Agricultural Impact on Groundwater Vulnerability to Nitrate in Northern Croatia

Marina BUBALO [1] (✉)
Davor ROMIĆ [1]
Monika ZOVKO [1]
Neven KUSPILIĆ [2]

Summary

There is noticeable negative impact on soil and water quality caused by nutrient leaching, especially nitrate. Five regions in Croatia are preliminary delineated as nitrate vulnerable zones, including potentially vulnerable zones (PVZ) and vulnerable zones (VZ), one of them being Varaždin County. Agricultural land spreads on 59% of its total area. The survey was carried out to analyze two available land use databases, ARKOD and CLC 2006, to determine relation between land use and vulnerability to nitrate. Results of on-going groundwater, soil and percolate research (nitrate concentrations) in the same area are used for more precise nitrate vulnerability determination. Database analysis revealed no significant difference in land use within VZ and PVZ. Groundwater monitoring shows no consistency between nitrate concentrations and PVZ/VZ designation. Furthermore, the difference in the amount of residual soil nitrogen in two years of research was determined. Results of lysimeter study show that up to 32% of applied nitrogen is percolated to deeper soil layers indicating high agricultural impact on groundwater vulnerability to nitrate.

Key words

agricultural impact, groundwater vulnerability, nitrate, soil

[1] University of Zagreb, Faculty of Agriculture, Svetošimunska cesta 25, 10000 Zagreb, Croatia
✉ e-mail: mbubalo@agr.hr
[2] University of Zagreb, Faculty of Civil Engineering,
Fra Andrije Kačića-Miošića 26, 10000 Zagreb, Croatia

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Introduction

Nitrate leaching to groundwater is a major concern throughout intensive agricultural areas. Depending on the land use, soil type and other, nitrate is washed out from soil into streams or rivers (i.e. surface waters), or leached down into porous rock aquifers (i.e. groundwater). While agriculture is the main source of nitrate in rural areas, nitrate may reach surface and ground water from different sources: fertilization, sewage treatment works, inadequate manure and waste storage (Romić et al., 1997). There are two main areas of concern associated with this loss of nitrate: public health and environmental harm. High nitrate levels in drinking water can cause serious health problems, and therefore the Drinking Water Directive (80/778/EEC) sets a limit of 50 milligrams per liter for nitrate in public water supplies. The principal harm caused by high nitrate levels from the environmental point of view is that "eutrophication" or the over-enrichment of water results in undesirable ecological changes, such as increase in phytoplankton mass and decrease of light penetration.

When it comes to measures for nitrate leaching reduction, then obviously climate conditions (precipitation) or natural soil properties (texture, soil depth) can not be controlled. However, land use and land management can be adapted to the given natural conditions. High-value, intensively managed crops, such as vegetables and other irrigated agricultural crops, to which large amounts of nitrogen fertilizer are usually applied, have a great potential for contributing to surface and ground water contamination by nitrate. In current Croatian agricultural practice there is noticeable negative impact on soil and water quality caused by nitrate leaching (Mesić et al., 2007; Filipović et al., 2012a). Nevertheless, combination of different measures such as soil management, crop rotation, fertilizer use, manure storage, livestock management, land use change and other, risk of surplus nitrate leaching can be significantly lower. Nitrate leaching on mulched surfaces, as one of possible management options, was lower in comparison with the treatment without mulching (Romić et al., 2003).

There are some other impacts that contribute to nitrate leaching, such as application of organic fertilizer (manure). Farmyard manure application in September resulted in a considerably higher nitrate leaching in the following leaching period, compared to unmanured lysimeters (Thomsen, 2005). Similar results are found in research done by Basso and Ritchie (2005), where the highest rates of nitrate losses were recorded in the manure treatment comparing to compost and inorganic N treatment. However, nitrate leaching depends in a large extent on soil type, solum depth, aquifer characteristics – hydrogeology, climate conditions and irrigation practice.

