Risk assessment of an urban aquifer based on environmental tracers

Ocena ranljivosti urbanega vodonosnika na osnovi okoljskih sledil

Branka TRČEK1, Primož AUERSPERGER2, Albrecht LEIS3 & Jürgen SÜLTENFUSS4

1Faculty of Civil Engineering, University of Maribor, SI 2000 Maribor, Slovenia; e-mail: braneka.trcek@um.si
2Water Supply Company Vodovod-Kanalizacija, Vodovodna 90, SI - 1000 Ljubljana Slovenia; e-mail: primoz.auersperger@vo-ka.si
3Laboratory Centre for Isotope Hydrology and Environmental Analytics, Joanneum Research, Elisabethstrasse 18/II, A 8010 Graz, Austria; e-mail: albrecht.leis@joanneum.at
4Institute of Environmental Physics, Department of Oceanography, University of Bremen, Bremen, Germany; e-mail: sue.suelten@uni-bremen.de

Prejeto / Received 15. 4. 2013; Sprejeto / Accepted 11. 6. 2013

Key words: urban area, intergranular aquifer, contamination risk, environmental tracers

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.

Izvleček

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 slovenskih urbanih območjih testirala uporaba sledil 3H-3He, CFCs in SF6. Razuljati so pokazali, da je za določanje starost podzemne vode v proučevanem urbanem vodonosniku najbolj uporabna 3H-3He tehnika, saj na koncentracije SF6, zlasti pa CFC, vpliva lokalno onesnaženje. S pomočjo omenjenih tehnik je ugotovljeno, da je povprečna starost podzemne vode raziskovanega vojna območja med 10 in 30 let. Bolj so vrtine 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 sloniču 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 kromatografije 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 industrial 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 ($^3$H–$^3$He) age indicators were tested in the study urban aquifer, as they haven’t been used in Slovenia so far.

$^3$H, $^3$He, 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 $^3$H for groundwater age determination depends on knowledge of the $^3$H input precipitation concentration, which may be poorly known or vary with time. Studying the relation between $^3$H and its stable daughter product $^3$He in water samples offers the possibility of determining groundwater ages without knowing the $^3$H input function. The original $^3$H input concentration could be reconstructed from the amount of tritogenic $^3$He in solution due to $^3$H 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 $^3$He other than tritogenic should be identified and corrected.

Tritium is considered to be a conservative tracer 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 $^3$H 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 (Cass et al., 2007; Rose, 2007). $^3$H derived tritogenic $^3$He is built up in the groundwater as the contained tritium decays. Therefore, the $^3$H–$^3$He ratio decreases with age. The $^3$H–$^3$He 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 Ljubljanica 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 (~wQ1 and s-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 (s-g-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.
Risk assessment of an urban aquifer based on environmental tracers (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 Dravlje 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).
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, $^3$H/$^3$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 $^3$H and $^3$He 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 Ošter et al. (1986). 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 $^3$H/$^3$He technique. In the case of $^3$H-$^3$He dating, the initial $^3$H content of the water sample is reconstructed from measurements of both the parent isotope ($^3$H) and tritogenic $^3$He, while dating with CFCs and SF$_6$ requires prior knowledge of the initial condition (Han et al., 2006). The $^3$H-$^3$He 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 $^3$He other than tritogenic were estimated on the bases of Ne and $^3$He 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., 2005).

The CFCs and SF$_6$ measurements were performed at Spurenestflabor, 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 $^3$H and $^3$He measurements were carried out with the $^3$He-ingrowth method (Sultenfuss et al., 2006) at the Institute of Environmental Physics, University of Bremen, Germany. $^3$H is expressed in tritium units – TU, which represents 1 $^3$H atom in $10^{18}$ atoms of $^3$H 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. $^4$He, $^{22}$Ne and $^{21}$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 (Sultenfuss et al., 2006). The system was calibrated with atmospheric air and controlled for stable conditions for the He and Ne concentrations and the $^4$He/$^4$He ratio. The precision of the He and Ne concentrations is better than 1 % and better than 0.5 % for the $^4$He/$^4$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 230 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-
result 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 & Buseck, 1999).

Concentrations of CFCs in groundwater samples are presented in Table 1. All concentrations, except CFC-113 of PU-39, were above the equilibrium value, 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 (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).

