Solute transport monitoring in the Ljubljana urban aquifer

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ABSTRACT
Groundwater from a Pleistocene sandy-gravel aquifer is an invaluable drinking water resource for the Ljubljana city (Slovenia), as well as for the Union brewery, which is located within an industrialized area near the centre of Ljubljana. A big part of the aquifer recharge area is highly urbanized, which represents a great risk for the groundwater quality assurance. The extensive monitoring of solute transport was performed in the brewery catchment area with the intention to analyze the contamination risk of drinking-water resources. It based on continuous measurements of hydrodynamic parameters and of physico-chemical water parameters (T, SEC) and on groundwater sampling for herbicide, isotope, trace elements and trace gas analyses. results indicated possible contaminant inflow into the Union brewery area. The results pointed out the risk of pollution breakthrough into the lower gravel aquifer and served for the development of a local hydraulic model.

1 INTRODUCTION

Groundwater from a Pleistocene sandy-gravel aquifer is an invaluable water resource for the Union brewery, which is located within a highly urbanised and industrialised area near the centre of Ljubljana (the capital of Slovenia) and supplies quality groundwater 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 quality groundwater is exploited from the lower gravel aquifer that is bounded by an impermeable barrier from the upper gravel aquifer that is contaminated.

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 with the intention of (a) assessing and predicting the directions of groundwater flow and contaminants transport through the unsaturated or/and saturated zone of the Pleistocene gravel aquifer and of (b) analysing 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.

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 the sequential subsiding. Its northern part is named Ljubljansko polje - Ljubljana Field, while its southern part is named Ljubljansko barje - Ljubljana Moor (Figure 1). The former is characterized by the Ljubljanica River with a karstic catchment and the latter by the Sava River with an alpine catchment. The recharge area of the Union brewery groundwater resources 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 geological composition of the study area is presented in Figure 1. The Quaternary fluvial and lacustrine deposits fill the Ljubljana basin. The fluvial sediments form an urban intergranular aquifer. This aquifer is opened in the NE part of the study area (t-wQ1 and š-a sediments in Figure 1). The impermeable or low permeable clay and sandy-clay layers cover the aquifer in other parts (šg-a, p-mQ2, j-mQ2 sediments in Figure 2). Locally lenses of these sediments divide the aquifer into two parts - the upper and lower aquifer, as it is a case in the Union brewery area (Figure 2).

Two isolated hills, the Šišenski hrib hill and the Ljubljana castle hill (Figure 1), have an important role in groundwater dynamics. They consist of impermeable Carboniferous-Permian sediments (Figure 1), hence they are characterised by a prevalent runoff. The area between two hills is called the Ljubljana door (Figure 1).

3 RESEARCH METHODOLOGY

The so-called quantity and quality monitoring was performed in the saturated zone of the observed sandy-gravel aquifer. The saturated zone of the upper and lower aquifer was monitored in 13 observation wells, located in

