ORIGINAL ARTICLE

Identifying the characteristics of groundwater flow in the Classical Karst area (Slovenia/Italy) by means of tracer tests

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Abstract Tracer tests are a widely used research method in karst hydrology. In the Classical Karst area on the border between Slovenia and Italy, they have a long history and for the most part they have been used to research the underground flow in the main karst conduits between the ponors and the springs. The results of the tracer test from 2013 presented in the article revealed new knowledge about the central part of the aquifer, less well researched to date, where the density of caves and the level of karstification are lower. Two tracers (uranine and amidorhodamine G) were used at two injection points (a research borehole in the central part of the aquifer and the karst surface at a distance of 2.5 km from a drinking water pumping station), and six springs, a pumping station, three boreholes and four karst caves were observed for tracer breakthrough for a full year after injection. The results were compared with findings from three other selected older tracer tests in which uranine was likewise used as a tracer but where hydrological conditions varied (very low, low and medium water levels), as did the methods of injecting tracer (in a sinking stream, in a fracture on the karst surface). The comparison showed how different modes of aquifer recharge and the heterogeneity of aquifer structure affect the characteristics of water flow and solute transport in complex karst aquifers.

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Introduction

Tracer tests using artificial tracers are a highly effective and widely used method for the study of the characteristics of underground water flow in karst (Käss [1998;](#page-11-0) Benischke et al. [2007](#page-11-0); Goldscheider et al. [2008](#page-11-0); Perrin and Luetscher [2008](#page-11-0); Kogovsek and Petric [2014](#page-11-0)). They also have an important place in the long history of research in the Classical Karst area on the border between Slovenia and Italy. In ancient times, Poseidonius of Apameria (135–50 BC) wrote about the underground connection between the Reka river, which loses itself underground in the Skocjan Caves on the south-eastern edge of the Classical Karst plateau, and the springs of the Timava/Timavo (Slovene/ Italian name) on the Gulf of Trieste (Shaw [1992\)](#page-11-0), a connection that was later confirmed by tracer tests. The first person known to have attempted to prove the connection in this way was Father F. Imperato in 1599, by means of ''floaters''. P. Kandler traced the Reka in 1864 using ''blue dye – indigo", while F. Müller did so in 1891 using uranine (Kranjc [2000](#page-11-0)). In the context of the search for better solutions for the supply of drinking water to the city of Trieste, these were in fact the first targeted studies of the directions of underground flow and retention time of water from the Reka in the karst underground (Müller [1891](#page-11-0)). Further studies were carried out up until the late 1920s by Boegan, Bertarelli and Timeus, who in addition to uranine were already using or testing new tracers in multi-tracer tests (Bertarelli and Boegan [1926](#page-11-0); Timeus [1928](#page-12-0)). In December 1907, for example, they used uranine in parallel with lithium chloride and proved the connection of the

Reka with the springs of the Timava/Timavo while also detecting tracer at a few other smaller springs.

In the following years, too, the main focus of attention was on the study of the characteristics of the underground flow of the Reka from the Skocjan Caves to the springs of the Timava/Timavo and its appearance in some deep caves in the Classical Karst region (Timeus [1928](#page-12-0); Mosetti [1965](#page-11-0)). Tracer tests also established connections between a number of other surface streams that disappear underground on the Classical Karst plateau and springs on the Gulf of Trieste (Timeus [1928;](#page-12-0) Habič [1989\)](#page-11-0). A new approach to tracer tests consisted of injecting tracer into a fracture on the karst surface near the Sežana municipal dump. This also enabled the study of the characteristics of authigenic recharge and the influence of the vadose zone on water flow and solute transport in karst aquifers (Kogovšek and Petrič [2007\)](#page-11-0).