According to The Nitrate Directive provisions (91/676/EEC), EU Member States should identify waters threatened by agricultural activities and areas subject to nitrate pollution, limit the application of nitrogen fertilizer and design and implement operational programs for the prevention of stated pollutions. There are five regions in Croatia which are classified as (preliminary) vulnerable zones (PVZ/VZ) to nitrogen losses and hence to nitrate pollution. Nitrate concentrations in water bodies show the integrated effect of all land uses on waters. The data from a national monitoring program, considering also land use and management data should be interpreted by integrating knowledge derived from scientific research.

Direct monitoring of nitrate losses in VZs provides evidence of losses under different farming systems and under a wide range of land use and management. Lysimeter installation is one of widely applied methods for direct nutrient and pollutant measurement in terrestrial and aquatic ecosystems (Romić et al., 1997; Aronsson and Bergström, 2000; Romić et al., 2003; Matlou and Haynes, 2006; Bubalo et al., 2013). Such research is set on three locations within Varaždin County.

Varaždin County represents intensive agricultural area: combination of mostly (85%) crop production, intensive vegetables production and livestock breeding. In addition, the entire area is under direct hydrogeological influence of the large river Drava and Mura. It is dominated by alluvial soil with shallow active profile mainly on gravel base and risk of nitrate leaching into watercourses and underground is high.

The main objectives of this study were:

— to put available scientific information on nitrate leaching from agriculture in the study area in relation to land use, land management, climate, and soil, by setting up the field lysimetric trial and

— to identify practical agricultural practices responsible for high nitrate leaching (fertilizer application, manure storage, soil and livestock management, plant rotation, land use change and combined measures) in the study area, that may generally contribute to the development of strategies for the necessary further reduction of leaching losses in nitrate vulnerable areas.

Materials and methods

Land use databases

There are two land use databases available in Croatia: ARKOD - Croatian national system of land parcels identification and land use records and CORINE LAND COVER (CLC 2006) for Croatia. ARKOD is a part of Integrated administrative and control system (IACS) which provides European Union state members to assign, monitor and control direct financial support to farmers, so it consists of only land use records in agriculture. Database is consisting of data for each registered agricultural plot: position, size, owner and class of defined land use. On the other hand, CLC 2006 is the database containing all types of land use; agricultural land use is just one segment of it. The standard approach for creating CLC database is based on visual interpretation of satellite images by the accepted methodology, which produces vector data at the scale of 1:100,000. ARKOD is more detailed single agricultural plot identification database created from Croatian farmers register (Fig. 2).

Field research

Study area

One of five designated PVZ/VZs in Croatia is situated in northern part of Varaždin County (zones are shown in Fig. 1). Delineation of those zones is done using GIS database of all water bodies and catchments boundaries, hydro geological map, map of natural groundwater vulnerability, available land use databases and according to ground, surface, transitional and coastal waters monitoring (Hrabánková and Datel, 2012). Vulnerability of Varaždin County to nitrate pollution is caused by its specific hydrogeologic conditions. The hydrogeology of the area is influenced by the large rivers Drava and Mura on its border – the aquifer is composed of gravel and sand with variable portions of silt (Urumović et al., 1990). At utmost north-western part of the area aquifer thickness is less then 5 meters and is gradually increasing in downstream direction reaching its maximum of roughly 105 meters in eastern part (Lavra and Marković, 2007). The area is dominated by alluvial soils with shallow active profile mainly on gravel base as a consequence of the covering layer of the aquifer. It is not continuously developed – in some parts it exceeds 2 meters and in some it completely disappears. That is considered as favorable from the aspect of aquifer recharge but this makes aquifer quite vulnerable (Lavra and Marković, 2007).

On the other hand, Varaždin County is heavily impacted agricultural area where 59% of its total area represents agricultural land, used for various types of agricultural production. According to Statistical Yearbook of the Republic of Croatia from 2003, there is 156,837 parcels on 36,813 ha, which means that average parcel size is 0.23 ha. This is twice smaller then average parcel size of 0.45 ha, according to the same inventory. Besides typical field crops production, which is the most common type of agricultural production in this county (Vincek and Ernoić, 2009), there is also highly developed intensive vegetables production with large amount of fertilizers application and a significant number of cattle and chicken farms on a relatively small area. All stated indicates that this area is very subject to nutrient, especially nitrates, pollution from agricultural sources.

