

Risk assesment of an urban aquifer based on environmental tracers

Ocena ranljivosti urbanega vodonosnika na osnovi okoljskih sledil

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Abstract

Groundwater from a Pleistocene sandy-gravel aquifer is a drinking water resource for the Union brewery, located near the centre of Ljubljana (Slovenia). A large part of the aquifer recharge area is highly urbanized, which represents a great risk for the groundwater quality assurance. The groundwater dating techniques were used to study the contamination risk of this drinking-water resource. The application of chlorofluorocarbons (CFCs), sulphur hexafluoride (SF₆) and tritium-helium-3 (³H-³He) age indicator was tested, as they haven't been used in Slovene urban areas so far. The results reflect that the ³H-³He dating technique is the most suitable for a groundwater age determination in the study urban aquifer, since SF₆ and particularly CFCs concentrations could be affected by the local contaminations. They indicated that average groundwater residence times range from 10 to 30 years. Boreholes that are more distant from the Šišenski hrib hill are more vulnerable to contamination due to flow of young groundwater from a direction of the main aquifer, which is exposed to the urban pollution. The presented results were supplemented with chemical investigations of groundwater organic pollutants. An unknown trace organic pollutant with a base ion mass-to-charge ratio 147 was put into focus. Its identification based on chromatographic separation and a mass spectrometric detection with GC-MS, LC-MS and LC-TOF MS techniques. The newly detected trace organic pollutant in sampled groundwater represents together with the ³H and ³He data a new technique to study the flow paths and contaminant transport in the urban aquifer in both, the lateral and vertical directions.

Izveleček

Podzemna voda pleistocenskega peščeno-prodnega vodonosnika je vir pitne vode Pivovarne Union, v neposredni bližini centra Ljubljane. Velik del napajalnega območja vodonosnika je urbaniziran, kar lahko ogroža kvaliteto pitne vode. Tveganje onesnaženja obravnavanega vira pitne vode se je proučevalo s pomočjo tehnik za določanje starosti podzemne vode. V ta namen se je prvič v v slovenskih urbanih območjih testirala uporaba sledila ³H-³He, CFCs in SF₆. Rezultati so pokazali, da je za določanje starosti podzemne vode v proučevanem urbanem vodonosniku najbolj uporabna ³H-³He tehnika, saj na koncentracije SF₆, zlasti pa CFC, vpliva lokalno onesnaženje. S pomočjo omenjene tehnike je ugotovljeno, da je povprečna starost podzemne vode raziskovanega območja med 10 in 30 let. Bolj ko so vrtnice oddaljene od Šišenskega hriba, bolj so ranljive na onesnaženje, ker so pod vplivom dotoka mlade vode s centralnega območja vodonosnika, ki je izpostavljeno urbanemu onesnaženju. Kemijske raziskave organskih onesnaževal v podzemni vodi dopolnjujejo predstavljene rezultate. Le te slonijo na nepoznanem slednem organskem onesnaževalu z osnovnim ionom, v katerem je razmerje med maso in električnim nabojem 147. Omenjena spojina se je odkrila s pomočjo kromatografske separacije in različnimi sklopljenimi tehnikami – plinsko kromatografijo z masno spektrometrijo (GC-MS), tekočinsko kromatografijo z masno spektrometrijo (LC-MS) in tekočinsko kromatografijo z masno spektrometrijo na čas preleta ionov (LC-TOF MS). Odkrito sledno organsko onesnaževalo predstavlja, skupaj s ³H in ³He podatki, novo tehniko za proučevanje toka podzemne vode in prenosa onesnaženja v urbanem vodonosniku, tako v lateralni kot v vertikalni smeri.

Introduction

Groundwater from a Pleistocene sandy-gravel aquifer is an invaluable water resource for the Union brewery, which is located within an industri-

alized area near the centre of Ljubljana (Slovenia) and supplies quality groundwater from four production wells. A large 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 began in 2006 in the catchment area of the brewery groundwater resources with the intention of assessing and predicting the directions of groundwater flow and contaminants transport through the Pleistocene sandy-gravel aquifer and of analysing the contamination risk of drinking-water resources in the lower Pleistocene aquifer. Knowledge of groundwater residence time is of great importance for understanding the key issues in the water quality evolution. For that purpose the groundwater dating techniques based on chlorofluorocarbons (CFCs), sulphur hexafluoride (SF_6) and tritium-helium-3 (^3H - ^3He) age indicator were tested in the study urban aquifer, as they haven't been used in Slovenia so far.

^3H , ^3He , CFC and SF_6 are environmental tracers. Their concentrations in groundwater could be affected by numerous physical and chemical processes (PLUMMER & BUSEMBERG, 2006), therefore a multi-tracer approach was essential to resolve estimates of sampled water ages in the study urban area.

Large-scale production of CFC-12 began in the early 1940s, followed by CFC-11 in the 1950s and by CFC-113 in the 1960s (PLUMMER & BUSEMBERG, 2006). Inevitably they leaked into the environment, with atmospheric concentrations rising until the 1990s, when production was cut back to protect the ozone layer.

SF_6 has been detectable in the atmosphere since 1953 and is still rising strongly in concentration. It is a stable gas for which no chemical reactions are known to occur in shallow groundwater conditions, and it has a well-known input function (BUSEMBERG & PLUMMER, 2000). The dating range of water with SF_6 is from 1970 to modern. The SF_6 data are particularly useful for dating post-1993 groundwater and yield excellent results in urban areas that are often contaminated with CFCs and other VOCs (BUSEMBERG & PLUMMER, 2000).

