Risk Assessment of the Agricultural Pollution with Nitrates in Latvia
Lauksaimniecības izraisītā nitrātu piesārņojuma riska analīze Latvijā

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Abstract. The legislation of the EU and Latvia obligate the control and mitigation of the environmental impact of the agriculture (nitrate pollution). The article summarises the main results arising from long-term measurements of nutrient concentrations within agricultural run-off monitoring programme. The assessment of the long time data series (1994-2007), obtained from the non point source agricultural run-off monitoring programme, has shown that nitrate nitrogen concentrations depend on the scale of monitoring system (drainage plot, drainage field, small catchment) and intensity of agricultural production system. The available long-term data series and use of the probability curves allow the assessment of the variations of nitrate concentration on the scale of the plot, drainage field and small catchments. The article provides the estimation of risk exceeding the threshold limits (11.3 mg L⁻¹ NO₃-N) of the nitrates concentrations. High risk to reach nitrates concentrations over the limits has been found (about 30% of samples) in the field drainage of Bērze monitoring site. With regard to the small catchments’ scale nitrates concentrations over limits could be expected (15% of samples) in the Bērze catchment with high intensity of agriculture. To some degree the presented study and interpretation of nitrate data may be used for designation of water quality standards and designation of nitrate vulnerable zones.

Key words: agriculture, nitrates, pollution risk.

Introduction
Most of the human activities may have a significant impact on the environment. For agriculture the pollution risk is related to accumulation of persistent contaminants and to leaching of nutrients to the groundwater and surface water (European Environment Agency, 2005; Executive Summary …, 2003). At the moment HELCOM is working extensively to control the environmental impact of agricultural sector in the Baltic Sea coastal states (HELCOM Baltic …, 2007). Intensive farming production systems result in the nutrient pollution of inland waters. According to the PLC assessments agriculture by far is the polluter number one for the Baltic Sea basin (The Baltic Marine …, 2003; Executive Summary …, 2003) and the main source of nitrogen implication as the basic nutrient in the development of algal blooms, whether in fresh, estuarine, coastal or marine waters.

Certainly the share of agricultural contribution to the non-point source pollution varies widely due to a complex impact of land use, cropping system, soil type, climate, topography, hydrology, animal density and nutrient management techniques (Position Statement …, 2000). However, it is clearly set out that in the natural water ecosystems nutrient pollution always is presented to some extent and could be determined by the background concentrations. In other words, water quality is a net result of both natural and anthropogenic factors due to the different origin of the nutrients. Most often, we are not being able to see visually poor run-off quality in the tile drains, drainage channels, and small streams. However, it is clearly set out by many authors (Vagstad et al., 2001a; 2001b; Haygarth, Jarvis, 2002; Guidelines for the Monitoring …, 2004; Kyllmar et al., 2006) that water leaching from the soil transports large amount of the nutrients (N; P, K and microelements) that can contribute to the nutrient enrichment of the surface water ecosystems and eutrophication.

Both the EU Nitrates Directive (ND) and Water Framework Directive (WFD) require that Latvia like all the Member States control the impact of agriculture on the surface and ground waters (Jansons et al., 2005). When assessing the results of water monitoring, it should be considered whether all the territory of Latvia or only part of it, with the highest
impact of agriculture measured in terms of high nitrate content (≥50 mg L⁻¹) or eutrophication phenomena, should be designated as nitrate vulnerable zones (NVZs). In addition, the risk that in the near future freshwater bodies or marine waters may contain more than 50 mg L⁻¹ nitrates (11.3 mg L⁻¹ NO₃⁻N) become eutrophic, if actions in agriculture are not taken, also is a relevant aspect for designation of the NVZs. Due to the lack of monitoring data the first designation of vulnerable zones in Latvia was performed using GIS Multi-Criteria decision-making analysis. The risk assessment was based on the data on soil and groundwater media, run-off, potential erosion risk, agricultural activities, such as agricultural land and arable land use, animal density, soil drainage, and application of fertilizers (Jansons et al., 2005). Factor weights have been computed according to the results of expert evaluation. The resulting impact data layer yields a map for the potential agricultural risk areas in Latvia. Finally, part of the territory in the central part of country, in the Lielupe river basin or Dobele, Jelgava, Bauska and Riga administrative regions, with the most intensive agricultural production and highest pollution risk today, was designated as NVZs. The designation of NVZs should be revised every four years; unless not the whole territory of the country is designated as NVZ.