The tracer tests mentioned here have reliably proved an underground water connection in the southern part of the Classical Karst aquifer, in which the underground Reka represents the principal water artery. Despite some tracings of sinking streams from the northern edge of the aquifer, less was known about water flow in the central part of the aquifer, where the density of caves and degree of karstification are lower. Accordingly, as part of the Hydrokarst project (Cucchi et al. [2015\)](#page-11-0), two injection points in this area were selected and, in 2013, a multi-tracer test was carried out. The results revealed new knowledge about the characteristics of underground flow in hitherto less well researched parts of the Classical Karst, while based on a comparison with the results of earlier tracings it was possible to gain some new information about the influence of hydrological conditions, location and tracer injection method on the characteristics of tracer transport through the karst aquifer. Original contribution of the article is improved understanding of the role of various modes of aquifer recharge and of how the heterogeneity of aquifer structure affects the characteristics of water flow and solute transport in complex karst aquifers.

Study area

The Classical Karst region of southwestern Slovenia and north of Trieste in Italy (originally called Kras/Carso) is a transboundary karst plateau that rises at the heights up to around 600 m above the Adriatic Sea at the Gulf of Trieste. It is approximately 40 km long and up to 13 km wide, covering an area of around 440 km^2 (Kranjc [1997\)](#page-11-0). In this area the first systematic research of karst phenomena in the world began at the start of the twentieth century and from its name the international term karst is derived.

Geological characteristics are summarised from Jurkovšek et al. (2010) (2010) and Cucchi et al. (2015) (2015) . The plateau itself is formed by the large overturned Trieste–Komen anticline that plunges to the northwest, extending along the Adriatic coast. Its central part is built predominantly of karstified and highly permeable Cretaceous limestones and, in part, dolomites in a thickness of greater than 1000 m. In the north, south and east, the Cretaceous rocks give way to marly and platy limestone of Palaeocene and Eocene age, which is also fractured and karstified (Fig. [1\)](#page-2-0). This anticline is bounded by two large thrust faults in the NW–SE direction along the Adriatic coast on the southwest and northeast sides which form hydrogeologic boundaries along the edge by bringing up the relatively impermeable Eocene flysch layers into contact with the karstified limestones. The result is that the karst plateau is effectively bound by less permeable rocks on its northern and southern borders, as well as at depth.

In the areas where the contact limestone-flysch is the lowest, numerous karst springs emerge on the Gulf of Trieste. The largest of them are the springs of the Timava/ Timavo, with discharges of between 9.1 and 127 $\text{m}^3\text{/s}$ and a mean discharge of 29.3 $m³/s$. Numerous smaller springs are also found further inland at heights above sea level ranging between 0.4 and 12 m. The most important among the submarine springs along the coast towards Trieste is the Brojnica pri Nabrežini/Aurisina spring. The total mean discharge of all these smaller springs is estimated at around 6 m^3 /s (Civita et al. [1995](#page-11-0)). There are no springs in the Slovene part of the karst plateau, but a pumping station has been set up in Klariči to supply drinking water, where 250 L of water per second can be pumped from three 70 m deep wells with diameters of 400 and 500 mm and a total capacity of 250 L/s. Usually around 100 L/s are pumped, however, when simultaneously supplying the Coastal area, around 200 L/s are extracted (Urbanc et al. [2012](#page-12-0)). Depth to the water table fluctuates due to changes in pumping rate; however, on average the water table is approximately 2 m.a.s.l.

Authigenic recharge of the karst aquifer in the Classical Karst region, where mean annual rainfall ranges from 1400 to 1650 mm (Frantar [2008\)](#page-11-0), represents around 65% of recharge in the overall water balance (Civita et al. [1995](#page-11-0)). Additional recharge is represented by sinking streams from the flysch margin, in particular the Reka, which disappears underground in the Skocjan Caves on the SE edge. Between 1971 and 2000, the hydrological station roughly 7 km upstream of the ponor measured a minimum discharge of $0.18 \text{ m}^3/\text{s}$ for the Reka, while mean discharge was 7.84 m^3 /s (Frantar [2008\)](#page-11-0). When the water level is very high, discharge can increase to above $300 \text{ m}^3/\text{s}$. The contribution of sinking streams from the flysch in the NE margin is significantly smaller, while the quantities of water flowing into the karst aquifer from the alluvial aquifer along the Soča/Isonzo and Vipava/Vipacco rivers

Fig. 1 Hydrogeological map of the study area

are unknown. These are estimated to be approximately 10 m³ /s (Zini et al. [2013\)](#page-12-0).

