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title: **Groundwater hydrochemistry of the quaternary alluvial aquifer in Varaždin region — Croatia**

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INTRODUCTION

High nitrate concentrations in surface waters and groundwater have emerged as s globally growing problem for drinking and agricultural purpose (Halberg, Keendy, 1993; Spalding, Exner, 1993; Nolan, 2001). The adverse health effects of high nitrate levels in drinking water have been well documented, that include gastric cancer, non-Hodgkin's lymphoma and methemoglobinaemia (Walton, 1951; Winnerberger, 1982; WHO, 1985; Ward et.al., 1994; Fan, Steinberg, 1996).

The study area is situated in the north-western part of Croatia (Fig. 1) in the Drava river valley.

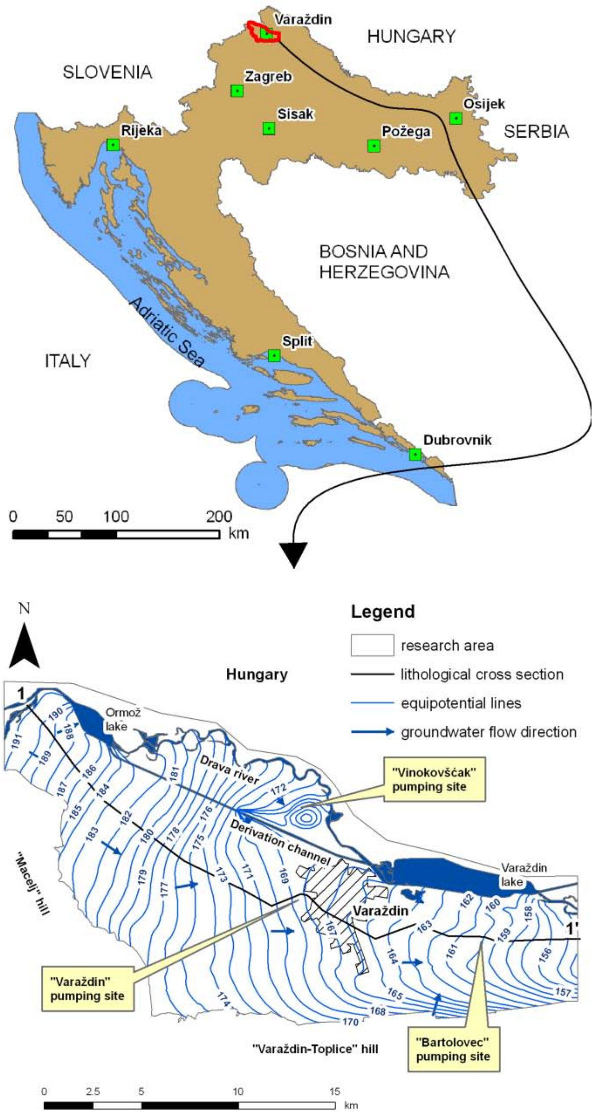

Figure 1. Location map showing equipotential lines and groundwater flow direction.

It is quite developed region where agricultural production is among the most important economic branches. Groundwater accumulated in the Drava alluvial aquifer represents valuable natural resource. As a result of favourable natural conditions, three pumping sites ("Varaždin", "Vinokovšćak" and "Bartolovec") have been developed for the purpose of drinking water supply. The natural quality of groundwater complies with the provisions of the Regulation on health safety of drinking water (OG 47/08), but during the years inadequate land use management took its toll, which became obvious in 1970s when high concentration of nitrates in groundwater was noticed for the first time. Today, high concentrations are observed in the first aquifer and, as a consequence, groundwater abstraction from the first aquifer at "Varaždin" pumping site has recently been terminated. This work was initiated to examine the nitrates behaviour in the first and the second alluvial aquifer of the study area.

HYDROGEOLOGICAL SETTING

The aquifer is composed of gravel and sand with variable portions of silt (Babić et.al., 1978; Urumović, 1971; Urumović, et.al., 1990). It is formed during Pleistocene and Holocene as the result of accumulation processes of the Drava river (Prelogović, Velić, 1988). In the north-westernmost area its thickness is less than 5 meters (Fig. 2). Going downstream the aquifer thickness gradually increases and reaches its maximum of roughly 105 meters in the eastern part of investigated area. It is noticed that particle sizes change going from the north-western part downstream, i.e. the size of gravel and sand particles gets gradually smaller as result of energy decrease of the Drava river. In accordance with variation of the particle size the values of hydraulic conductivity vary in the range from 100 to 300 m/day. In the central part, near Varaždin town, a tiny aquitard appears dividing the aquifer in two hydrogeological units (Fig. 2).