In conformity with the EU and national legislation (LR MK noteikumi Nr. 531, 2001) Water monitoring and Action Programme should be implemented in Latvia for water quality assessment and nutrient pollution control. The environmental conditions of the Baltic Sea, and particularly the Gulf of Riga, are still a matter of great concern. The results from the Gulf of Riga project showed that eutrophication still prevail with a moderately high primary production. The results have also showed that the Gulf of Riga is basically nitrogen limited (Stalnacke et al., 1999; Vagstad et al., 2000).

The considerable amount of the nitrogen concentration data and information necessary to carry out risk assessments is already accumulated during the implementation of the agricultural run-off monitoring programme in Latvia University of Agriculture. However, the study also shows that the agricultural contribution to the nutrient loads is extremely variable over time and space (between catchments). Therefore nutrient concentrations usually vary considerably from year to year and interannually (Haygarth, Jarvis, 2002; US Geological Survey, 1999; Stalnacke, 1996). That large amount of data and information is far from being fully and adequately used. There is need to develop capacities to interpret data and to carry out risk assessments to be able to conduct a detailed evaluation of nitrogen concentrations, and making it more easy to draw conclusions on the vulnerability of agricultural territories.

Materials and Methods

HELCOM recognizes (HELCOM Baltic …. 2007) that countries should apply harmonised principles and methods for quantifying non point losses throughout the Baltic Sea catchment area in order to obtain comparable and reliable estimates on the waterborne inputs from both point sources and non-point sources entering into the Baltic Sea. The similar task is proposed and attempts on harmonisation have been made in different EU documents and research papers (Implementation of Council Directive …, 2002; Guidelines for the Monitoring …, 2004; Ital, 2005). Agricultural run-off monitoring network in Latvia was established with the assistance of the Nordic countries (Sweden, Norway) using the same monitoring methods and technologies (Jansons, 1998; Vagstad, 2001a; Lauksaimniecības noteču …, 2003; Deelstra et al., 2004).

The soils at the monitoring sites are imperfectly to poorly drained. Therefore most of the agricultural land in the small catchments is drained with tile drains (depth 1.1-1.3 m, and internal spacing between drains 10-32 m). Tile drainage in drainage fields has surface run-off inlets, which may result in direct inflow of eroded soil particles during flood periods. Due to the presence of a calcareous material soil pH is rather high (pHₑᵤₜ=6.7-7.9). The status of major plant nutrients ranges from good (Bērze site: Cₑᵣₑ=1.2%, N=0.15%, Pₐₒₚₐₜₑₐₑₑₒₑ=10.5 mg 100 g⁻¹) to moderately good (Mellupīte site: Cₑᵣₑ=1.2%, N=0.08%, Pₐₒₚₐₜₑₐₑₑₒₑ=8.3 mg 100 g⁻¹).

Due to the specific water balance conditions of humid climate (Jansons, 1998; Vagstad et al., 2000; Deelstra et al., 2005; Ital, 2005; Kyllmar et al., 2006), the assessment of the nutrient leakage in Latvia has been implemented in 3 geographical scales/levels (Fig. 2):

firstly, soil, plant, nutrient, and water relationships could be studied on the plot level. In such experiments data of the nutrient leaching from farmland with both different application rates and times of mineral or organic fertilizers for various crops and soil management might be studied;
secondly, nutrient losses from arable land could be measured on a field level. Field scale run-off represents an integrated effect of farming practice, crop rotation, application of fertilizers, etc. on the water quality;

the third level is a small catchment (watershed) scale. The climate and agricultural practices influence the nutrient transport in a stream. There are no point sources in the catchments. The integrated influence on run-off of variations in farming practices, erosion, soil, and topography within the drainage basin might be studied in a better way than in the field scale.

The measurements (Table 1) in Bērze, Vienziemīte and Mellupīte catchments were based on fixed measurement structures, i.e., Crump, V-shape and combined profile weirs and automatic data loggers, and sampling equipment for continuous water level registration and automatic water sampling. Collection of the composite water samples were based on a flow-proportional sampling procedure. One flow-proportional composite sample consists of a large number of sub-samples gathered during a period of one month. Logger triggered sampling frequency was 10-15 sub-samples per day. Tipping buckets with magnetic switches are installed in the cellar of a monitoring station and have been used for drainage plot discharge recording and water sampling. The measurements in the Bērze and Vienziemīte catchments were started in 1994, while in 1995 they were started in the Mellupīte catchment.

