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Sustainable Management of the Union Brewery Groundwater Resources, Ljubljana (Slovenia)

Nachhaltige Bewirtschaftung der Grundwasserreserven der Unionbrauerei, Ljubljana (Slowenien)

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1. Introduction

Groundwater from a Pleistocene sandy-gravel aquifer is an invaluable water resource for the Union brewery, which is located within a highly urbanized and industrialized area near the centre of Ljubljana (the capital of Slovenia) and supplies groundwater with high quality from four production wells. A big part of the aquifer recharge area is highly urbanized, which represents a great risk for the groundwater quality assurance. The discussed aquifer is divided into two parts - the upper and lower gravel aquifer. The groundwater with higher quality is exploited from the lower gravel aquifer which is bounded by an impermeable barrier from the contaminated upper gravel aquifer. Fortunately, the upper gravel aquifer has not influenced the present brewery production wells, owing to their successful reconstruction during the last decade. Nevertheless, the managers of the brewery were aware that sustainable groundwater resources management should be assessed and improved. Hence, an extensive study of groundwater flow and solute/contaminant transport was performed in the catchment area of the Union brewery groundwater resources in the framework of "Competence Network Water Resources and their Management" (Knet Water), work package WP 6.2.1: Best Management Practices – Pivovarna Union d.d. (BMP-PU).

The goal of the study was to

- (a) assess and predict the directions of groundwater flow and contaminants transport through the unsaturated or/and saturated zone of the Pleistocene gravel aquifer and to
- (b) analyze the contamination risk of drinking-water resources in the lower Pleistocene gravel aquifer.

Complex geological, hydrogeological, chemical, geochemical and isotopic investigations were performed and integrated with results of previous investigations and with administrative and economic needs with the aim

- (a) to establish a data base, connected with a GIS-system;
- (b) to prepare the detailed geological and hydrogeological maps of the study area;
- (c) to ascertain a hydrodynamic functioning of the investigated aquifer and a pollution degree of soil and groundwater;
- (d) to construct a hydraulic model of the study area, which can provide the ability
 - (i) to simulate groundwater flow and solute transport in the aquifer system, particularly in dependence on discharge,
 - (ii) to predict the aquifer system behavior during further exploitation,
 - (iii) to define and predict interdependence between aquifers;
- (e) to assess the optimal balance between environmental protection and economic use of the brewery groundwater resources;
- (f) to develop a protection strategy of the investigated urban drinking-water resources.

2. Study area

The Union brewery is located in the Ljubljana basin, which is a large tectonic depression, surrounded by hills and mountains (up to 1300 m a. s. l.). The Ljubljana basin was formed in Plio-Quaternary by sequential subsiding. Its northern part is named the Ljubljana Field, while its southern part is named the Ljubljana Moor (Fig. 1, Plio-Quaternary). The former is characterized by the Ljubljanica River with a karstic catchment and the later by the Sava River with an alpine catchment. The Union brewery water body is situated close to the boundary line of the Ljubljana Moor and Field, while the Dravlje valley borders its western part. This valley has a dolomite catchment area.

The Quaternary fluvial and lacustrine deposits fill the Ljubljana basin. The fluvial sediments form the urban aquifer. Lenses of practically impermeable layers divide the aquifer into the upper and lower part (Fig. 4). It was already mentioned in the previous chapter that the upper aquifer is contaminated.

Two isolated hills, the Šišenski hrib hill and the Ljubljana castle hill (Fig. 1), have an important role for the groundwater dynamics. They consist of less permeable Carboniferous-Permian sediments (sandstones and shale), hence they are characterized by a high portion of surface flow. The area between two hills is called the Ljubljana door (Fig. 1).

3. Research methodology

3.1. Data base establishment

At the beginning of the work a uniform data base was established, which collected archive geological, hydrogeological, chemical, geochemical and isotopic data. Data were geo-referenced and adjusted to a geological and hydrogeological GIS-system. The data base was simultaneously supplemented with new data.

3.2. Study of the field geology and hydrogeology

The structure and geology of the investigated water body is controlling hydrodynamic processes and solute transport. Hence, a detailed geological and hydrogeological mapping of the study area was performed for a precise definition of the brewery groundwater resources catchment area. The boundary conditions with the river basins were put into the focus, as well as with the brewery adjacent hill Šišenski hrib which is characterized by a meteoric water discharge (Fig. 1).