The application of ^3H for groundwater age determination depends on knowledge of the ^3H input precipitation concentration, which may be poorly known or vary with time. Studying the relation between ^3H and its stable daughter product ^3He in water samples offers the possibility of determining groundwater ages without knowing the ^3H input function. The original ^3H input concentration could be reconstructed from the amount of tritogenic ^3He in solution due to ^3H decay when no helium has been lost from the solution (SOLOMON et al., 1993). However, for this dating technique the recharge temperature, excess air and other sources and sinks which result from possible gains and losses of ^3He other than tritogenic should be identified and corrected.

Tritium is considered to be a conservative trac-

er for most hydrologic studies. Its natural abundance drastically increased due to anthropogenic sources produced during nuclear weapons testing in the late 1950s and early 1960s. The present ^3H concentration is several magnitudes lower than during the period of the weapons testing and it continues to decrease. Groundwaters are typically in the 5–10 TU range today (CRISS et al., 2007; ROSE, 2007). ^3H derived tritogenic ^3He is built up in the groundwater as the contained tritium decays. Therefore, the ^3H - ^3He ratio decreases with age. The ^3H - ^3He technique can be used to date groundwater that is not more than few years old, which is an advantage in comparison with a CFC dating (HAN et al., 2006).

The results of groundwater dating were supplemented with chemical investigations of groundwater organic pollutants. A newly detected unknown trace organic pollutant was put into focus in order to study its source and application for risk assessment of the study urban aquifer.

Study area

The Union brewery is located in the Ljubljana city at an altitude of 300.3 m asl. The Ljubljana area is a large tectonic depression, surrounded by hills and mountains (up to 1300 m asl). It was formed in Plio-Quaternary by the sequential subsiding. Its northern part is named Ljubljana Field – Ljubljansko polje, while its southern part is named Ljubljana Moor – Ljubljansko barje (Fig. 1). The former is characterized by the Ljubljana River with a karstic catchment and the latter by the Sava River with an alpine catchment. The recharge area of the brewery groundwater resources is situated close to the boundary line of the Ljubljana Moor – Ljubljansko barje and Ljubljana Field – Ljubljansko polje, 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 Fig. 1. The Quaternary fluvial and lacustrine deposits fill the Ljubljana depression. The fluvial sediments form an urban intergranular aquifer that is opened in the NE part (t-wQ1 and š-a sediments in Fig. 1). The depth of sandy-gravel sediments increases in the Ljubljana Field – Ljubljansko polje from NW to S and SE where it exceeds 80 m. It varies between 30 and 90 m in the central part of the Ljubljana Field – Ljubljansko polje, where the Union brewery is located. Fig. 2 illustrates that the aquifer is approximately 90 m deep in the brewery area.

In other parts of the Ljubljana depression the impermeable or low permeable clay and sandy-clay layers (šg-a, p-mQ2, j-mQ2 sediments in Fig. 1) cover the aquifer. Locally lenses of mentioned sediments divide the aquifer into two parts – the upper and lower aquifer, as it is a case in the Union brewery area (Fig. 2).

Two isolated hills – the Šišenski hrib hill and the Ljubljana castle hill (Fig. 1) have an important role in groundwater dynamics. They consist of impermeable Carboniferous-Permian sediments

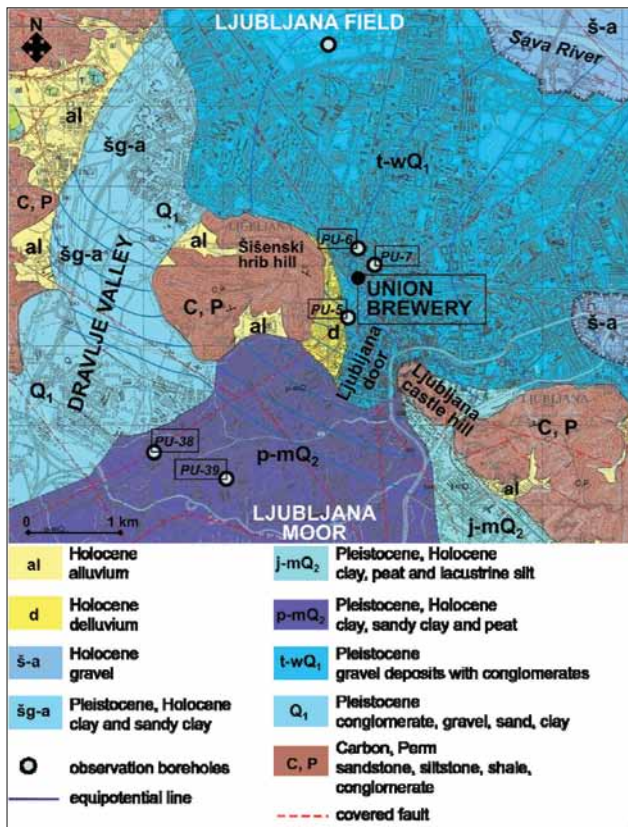


Fig. 1. Geological map of the Union brewery catchment area (PETAUER & JUREN, 2006 a)

Sl. 1. Geološka karta vplivnega območja Pivovarne Union (PETAUER & JUREN, 2006 a)