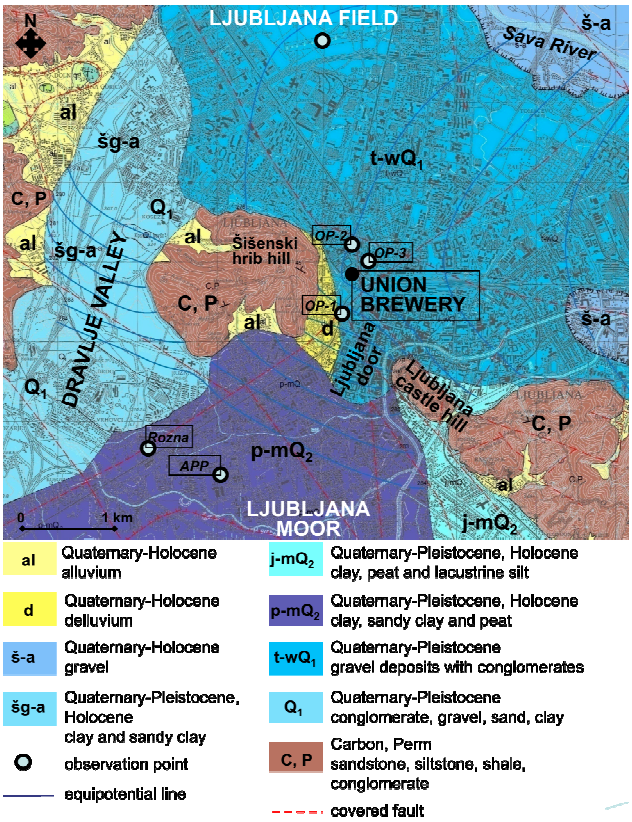

Figure 1. Catchment area of the Union brewery groundwater resources with geological characteristics and observation wells (after Petauer and Juren, 2006)

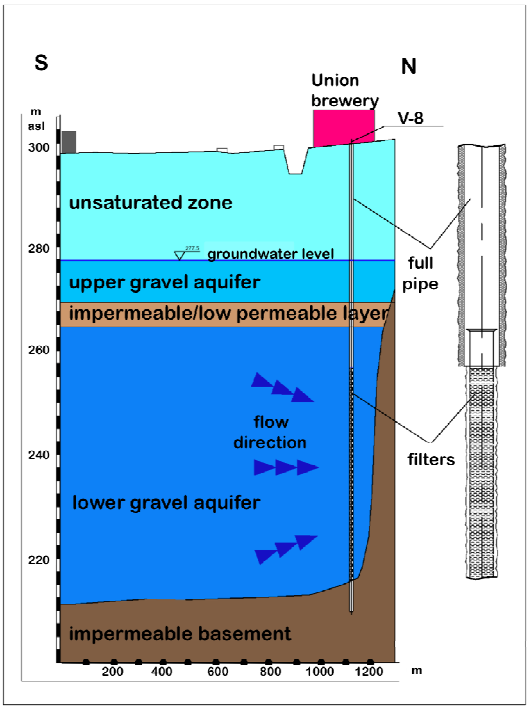

Figure 2. Schematic aquifer cross-section in the Union brewery area (N-S direction) (Juren et al., 2008)

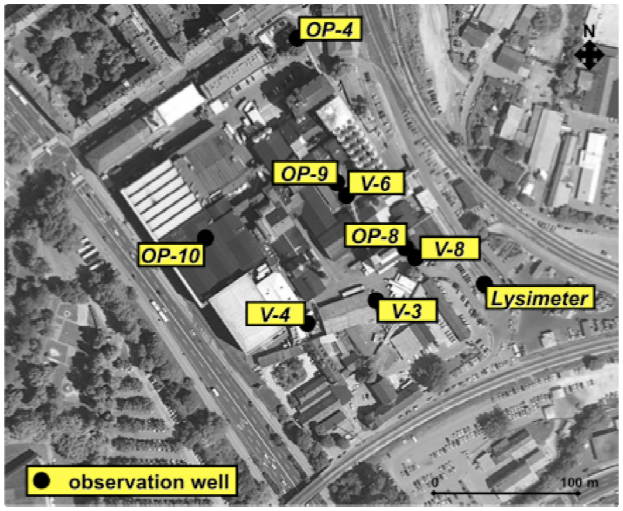

Figure 3. Observation wells in the Union brewery (modified Google Image Terra Matrics, 2008)

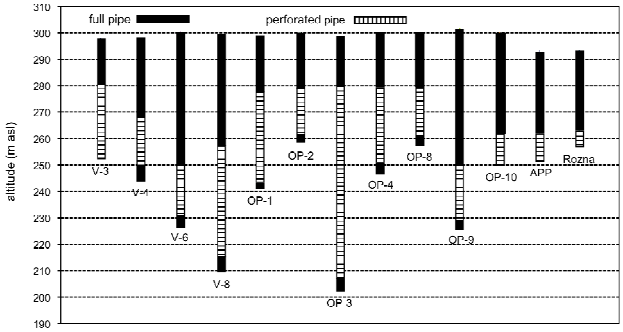

Figure 4. Profiles of observation wells in the Union catchment

the Union brewery and its catchment (Figure 2). The observation wells capture (a) groundwater of the lower aquifer, (b) groundwater of the upper aquifer or (c) both of them (Figure 3). The monitoring included a) continuous measurements of hydrodynamic parameters (groundwater level) and of physico-chemical water parameters (T, SEC) and b) groundwater sampling for herbicide, isotope and trace gas analyses.