Various sources of recharge are reflected in some differences in chemical and isotopic composition of the water and the springs can be classified in several groups (Reisenhofer et al. [1998;](#page-11-0) Ballarin et al. [2000;](#page-11-0) Doctor et al. [2000\)](#page-11-0). The main group of the Timava spring is characterised by typical karst water which is mainly fed by authigenic recharge. Especially at high waters an increased influence of the Reka sinking stream can be noticed. Springs situated inland towards north show higher share of recharge from the alluvial aquifers along the Soča/Isonzo river. For all springs, significant changes of chemical and isotopic composition with hydrological conditions are characteristic. The proportions of Soča/Isonzo water increase under drier conditions and decrease under wetter conditions. Urbanc and Kristan [\(1998](#page-12-0)) confirmed that in the area of Klariči in the rainy season the aquifer is mainly recharged from the karst area, but during summer dry periods as much as 50–60% of the aquifer's water is fed by the water from the alluvial aquifer.

The characteristics of underground flow towards the springs of the Timava/Timavo have been studied by numerous tracer tests. Apparent flow velocities of between 47 and 162 m/h (Peric [2012](#page-11-0); Timeus [1928](#page-12-0)) have been identified under various hydrological conditions for the connection with the Reka sinking stream; for the connection with sinking streams in the NE margin, apparent flow velocities are between 20 and 30 m/h (Habič [1989\)](#page-11-0). An apparent flow velocity of 39 m/h was calculated during tracing from the surface near Sežana at medium water level (Kogovšek and Petrič 2007).

The main flow along large karst conduits may be observed in numerous deep karst caves (e.g. Kačna jama, Jama v Kanjaducah 1, Labodnica/Abisso di Trebiciano) in the southern part of the aquifer between the Skocjan Caves and the springs of the Timava/Timavo. The central and north-eastern parts are less karstified, and the density of caves is lower. Research boreholes in this area have indicated great heterogeneity, with large differences in permeability, which, however, is generally lower than in the main flow of the underground Reka. For example, by pumping tests, the following values of hydraulic conductivity K were defined: $K > 10^{-3}$ m/s for the borehole of Klariči, $K = 7 \times 10^{-5}$ m/s for the borehole B7 (Fig. 1), and $K < 10^{-9}$ m/s for the borehole V2 in the north-eastern part of the aquifer (Krivic [1983](#page-11-0)).

As part of the Hydrokarst project, the Geological Survey of Slovenia (Urbanc et al. [2015](#page-12-0)) drilled in the period from 29 November to 10 December 2012 a 250 m deep research

borehole near the village of Štorie (surface at 365 m.a.s.l.). Only the initial part of this borehole is piped, and it is located entirely within the area of Upper Cretaceous limestone. The diameter of the borehole is 203 mm. The level of groundwater is around 168 m.a.s.l., and it increases after more intensive precipitation events. The drilling process (rotary percussion drilling) and logging in the borehole (temperature, conductivity, borehole video camera) indicated the existence of karst conduits at various depths (in the lower part caverns at the altitudes from 165 to 168 m, and 149 to 155 m.a.s.l.), on the basis of which it was concluded that the rapid flow of the injected tracer from the borehole into the karst aquifer would be possible. This new borehole, which is at the moment used only for research purposes, was selected as an injection point for the tracer test presented in this article.

Materials and methods

Tracer test in 2013

On 2 April 2013, following frequent rainfall in the second half of March 2013, the discharge of the Timava/Timavo spring reached a peak of $134 \text{ m}^3\text{/s}$ and then declined slowly. On 10 April 2013, while the water level was falling, a solution of 48 kg of uranine (three 100 L containers) was injected into the Storje-1/12 borehole. Before injecting the first container of tracer solution, 2 m^3 of water from a tank was poured into the borehole, then followed by approximately 1 $m³$ of water before emptying each subsequent tracer container. After rinsing out the containers, the remainder of the water from the tank was poured into the borehole—a total of 14 m^3 . Measurements in the borehole using a multiparameter probe with data recorder showed initial water level of 184 m, and then a rapid rise in the level by 20 m on injection of the tracer and water and a fall of a few metres while rinsing the containers (Urbanc et al. [2015\)](#page-12-0). When the remainder of the water was poured into the borehole the water level again rose to 20 m above its starting value before injection and then fell very rapidly to its starting value. Thus, in the space of 2.5 h, the entire 14 m^3 of water poured into the borehole had drained away—thereby confirming the good communication of the borehole with the surrounding aquifer.