The Bērze catchment is characterised by relatively intensive crop production as compared to the present average conditions in Latvia. The landscape is flat lowland and 98% of the catchment soils are cultivated. Due to natural high soil fertility, winter wheat, sugar beets and winter rape have become the main crops in the Bērze catchment. The share of arable crops increased up to 80-90% during 1997-2007. Farmers use modern equipment, and rather intensive technology for the Baltic conditions, e.g., an average fertilizer application amounting to 100 kg N ha$^{-1}$ year$^{-1}$, but in few fields the use of fertilizers reached 300 kg N ha$^{-1}$ year$^{-1}$ in 2007.
The landscape in Vienziemīte catchment is rather hilly for the Baltic conditions. Soil, slopes, and market conditions are less favourable for agriculture, and only two farms in the catchment are producing something for the market. Almost no fertilizers (only 4-5 kg N ha\(^{-1}\) year\(^{-1}\)) were applied in the catchment. During the measurement period 1994-2007 most of the farmland was abandoned land or low productivity grassland. The Vienziemīte catchment is a typical example of low input agricultural land use, and can be used as a reference site for diffuse pollution.

The Mellupīte catchment represents the average farming conditions and could be considered typical for the present agriculture in Latvia. Several large farms are using intensive agricultural technology, whereas a few farms are producing only for self-consumption with low fertilization rates and without pesticides. During the period of 1994-2007 the use of the fertilizers and pesticide increased slowly, the average use of mineral fertilizers changed from 10 to 70 kg N ha\(^{-1}\) year\(^{-1}\). The highest application rates in farms with intensive technology reached 155 kg N ha\(^{-1}\) year\(^{-1}\) in 2007.

Nitrogen analyses of water samples (N\(_{\text{tot}}\), NO\(_3\)-N, NH\(_4\)-N) were carried out according to the standard methods (LVS 340:2001, LVS 339:2001, LVS ISO 7150/1-1984). Laboratory analyses with the standard methods were combined with measurements of nitrate concentrations with the multiparameter sonde YSI 6920-C-M. Sonde monitors several water quality parameters simultaneously at the user-selectable intervals. In order to provide an accurate assessment of the short term changes, in response to the changes in precipitation and discharge, the measurements with sonde were started in autumn 2006. Nitrate sensor application range is 0-200 mg L\(^{-1}\) for NO\(_3\)-N, resolution (0.001-1 mg L\(^{-1}\) for NO\(_3\)-N) depends on the measurement range, and sensor accuracy is ±10% of reading. The analyses of the soil mineral nitrogen were carried out in the “Centre for Agrochemical Research” with standard methods (LVS EN ISO/IEC 17025).

**Results**

**Nitrate Concentrations**

**Small catchment and drainage field scale.** Generally, during dry periods in summer drainage and sometimes run-off in the catchment scale was not observed. Composite water samples in drainage and catchments’ scales were analysed once a month. Total number of analysed (1994-2007) water samples depended on site, and both in drainage and catchments’ scale ranged between 120 and 170.

The highest average nitrate concentrations were observed in Bērze monitoring station (Table 2).
Nutrient concentrations in all monitoring sites varied throughout the year, largely in response to the changes in precipitation, ground water level and flow rate. The coefficient of the variation ranged from 42% to 99%. In the autumn of 2006, after dry and hot summer, the highest nitrate values were measured. With regard to the Nitrate Directive, it should be noted that the threshold values of nitrate (11.3 mg L\(^{-1}\)) established by directive was often exceeded.

Nitrogen concentrations in drainage run-off from fields with intensive farming were higher than in the catchment scale in Bērze and Mellupīte monitoring sites. These monitoring sites both catchments’ and field scale nitrate concentrations show up ward trend (Fig. 3). In Vienziemīte site the variation of nitrate content between the field and catchment scale in not high, and concentrations are close to natural background values. There, with low input agriculture,
long term water quality data does not show nitrate upward trend.

**Drainage plot scale.** Due to the limited size of one plot (0.12 ha), and therefore relatively small total length of drainage pipes collecting water flow, the duration of run-off period, total discharge and number of collected samples was smaller than in the field and catchments’ level. Plot drainage discharge most often occur during spring and autumn flood periods. Plots have no structures for surface run-off inflow, i.e., the impact of water erosion on water quality is excluded. Therefore, it is not surprising that nitrate content variation that ranged from 41% to 59% (Table 3) was lower than in drainage field and catchments’ scale.