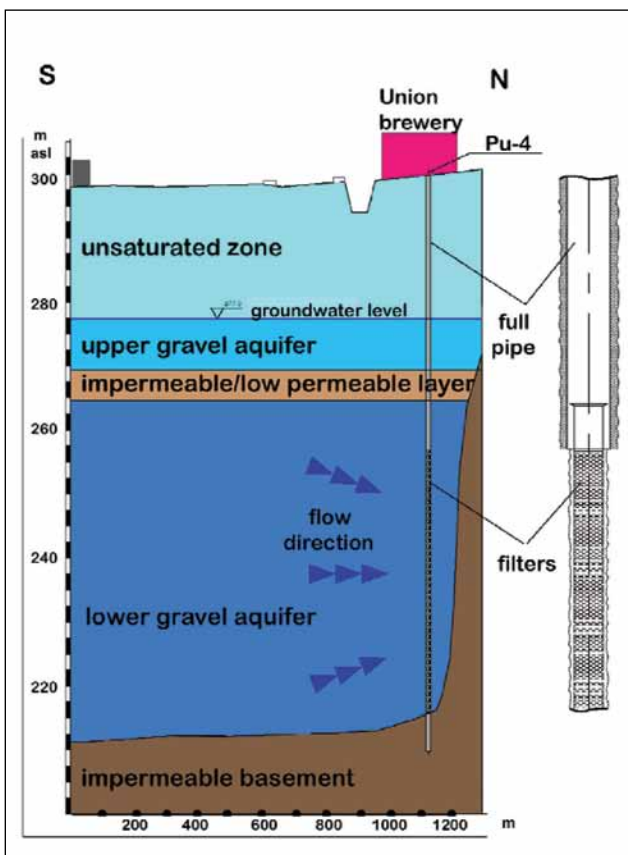


Fig. 2. Schematic aquifer cross-section in the Union brewery area, N-S direction (PETAUER & JUREN, 2006 b)

Sl. 2. Shematski prerez vodonosnika na območju Pivovarne Union, smer S-J (PETAUER & JUREN, 2006 b)

(Fig. 1), thus they are characterised by a prevalent runoff. The area between the hills is called the Ljubljana Door (Fig. 1).

The Pleistocene sandy-gravel aquifer of the Ljubljana Field – Ljubljansko polje is recharged by precipitation and inflows from the Sava and Ljubljanica Rivers. The groundwater flow from the Ljubljana Moor –Ljubljansko barje direction is additionally recharging the discussed aquifer through sediments of the Dravljje valley and the Ljubljana Door (JUREN et al., 2008). Surface and subsurface run-off from the Šišenski hrib hill represent an additional recharge of the aquifer in the catchment area of the Union brewery groundwater resources. In this area groundwater table is 18–22 m below the surface under law water conditions (JUREN et al., 2008).

Research methodology

The so-called quantity and quality monitoring was performed in the catchment area of the Union brewery groundwater resources in the period 2006–2009. The Pleistocene sandy-gravel aquifer was monitored in 13 observation boreholes, located in the Union brewery area and its catchment (Figs. 2 and 3). The observation boreholes capture groundwater of the lower aquifer, groundwater of the upper aquifer or both of them (Fig. 4).

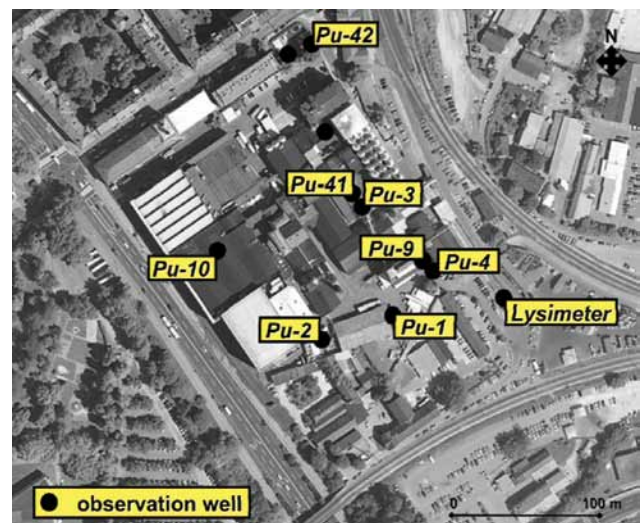


Fig. 3. Observation boreholes in the Union brewery area (Internet)
Sl. 3. Opazovalne vrtine na območju Pivovarne Union (Internet)

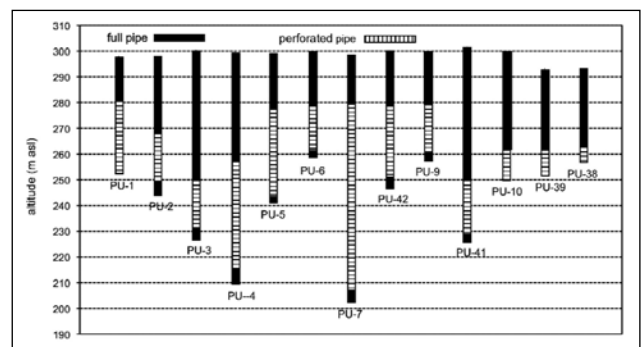


Fig. 4. Profiles of observation boreholes in the study area
Sl. 4. Profili opazovalnih vrtin na raziskovalnem območju

The discussed monitoring included continuous measurements of groundwater table and physico-chemical water parameters (T and SEC) and groundwater sampling for isotope, trace gas, noble gas and herbicide analysis. Groundwater table and physico-chemical water parameters were measured hourly by DMS (Data Merilni Sistemi d.o.o) data loggers.

On the basis of CFCs, $^3\text{H}/^3\text{He}$ and SF_6 data the groundwater ages were estimated. Groundwater sampling for CFCs and SF_6 analyses was performed on June 5, 2009 and for ^3H and ^3He measurements on September 1, 2009. Water samples for tritium analysis were collected in 100 mL HDPE bottles and 1L PE bottles, respectively. CFCs and SF_6 samples were collected unfiltered and without atmospheric contact in glass bottles contained within metal cans by the displacement method of OSTER et al. (1996). This method ensures that the sample is protected from possible atmospheric contamination by a jacket of the same water. Water for noble gas analysis was pumped with a submersible pump (Grundfos MP1) through a transparent hose into a copper tube (volume 40 mL, outer diameter 1 cm). A transparent hose with a regulator clamp was attached to the outlet of the copper tube. The clamp was used to squeeze the hose to increase pressure in order to suppress potential degassing and the transparent hose was constantly checked for bubbles. Pumping proceeded until steady state conditions with regard to temperature and conductivity were reached. The copper tubes were subsequently pinched off with stainless steel clamps to maintain highly vacuum tight sealing.