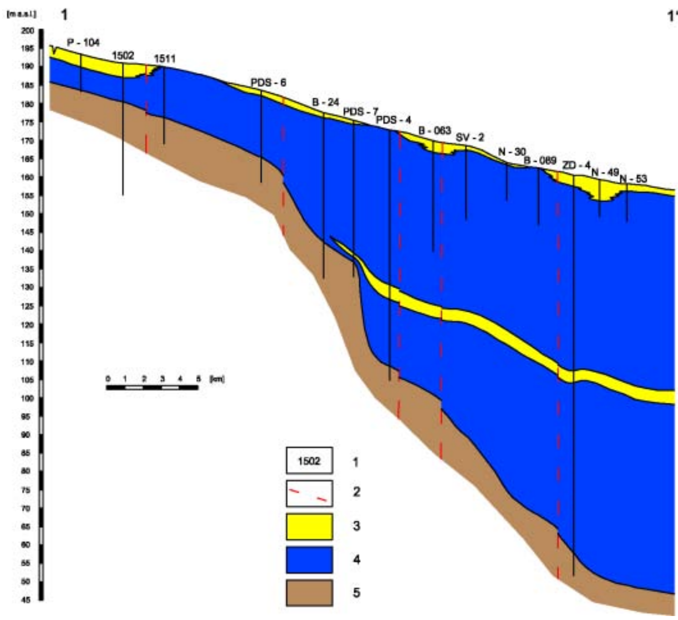

Figure 2. Lithological cross section. 1 — borehole; 2 — supposed fault; 3 — aquitard; 4 — aquifer; 5 — impermeable rocks.

It has regional significance and can be tracked even downstream of investigated area. It is composed of clay and silt and its thickness does not exceed 5 meters. The covering layer of the first aquifer is not continuously developed. In central part and near the Drava river it rarely exceeds two meters, while often there is no covering layer at all. Such conditions are favourable if they are considered from the aspect of aquifer recharge, but on the other hand tiny or non-existing covering layer composed of clay, silt and sand particles mixed with various content of organic matter, makes the aquifer quite vulnerable.

The aquifer is unconfined except its marginal part in the vicinity of "Varaždin-Toplice" hill where, locally, the covering layer gets thicker, at some places more than 10 meters. The recharge of the first aquifer occurs by means of precipitation infiltration and percolation of surface water, while the lower aquifer is recharged by the slow percolation of groundwater through aquitard.

The general groundwater flow direction is NW-SE and is parallel to the Drava river (Fig. 1). It is noteworthy that the piezometric head distribution and the flow net have been significantly changed consequential to building of two accumulation lakes for hydropower plants. Namely, prior to this intervention the groundwater had flown towards the Drava river where the aquifer had been drained and most of the recharge had been achieved by infiltration of precipitation. After construction of the Ormož and Varaždin accumulation lakes, the regional flownet changed leading to percolation of the water from the lakes to the aquifer. Besides, the groundwater levels increased leading to washing out of nitrates from unsaturated zone.

METHODS

In various hydrological conditions water samples were taken from wells and surface waters - Drava river, lakes, gravel pit (Figure 3).

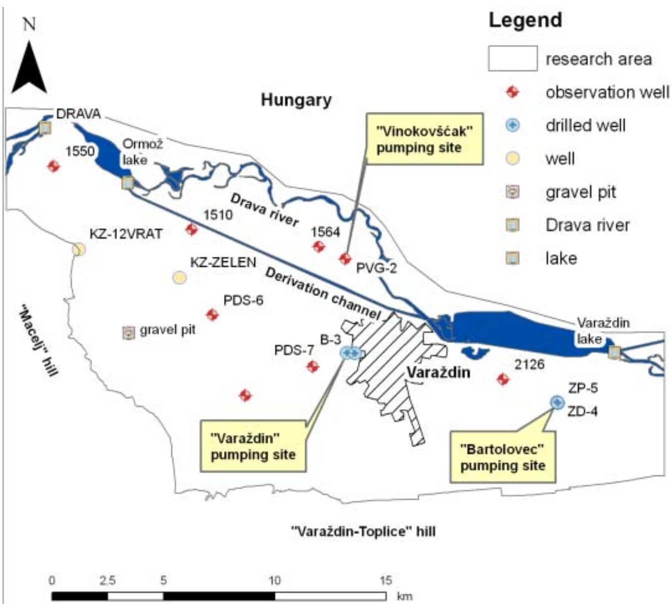

Figure 3. Sampling sites.