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:

\[
\text{Groundwater Age (years)} = - 17.8 \times \ln \left( 1 + \frac{3 \text{He}}{3 \text{He}_{\text{eq}}} \right)
\]

(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–tritiogenic sources of 3He that based on Ne and 4He data (Tab. 3). All groundwater samples show significant concentration of 3He from radiogenic sources (Fig. 5). The solubility equilibrium concentrations of all

| Sampling point | Sampling date | CFCs [pmol/l] | SF6 [fmol/l] |
|----------------|--------------|--------------|--------------|
|                |              | CFC-12 | CFC-11 | CFC-113 | SF6 |
| 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

| 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
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 lower aquifer.

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

| Sampling point | Tritium [TU] (1.9.2009) | Ne excess [%] | $^4$He radiogenic [ccSTP/kg] | $^3$He 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                            |

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

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

Except for the PU-10 groundwater sample the concentrations of $^3$H and tritiogenic $^3$He match the $^3$H concentration in precipitation quite well (Fig. 6). Hence, average residence times of sampled groundwater were determined quite well with the $^3$H-$^3$He 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 $^4$He 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 $^4$He is assumed in the study area, because the $^4$He 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 $^4$He. It is assumed that radiogenic $^4$He 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 $^4$He could be accumulated in large amounts in this stagnant water and the
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 mS·cm⁻¹/25 °C (Fig. 7). The lowest SEC values, 200–300 mS·cm⁻¹/25 °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 mS·cm⁻¹/25 °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 mS·cm⁻¹/25 °C were measured in boreholes PU-7, PU-9 and PU-42 that capture groundwater of the upper aquifer, which is locally contaminated (Tirček & 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
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 bicyclical 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 µgL-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 C8H10N3, less probable C9H10NO), (b) MH+ m/z 134 (most probable C7H8N3, less probable C8H8NO) and (c) MH+ m/z 120 (most probable C6H6N3, less probable C7H6NO) and that the most probable molecular formula of the unknown chemical tracer is C8H9N3. 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.

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 bicyclical 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 µgL-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 C8H10N3, less probable C9H10NO), (b) MH+ m/z 134 (most probable C7H8N3, less probable C8H8NO) and (c) MH+ m/z 120 (most probable C6H6N3, less probable C7H6NO) and that the most probable molecular formula of the unknown chemical tracer is C8H9N3. 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.

The NIST05 library of GC-MS mass spectra search gave more than 100 possible results for the unknown compound, containing a bicyclical 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 µgL-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 C8H10N3, less probable C9H10NO), (b) MH+ m/z 134 (most probable C7H8N3, less probable C8H8NO) and (c) MH+ m/z 120 (most probable C6H6N3, less probable C7H6NO) and that the most probable molecular formula of the unknown chemical tracer is C8H9N3. 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](image1)

[Sl. 8. GC-MS masni spekter neznane spojine, ki je bila odkrita na raziskovalnem območju](image2)
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 SF₆ 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, Dravlje 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.

Acknowledgement

The authors would like to acknowledge the Union brewery and K_w Water for the financial support of researches. Moreover the authors acknowledge dr. Harald Oster (Spurenstofflabor Wachenheim, Germany) for the CFC and SF₆ analysis and dr. Dušan Žigon (Jožef Stefan Institute) for analysis with for analysis with LC-TOF MS and LC-MS.

References

Auersperger, P., Lah, K., Kus, J. & Marsel, J. 2005: High precision procedure for determination of selected herbicides and their degradation products in drinking water by solid-phase extraction and gas chromatography-mass spectrometry. J. chromatogr., A, 1088/1–2: 234-241.

Auersperger, P., Lah, K., Jamnik, B. & Nartnik, M. 2009: Določitev racionalnega nabora organiških onesnaževal v podzemni vodi. In: Geološki zbornik. Ljubljana: 12-15.

Auersperger, P., Lah, K., Kramarič Zidar, V. & Mali, N. 2011: Kvalitativni monitoring organiških onesnaževal v podzemni vodi z uporabo pasivnega vzorčenja in plinske kromatografije z masno spektrometrijo = Qualitative monitoring of organic pollutants in groundwater by passive sampling and gas chromatography mass spectrometry. In: Kravanga, Z., Brodnjak-Vončina, D. & Bogataj, M. (eds.): Slovenski kemijski dnevi 2011, Portorož, 14–16 september 2011. FKKT, Maribor: 1-10.

Busemberg, E. & Plummer, L.N. 2000: Dating young groundwater with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. Water Resources Research, 36/10: 3011–3030.

Cook, P.G. & Solomon, D.K. 1997: Recent advances in dating young groundwater: chlorofluorocarbons. ³H/³He and ⁸⁵Kr. J. Hydrol., 191: 245-265.

Crisis, R.E., Davisson, M.L., Surbeck, H. & Winston, W.E. 2007: Isotopic Techniques. In: Goldscheider, N. & Drew, D. (eds.): Methods in karst hydrogeology. International contribution to hydrogeology 26, Taylor and Francis, London: 123–145.