An important distinction can be made between dating based on CFCs and SF_6 and dating by a $^3\text{H}/^3\text{He}$ technique. In the case of ^3H - ^3He dating, the initial ^3H content of the water sample is reconstructed from measurements of both the parent isotope (^3H) and tritiogenic ^3He , while dating with CFCs and SF_6 requires prior knowledge of the initial condition (HAN et al., 2006). The ^3H - ^3He technique can be used to date groundwater that is not more than few years old, which is an advantage in comparison with a CFC dating (HAN et al., 2006). For this dating technique the recharge temperature, excess air and other sources and sinks which result from possible gains and losses of ^3He other than tritiogenic were estimated on the bases of Ne and ^4He isotope analyses (COOK & SOLOMON, 1997).

Groundwater dating with CFCs and SF_6 refers to the process of estimating the historical date at which a parcel of water was recharged to a groundwater system. These techniques may provide reliable dating information only if physical and chemical processes affecting trace gas concentrations in groundwater are accounted for. For this purpose additional measurements were made – measurements of dissolved oxygen concentration for determination of potential for microbial degradation and noble gas measurements for defining recharge temperature and excess air (PLUMMER et al., 2006).

The CFCs and SF_6 measurements were performed at Spurenstofflabor, Wachenheim, Germany by gas chromatography using an electron capture detector (GC ECD) after pre-concentration using a purge-and-trap technique (BUSENBERG & PLUMMER, 2000). The detection limit of this method was 0.01 pmol/l for CFCs and 0.1 fmol/l for SF_6 .

The ^3H and ^3He measurements were carried out with the ^3He -ingrowth method (SÜLTENFUSS et al., 2006) at the Institute of Environmental Physics, University of Bremen, Germany. ^3H is expressed in tritium units – TU, which represents 1 ^3H atom in 10^{18} atoms of ^1H or an activity of 0.118 Bq/kg in water. The uncertainty is typically less than 3 % for samples of >1 TU and 0.01 TU for very low concentrations.

Isotopic analysis of He and Ne were performed at the Institute of Environmental Physics, University of Bremen, Germany. ^4He , ^{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). The system was calibrated with atmospheric air and controlled for stable conditions for the He and Ne concentrations and the $^3\text{He}/^4\text{He}$ ratio. The precision of the He and Ne concentrations is better than 1 % and better than 0.5 % for the $^3\text{He}/^4\text{He}$ ratio.

During the monitoring period the herbicides were analysed in groundwater samples seasonally at the laboratory of JP Vodovod-kanalizacija d.o.o., alternately qualitatively and quantitatively (AUERSPERGER et al., 2005 and 2009). The qualitative analyses detected the unknown trace organic pollutant with the source in the borehole PU-9. Therefore, the passive inox samplers with granular active carbon were installed into the borehole in order to identify this compound. The organic compounds were absorbed in the passive sampler for approximately 3 months and then analysed at the laboratory of JP Vodovod-kanalizacija d.o.o. and at the Jožef Stefan Institute, Department of environmental sciences (AUERSPERGER et al., 2011). The identification of the unknown trace organic pollutant based on a pre-concentration by liquid-liquid extraction, solid-phase extraction, a chromatographic separation and a mass spectrometric detection with gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS) and liquid chromatography-time of flight mass spectrometry (LC-TOF MS).

Results and Discussion

In the period 2006–2009 the groundwater table varied between 276 and 280 m asl in the study area. The annual parameter range was more than 2 m in 2009, while it was 1–1.5 m in other years.

The groundwater temperature ranged from 11 to 17 °C. The increased temperature values were measured in the brewery area in boreholes PU-41, PU-9 and PU-42 (Figs. 3 and 4), which could re-

sult from technological processes or a wastewater leakage.

Data of groundwater ages were essential for assessing the groundwater vulnerability to contamination. Trace gas, noble gas and tritium investigations provided valuable information on recharge temperatures and average residence times of sampled groundwater.

The use of CFCs and SF₆ as indicators of residence time is based on the known rise of their atmospheric concentrations over the past 60 years, the observation that they are well-mixed in the atmosphere (unlike ³H), and the assumption that they dissolve in water according to their Henry's Law solubility at the temperature of recharge (PLUMMER & BUSENBERG, 1999).

Concentrations of CFCs in groundwater samples are presented in Table 1. All concentrations, except CFC-113 of PU-39, were above the equilibrium values, suggesting some anthropogenic addition of CFC. Such CFC excess values are typical for densely populated urban areas. In such cases the age dating based on CFCs isn't possible. Nevertheless, the site-specific excess values give information about the groundwater flow direction and mixing processes. It is remarkable that all three CFC species are simultaneously in excess. The excess is observed more often for CFC-12/CFC-11 or CFC-113, respectively. This structure results from different use patterns of these substances in former times.

Table 1 presents also concentrations of SF₆ in groundwater samples. All samples had values near or below the recent equilibrium value with the atmosphere, except samples PU-9 and PU-4. This indicates that groundwater samples contain post-1970's water (KIPFER et al., 2002). Under the assumption of the piston flow in the study aquifer groundwater ages were derived from the SF₆ data. A piston-flow model is a very common and frequently used approach in groundwater hydrology. Several researchers used it for age determination in alluvial aquifers (HUNT et al., 2005). However, the piston-flow model is a simplification showing a mean groundwater age, which is identical to an advective age in the case if dispersion and diffusion are zero.