Prior to taking water samples from individual springs, the following parameters were measured "in situ" by probes of WTW company: EC, TDS, T and pH content in waters. At the Hydrochemical Laboratory of the Department of Hydrogeology and Engineering Geology — Croatian Geological Survey, the concentrations of the basic anions and cations were measured. The content of chlorides, sulphates and nitrates were measured by ion chromatograph of the LabAlliance company, whereas the concentrations of orthophosphates and ammonium were measured by the spectrophotometer DL/2010 of the HACH company. The concentrations of calcium, manganese, sodium and potassium were measured by the atomic adsorber of the Perkin Elmer company. The content of HCO_3^- was determined by titration. The results for ions were processed using the Netpath software. Data quality was further assessed using the charge balance between the sum of cations and anions (expressed in meq/l), which was always <±5%. Also, periodical chemical analysis made by VARKOM was used for interpretation.

RESULTS AND CONCLUSIONS

According to the chemical composition, groundwater from the Varaždin aquifer belongs to the $CaMg\text{-}HCO_3$ hydrochemical type. This is the primary water type which is principally derived from dissolution of carbonate minerals (calcite and dolomite) that compose the aquifer.

The pH of the analyzed water samples varies from 6.96 to 7.94 (slightly acid to alkaline). The EC values vary from 596 to 720 μS/cm and depend on amount of dissolved solids in water. Nitrate concentrations vary from 3 to 89 mg/l (Fig. 4, 5). The highest value was measured in groundwater from the catchment area of Varaždin pumping site. In the most samples from the first aquifer of Varaždin pumping site, measured concentrations of nitrate are over the MPC value. Nitrates concentrations from the wells located at the catchment areas of Vinokovšćak and Bartolovec pumping sites, vary from 3 to 38 mg/l in waters (Figure 4).

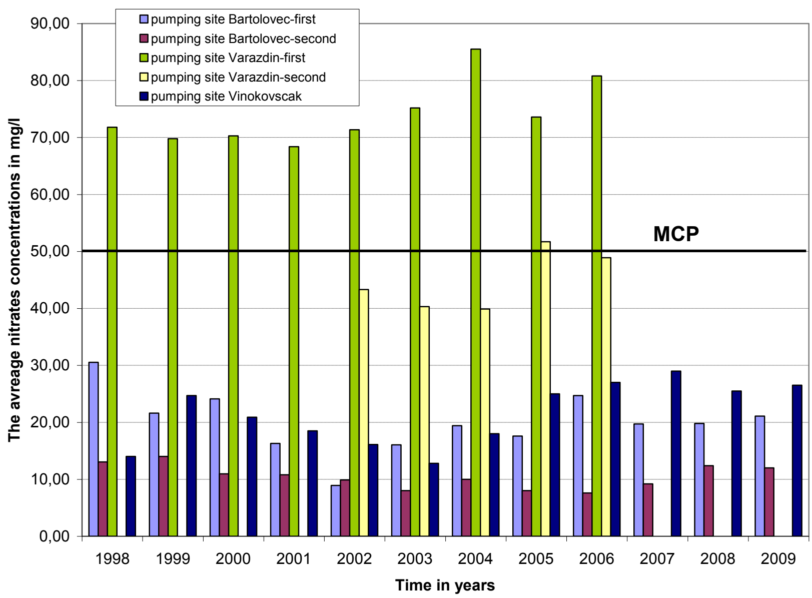

Figure 4. Distribution of average nitrates concentrations over 11 year period at pumping sites of Varaždin area.