As the groundwater direction has not been known in the study area four new piezometers have been drilled in the catchment.

3.3. Study of groundwater flow and solute/contaminant transport

The study of groundwater flow and solute transport was based on quantity and quality monitoring. It was performed in the unsaturated and saturated zone of the observed aquifer. The main goal of the saturated zone monitoring was to investigate sources of contaminants and to identify their flow paths and sinks. On the other hand the main goal of the unsaturated zone monitoring was to study possible contamination in the vicinity of the brewery and to evaluate the role of the unsaturated zone in groundwater protection.

The saturated zone of the upper and lower aquifer was monitored in 20 observation wells, located in the Union brewery and its catchment (Fig. 1, 2 and 4). The observation wells capture groundwater of the lower aquifer, groundwater of the upper aquifer or both of them.

The aquifer unsaturated zone was monitored at the urban lysimeter (A. JUREN et al., 2003, B. TRČEK, 2005), adjacent to the brewery (Fig. 2), in boreholes that are distributed at depths of 0.3–4.0 m and equipped with suction cups for groundwater sampling (Fig. 3). A total of 18 observation points were established on right lysimeter side, under



Fig. 1: Catchment area of the Union brewery groundwater resources. Einzugsgebiet des Grundwasserkörpers der Unionbrauerei.

the industrial railway tracks, while other observation points are located on left side of the lysimeter, beneath the asphalt surface. The boreholes penetrate four layers: sandy gravel, silt-sandy gravel, clayey silt-sandy silt with gravel grains and gravel with sand and silt. The upper three layers are not autochthonous; therefore they are called artificial layers. However, the fourth layer is autochthonous and consists of river deposits.

The quantity and quality monitoring included

- (a) continuous measurements of hydrodynamic parameters (water table, discharge) and of physico-chemical water parameters (pH, temperature, specific electric conductivity) and
- (b) analyses of trace elements, herbicides, environmental isotopes (¹⁸O and ²H) and artificial tracers in groundwater, surface water and precipitation.

The vulnerability of groundwater resources to various contaminants was assessed with scanning procedures, performed at least twice per year.

For the purpose of defining recharge processes and predicting contaminant transport through and/or between different aquifer zones tracer tests are of particular value. A new compound that was detected with the scanning technique served as a tracer in the aquifer saturated zone. At the lysimeter two tracer tests were performed. In the framework of the preliminary test 75 g of uranine was mixed with 20 L of water and injected into a



Fig. 2: Observation wells and lysimeter in the Union brewery. Beobachtungsbrunnen und Lysimeter in der Unionbrauerei.



Fig. 3: Scheme of the Union urban lysimeter. Schema des Stadtlysimeters in der Unionbrauerei.

point in the middle of the right lysimeter side. The principal test was performed in the same location, but it based on three tracers $- {}^{2}$ H, eosin and UV tracer.

State-of-the-art chemical, geochemical and isotopic analytical methods and techniques were applied and tested in the framework of the quality monitoring. The analyses were made by laboratory of JP Vodovod-kanalazicaija d.o.o., laboratory of Acme Analytical Laboratories Ltd., laboratory of Helmholtz Zentrum München – Institute for Groundwater Ecology and laboratory of JOANNEUM RESEARCH – Institute of Water Resources Management, respectively.

A new Gas Chromatography-Mass Spectrometry (GC-MS) method was applied for chemical analyses and a new High-Performance Liquid Chromatography with Fluorescence Detection (HPLC-FD) method was used for the separation and quantitative determination of the fluorescent dyes and 1,5-naphthalene disulfonate (1,5-NDS) in percolation water samples.

HPLC analyses were performed using a Dionex Summit[®] HPLC System equipped with a gradient pump (P 680), an automatic sample injector (AS-100), chromatography oven (TCC-100), a diode array detector (UVD 340U) and a programmable fluorescence detector (FD) (FP 920) from Jasco. A Gemini 250 × 5 μ m C6-Phenyl column and a security guard cartridge Gemini C6-Phenyl 4 × 3.0 mm (Phenomenex, Eschborn, Germany) were used. The injection volume was 50 μ L.