Ages of groundwater in the study area, derived from the SF₆ concentrations are listed in Table 2. The groundwater average residence time based

on the SF₆ measurements is in the range between 10 and 16 years. In the brewery area the youngest groundwater is captured from the upper sandy-gravel aquifer that is the most distant from the Šišenski hrib hill (PU-6, Figs.1-4). On the other hand, groundwater captured from boreholes close to the Šišenski hrib hill has the longest residence time (PU-5 and PU-10, Figs.1-4).

Sampling point	Model ages (years)
PU-1	≈12
PU-4	
PU-5	≈15
PU-6	≈10
PU-9	
PU-10	≈16
PU-38	≈11
PU-39	≈14

Table 2. Ages of groundwater in the study area, derived from the SF₆ concentrations under the assumption of the piston flow model

Tabela 2. Starost podzemne vode na raziskovalnem območju, izračunana na podlagi koncentracij SF₆ ob upoštevanju modela batnega toka

The ³H/³He ratio in groundwater samples was used to reconstruct the initial ³H concentration in sampled groundwater during the infiltration period and to provide an independent check of dating results obtained from CFC and SF₆ data. Namely, the common effects that affect the CFC and SF₆ based ages, such as local contaminant sources, chemical processes and mixing fractions do not have an impact on the ³H/³He based ages (HAN et al., 2006). Ages were determined from the following relationship:

$$\text{Groundwater Age (years)} = -17.8 \times \ln(1 + {}^3\text{He}_{\text{trit}}/{}^3\text{H}) \quad (1)$$

The longtime data series of annual weighted values of ³H in Vienna precipitation (Fig. 6) were used to calculate the ³H input function.

The results of ³H and ³He measurements in groundwater samples are given in Table 3. The ³H-³He dating technique required corrections, related to excess air and non-tritogenic sources of ³He that based on Ne and ⁴He data (Tab. 3). All groundwater samples show significant concentration of ⁴He from radiogenic sources (Fig. 5). The solubility equilibrium concentrations of all

Sampling point	Sampling date	CFCs [pmol/l]			SF ₆ [fmol/l]
		CFC-12	CFC-11	CFC-113	
PU-1	05.06.2009	7,1 ±0,8	83 ±25	24 ±5	1,9 ±0,2
PU-4	05.06.2009	7,1 ±0,8	22 ±5	8 ±2	3,5 ±0,4
PU-5	05.06.2009	8,0 ±0,8	13 ±3	2,1 ±0,3	1,5 ±0,2
PU-6	05.06.2009	3,3 ±0,2	58 ±18	11 ±3	2,1 ±0,3
PU-9	05.06.2009	4,5 ±0,5	37 ±8	15 ±3	3,8 ±0,4
PU-10	05.06.2009	5,8 ±0,3	cca 490	ca. 75	1,4 ±0,2
PU-38	05.06.2009	4,8 ±0,3	15 ±3	1,5 ±0,2	2,0 ±0,2
PU-39	05.06.2009	3,5 ±0,2	7,8 ±0,8	0,49 ±0,05	1,6 ±0,2

Table 1. CFCs and SF₆ concentrations in groundwater samples

Tabela 1. Koncentracije CFC in SF₆ v vzorcih podzemne vode

groundwater samples were calculated assuming the mean annual temperature of 10°C for the period of infiltration. The portion of the He excess is typical, namely in the order of 15–30% of the equilibrium value.

Average ages of sampled groundwater determined with the ^3H - ^3He dating technique are presented in Table 3. As in the case of groundwater dating with the SF_6 technique the piston flow conditions were assumption in the study aquifer. Groundwater ages vary between 4 and 33 years. Groundwater of the upper sandy-gravel aquifer, captured in the borehole PU-9 is the youngest, while the oldest groundwater recharges the borehole PU-10 with a perforated pipe in the lower aquifer (Figs. 1-3).

Sampling point	Tritium [TU] (1.9.2009)	Ne excess [%]	^4He radiogenic [ccSTP/kg]	^3He tritiogenic [TU]	Age [y] normalized to (1.9.2009)
PU-1	5.35 ±0.1	21	5.25 E-5	9	18±1
PU-4	5.3 ±0.2	16	4.6 E-5	4.5	11±1
PU-9	5.7 ±0.2	20	4.2 E-6	1.5	4±1
PU-10	4.4 ±0.1	30	3.5 E-5	25	33±2
			error: 1E-6	error: 0.5 TU	error: 1 year

Table 3. Tritium and noble gases values in groundwater samples and groundwater ages, derived from ^3H - ^3He dating

Tabela 3. Vrednosti tricija in žlah-tnih plinov v vzorcih podzemne vode ter starost podzemne vode, določena na osnovi ^3H in ^3He

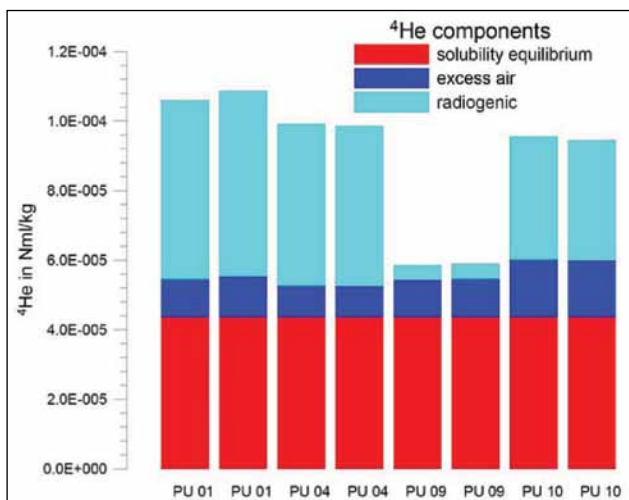


Fig. 5. Separation of ^4He concentration by origin (double measurement included)

Sl. 5. Delitev koncentracije ^4He glede na izvor (vključene so dvojne meritve)

Except for the PU-10 groundwater sample the concentrations of ^3H and tritiogenic ^3He match the ^3H concentration in precipitation quite well (Fig. 6). Hence, average residence times of sampled groundwater were determined quite well with the ^3H - ^3He dating technique. PU-1, PU-4 and PU-9 groundwater samples do not contain any tritium-free water, while the PU-10 groundwater sample falls a little below the precipitation line (Fig. 6). This indicates that the PU-10 groundwater sample contains a portion of tritium-free water infiltrated into the aquifer before 1955. The tritium-free portion could be in the order of 20–50 %.