Groundwater nitrate concentrations

Croatian Waters have carried out groundwater monitoring using 15 m deep piezometers on national level since 2006, in order to monitor groundwater pollution from different sources. Ten of those piezometers are set within the study area (Fig. 1). Water samples have been continuously collected for six years.

Groundwater samples from piezometers were collected twice a year in 2006/2007 and four times a year in period 2008-2011. All collected groundwater samples, what makes total of 180, were analyzed for nitrate concentrations.

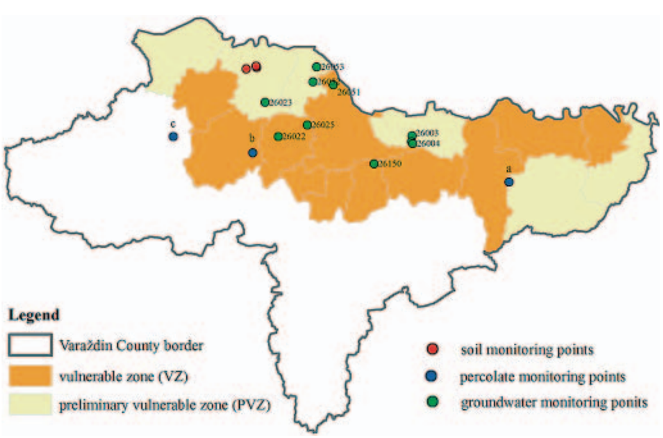

Figure 1. Position of soil and water sampling points within nitrate (preliminary) vulnerable zones

Soil residual N

For soil residual N calculation, soil samples from three depths (0-30, 30-60 and 60-90 cm) are collected twice a year (in early spring and late autumn) in period 2010-2012. Each soil sample is analyzed for nitrate concentration and soil layer density. The calculation of residual N is performed for each soil layer individually as a product of nitrate concentration, soil layer density and layer height. Eventually, total N load over the sampled profile is the sum of the N content in three layers (Vandecasteele and Romić, 2013).

Lysimeter installation and percolate analysis

In 2011, three sets of three field lysimetres were installed on agricultural parcels (one in VZ, one in PVZ and one outside both zones) with different production systems on different soil types.

Each lysimeter is installed in open soil profile at a depth above less permeable horizon or at the solum-gravel contact. Room for its placement was additionally excavated so the soil layer above lysimeter remains undisturbed. PVC reinforced hose was connected to lysimeter drain and set with sufficient slope to ensure the flow of percolate. Percolate water is collected in a plastic container. Vertical stiff PVC pipe was integrated in the same container and it has perforations along the wall to allow the pumping of the percolate. Vertical pipe is sealed with a plastic cap to prevent possible contamination of the percolate. In the final stage, opened pedological profile is filled with excavated soil and additionally compacted to prevent the peripheral flow of groundwater towards the open profile. The unobstructed breeding measures are enabled in such way.

Percolate samples were collected by pumping twice a month or after abundant rainfall; 3-11 times, varying from on location to another, in period July 2011-December 2012. Nitrate concentrations were determined spectrophotometrically using segmented flow on the Skalar San++Analyzer (Skalar, Breda, The Netherlands).

Results and discussion

Land use

According to available digital PVZ/VZ database, 51.3% of total Varaždin County area is area with some level of groundwater vulnerability to nitrate. Data show that 30.6% of total County area is classified as nitrate VZ and 20.7% as PVZ (Fig. 1).

Results presented in Table 1. show that there is substantial difference between land use records in two used databases; i.e. agricultural land within VZ covers 38.2% area according to ARKOD and 69.9% according to CLC 2006. Difference is noticeable also within different categories indicating diverse methodology used to create these databases. However, according to both ARKOD and CLC 2006 the most of agricultural plots, 86% and 89%, respectively, are used as arable land. This corresponds to average value of 85% on agricultural land use data within Varaždin County according to Statistical Yearbook of the Republic of Croatia for 2012.