In piezometer PDS-7 (near Varaždin pumping site) concentrations of nitrite are high, while, at the same time, concentrations of nitrate are low (Fig. 5). Nitrate contamination is generally high in oxygenated aquifers where nitrate is relatively stable and mobile, while nitrate can be naturally attenuated by denitrification under reducing aquifer conditions (Edmunds, Walton, 1983; Trudell et al.,1986; Frind et al.,1990; Postma et al.,1991; Geyer et al., 1992; Canter, 1997; Hamilton, Helsel, 1995; Pauwels et al., 2000; Böhlke, 2002; Jang, Liu, 2005; Thayalakumaran et al., 2008; Kim et.al., 2009). The redox state of an aquifer can be changed by the variability of geologic and geochemical properties and may determine the spatial distribution and biogeochemical behavior of nitrate and other redox-sensitive species. For example, reducing conditions required for denitrification can be facilitated within a silty aquifer where organic matter (as an important electron donor) is abundant and groundwater flow is retarded (Postma et al., 1991; Smith et al., 1991; Starr, Gillham, 1993; Robertson et al., 1996; Chae et al., 2004a; Thayalakumaran et al., 2008; Kim et.al., 2009). Such conditions are present in the surrounding area of the piezometric well PDS-7. Generally higher concentrations of nitrite were measured in water samples taken in the vicinity of the Varaždin pumping site, while they are low in other catchments.

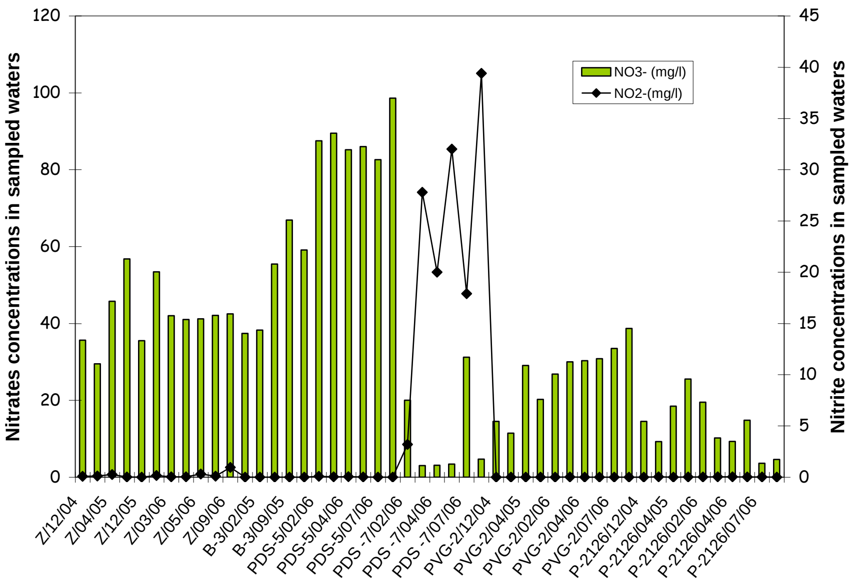

Figure 5. Distribution of nitrates and nitrite in monitored waters.

Ammonia and orthophosphate concentrations are higher in the water samples from wells located in catchment area of Varaždin pumping site then on the other sampling locations. The reasons for higher values of parameters in the groundwater from the first aquifer in the catchment area of Varaždin pumping site compared to the ones obtained for the water samples in the catchment areas of Bartolovec and Vinokošćak pumping sites area are: the lack of covering layer, thinner aquifer, numerous poultry farms as well as intensive cabbage production. Other values of chemical parameters measured in groundwater from the second aquifer are mostly under MPC levels.

The excessive concentrations of nitrates in groundwater from the shallow aquifer at the catchment area of Varaždin pumping site led to gradual decreasing of groundwater abstraction rate and directed the majority of abstraction to the other pumping sites — Bartolovec and Vikonovšćak, where concentrations of nitrate still do not exceed the MPC values. It's necessary to make improvements in agricultural production, as well as in Varaždin infrastructure, in order to reduce concentrations of contaminants in groundwater and enable sustainable groundwater management and development of the entire region.

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REFERENCES

Babić Ž., Čakarun I., Sokač A., Mraz V., 1978: *On geological features of quaternary sediments of Drava basin on Croatian territory.* Geol. vjesnik, 30/1, pp. 43–61.

Böhlke J.K., 2002: *Groundwater recharge and agricultural contamination.* Hydrogeol. J. 10, pp. 153–179.

Canter L.W., 1997: *Nitrates in Groundwater.* Lewis Publisher, Florida.

Chae G.T., Kim K., Yun S.T., Kim K.H., Kim S.O., Choi B.Y., Kim H.S., Rhee C.W., 2004a: *Hydrogeochemistry of alluvial groundwaters in an agricultural area: animplication for groundwater contamination susceptibility.* Chemosphere 55, pp. 369–378.

Edmunds W.M., Walton N.R.G., 1983: *The Lincolnshire limestone hydrogeochemical evolution over a ten-year period.* J. Hydrol. 61, pp. 201–211.