**Discussion**

**Evaluation of the nitrate pollution risk.** The contribution of agriculture to the non-point source pollution varies widely as a complex function of land use, cropping system, soil type, climate, topography, hydrology, animal density, and nutrient management techniques (Position statement …, 2000). Moreover, long term data series of nutrient values (1994-2007) reflect the variation in water quality in both spatial and temporal terms, e.g., from year to year and interannually. Probability analysis that is a common method in hydrologic studies could be used to describe the water quality, e.g., the likelihood of an event where an event is defined as occurrence of a specified value of the random variable (McCuen, 1998; Ward, Robinson, 2000; Gordon et al., 2004). A number of different probability functions can be used to represent a random variable (water sample), and to determine the probability of occurrence. A probability curve is presented as a cumulative distribution function. Gamma frequency curve was recommended by Sudars et al. (2005) to evaluate risk of the water pollution in agricultural point source monitoring catchments. Small catchments’ run-off quality described with the probability curves for the nitrate values are presented in Figure 4. Comparison of all water samples, tested with these reference values, showed that approximately 85% of the Bērze catchments samples (Fig. 4) and over 70% of the field drainage samples had values below the threshold level.

In the Mellupīte site only few water samples from both catchment and drainage field values had exceeded threshold limits of the directive. In the Vienziemīte site high nitrate pollution risk was not observed.

Both winter (October to March) and the concentrations in early spring, measured just before the significant algal growth started in water bodies, should be estimated as an important factor contributing eutrophication phenomena of surface water bodies (Guidelines for the Monitoring …, 2004). Moreover, the relatively large proportion of N loss during the winter period indicates that a considerable part of diffuse pollution has been generated through infiltration into the frozen or partly frozen soils. Therefore the assessment of winter concentrations of nitrates in the drainage (Fig. 5) and small catchments’ run-off has high importance considering control of the nutrient leakage.

The average nitrate concentration has a tendency to increase in the plots with higher fertilization rate and with animal manure applications, e.g., nitrate concentration in run-off from non fertilized plots was lower by 2.1 mg L\(^{-1}\) than from plots with slurry application. Difference of the mean values is small. In that context, it can be mentioned that the nitrate trends have not statistical significance for the given number of samples and confidence level \(\alpha=0.05\). Therefore, our risk analysis is based on the preposition that concentrations of nitrates in the discharge from plot drainage represent one sample population.

**Extremes of the nitrate concentrations.** Monthly sampling frequency is insufficient to cope with the high variability of nutrient concentrations. Especially for the smaller catchments and field drainage run-off, the monitoring results suggest the necessity to consider hourly water quality measurements for better

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**Table 3**

<table>
<thead>
<tr>
<th>Fertilization</th>
<th>Number of samples</th>
<th>(\text{NO}_3^-\text{N concentrations, mg L}^{-1})</th>
<th>Standard deviation</th>
<th>CV, %</th>
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<tr>
<td></td>
<td></td>
<td>average</td>
<td>minimal</td>
<td>maximal</td>
</tr>
<tr>
<td>Without fertilizers</td>
<td>52</td>
<td>9.37</td>
<td>3.65</td>
<td>23.96</td>
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<tr>
<td>Normal fertilization</td>
<td>49</td>
<td>10.02</td>
<td>3.00</td>
<td>30.10</td>
</tr>
<tr>
<td>rate</td>
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<td>48</td>
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<td>23.76</td>
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<tr>
<td>rate</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Solid manure</td>
<td>48</td>
<td>11.11</td>
<td>3.80</td>
<td>39.97</td>
</tr>
<tr>
<td>Slurry</td>
<td>48</td>
<td>11.44</td>
<td>5.00</td>
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</table>
interpretation of hydrological processes and their possible effects on nutrient loss. Nitrate monitoring with sonde at the user-selectable short time intervals started in autumn 2006. Surprisingly high nitrate values in Bērze drainage field run-off were found in November 2006, when drainage run-off appeared after dry summer-autumn period (Fig. 6). Nitrate concentration (41.6 mg L⁻¹ in 21 November 2006) found in the water sample analysed in laboratory, proved the accuracy of measurement results with sonde.