The concentration of radiogenic ^4He can be used as an indicator for older waters (HAN et al.,

2006). A concentration in the order of the equilibrium value marks hundreds to 1000 years old groundwater in sandy aquifers. A quite intensive source of radiogenic ^4He is assumed in the study area, because the ^3H - ^3He data reflects that groundwater samples do not contain any water from before 1955, except PU-10 groundwater sample (Fig. 6). Even the youngest groundwater of the borehole PU-9 shows a significant concentration of radiogenic ^4He . It is assumed that radiogenic ^4He is accumulated in stagnant water close to the aquifer contact with the Šišenski hrib hill (Figs. 1-3). In this area groundwater could be trapped since the subsidence process and physical heterogeneities of the aquifer. Radiogenic ^4He could be accumulated in large amounts in this stagnant water and the

petro-physical heterogeneities of the aquifer give rise to the coexistence of slow-velocity older waters residing in stagnant zones and fast-velocity younger waters of high-permeability zones (PINTI & MARTY, 1998).

The differences in age estimates of sampled groundwater with different dating techniques are noticeable (Tabs. 2 and 3), which is not surprising, since all dating techniques have certain advantages and limitations in the application to specific hydrological problems. Numerous processes in the groundwater environment can affect tracer concentrations and consequently the groundwater age determination. A multi-tracer approach generally yields more information and helps to resolve conflicting results. Hence, the CFCs, SF_6 and ^3H - ^3He techniques were used to compare the timescales derived from different tracers. The researches point out that the CFCs and SF_6 data could be influenced by the aquifer local contaminations and can yield wrong age estimates of groundwater in urban areas. Natural conditions are only reflected by the ^3H - ^3He technique in the study area. Nevertheless, results of both – the SF_6 and ^3H - ^3He dating techniques indicate that in the brewery area the oldest groundwater is stored in the aquifer part that is the most close to the Šišenski hrib hill.

On the basis of the ^3H - ^3He dating the mixing of old and young groundwater was evidenced in the sandy-gravel aquifer due to the aquifer petro-physical heterogeneities. It is assumed that the old groundwater is stored in stagnant zones close to the aquifer contact with impermeable sediments of the Šišenski hrib hill (Figs. 1-3). Under the influence of the surface and subsurface run-off from the hill this water flows with a slow velocity towards high-permeability zones of the upper and

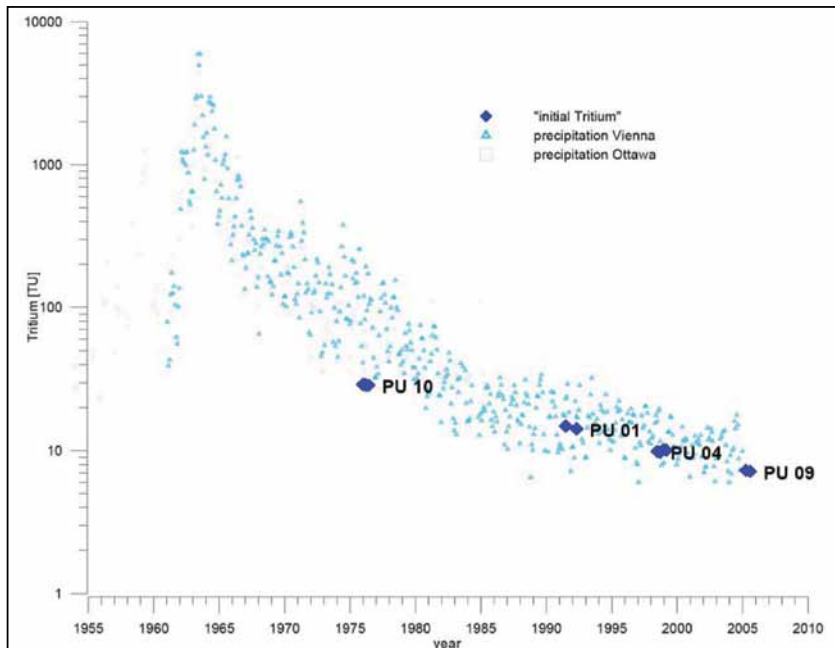


Fig. 6. Initial ^3H concentrations in sampled groundwater during the infiltration period, calculated from the ^3H and ^3He measurements in groundwater samples and ^3H concentrations in Vienna and Ottawa precipitation (symbols represent multiple measurements of the same sample)

Sl. 6. Začetne koncentracija ^3H v vzorčni vodi v obdobju infiltracije, izračunane na podlagi ^3H in ^3He meritev v vzorcih podzemne vode ter koncentracije ^3H v padavinah na Dunaju in v Otavi (simboli predstavljajo večkratne meritve istega vzorca)

lower sand-gravel aquifer. Hence, the youngest groundwater with the mean age of 4 years was determined in the borehole PU-9, which is the most distant from the hill and capture only the upper aquifer (Figs. 1-4). This water reflects fast flow velocities, typical for the main Ljubljana urban aquifer (JUREN et al, 2008).

The borehole PU-4 is only 2 m distant from the borehole PU-9, but it captures deeper groundwater of the lower sandy-gravel aquifer (Figs. 2-4). The mean age of its groundwater is 11 years, which reflects the lateral and vertical components of the groundwater flow in the study aquifer.