HPLC parameters established for the analysis of fluorescent dyes were as follows. The mobile phase (A) consisted of a solution of 1 mmol acetic acid and 1 mmol tributylamine in 25% meOH. HPLC grade acetonitrile was used as eluent B. The following gradient elution was used: 0 min 25% B, 12 min 60% B, 15 min 90% B, 17 min 90% B, 19 min back to the initial conditions at 25% B, followed by 6 min of equilibration. The flow rate was 1.0 ml/min, column temperature was maintained at 40 °C and the

injection volume was 50 μ L. The UV-absorption wavelength was 228 and 523 nm with a reference wavelength of 550 nm. The initially FD excitation wavelength was 227 nm, changed to 525 nm after 6 min. The acquired emission wavelength was 333 nm, changed to 525 nm after 6 min. The substances were identified based on their absorption and emission wavelengths and their retention times in the Ultraviolet-Visible Spectroscopy (UV-Vis) and FD chromatograms.

3.4. Statistical processing and modelling of data

Data, collected in the data base, were statistically processed with state-of-the art methods. The multivariate cluster analysis and R-mode factor analysis were used to reveal the associations of chemical elements in sample media (R. ŠAJN, 1999, A. JUREN & B. TRČEK, 2008, A. JUREN et al., 2008). The factor analysis was performed on variables standardized to zero mean and unit standard deviation (R. ŠAJN, 1999). As a measure of similarity between variables, the product-moment correlation coefficient was applied. For orthogonal rotation the varimax method was used.

The collected data were synthesized in a conceptual model of the study area. It served for a three-dimensional mathematical model development of intergranular aquifers of the Ljubljana Moor, Dravlje valley and Ljubljana Field with a VISUAL MODFLOW 4.2 modelling code (A. JUREN & B. TRČEK, 2008, A. JUREN et al., 2008). The model was validated and verified on the basis of geological, hydrogeological, hydrological and geochemical data. It was applied for simulations of contaminant transport in the investigated water body. The simulations were conducted with the MODFLOW 2000, MODPATH and M3DM modelling tools (A. JUREN & B. TRČEK, 2008, A. JUREN et al., 2008).

4. Results

4.1. Study of the field geology and hydrogeology

The study of the field geology and hydrogeology resulted in new geological and hydrogeological maps of the Union brewery groundwater catchment area and in the map of boreholes of the Union brewery groundwater catchment area in scale 1:25000 (D. PETAUER & A. JUREN, 2006a, 2006b, 2006c). The geological model of intergranular aquifers of the Ljubljana Moor, Dravlje valley and Ljubljana Field was illustrated with the map of the Pre-Quaternary basement in scale 1:25000. Data of 178 structural and piezometric boreholes were applied for the model construction.

The Ljubljana Field, Dravlje valley and Ljubljana Moor (Fig. 1) are tectonic depressions, filled with Quaternary clayey-silt and sandy-gravel sediments that are locally transformed into lenses of porous conglomerates.

The depth of sandy-gravel sediments increases in the Ljubljana Field from NW to S and SE where it exceeds 80 m. In the central part of the Ljubljana Field the depth of sandy-gravel sediments varies between 30 and 90 m. The aquifer cross-section in the Union brewery area is presented in Fig. 4.

The Dravlje depression is filled with sandy-gravel sediments with lenses of conglomerates that are 50-80 m deep. They are covered with clayey layers that are up to 20 m thick.



Fig. 4: Schematic aquifer cross-section in the Union brewery area (N-S direction). Schematisches Profil des Aquifers im Bereich der Unionbrauerei (N-S-Richtung).

In the central part of the Ljubljana Moor a distinctive doorstep is present in the Pre-Quaternary basement. The sandy-gravel sediments are 50–60 m deep north of the doorstep. They are covered with silty-clay layers that are more than 20 m thick. The depth of the discussed sediments varies between 100 and 150 m south of the doorstep.