The chemical analyses based on solid-phase extraction and GC-MS, LC-MS and LC-MS TOFMS analysis. Deuterium (δ^2H) was measured in continuous flow mode by chromium reduction using a ceramic reactor slightly modified from Morrison et al. (2001). The oxygen isotopic composition ($\delta^{18}O$) of the water was measured by the classic CO_2–H_2O equilibrium technique (Epstein and Mayeda, 1953) with a fully automated device adapted from Horita et al. (1989) coupled to a Finnigan DELTAplus Mass Spectrometer. The carbon isotopic composition of DIC ($\delta^{13}C$-DIC) was analyzed using a fully automated peripheral continuous-flow gas preparation device Gasbench II, which was connected to a Finnigan Delta^{plus} XP mass spectrometer. The measurement of radiocarbon (^{14}C) was carried out using the conventional liquid scintillation counting of benzene produced from barium carbonate. The Chlorofluorocarbons and sulfur-

hexafluoride samples were analyzed by using a gas chromatograph equipped with an Electron Capture Detector (ECD) (Oster et al., 1996). The detection limit of the method was 0.01 pmol/l whereas SF6 was 0.1 fmol/l.
The measurements of tritium and noble gases were carried out with the ^{3}He-ingrowth method (Sültenfuß et al., 2006). ^{4}He, ^{20}Ne and ^{22}Ne were measured with a quadrupole mass spectrometer (Balzers QMG112A). Helium isotopes were analyzed with a high-resolution sector field mass spectrometer (MAP 215–50) (Sültenfuß et al., 2006).

4 RESULTS

The comparison of parameters presence and concentrations at and between different observation points in the catchment area of the Union brewery groundwater resources 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 groundwater level varied in the Union catchment area between 276 and 280 m asl between 2006 and 2009.The annual parameter range was the maximal - more than 2 m in 2009, while it was 1-1.5 m in other years. The groundwater temperatures ranged between 11 and 17 °C. The increased temperature values were measured in the brewery area in piezometers OP-9, OP-8 and OP-4 (Figures 3 and 4), which could result from technological processes or wastewater leakage.
The values of specific electroconductivity (SEC) oscillated in observation wells between 200 and 1100 µS·cm^{-1}/ 25 °C (Figure 5). The high values (700-1100 µS·cm^{-1}/ 25 °C) were measured in piezometers OP-3, OP-8 and OP-4 that capture groundwater of the upper gravel aquifer, which is locally contaminated. The piezometer OP-3 is located in the brewery vicinity (Figures 1 and 4) and the other two piezometrs in the brewery area (Figures 3 and 4). The lowest values (200-300 µS·cm^{-1}/25 °C) refer to piezometers OP-9 and OP-10 that are probably recharged by waters from the Šišenski hrib hill (Figure 1). The SEC data of production wells varied between 400 and 500 µS·cm^{-1}/25 °C and indicate a little contamination load. They are mostly recharged by the lower gravel aquifer (Figures 2 and 4). The piezometers OP-3, OP-8 and OP-4 have also the highest SEC ranges, which reflect an intensive groundwater dynamics and contaminant transport (oscillation in OP-10 results from the pumping for groundwater sampling). This was inferred also from results of the herbicides monitoring (Juren et al., 2008; Trček & Juren, 2006, 2007). The piezometer OP-8 should be exposed. Namely, on the basis of previous isotopic investigations (Juren et al., 2008; Trček, 2006) the risk of contamination spread through the upper gravel aquifer is evident here as well as the possibility of contaminants breakthrough into the lower gravel aquifer. The unknown compound with base ion m/z 147 has been determined with GC-MS analysis (Figure 6). NIST05 library search gave more than 100 possible results for the unknown compound with the similar probability, containing bicyclic heteroaromatic ring with N and or O. One group of them confirms the chemical class of benzimidazoles with wide-spread use - mostly as fungicides, lubricants, metal corrosion inhibitors and pharmaceuticals. In same samples there was few other similar compounds identified by NIST05: 5-methylbenzotriazole (CAS 136-85-6; metal corrosion inhibitor, antioxidant), 2-methyl-2H-benzotriazole (CAS 16584-00-2; pesticide formulations, antimicrobial agents), 5,6-dimetilbenzotriazol (CAS 4184-79-6; lubricants, metal corrosion inhibitor, heat transfer fluids).