About 40% of the Bērze drainage water samples (Fig. 4) and over 5% of the Mellupīte field drainage samples had values higher than the threshold level.
Due to the climate in Latvia the cycles of drying and wetting may have a significant effect on the rate of mineralization, and freezing and thawing of the soil may stimulate elevated soil nitrate concentration upon thawing. The nitrate anion is highly soluble in water, and therefore subject to movement in any water leaving the soil by drainage down the profile and run-off from the soil surface. Most of run-off and erosion events take place during winter conditions. Both winter and annual concentration values obtained from probability curves are presented in Table 4. Generally, except part of Mellupite drainage field data, winter data show higher pollution risk than full year data set. The problem, with regards to mitigation of nitrate leakage, is that farmers have not wide variation of actions needed to achieve the agreed environmental objectives during winter and spring flood period when the highest concentrations and nutrient loads take place.

Risk of the nitrate run-off extremes. As it was shown in Figure 6, the nitrate concentration may be extremely high. VSIA “Centre for Agrochemical Research” in several fields of Jaunbērze municipality has analysed mineral nitrogen. Data of the soil mineral nitrogen, presented in Table 5, provide the information on soil leakage potential in the autumn of
2006 resulting in high concentrations when drainage run-off started in November. Run-off transported considerable amount of the nitrogen that was accumulated in soil during summer and early autumn due to the dry and hot weather conditions. In addition, soil has many cracks and macropores (Fig. 7).

<table>
<thead>
<tr>
<th>Field</th>
<th>Soil layer, cm</th>
<th>Content of the mineral nitrogen, mg kg⁻¹ dry soil</th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>autumn 2006</td>
<td>spring 2007</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>NO₃⁻N</td>
<td>NH₄⁻N</td>
<td>NO₂⁻N</td>
<td>NH₄⁻N</td>
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<tr>
<td>Silarāji</td>
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<td>6.6</td>
<td>2.6</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30-60</td>
<td>6.8</td>
<td>3.3</td>
<td>6.1</td>
<td>3.1</td>
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<tr>
<td></td>
<td>60-90</td>
<td>1.3</td>
<td>2.7</td>
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<td>7.1</td>
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<tr>
<td></td>
<td>60-90</td>
<td>0.9</td>
<td>3.4</td>
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<td>1.7</td>
<td>3.1</td>
<td>3.1</td>
<td>3.2</td>
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<tr>
<td></td>
<td>60-90</td>
<td>1.3</td>
<td>2.6</td>
<td>2.4</td>
<td>2.7</td>
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<tr>
<td>Vāverītes</td>
<td>0-30</td>
<td>14</td>
<td>4.1</td>
<td>3.5</td>
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<td>30-60</td>
<td>9.6</td>
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<td>4.9</td>
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<td>7.9</td>
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<tr>
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<td>60-90</td>
<td>7.1</td>
<td>3.2</td>
<td>11.3</td>
<td>3.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 5

Content of the soil mineral nitrogen, autumn 2006-spring 2007, data of the Centre for Agrochemical Research.

Fig. 7. Soil cracks in Bērze drainage field on June 19, 2006 (LLU data).
This nitrate leaking risk depends upon a number of factors, such as the climatic, hydrological, and soil conditions. In the case of drainage run-off, for example in Bērze site, vulnerability to pollution by nitrates (and other soluble contaminants) is greatest when:
- temperature and moisture regimes in summer promote the nitrate accumulation and probability of high soil nitrate levels;
- the composition of the unsaturated zone (including top soil) is coarse and/or has macro pores and cracks;
- intensive precipitation produce fast drainage discharge with high rate, when the period of hydrological activity started in autumn.

Conclusions
1. Long term water monitoring data (1994-2007) from agricultural run-off monitoring sites indicates that most important nitrate leaching risk factor is intensity of farming (share of arable land and land use).
2. Monitoring data in several geographical scales (plot, field and catchment) shows that the highest nitrate values exceeding 11.3 mg L⁻¹ NO₃-N belong to run-off from drainage plots. Retention of nitrates decreased nitrate concentrations in field and small catchments’ scale.
3. The results of risk assessment shows that the highest impact of agriculture measured in terms of high nitrate content was observed in the territory designated as nitrate vulnerable zones (Bērze monitoring station).
4. The real time measurements with nitrate sensor shows that concentration peaks are observed relating to high flow conditions and high content of the mineral nitrogen in soil. The risk of nitrate pollution is greatest when levels of available nitrate in the soil profile (especially in the soil surface) are high, and coincide with other circumstances which add to the vulnerability of underlying or adjacent waters to diffuse pollution.
5. Extreme weather conditions in summer and winter, due to the climate change in the future, might increase the nutrient concentration in agricultural run-off and role of diffuse pollution.

References
Anotācija