The borehole PU-1 captures groundwater from the upper and lower aquifer. It is located between boreholes PU-10 and PU-4. Although it is shallower from the borehole PU-4 its groundwater is older for approximately 7 years (Tab. 3, Figs. 2-4). This indicates that the discussed borehole is not influence a lot with young groundwater flow from a direction of the main aquifer, which is exposed to an urban pollution.

The results of groundwater dating were supplemented with chemical investigations based

on data of specific electroconductivity (SEC) and the unknown trace organic pollutant in sampled groundwater to study the possibility of contamination spread through the upper gravel aquifer and its breakthrough into the lower sandy-gravel aquifer.

The values of specific electroconductivity (SEC) oscillated in observed boreholes between 200 and 1100 $\text{mS}\cdot\text{cm}^{-1}/25^\circ\text{C}$ (Fig. 7). The lowest SEC values, 200–300 $\text{mS}\cdot\text{cm}^{-1}/25^\circ\text{C}$ refer to boreholes PU-41 and PU-10 that are influenced by run-off from the Šišenski hrib hill (Fig. 1). The SEC values between 400 and 500 $\text{mS}\cdot\text{cm}^{-1}/25^\circ\text{C}$ were recorded in boreholes PU-1, PU-2, PU-3 and PU-4, which indicates a little contamination load. They are mostly recharged from the lower gravel aquifer (Figs. 2 and 4). High values, 700–1100 $\text{mS}\cdot\text{cm}^{-1}/25^\circ\text{C}$ were measured in boreholes PU-7, PU-9 and PU-42 that capture groundwater of the upper aquifer, which is locally contaminated (TRČEK & JUREN, 2006 a). The borehole PU-7 is located in the brewery vicinity and other two boreholes inside the brewery (Figs. 1-4). The discussed boreholes have also the highest SEC

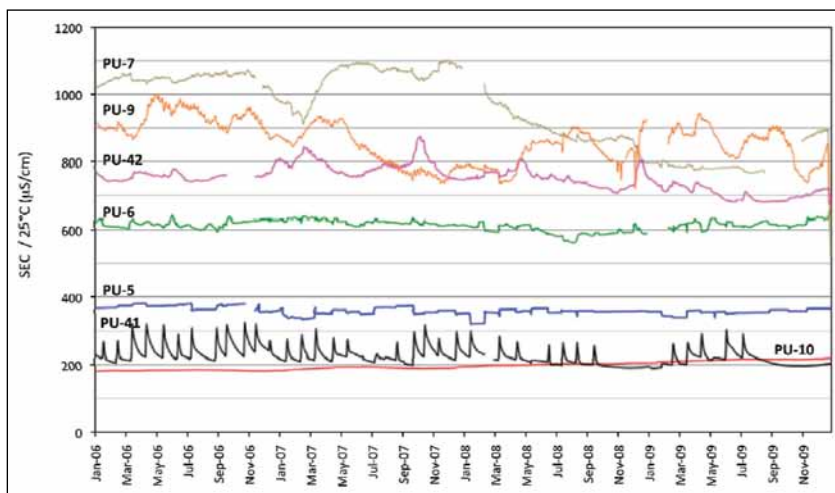


Fig. 7. Oscillation of groundwater specific electroconductivity in the study area in the period 2006-2009

Sl. 7. Nihanje specifične elektroprevodnosti podzemne vode na raziskovalnem območju v obdobju 2006-2009

ranges, which reflect the intensive groundwater dynamics and contaminant transport (oscillation in PU-10 resulted from the pumping for groundwater sampling).

The presented results confirm those based on groundwater dating techniques. The boreholes that are most distance from the Šišenski hrib hill and capture groundwater of the upper aquifer are contaminated, while those that are located closer to the hill are naturally protected from contaminated young groundwater that flows from a direction of the main aquifer.

The borehole PU-9 that captures the upper sandy-gravel aquifer should be exposed due to a high contamination load. A pollution sign was confirmed also by the unknown trace organic pollutant with a base ion mass-to-charge ratio (m/z) 147 (Fig. 8) that has been detected in this borehole with a GC-MS technique and additionally confirmed with LC-MS and LC-TOF MS techniques after pre-concentration by passive sampling on the active carbon.

The NIST05 library of GC-MS mass spectra search gave more than 100 possible results for the unknown compound, containing a bicyclic hetero aromatic rings with N and/or O (Fig. 8). One group indicated a chemical class of benzimidazoles with a widespread use – mostly as fungicides, lubricants, metal corrosion inhibitors and pharmaceuticals. The other compounds in same water samples could be: 5-methylbenzotriazole (CAS 136-85-6; metal corrosion inhibitors and antioxidants), 2-methyl-2H-benzotriazole (CAS 16584-00-2; pesticide formulations and antimicrobial agents) and 5,6-dimethylbenzotriazol (CAS 4184-79-6; lubricants, metal corrosion inhibitors and heat transfer fluids). A narrowing of the candidate list was conducted by the LC-MS techniques to confirm that the discussed compound is not a product of thermal degradation of a parent compound in the GC injector.

In the mean time a semi-quantitative monitoring of the unknown trace organic pollutant was established. The respond for the unknown compound was reporting relative to the internal standard calibration by a linear regression. 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 the target ion, while m/z 104, 77 for the unknown and m/z 163, 128 for the 3,4-dichloroaniline and its deuterated analogue were used to confirm the discussed ions. A simple Electrospray (ESI) LC-MS method indicated that the unknown compound is not a high volatile compound and that m/z 147 belongs to a molecular ion. Concentration estimates for the study compound in borehole PU-9 were on a $0,1 \mu\text{gL}^{-1}$ level or higher.

