sandy loam) [44]. The greatest amounts of organic substance were determined when the level of water fluctuated near to the earth’s surface (could get together with a surface flow) and near to the ground of well (the amount of organic substances in the water has increased through ground deposits) [45]. The highest pollution of well water with organic matters is observed in summer [46].

Figure 5. Nitrate concentration (a) and amounts of organic substance (b) in the drinking water wells. Wells 1–5 were identified in moraine sandy loam; wells 6 and 7 were identified in glacial lacustrine clay.
The study [42] shows that the type of soil (mineral and peat) and location of a well in respect of sinkholes have impacts on chemical composition of groundwater. Sum of ions (mineralization) in water of peat soil was a 1.1–1.2 times larger than in water of mineral soil (Table 6). According to the mineralization level and distribution of anions, the groundwater in a sinkhole (well 4) contained the largest amounts of hydro-carbonates (8.5 meq L\(^{-1}\)), calcium (5.9 meq L\(^{-1}\)), magnesium (2.9 meq L\(^{-1}\)) and potassium (0.26 meq L\(^{-1}\)); the distribution of cations was similar to the water samples collected from other wells (Ca\(^{2+}\) > Mg\(^{2+}\) > Na\(^{+}\) > K\(^{+}\)), but distribution of anions was different (HCO\(_3\)\(^{-}\) > Cl\(^{-}\) > SO\(_4\)\(^{2-}\) > NO\(_3\)\(^{-}\)) that is SO\(_4\)\(^{2-}\) ions were replaced by Cl\(^{-}\).

Groundwater level fluctuation is influenced by precipitation and melting snow water amount. The most distinct fluctuations of groundwater level were observed in mineral soil where the difference was 3.2 m and in peat soil groundwater level fluctuations were 1.7 (well 2 installed near the stream) and 0.85 m (well 4 installed in a sinkhole).

The hot and dry summers, recurrent droughts, very uneven distribution of rainfall (over the year and in the territory) had a negative impact on groundwater resources [47]. Changes of groundwater level regime, especially seasonal, will not necessarily be useful for other elements of the environment to which groundwater is closely linked [48]. Changes of groundwater mineralization depend on its level fluctuation [42]. A larger ion sum results in lower groundwater level. A stronger correlation was determined between groundwater levels and chemical compounds (Ca\(^{2+}\), Mg\(^{2+}\), SO\(_4\)\(^{2-}\) and HCO\(_3\)\(^{-}\)) concentrations inducing groundwater mineralization. During the vegetation period (April–October), when water level was raised nearer by ground surface in mineral soil, nitrate concentration was increasing. The water levels subside for concentrations amount was insignificant. In peat, the groundwater level fluctuation and NO\(_3\)\(^{-}\) concentration have no connection.

<table>
<thead>
<tr>
<th>Well No</th>
<th>K(^{+})</th>
<th>Na(^{+})</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>NH(_4)(^{+})</th>
<th>HCO(_3)(^{-})</th>
<th>SO(_4)(^{2-})</th>
<th>Cl(^{-})</th>
<th>NO(_3)(^{-})</th>
<th>Ion sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>0.03</td>
<td>0.05</td>
<td>0.31</td>
<td>0.25</td>
<td>0.05</td>
<td>0.24</td>
<td>0.32</td>
<td>0.06</td>
<td>0.03</td>
<td>1.34</td>
</tr>
<tr>
<td>Groundwater in mineral soil</td>
<td>1</td>
<td>0.05</td>
<td>0.31</td>
<td>5.2</td>
<td>2.4</td>
<td>0.02</td>
<td>6.7</td>
<td>0.62</td>
<td>0.26</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>0.21</td>
<td>5.0</td>
<td>2.1</td>
<td>0.04</td>
<td>6.7</td>
<td>0.21</td>
<td>0.18</td>
<td>0.12</td>
<td>14.6</td>
</tr>
<tr>
<td>Groundwater in peat</td>
<td>2</td>
<td>0.11</td>
<td>0.44</td>
<td>5.2</td>
<td>2.4</td>
<td>0.45</td>
<td>8.0</td>
<td>0.16</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>0.16</td>
<td>0.23</td>
<td>5.9</td>
<td>2.9</td>
<td>0.24</td>
<td>8.5</td>
<td>0.20</td>
<td>0.28</td>
<td>0.02</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Table 6. Average chemical composition (meq L\(^{-1}\)) of precipitation and groundwater between 1997 and 2002 [42].