Narrowing of the candidate list was conducted by LC-MS techniques. In meant time a semi-quantitative monitoring of the unknown compound was established. The respond for the unknown compound was reporting relative to the respond of internal standard calibration by 3,4-dichloroaniline / 3,4-dichloroaniline D2 calculated by

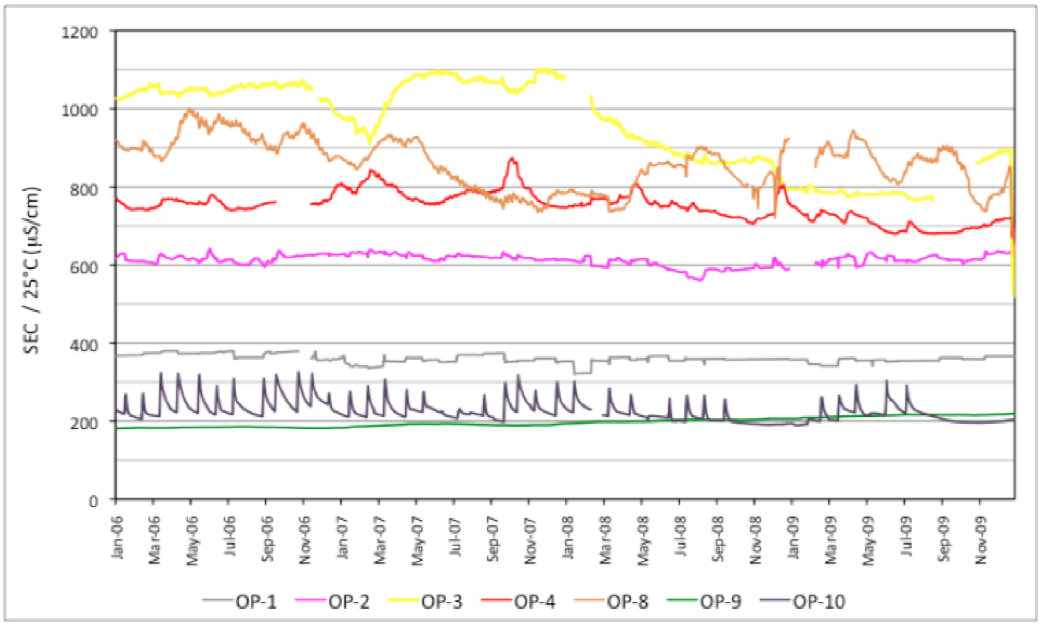

Figure 5. *Oscillation of groundwater specific electroconductivity in the Union catchment area in the period 2006-2009*