Investigations with high resolution LC-TOF MS resulted in determination of a molecular formula of the unknown trace organic pollutant. Several chromatographic peaks identified that the study compound could be (a) MH^+ m/z 148 (most probable $\text{C}_8\text{H}_{10}\text{N}_3$, less probable $\text{C}_9\text{H}_{10}\text{NO}$), (b) MH^+ m/z 134 (most probable $\text{C}_7\text{H}_8\text{N}_3$, less probable $\text{C}_8\text{H}_8\text{NO}$) and (c) MH^+ m/z 120 (most probable $\text{C}_6\text{H}_6\text{N}_3$, less probable $\text{C}_7\text{H}_6\text{NO}$) and that the most probable molecular formula of the unknown chemical tracer is $\text{C}_8\text{H}_9\text{N}_3$. Its pollution sources could be a lubricant containing alkyl-substituted benzotriazoles, a metal corrosion inhibitor or a degraded fungicide.

The unknown trace organic pollutant could be 2,4-dimethyl-2H-benzotriazole with traces of 2-methyl-2H-benzotriazole. Its origin is still not well explained. Lack of commercial available source for mentioned compounds could be explained by degradation and/or transformation of parent compounds containing triazoles. Nevertheless, the main characteristics of the discussed tracer are known, as well as the monitoring methods. This is very important, because the newly detected trace organic pollutant with the source in the upper sandy-gravel aquifer, in borehole PU-9 resents a valuable tool to study the flow paths and contaminant transport in the study aquifer in both, the lateral and vertical directions. As it has been already mentioned, the borehole PU-4 is only 2 m distant from PU-9 and captures the lower sandy-gravel aquifer (Figs. 2-4). Therefore, the two boreholes are an ideal polygon to study the risk of contamination

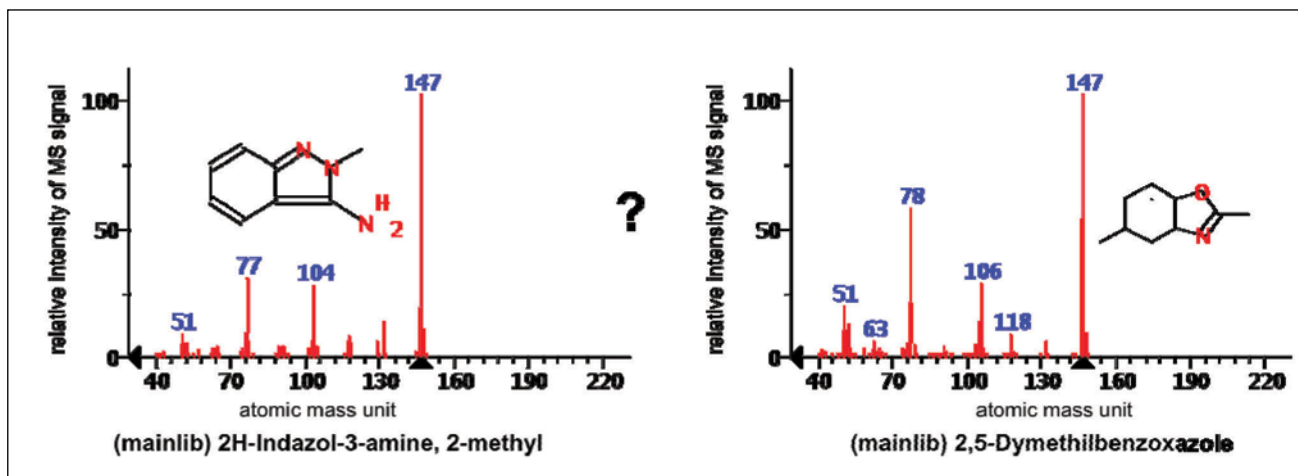


Fig. 8. GC-MS mass spectra of the unknown compound, detected in the study area

Sl. 8. GC-MS masni spekter neznanne spojine, ki je bila odkrita na raziskovalnem območju

breakthrough from the upper into the lower aquifer, which was detected in this location with previous investigations (TRČEK, 2006; JUREN et al, 2008).

Conclusions

The researches point out that the ^3H - ^3He dating technique is the most suitable for groundwater age determination in the study urban aquifer, since SF_6 and particularly CFCs concentrations could be affected by the aquifer local contaminations. Its results, supported with SEC measurements provided an insight into groundwater age structure in the observed aquifer and hence into the aquifer hydraulic behaviour. The comparison of parameter presence at and between different sampling points gave important information on recharge conditions, groundwater residence times and mixing processes and with that on hydrodynamic connections and solute transport in the urban aquifer.

The results reflect that boreholes of the brewery area that are more distant from the Šišenski hrib hill are more vulnerable to contamination due to flow of young groundwater from a direction of the main aquifer, which is exposed to the urban pollution. On the other hand the boreholes located closer to the hill are naturally protected from contamination as they capture old groundwater, which flows towards central high-permeability zones of the upper and lower sand-gravel aquifer. The presented information is closely connected with flow velocities in the study aquifer, which decreases towards the Šišenski hrib hill.

The newly detected trace organic pollutant in sampled groundwater with a base ion mass-to-charge ratio (m/z) 147 represents together with the ^3H and ^3He data a new technique to study the flow paths and contaminant transport in the study urban aquifer in both, the lateral and vertical directions. It could be used for calibration of the hydraulic mathematical model of the Ljubljana Moor, Dravljje valley and Ljubljana Field aquifer (JUREN et al., 2008) and for reconstruction of the contaminant load to the aquifer. For this purpose the transport of trace organic pollutant should be simulated and groundwater age data compared with travel times computed with the mention model.

The described approach needs further investigations. The monitoring of the unknown trace organic pollutant should continue in the unsaturated and saturated zone of the observed aquifer to obtain information of its distribution and concentrations.

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