6. Water protection

Based on the geological and hydrogeological studies, the karst area was divided into two parts. The first part is territory of active karst development. The second part is karst protection
zone [4]. Depending on the degree of vulnerability of the karst terrain (thickness of overlying sediments, density of sinkholes, recharge-discharge characteristics and the amount of groundwater pollution), the active karst zone was subdivided into four land groups (Figure 6).

Each of these land groups has a different level of restriction imposed on agricultural activity within it [49]. These are land group 1 (from 5 to 20 sinkholes km\(^{-2}\))-perennial grass should compose at least 20% of crops. Fertilizers are limited up to 100 kg ha\(^{-1}\) total nitrogen of mineral fertilizer and manure. Land group 2 (from 21 to 50 sinkholes km\(^{-2}\))-perennial grass should compose at least 30% of crops. Fertilizers are limited up to 80 kg ha\(^{-1}\) total nitrogen of mineral fertilizer and manure. Land group 3 (from 51 to 80 sinkholes km\(^{-2}\))-perennial grass and grazing should compose at least 40% of crops. Fertilizers are limited up to 70 kg ha\(^{-1}\) total nitrogen of mineral fertilizer and manure. Land group 4 (>80 sinkholes km\(^{-2}\))—meadows and forest are allowed. Melliferous and drug plants should be grown. Fertilize can only use manure.

Figure 6. Scheme of distribution of karst area according to number of sinkholes: (1) state’s border; (2) North Lithuanian karst region border; (3–6) land group (3—from 5 to 20 sinkholes km\(^{-2}\); 4—from 21 to 50 sinkholes km\(^{-2}\); 5—from 51 to 80 sinkholes km\(^{-2}\); 6—>80 sinkholes km\(^{-2}\)) (according to the literature [49]).
In all land groups, a 5 or 10 m (according to the slope of the surface) width protection zone is required around each sinkhole.

In an alternative approach, the protection of karst water from pollution in the agriculture area is sustainability agriculture practce.

7. Summary

North Lithuanian karst region, as the mostly Lithuanian territory, is used for agricultural practise. The leaching of nutrients from agricultural fields is one of surface and groundwater pollution sources. Polluted drinking groundwater is dangerous for people’s health. The salt-saturated water becomes more aggressive and intensifies karst process of the rocks lying below, which definitely causes a risk to people’s property or event life.

Most chemical matter contained in the soil is water-soluble; therefore, hydrological regime changes in the ecosystem are closely related to changes in nutritive leaching. By means of drain, much nitrate nitrogen and other elements contaminating the stream (drainage receivers’) water are leached out. The stream water mineralization was determined by soil texture, type of land use and fertilizers applied in the areas drained. Higher amount of nitrogen and phosphorus are leached out in winter and spring periods and at the onset of run-off after a dry period (due to the leaching of nitrogen that was not used during the dry period).

The bigger rivers have more intensive agitation processes in the flow and receive run-off from greater areas, while quality of small streams is under immediate impact of local factors and distinguished impact of particular factors in the catchments. The concentration of nitrate nitrogen is up to 2.1 times smaller in the rivers than it is in the stream.

Chemical composition of groundwater is mostly depended on the type of soil and location of a well in respect of sinkholes and meteorological conditions. In the dry period, peat-filled sinkhole water is at higher level and less polluted with nitrate nitrogen, chlorine and sulphate compounds.

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