The sandy-gravel sediments of the Ljubljana Field represent an important urban intergranular aquifer. It is recharged by precipitation and inflows from the Sava and Ljubljanica River. The groundwater flow from the Ljubljana Moor direction is additionally recharging the discussed aquifer through sediments of the Dravlje valley and the Ljubljana door (Fig. 1).

The sandy-gravel sediments of the Ljubljana Field aquifer are very heterogeneous as they are divided with conglomerates and silty-clay lenses. On the basis of archive data the permeability k was estimated to 2×10^{-2} to 5×10^{-3} m/s in the central part of the Ljubljana Field where the Union brewery is located. Lenses of clay, silty clay, clayey sand and clayey gravel are present in depths between 8 and 18 m. Their permeability is very low, so they divide the aquifer into the upper and lower part (Fig. 4). The upper aquifer is recharged by precipitation and surface and underground inflows from the Šišenski hrib hill (Fig. 1). The groundwater level of the intergranular aquifer of the Ljubljana Field is 6–22 m below the surface. It is at depths between 18 and 22 m in the Union brewery area (Fig. 4). The sandy-gravel sediments with lenses of conglomerates compose an intergranular aquifer of the Dravlje valley with the permeability coefficient $k > 10^{-4}$ m/s. The ground-water level is at depths 17–25 m. The aquifer is protected with a cover of low permeable or impermeable clayey layers that are 14–20 m thick.

Owing to the variegated geological composition three aquifers are in existence in the Ljubljana Moor: the Holocene, upper Pleistocene and lower Pleistocene aquifer. They are separated with thick layers of silty and sandy clay that have very low permeability. Hence, the hydrostatic pressure is different in each aquifer and the aquifers interact only in contact zones.

4.2. Study of groundwater flow and solute/contaminant transport

The comparison of parameters presence and concentrations at and between different observation points in the catchment area of the Union brewery groundwater resources (Fig. 1 and Fig. 2) gave important information on the recharge conditions, solute/contaminant behaviour, mixing processes and groundwater residence times and with that on hydrodynamic connections among individual aquifers.

The water table varied between 276 and 280 m a.s.l. in most of observation wells, except in Pu-37 and Pu-40, which are influenced by the Ljubljana Moor, and Pu-8 and Pu-43, which should be recharged from hanging aquifers (Fig. 5).

The values of specific electric conductivity (SEC) oscillated in observation wells between 200 and 2500 μ S·cm⁻¹/25 °C (Fig. 6). High SEC (600–1100 μ S·cm⁻¹/25 °C) was measured in piezometers that capture groundwater of the upper gravel aquifer that is locally contaminated (Pu-6, Pu-7, Pu-9, Pu-11, Pu-42). The highest parameter range was registered in the piezometer PU-9, which reflects an intensive groundwater dynamics and contaminant transport. The lowest SEC values (150–350 μ S·cm⁻¹/25 °C) refer to piezometers that are probably recharged by waters from the Šišenski hrib hill (Pu-10 and Pu-41). The SEC data of remaining wells (350–500 μ S·cm⁻¹/25 °C) indicate a little contamination load. Most of them are recharged from the lower gravel aquifer.

The SEC values of the lysimeter sampling points are presented in fig. 7. They varied between 200 and 600 μ S·cm⁻¹/25 °C. The highest values were measured in sampling points on level III (Pu-vr14, Pu-vr23), which is located near the clayey layer. The measurements indicated that the clayey layer acts as a semi-permeable membrane and significantly influence on groundwater dynamics. The water balance of the lysimeter sampling points demonstrated that the bulk of water was discharged to sampling points on level III that is located near the contact between two structurally different layers: silt-sandy gravel and underlying clayey silt-sandy silt with gravel grains (B. TRČEK & A. JUREN, 2007). The hydraulic conductivity of the upper layer is higher from the lower one, which could result in a development of a lateral flow component near this contact. It is presumed that this is the main reason for high SEC values of groundwater near the level III.

The variation of oxygen isotopic composition (δ^{18} O) in sampled waters is illustrated in fig. 8 (B. TRČEK, 2006). It is the most intensive in piezometer Pu-9 (Fig. 8), which reflects intensive groundwater dynamics and mixing of waters from different aquifer layers. Figure 8 indicates a breakthrough process that is particularly evident in January 2006 (after a period of very high water conditions) – groundwater with the similar δ^{18} O like in piezometer Pu-10 was pushed into piezometer Pu-9. Influences of other water masses are evident also in Pu-4 and Pu-10.