On the same day, in order to determine the characteristics of underground flow in the catchment area of the Klariči pumping station, 1.1 kg of amidorhodamine G dissolved in 50 L of water was injected into the surface near Sela na Krasu at the altitude of 240 m.a.s.l. (2.5 km to the NE and approximately 230 m above the level of the water at the pumping station). The surface here is bare or covered with a few centimetres thick soil with grass.

Preliminary irrigation with 1 m^3 of water from a tank had indicated very good infiltration capacity. Water from a tank was used to create artificial rain and irrigate the injection area with a further 9 $m³$ of water.

Even before injecting the tracers, regular manual or automatic regular sampling (using ISCO 6712 automatic samplers) at selected springs (Timava/Timavo, Brojnica pri Nabrežini/Aurisina, Sardoč/Sardos, Moščenice/Moschenizze N and S, Laško jezero/Lago di Pietrarossa), at the Klariči pumping station and in boreholes (P1—Pliskovica, V2—Avber, B7—Klariči), and occasionally in karst caves with water flows (Kačna jama, Jama v Kanjaducah 1, Labodnica/Abisso di Trebiciano, Jama pri Komarjih/Cavernetta di Comarie) (Fig. [1\)](#page-2-0) was organised. In the case of the Timava/Timavo spring, sampling by automatic sampler initially took place once a day, then twice a day, before returning to a frequency of once a day until the end of February 2014. Sampling at the Klariči pumping station was carried out twice a day until mid-June 2013. At both locations, throughout the period of observation until the beginning of March 2014, parallel measurements in 30-min intervals with Gotschy Optotechnik LLF-M field fluorometers (detection limits 0.02 mg/m³ for uranine and 0.04 mg/m^3 for amidorhodamine G) were also carried out. Sampling with an automatic sampler at the Brojnica pri Nabrežini/Aurisina spring, which took place twice a day, was interrupted in July 2013 because of problems of organisation. A Gotschy Optotechnik LLF-M field fluorometer was in place from September 2013 to March 2014. An automatic sampler with a sampling frequency of once a day was in place at the Sardoč/Sardos spring until the beginning of July 2013. At all other points, periodic manual sampling was carried out (until mid-June 2013 at the latest). Sampling was carried out at some locations with the help of partners from the Hydrokarst project (ACE-GASApsAmga; Department of Mathematics and Geosciences, University of Trieste; Geological Survey of Slovenia) and Mr Rikardo Vrabec of Pliskovica.

In order to estimate the retention time of the tracer in the borehole, the first sample of water from the Storje-1/12 borehole was taken approximately 8 months after injection. This was followed by a further two samples before April 2014.

All the water samples were analysed in the laboratory using a PerkinElmer LS 45 fluorescence spectrometer. Uranine was detected at $E_{ex} = 491$ and $E_{em} = 512$ nm with a detection limit of 0.005 mg/m³; amidorhodamine G was detected at $E_{ex} = 531$ and $E_{em} = 552$ nm with a detection limit of 0.01 mg/m³.

Figures for rainfall in the catchment and discharges for the Reka upstream of the ponor were obtained from the website of the Slovenian Environment Agency [\(2013](#page-12-0)), while discharges for the Timava/Timavo and Brojnica pri Nabrežini/Aurisina springs were provided by project partners ACEGASApsAmga and Direzione Centrale Ambiente ed Energia, Autonomous Region of Friuli Venezia Giulia. An Onset HOBO Water Level Logger in the Gabranca Cave was used for monitoring hydrological conditions in the karst aquifer eastern from the Štor je-1/12 borehole (upstream of the water flow from the borehole towards the main underground flow of the Reka).