According to ARKOD the most agricultural area is used as arable land and meadow. Arable land covers 32.5% area within VZ and 32.1% area within PVZ; 4.1% of VZ area and 3% of PVZ area is classified as meadow. Other land use categories defined in

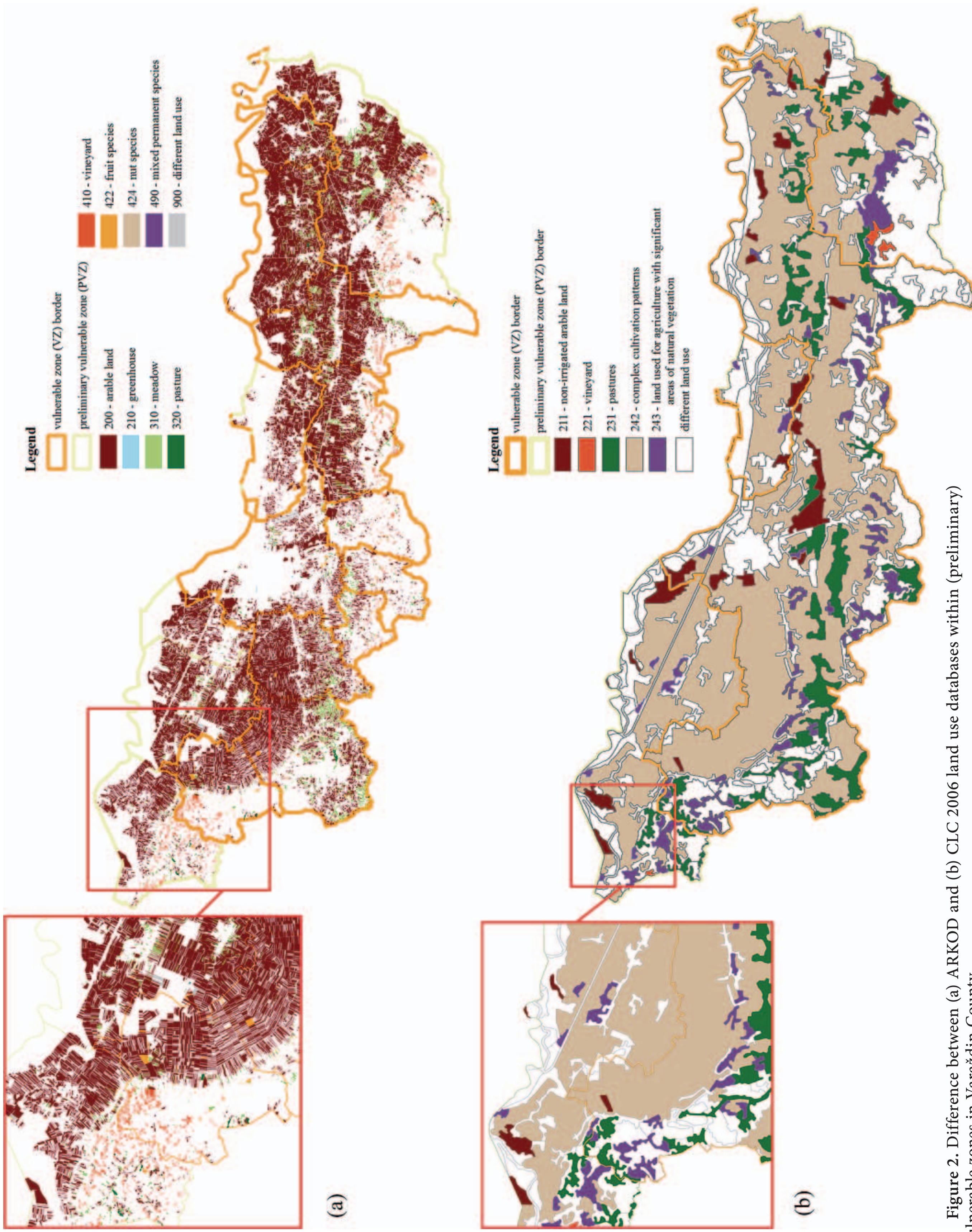

Figure 2. Difference between (a) ARKOD and (b) CLC 2006 land use databases within (preliminary) vulnerable zones in Varaždin County