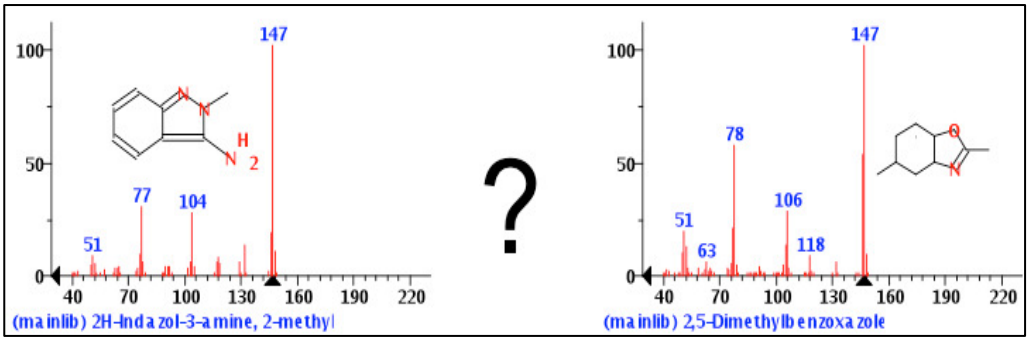

Figure 6. Properties of the unknown compound with a source in the Union brewery, piezometer OP-8

linear regression (Auersperger and Kus, 2002). M/z 147 of the unknown, m/z 161 of the 3,4-dichloroaniline and m/z 165 of the 3,4-dichloroaniline D2 were used for target ion. M/z 104, 77 for the unknown and m/z 163, 128 for the 3,4-dichloroaniline and its deuterated analogue were used for confirmation the discussed ions. By simple electrospray (ESI) LC-MS method it was indicated that the unknown compound is not a high volatile compound and m/z 147 belongs to molecular ion.

After that more complex TOF MS system was used. The LC-MS-TOF MS analyses enabled to study fragmentation and to obtain molecular formula of the unknown compound. Hence, the candidate list was narrowed. With LC with mass spectrometric detection several chromatographic peaks were identified. The unknown compound could be: a) MH+ m/z 148 (most probable $C_8H_{10}N_3$, less probable $C_9H_{10}NO$), b) MH+ m/z 134 (most probable $C_7H_8N_3$, less probable C_8H_8NO), c) MH+ m/z 120 (most probable $C_6H_6N_3$, less probable C_7H_6NO). It was concluded that the molecular formula of the unknown compound is the most probably $C_8H_9N_3$. The sources of pollution could be lubricant containing alkylsubstituted benzotriazoles, metal corrosion inhibitor or degradation of fungicide.

The data of absolute groundwater age are also essential for the sustainable management of discussed groundwater resources. Trace gas measurements, tritium investigations and dissolved noble gas concentrations in groundwater can provide valuable information on recharge temperatures and enable ^3H–^3He age-dating with the use of physically based interpretive models.

Table 1 shows the concentrations of CFCs and SF_6 found in groundwater samples. All of the groundwater samples have SF6 concentrations below modern atmospheric concentrations whereas nearly all CFC concentrations (except for CFC-113 of App) of these water samples are above the equilibrium values, suggesting some anthropogenic addition of CFC. Such CFC excess values are found especially in densely populated urban regions. In such cases age dating based on CFC`s isn't possible. However in some cases the site–specific excess values can give information about the flow direction of the groundwater or mixing processes etc. like a dye. Remarkable is that all three CFC species are simultaneously in excess. More often an excess is observed for CFC–12/CFC–11 or CFC–113, respectively. This structure results from the different use patterns of these substances in former times. For the tracer SF_6 the situation is completely different. All of the samples have a

Table 1. Measured chlorofluorocarbon (CFC) and sulfur-hexafluoride (SF_6) concentrations in groundwater

Sampling point	Sampling date	CFC [pmol/l]			SF_6 [fmol/l]
		F12	F11	F113	
V-3	05.06.2009	7,1 ±0,8	83 ±25	24 ±5	1,9 ±0,2
V-8	05.06.2009	7,1 ±0,8	22 ±5	8 ±2	3,5 ±0,4
OP-1	05.06.2009	8,0 ±0,8	13 ±3	2,1 ±0,3	1,5 ±0,2
OP-2	05.06.2009	3,3 ±0,2	58 ±18	11 ±3	2,1 ±0,3
OP-8	05.06.2009	4,5 ±0,5	37 ±8	15 ±3	3,8 ±0,4
OP- 10	05.06.2009	5,8 ±0,3	ca. 490	ca. 75	1,4 ±0,2
Rozna	05.06.2009	4,8 ±0,3	15 ±3	1,5 ±0,2	2,0 ±0,2
App	05.06.2009	3,5 ±0,2	7,8 ±0,8	0,49 ±0,05	1,6 ±0,2

SF_6 concentration near or below the recent equilibrium value with the atmosphere (except for OP-8 and V-8). This indicates that the water contains post–1970's water. The piston flow model ages derived from the SF_6 concentration are listed in the table below (Table 2).