Data of trace elements in sampled water were applied in combination with archive data of trace elements contents in soil and water (R. ŠAJN, 1999) for geochemical studies,



Fig. 5: Oscillation of water table in observation wells in the catchment area of the Union brewery groundwater resources. Schwankungen des Grundwasserspiegels in Beobachtungsbrunnen im Einzugsgebiet des Grundwasserkörpers der Unionbrauerei.



Fig. 6: Oscillation of groundwater specific electric conductivity (SEC) in observation wells in the catchment area of the Union brewery groundwater resources. Schwankungen der spezifischen elektrischen Leitfähigkeit (SEC) in Beobachtungsbrunnen im Einzugsgebiet des Grundwasserkörpers der Unionbrauerei.



Fig. 7: Oscillation of groundwater specific electric conductivity (SEC) at the lysimeter sampling points. Schwankungen der spezifischen elektrischen Leitfähigkeit (SEC) in den Beobachtungsstellen des Lysimeters.



Fig. 8: Time series of the oxygen-18 isotopic composition in groundwater, sampled in observation wells in the catchment area of the Union brewery groundwater resources and in precipitation. Zeitreihen der Sauerstoff-18-Konzentration im Grundwasser aus Beobachtungsbrunnen im Einzugsgebiet des Grundwasserkörpers der Unionbrauerei und im Niederschlag.

which enabled to define the geogenic background of sampled waters and to evaluate anthropogenic impacts. In the final multivariate factor solution 46 elements were retained that are presented with five statistical factors (B. TRČEK & R. ŠAJN, 2009). The statistical factor 1 represents a natural distribution of trace elements that are typical for sediments that compose flysch (Co, Dy, Er, Ho, Lu, Ni, Y, Yb), the statistical factor 2 reflects anthropogenic impacts of industry (B, Cd, Cu, Li, Mo, P, Pb, Sb, Se, Sn, U, V, W, Zr), the statistical factor 3 associates trace elements of clay origin (Al, Ce, Gd, La, Nd, Pr, Sm), the statistical factor 4 presents a variation of the iron group elements (As, Fe, Mn, S, Sc, Si), while the statistical factor 5 reflects the anthropogenic urban impacts (Ba, Br, Ca, Cl, Cr, Cs, K, Na, Rb, Re, Sr).

The most important results of geochemical investigations are summarized in fig. 9, which illustrates the anthropogenic impacts of urbanization – particularly waste water (Factor 5) on sampled groundwater. Factor 5 demonstrates that piezometers of the upper gravel aquifer (Pu-6, Pu-7, Pu-9) are significantly impacted by urban contamination. These impacts are very low in shallow production wells of the lower gravel aquifer (Pu-1 and Pu-2) and practically negligible in deep production wells (Pu-3, Pu-4).

Within the framework of WP 6.2.1 a new HPLC-FD method for the separation and quantitative determination of the fluorescent dyes 2,4,5,7-Tetrabromofluorescein, sodium salt (eosin) and 1,5-naphthalene disulfonate (1,5-NDS) in percolation water samples was developed. This method allowed the chromatographic separation of both fluorescent dyes from each other as well as from the other organic trace compounds. Moreover, the HPLC method has low detection limits (0.01 μ g/L eosin, 0.2 μ g/L 1.5-NDS), good accuracy and precision as well as simple handling and instrumentation make this rapid and robust method ideally suited for routine analyses of tracer samples.



Fig. 9: Distribution of factor 5, reflecting anthropogenic impacts of urbanization on groundwater, sampled in the catchment area of the Union brewery groundwater resources. Verteilung des Faktors 5, der anthropogene urbane Auswirkungen auf das Grundwasser repräsentiert, basierend auf Probennahmen im Einzugsgebiet des Grundwasserkörpers der Unionbrauerei.