Table 1. Data on agricultural land use according to ARKOD and CLC 2006

Land use	ARKOD	
	Percentage of VZ area	Percentage of PVZ area
Arable land	32.51	32.08
Greenhouse	0.05	0.03
Meadow	4.14	2.99
Pasture	0.13	0.07
Vineyard	0.49	0.63
Fruit species	0.46	0.43
Nut species	0.18	0.11
Mixed permanent species	0.01	0.02
Different land use	0.22	0.12
Total	38.19	36.48
	CLC 2006	
	Percentage of VZ area	Percentage of PVZ area
Non-irrigated arable land	3.37	4.04
Vineyard	0.00	0.66
Pastures	10.85	3.67
Complex cultivation patterns	50.51	47.36
Land used for agriculture with significant areas of natural vegetation	5.15	5.67
Total	69.88	61.40

ARKOD have very small portion, less then 1%, in overall agricultural area. CLC 2006 database analysis shows that most area both in VZ and PVZ, respectively 50.5% and 47.4%, is classified as agricultural land with complex cultivation patterns. There is also no evident difference, less then 1%, within VZ and PVZ in categories non-irrigated arable land, vineyard and land used for agriculture with significant areas of natural vegetation. Only substantial difference within VZ and PVZ according to CLC 2006 is recorded in pastures area, respectively 10.9% and 3.8%. It can be concluded that analysis of both available databases did not confirm substantial land use differences between VZ and PVZ.

Groundwater sampling results

Groundwater analysis results partly confirm designation of nitrate PVZ and VZ within Varaždin County (Table 2). Average nitrate concentration in period 2006-2011 in piezometers within PVZ is 4.7 mg/l and in piezometers within VZ is 13 mg/l. That is in ordinance with the Drinking Water Directive regulations: maximum allowed concentration (MAC) of 50 mgNO_3/l or 11.2 mgNO_3-N/l. However, there is one piezometer 26023 within PVZ which NO_3-N concentration continuously exceeds MAC: average of 15 mg NO_3-N/l and maximum of 23 mg NO_3-N/l (Fig.3). Data show the opposite situation regarding piezometers 26051 and 26150 within VZ. Average concentrations in piezometers 26051 and 26150 are, respectively, 1.3 mg/l and 8.1 mg/l. Maximum concentration on both piezometers does not exceed MAC in research period. Based on their position (Fig. 1), groundwater monitoring results and databases analysis from previous paragraph, they could easily be part of zone opposite to the one they are now in.

Maximum nitrate concentration of 29 mg/l was recorded in piezometer 26022 in 2006 and minimum of 0.3 mg/l in piezometer 26053 in 2008. The nearest groundwater sampling point to soil sampling points for residual N balancing is piezometer 26023 situated in PVZ.

Table 2. Data on groundwater sample analysis in period 2006-2011

	Piezometer label	Minimum NO_3-N concentration (mg/l)	Maximum NO_3-N concentration (mg/l)	Average NO_3-N concentration (mg/l)	Average NO_3-N (mg/l)
PVZ	26002	2.0	5.0	2.6	4.7
	26003	3.3	7.2	4.2	
	26004	2.2	5.4	3.4	
	26023	12	23	15	
	26052	0.5	8.9	2.0	
	26053	0.3	5.4	1.8	
VZ	26022	10	29	22	13
	26025	0.3	25	21	
	26051	0.4	9.4	1.3	
	26150	0.4	8.9	8.1	

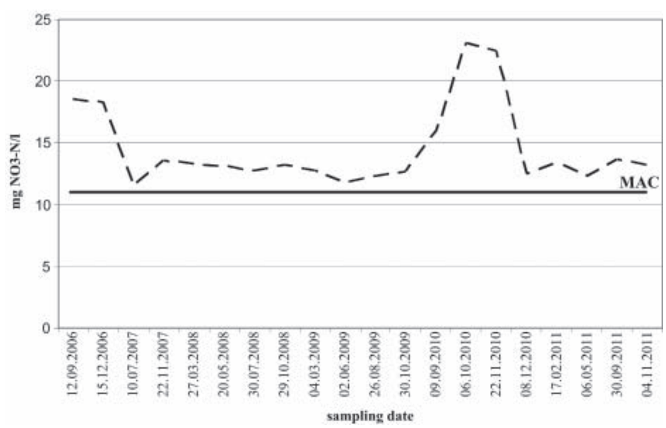

Figure 3. Dynamics of nitrate concentrations in piezometar 26023 in period 2006-2011 (MAC:11.2 mgNO_3-N/l)