Table 2. Model ages derived from the measured SF_6 concentration

Sample ID	Dating tracer	model ages in years
V-3	SF_6	≈12
V-8	SF_6	
OP-1	SF_6	≈15
OP-2	SF_6	≈10
OP-8	SF_6	
OP-10	SF_6	≈16
Rozna	SF_6	≈11
App	SF_6	≈14

The range of the residence time based on the SF_6 measurement is between about 10 years to 16 years.

The results of the tritium measurements and trace gas analysis are given in Table 3. Tritium concentrations and ages refer to 1st September 2009 under the assumption of piston flow conditions in the aquifer. All samples show significant concentration of ^4He from radiogenic sources. The concentration of tritium and tritiogenic ^3He match the concentration of tritium in precipitation quite well, except for sample OP-10. This indicates that V-3, V-8 and OP-8 do not contain any tritium-free water. This means their ages of the complete water samples are determined quite well by the Helium-Tritium ages. Sample OP-10 falls a little below the precipitation line (Figure 7).

Table 3. Model ages derived from ^{3}H-^{3}He dating

Sample ID	Tritium [TU] (1.9.2009)	Excess Ne in %	^{4}He radiogenic [ccSTP/kg]	^{3}He tritiogenic [TU]	Age [y] normalized to (1.9.2009)
V-3	5.35 ±0.1	21	5.25 E-5	9.0	18±1
V-8	5.3 ±0.2	16	4.6 E-5	4.5	11±1
OP-8	5.7 ±0.2	20	4.2 E-6	1.5	4±1
OP-10	4.4 ±0.1	30	3.5 E-5	25	33±2
			error: 1E-6	error:0.5 TU	error: 1 year