4.3. Statistical processing and modelling of data

The mathematical model of the Ljubljana Field and Moor was constructed (A. JUREN & B. TRČEK, 2008, A. JUREN et al., 2008). It consists of the network of 320×276 square elements that have a 50 m side length. Each element is defined with the groundwater horizon thickness, the permeability coefficient (k), the specific outflow (Sy), the porosity (n), the effective porosity (ne), the infiltration of precipitation and the initial water table. The thickness of groundwater horizon was determined on the basis of measurements of water table (Fig. 5) and the thickness of sandy gravel sediments given with the thickness to the Pre-Quaternary basement.

The modelling area was vertically divided into four layers that were determined on the basis of thickness of the permeable and impermeable strata in the research area. In areas of the Sava and Ljubljanica River beds the elements were described with a bed bottom, a bed water level and a permeability of the river bed, which represents a flow resistance in the zone between surface and groundwater. On the other hand the mean



Fig. 10: Main directions of groundwater flow in the Union catchment. Hauptfließrichtungen des Grundwassers im Einzugsgebiet der Unionbrauerei.

annual quantities of discharged groundwater were taking into account for the production wells of the Ljubljana waterworks and Union brewery.

In the second phase the mathematical model of the Ljubljana Field and Moor was validated on mean water table and verified with data of the quality monitoring.

The model was applied for simulations of groundwater flow and contaminant transport in the catchment area of the Union brewery groundwater resources. It indicated that groundwater flows into the Union brewery area from the Ljubljana door direction (Fig. 10 and 1). Hence, if the contamination occurs in the area of the Ljubljana door and the contamination is not sanitized in a time of more than one year, then the quality of the brewery groundwater resources could be threatened. The results illustrate that observation wells that are more distant from the Šišenski hrib hill are more vulnerable to contamination, which is in accordance with results of the quality monitoring.

Summary and conclusions

The presented results indicated anthropogenic impacts on groundwater and directions of possible contaminant inflow into the Union brewery area, Ljubljana, Slovenia. They pointed out the risk of pollution breakthrough into the lower gravel aquifer and served for the development of a local hydraulic model that enables scenario simulations on movement of contaminants towards the saturated zone of the lower intergranular aquifer.

The results were used for improvement of exploitation methods of brewery groundwater resources as well as for the methodology improvement of quality and quantity control of brewery water resources.

In a case that groundwater is contaminated in whichever location in the Union catchment area the model could be used to find out the threading degree of ground-water resources that are supplied with brewery production wells and hence to develop a protection strategy in water treatments.

The synthesis of project results enabled

- (a) a precise definition of the Union brewery water body,
- (b) the optimization of groundwater protection zones and
- (c) the protection strategy improvement.

If mechanisms of flow and solute transport are adequately understood, then also efficacious monitoring and protection strategies for sustainable management of investigated groundwater resources can be recommended.

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Zusammenfassung

Eine detaillierte Studie betreffend Grundwasserströmung und Stofftransport wurde im Gebiet des Grundwasserkörpers der Unionbrauerei in Ljubljana, Slowenien, durchgeführt mit den Zielen:

- a) Beurteilung und Vorhersage der Grundwasserfließverhältnisse und des Transports urbaner Schadstoffe durch die ungesättigte und/oder gesättigte Zone des pleistozänen Schotteraquifers und
- b) Analyse des Risikos des Transports von Schadstoffen zu Trinkwasserversorgungen im tieferen pleistozänen Aquifer.

Für diese Zwecke wurden umfangreiche geologische, hydrogeologische, chemische, geochemische und isotopenhydrologische Untersuchungen vorgenommen, sie wurden in die Ergebnisse früherer Untersuchungen integriert und mit administrativen und ökonomischen Bedürfnissen abgestimmt. Die Ergebnisse wurden statistisch bearbeitet und mit Hilfe spezifischer Software zur Simulation von Transport, Akkumulation und Auswaschung von Schadstoffen im Untersuchungsgebiet modelliert. Dies wird Szenariosimulationen und damit die Entwicklung einer Schutzstrategie ebenso ermöglichen wie Decision-Support-Systeme und eine langfristige ökonomische Planung.

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Schlüsselwörter:	Ljubljana, städtischer Porenaquifer, Grundwasserströmung, Schadstoff-
	transport, nachhaltige Wasserwirtschaft.