Residual soil nitrogen

Total N budgeting was done on three nearby plots with similar agricultural practice: early fall plowing up to 45 cm depth; in fall and spring secondary tillage operations with rotary tiller; use of poultry manure: 20 t/ha in October, 300 kg/ha of NPK 15:15:15 in March and 150 kg/ha of CAN in June for three consecutive years. Those measures are part of the farmer's usual practice, without any other influence of control. Crop rotation on each plot in 2011-2012 was: maize -parsley, maize – beetroot, maize – beetroot.

Results of soil samples collected in 2011 from all three plots show the average nitrate content in top soil layer of 9.6 mg/kg in early spring and 8.7 mg/kg in late autumn. On the other hand, in 2012 there is significant increase (Fig. 4). Average nitrate value from all three plots in top soil is 22 mg/kg and 49 mg/kg in late autumn. This can be explained by excessive fertilizer use in combination with dry hydrological year. Similar values are

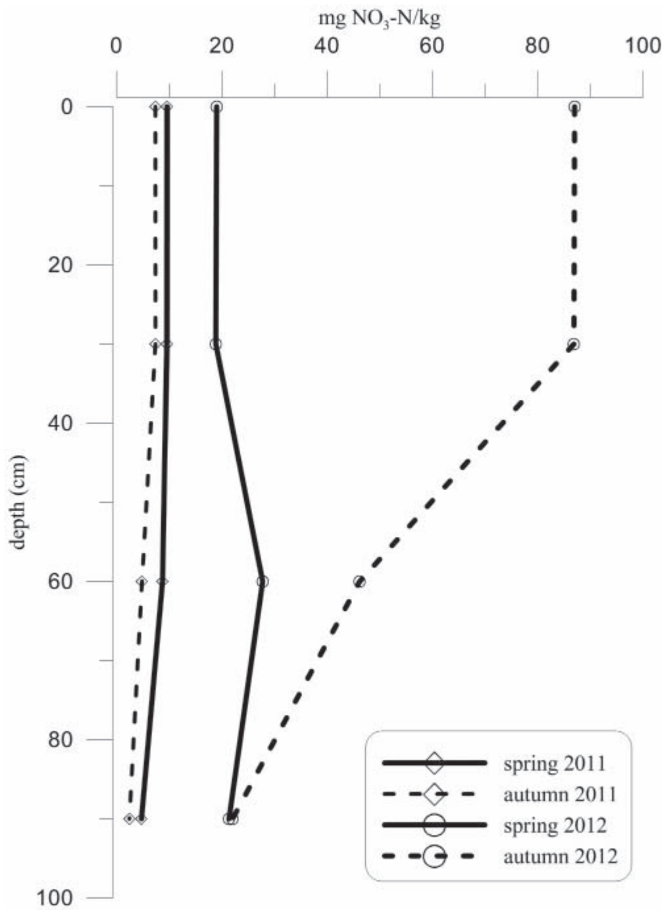

Figure 4. Nitrate content in one soil profile in period 2011-2012

recorded in fertilization trail conducted in central Croatia. In treatment N_{100}+P+K average nitrate value in top soil layer was 40 mg/kg (Jurišić et al., 2013) compared to overall average nitrate concentration of 36 mg/kg in this research.

Calculation of N budgeting for selected plots show that there is total of 150-700 kg/ha of residual nitrogen in 1 m deep soil profile in November, which can be easily, by rainfall, percolated to deeper layers and groundwater. High quantities of residual N require precision in fertilizers application and management strategies.

Percolate sampling results

Plant's inability to uptake all available nitrates followed by high precipitation resulted in surplus nitrate leaching (Romić et al., 2003). In current climatic conditions the risk of nitrogen leaching from the topsoil is highest during the autumn and winter (Šimunić et al., 1997; Romić and Borošić, 1998).