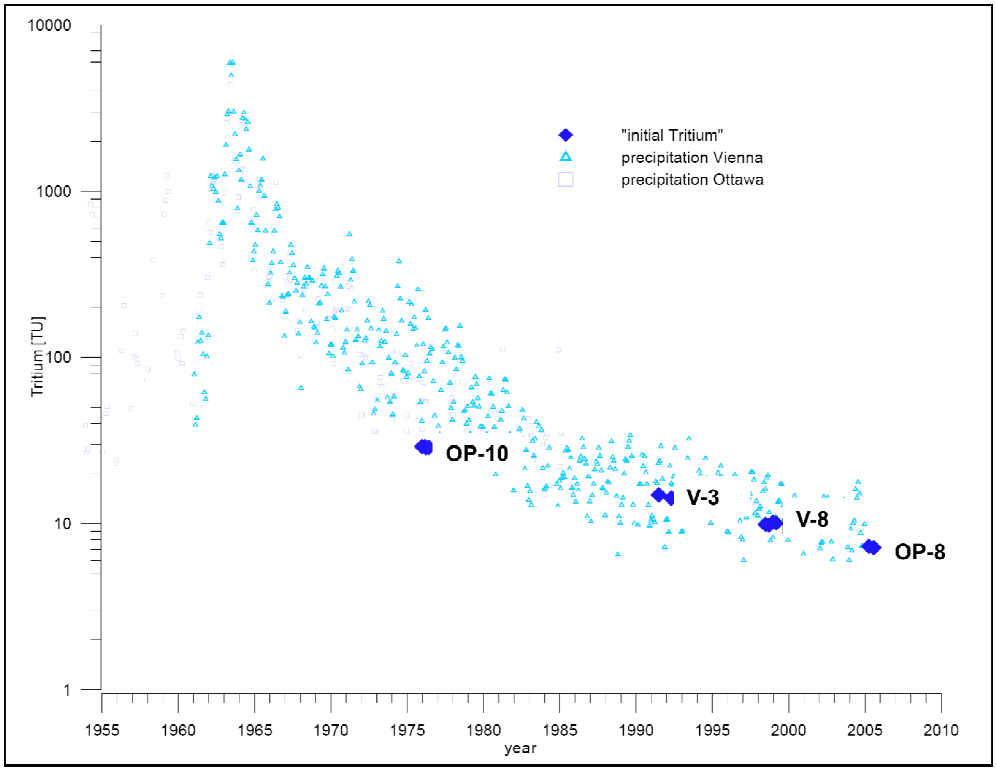

Figure 7. Sum of tritium and tritiogenic ^{3}He of the samples and the calculated infiltration period and compares the sum to concentration in precipitation for the Vienna. Symbols represent multiple measurements of the same sample

This clearly shows that sample OP-10 contains a portion of tritium–free water, which must have been infiltrated before 1955. This tritium-free portion could be in the order of 20–50%. The solubility equilibrium concentrations of all samples are calculated assuming mean annual temperature of 10°C for the period of infiltration. The portion of excess He is quite typical, namely in the order of 15–30% of the equilibrium value.
The concentration of radiogenic ^{4}He can be used as an indicator for older waters. For sandy aquifers a concentration in the order of the equilibrium value marks water of an age of some hundreds to 1000 years. Here I assume a quite intensive source for radiogenic ^{4}He, because the Tritium-^{3}Helium data show that the samples do not contain any water from before 1955 except for sample OP-10. Even the youngest sample OP-8 shows a significant concentration of radiogenic ^{4}He (Figure 8).

5 CONCLUSIONS

The results illustrate that observation wells of the brewery area that are more distant from the Šišenski hrib hill (Figures 1 and 3) are more vulnerable to contamination.

Groundwater from OP-10 that is the most close to the Šišenski hrib hill from among the observation wells is more than 30 years old (Table 3). Although the production well V-8 is deeper from V-3 the ^{3}H-^{3}He dating indicated that V-3 groundwater is older for approximately 7 years. The flow velocity decreases towards the Šišenski hrib hill and is the minimal close to the hill. On the other hand groundwater of the upper aquifer in piezometer OP-8 is the youngest (Table 3), which reflects higher flow velocities in this area and its vulnerability to contamination indicated also with the herbicide monitoring.

The results pointed out the risk of pollution breakthrough into the lower gravel aquifer and served for the development of a local hydraulic model. The protection strategy was upgraded and consequently, guidelines for the implementation of the quality and quantity monitoring were prepared.

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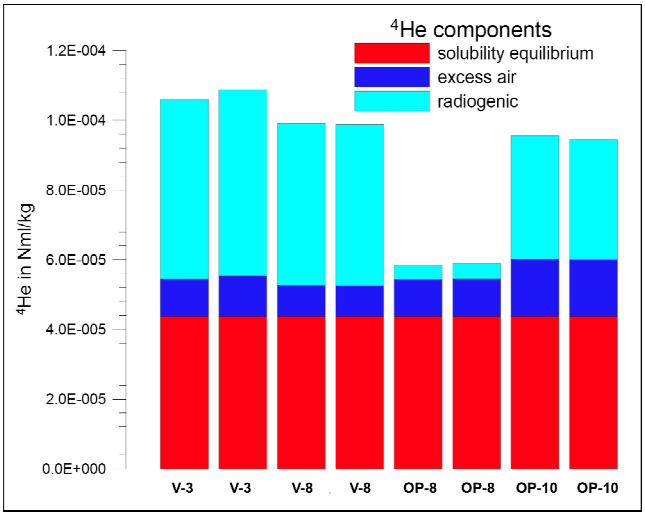

Figure 8. ^{4}He concentration separation by origin (double measurement included)

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