Han, L.F., Groning, M., Plummer, L.N. & Marsel, D.K. 2006: Comparison of the CFC technique with other techniques (³H, ³H/³He, ⁸⁵Kr). In: Use of Chlorofluorocarbons in Hydrology: A Guidebook, STI/PUB/1238. IAEA, Vienna: 191-198.

Hunt, R.J., Tyler B., Coplen, T.B., Haas, N.L., Saad, D.A. & Borcharidt, M.A. 2005: Investigating surface water–well interaction using stable isotope ratios of water. Journal of Hydrology, 302: 154–172.

Juren, A., Trček, B., Harum, T., Leis, A. & Petauer, D. 2008: Project A1.4, Water for beverage industry applying best management practices, final report, Phasing out. Kompetenznetzwerk Wasserressourcen GmbH, Graz: 38 p.

Kiffer, R., Aeschbach-Hertig, W., Peeters, F. & Stute, M. 2002: Noble gases in lakes and ground waters. In: Porcelli, D., Ballentine, C. & Wiel, R. (eds.): Noble gases in geochemistry and cosmochemistry. Rev. Mineral. Geochem., 47: 615–700.

Oster, H., Sonntag, C. & Münnich, C.O. 1996: Groundwater age dating with chlorofluorocarbons. Water Resources Research, 32/10: 2989–3001.

Petauer, D. & Juren, A. 2006a: Geological Map of the Union Brewery Groundwater Catchment Area in Scale 1: 25 000. GeoSI, Ljubljana: a CD-Rom.
Petauer, D. & Juren, A. 2006b: Hydrogeological Map of the Union Brewery Groundwater Catchment Area in scale 1: 25 000. GeoSI, Ljubljana: a CD-Rom.

Plint, D. & Marty, B. 1998: The origin of helium in deep sedimentary aquifers and the problem of dating very old groundwaters. In: Parnell, J. (ed.): Dating and Duration of Fluid Flow and Fluid Rock Interaction. Geological society, Special Publications 144, London: 53-68.

Plummer, L.N. & Busemburg, E. 1999: Chlorofluorocarbons. In: Cook, P. & Herczeg, A. (eds.): Environmental tracers in subsurface hydrology. Kluwer Academic Publishers Boston: 441-478.

Plummer, L.N. & Busemburg, E. 2006: Chlorofluorocarbons in aquatic environments. In: Use of Chlorofluorocarbons in Hydrology: A Guidebook, STI/PUB/1238. IAEA, Vienna: 1-8.

Plummer, L.N., Busemburg, E. & Cook, P.G. 2006: Principles of chlorofluorocarbons dating. In: Use of Chlorofluorocarbons in Hydrology: A Guidebook, STI/PUB/1238. IAEA, Vienna: 17-30.

Rose, S. 2007: Utilization of decadal tritium variation for assessing the residence time of base flow. Ground Water, 45/3: 309–317, doi:10.1111/j.1745-6584.2006.00295.x.

Solomon, D.K., Schiff, S.L., Poreda, R.J. & Clarke, W.B. 1993: A validation of the $^3$H/$^4$He method for determining groundwater recharge.

Water Resources Research, 29/9: 2951–2962, doi:10.1029/93WR00968.

Sultenfuss, J., Roether, W. & Rhein M. 2006: The Bremen mass spectrometric facility for the measurement of helium isotopes, neon, and tritium in water. In: Proceedings of the IAEA International Symposium on Quality Assurance for Analytical Methods in Isotope Hydrology, CN-119. IAEA, Vienna.

Trček, B. 2006: Isotopic investigations in the Union brewery water body. Geologija, 49/1: 103-112.

Trček, B. & Juren, A. 2006a: Vulnerability study of the Union Brewery water body. In: Proceedings of the IAH Symposium, Dijon, France.

Trček, B. & Juren, A. 2006b: Protection of drinking-water resources in the Union Brewery water body (Ljubljana, Slovenia). In: 34th Congress of International Association of Hydrogeologists, Beijing, China, October 9-13, 2006. Proceedings of the 34th IAH Congress, Beijing, China.

Trček, B. & Juren, A. 2006c: Best management practices - Pivovarna Union d.d. (BMP-PU). In: Trauner, L. & Vovk Korže, A. (eds.): Water resources management. Faculty of Arts, K-net Subcenter, Maribor: 58-63.

Internet: https://maps.google.si/maps?hl=sl&q=Google+Image+Terra+Matrices&ie=UTF-8 (15.12. 2008).