Percolate amount varied depending on soil type and hence amount of leached N ranged from 3% to 11% (from 4 kg N/ha to 19 kg N/ha) in 2011 and from 3% to 32% (from 5 kg N/ha to 56 kg N/ha) in 2012 (Fig. 5).

In eastern Croatia annual amount of leached nitrogen from agricultural plots varies from 4.1 kg N/ha to 63 kg N/ha (Filipović et al., 2012b). On one research plot (marked c on the

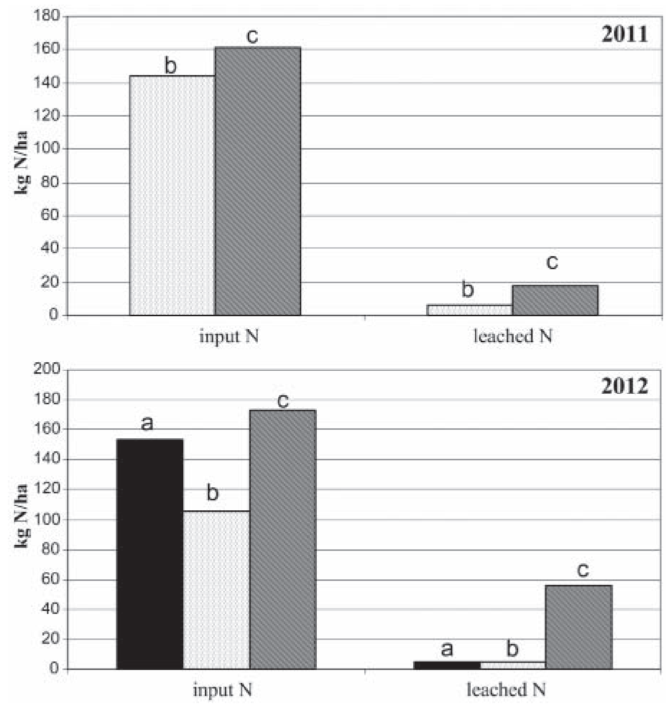

Figure 5. Preview of input and leached N from three locations (a, b, c) with installed lysimeters in 2011-2012

Fig. 5), where the highest content of leached N was recorded, regular fertilization implies use of mineral fertilizer in combination with manure.

Conclusion

Varaždin County is one of five nitrate vulnerable areas defined and delineated in Croatia. Vulnerability to nitrate in that area is classified either as vulnerable or as preliminary vulnerable. Land use analysis according to ARKOD and CLC 2006 databases did not confirm substantial land use differences between VZ and PVZ. Groundwater monitoring results show there are piezometers with continuously high nitrate concentration in both zones. Maximum of 32% leached N in 2012 shows there is direct agricultural influence on groundwater quality. Total N content in 1 m soil profile within research of 150-700 kg/ha in 2012 indicates on excessive fertilizer use. It can be concluded that Varaždin County is highly vulnerable to nitrate, especially those from agricultural origin. For more precise determination of VZs and PVZs it is necessary to create a model with detailed data on land use, including soil management, crop rotation, fertilizer use, manure storage, livestock management, in combination with more detailed continuous groundwater monitoring.

References

Aronsson, P.G., Bergström, L.F. (2001). Nitrate leaching from lysimeter-grown short-rotation willow coppice in relation to N-application, irrigation and soil type. Biomass and Bioenergy 21: 155-164.

Basso, B., Ritchie, J. T. (2005). Impact of compost, manure and inorganic fertilizer on nitrate leaching and yield for a 6-year maize–alfalfa rotation in Michigan. Agriculture, Ecosystems and Environment 108: 329-341.

Bubalo, M., Romić, D., Kuspilić, N., Filipović, V. (2013). Application of field lysimeters in groundwater pollution assessment. In Nakić, Z., Rubinić, J. (eds) 3rd International Conference Waters in Sensitive & Protected Areas. Croatian society for water protection, Zagreb: 34-38.

EC (1980). Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption. Off. J. Eur. Commun. L229, 11-29.