Fan A.M., Steinberg V.E., 1996: *Health implications of nitrate and nitrite in drinking water: an update on methemoglobinemia occurrence and reproductive and developmental toxicity.* Regul. Toxicol. Pharmacol. Sect. 23, pp. 35–43.

Frind E.O., Duynisveld W.H.M., Strebel O., Boettcher J., 1990: *Modeling of multicomponent transportwithmicrobial transformation in groundwater: the Führberg case.Water Resour.* Res. 26, pp. 1707–1719.

Geyer D.J., Keller C.K., Smith J.L., Johnstone D.L., 1992: *Subsurface fate of nitrate as a function of depth and landscape position in Missouri Flat Creek watershed, USA.* J. Contam. Hydrol. 11, pp. 127–147.

Halberg G.R., Keedny D.R., 1993: *Nitrate. In: Alley, W.M. (Ed.), Regional Groundwater Quality.* InVan Norstrand Reinhold, NewYork, pp. 297–322.

Jang C.S., Liu C.W., 2005: *Contamination potential of nitrogen compounds in the heterogeneous aquifers of the Choushui River alluvial fan, Taiwan.* J. Contam. Hydrol. 79, pp. 135–155.

Kim K.H., Yun S.T., Choi B.Y., Chae G.T., Joo Y., Kim K., Kim H.S., 2009: *Hydrochemical and multivariate statistical interpretations of spatial controls of nitrate concentrations in shallow alluvial aquifer around oxbow lake (Osong area, central Korea).* J. of Cont. Hyd., 107, pp. 114–127.

Nolan B.T. 2001: *Relating nitrogen sources and aquifer susceptibility of nitrate in shallow ground waters of the United States.* Ground Water 39, pp. 290–299.

OG 47/08: *Regulation on health safety of drinking water.*

Pauwels H., Foucher J. C., Kloppmann W., 2000: *Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes.* Chem. Geol. 168, pp. 307–324.

Postma D., Boesen C., Kristiansen H., Larsen F., 1991: *Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling.* Water Resour. Res. 27, pp. 2027–2045.

Prelogović E., Velić I., 1988: *Quaternary tectonic activity in western part of Drava basin.* Geol. vjesnik, 41, pp. 237–253.

Robertson W.D., Russell B.M., Cherry J.A., 1996: *Attenuation of nitrate in aquitard sediments of southern Ontario.* J. Hydrol. 180, pp. 267–281.

Smith R.L., Howes B.L., Duff J.H., 1991: *Denitrification in nitrate-contaminated groundwater: occurrence in steep vertical geochemical gradients.* Geochim. Cosmochim. Acta 55, pp. 1815–1825.

Spalding R.F., Exner M.E., 1993: *Occurrence of nitrate in groundwater: a review.* J. Environ. Qual. 22, pp. 392–402.

Starr R., Gillham R.W., 1993: *Denitrification and organic carbon availability in two aquifers.* Ground Water 31, pp. 934–947.

Thayalakumaran T., Bristow K.L., Charlesworth P.B., Fass T., 2008: *Geochemical conditions in groundwater systems: implications for the attenuation of agricultural nitrate.* Agric. Water Manag. 95, pp. 103–115.

Trudell M.R., Gillham R.W., Cherry J.A., 1986: *An in situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer.* J. Hydrol. 83, pp. 251–268.

Urumović K., 1971: *On quaternary aquifer complex in Varazdin area.* Geol. Vjesnik 24, pp. 183–191.

Urumović K., Hlevnjak B., Prelogović E., Mayer D., 1990: *Hydrogeological conditions of Varaždin aquifer.* Geol. vjesnik 43, pp. 149–158.

Walton B., 1951: *Survey of literature relating infant metemoglobinemia due to nitrate contaminated water.* Am. J. Public Health 41, pp. 986–996.

Ward M.H., Zahm S.H., Blair A., 1994: *Dietary factors and non-Hodgkin's lymphoma.* Cancer Causes Control 5, pp. 422–432.

WHO (World Health Organization), 1985: *Health Hazards from Nitrates in Drinking Water,* Report on a WHO Meeting in Copenhagen, 5–9 March 1984, Regional Office for Europe, Copenhagen, 3, pp. 49–66.

Winneberger J.H., 1982: *Nitrogen, Public Health and the Environment.* Ann Arbor Science Publishers Inc., Ann Arbor, Michigan.

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