EC (1991). Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. Off. J. Eur. Commun. L375, 1-8.

Filipović, V., Petošić, D., Nakić, Z., Mustać, I., Ružičić, S., Zovko, M., Bubalo, M. (2012a). Identifying spatial and temporal variation of nitrate concentration in shallow groundwater aquifer. Journal of Food Agriculture & Environment. 10, 3&4: 1001-1004.

Filipović, V., Petošić, D., Rubinić, V., Marković, M. (2012b). Impact of agriculture on the quality of percolating water: Case study in eastern Croatia. Journal of Food Agriculture & Environment. 10, 3&4: 1335-1336.

Hrabánková, A. and Datel, J. V. (2012). [in Croatian]. Methodology and criteria for nitrate vulnerable zones delineation. Ministry of Agriculture Republic of Croatia, Zagreb.

Jurišić, A., Mesić, M., Šestak, I., Zgorelec, Ž. (2013). Horizontal and vertical nitrate-nitrogen distribution under different nitrogen fertilization levels. Novenytermeles/Crop production. 62, Supplement: 29-32

Lavra, O., Marković, T. (2007). Grounwater bodies at risk. Further characterization – case study: Varazdin region, Croatia. In Ribeiro, L., Condesso de Melo, M.T. (eds) XXXV Congress of the International Assosiation of Hydrogeologists, Groundwater and Ecosystems. International Association of Hydrogeologists, Lisbon: 175-177.

Matlou, M. C., Haynes, R. J. (2006). Soluble organic matter and microbial biomass C and N in soils under pasture and arable management and the leaching of organic C, N and nitrate in a lysimeter study. Applied Soil Ecology 34: 160-167.

Mesić, M., Bašić, F., Kisić, I., Butorac, A., Gašpar, I. (2007). Influence of mineral nitrogen fertilization on corn grain yield and nitrogen leaching. Cereal Research Communications, 35/2: 773-776.

Republic of Croatia - Central bureau of statistics. (2003). Statistical Yearbook of the Republic of Croatia, Zagreb

Republic of Croatia - Central bureau of statistics. (2012). Statistical Yearbook of the Republic of Croatia, Zagreb

Romić, D., Romić, M., Klačić, Ž., Petošić, D., Stričević, I. (1997). Effect of land use upon the leaching of nitrogen into groundwater in area of the future water pumping station. Bericht Uber die 7. Lisimetertagung "Lysimeter und nachhaltige Landnutzung", BAL Gumpenstein, Austria

Romić, D., Borošić, J. (1998). Agricultural practices in the function of ground and surface water protection (Croatian experience). International Workshop on Protection of Natural Resources in agriculture of Central and Eastern Europe, Prague, Czech Republic, pp 85-88.

Romić, D., Romić, M., Borošić, J., Poljak, M. (2003). Mulching decreases nitrate leaching in bell pepper (*Capsicum annuum L.*) cultivation. Agricultural Water Management 60: 87–97.

Šimunić, I., Tomić, F., Drevenkar, V., Klačić, Ž., Petošić, D., Stričević, I., Rus, B. (1997). The concentration of NO_3 and atrazine in drainage water of different drainage systems in pseudogley-gley soils. In Proceedings of Abstracts XXXIII. Croatian Scientific Conference on Agriculture with International Participation, 11, Pula, Croatia, pp 11.

Thomsen, I.K. (2005). Crop N utilization and leaching losses as affected by time and method of application of farmyard manure. European Journal of Agronomy 22: 1-9.

Urumović, K., Hlevnjak, B., Prelogović, E., Mayer, D. (1990). Hydrogeological conditions of Varaždin aquifer. Geološki vjesnik vol. 43: 149-158.

Vincek, D., Ernoić, M. (2009). [in Croatian]. Nitrate Directive and agricultural production in Varaždin County. Animal Science 63 (4): 309-316.

Vandecasteele, B., Romić, M. (2013). Manual: Quality assessment/quality control of soil sampling procedures and soil analysis. Institute for Agricultural and Fisheries Research (ILVO), Belgium and University of Zagreb Faculty of Agriculture.

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