Results of the tracer test in 2013

Timava/Timavo spring

The first traces of uranine in the Timava/Timavo spring were obtained 15 days after injection (25 April 2013), coinciding with a decline in discharge, which at that time reached a value of $45 \text{ m}^3/\text{s}$, and when the contribution of the Reka was small. A first tracer pulse formed with two clear peaks and lasted for over a month (Fig. [2](#page-5-0)). The Timava/Timavo reached its highest concentration of uranine (0.21 mg/m^3) one month after injection, before its discharge began to increase again.

The subsequent increase in discharge of the Timava/ Timavo, when a significant part of the water was also contributed by the Reka, caused a fall in the uranine concentration in the Timava/Timavo. Nevertheless, each occurrence of rainfall in the catchment area pushed the injected uranine through the aquifer with greater intensity. This was only reflected, after a delay of 2–3 days, in small increases in the concentration of the uranine discharging in the Timava/Timavo, as a result of significant dilution or increased inflow of water from the wider catchment area. Roughly 2 months after injection, when the constantly declining discharge of the Timava/Timavo reached a level of 43 m^3 /s and the contribution of the Reka was small, the more pronounced transport of uranine resumed. In similar hydrological conditions to the first tracer pulse, a second tracer pulse formed, lasting 2 months and with two peaks.

With regard to the maximum achieved concentration, the apparent dominant flow velocity is 38 m/h, while the apparent maximum velocity, with regard to the first appearance of tracer, is 75 m/h (Table [1](#page-5-0)).

A detailed comparison of the tracer breakthrough curve and hydrological conditions in the aquifer revealed that in the time of higher discharges of the Reka sinking stream, the inflow from the broader area of the aquifer into the main conduits of the underground Reka flow in the southern part of the aquifer is limited due to higher hydraulic head in these conduits. Consequently, higher water levels persist in this broader area [e.g. high water levels above 405 m.a.s.l. in the Gabranca Cave (Fig. [3](#page-6-0))]. This inflow starts only when significant decrease of discharges of the Reka and lower hydraulic heads in the main conduits occur and is reflected by water level decrease for several tens of metres in the Gabranca Cave. The discharge of Reka decreases below $4 \text{ m}^3/\text{s}$, and of Timava below 45 m^3 /s. The return of high waters restores previous conditions. Described characteristics are confirmed by the two main tracer pulses which both occur in the time of decline in discharge of the Reka and increased inflow from the broader area of the aquifer into the main drainage conduits.

Subsequently, despite occasional rainfall (lower effective infiltration in the summer and autumn months), the concentration of uranine at low to medium discharges of the Timava/Timavo persisted at the detection limit, which means that transport was minimal or absent (Fig. [2](#page-5-0)). Only following precipitation events from November 2013 onwards (210 days after injection), when the highest discharges of the entire period of observation were reached, did occasional minor but continuous increases in uranine concentration occur. The cause of this was the more intensive flushing of the residual uranine in the aquifer and the borehole, following significant dilution. The presence of uranine in the borehole was confirmed by analyses of water samples from the borehole, when a concentration of 2.2 mg/L was measured on 9 December 2013.

In the second half of February 2014 (313 days after injection), the concentration of uranine in the Timava/Timavo fell below the detection limit. The concentration of uranine in the borehole was also significantly lower (0.07 mg/L). Evidently the exceptionally heavy rainfall (272 mm in 2 weeks at the Godnje station) had flushed out a large part of the residual uranine. A 6-week flood pulse with a maximum level 20 m above the starting value was measured in the Storje-1/12 borehole (Urbanc et al. [2015](#page-12-0)). One year after injection, however, on 1 April 2014, with the level having fallen and with the discharge of the Timava/Timavo below 40 m^3 /s, an increased concentration of uranine (1.1 mg/L) in the borehole was recorded again. This is assumed to be a local increase in uranine content resulting from the debris in the borehole, which had adsorbed some of the injected uranine.

In the Timava/Timavo, the fluorescence of the uranine was also measured with an LLF-M field fluorometer, where the results coincided well with the analyses of the samples taken. Two days before the continuous growth of uranine in the first tracer pulse, however, the field fluorometer detected a marked continuous increase in the concentration of uranine. Since this only lasted 12 h, it was not detected by the once-daily analysis of samples (Fig. [4](#page-6-0)). On the basis of the data collected, no adequate explanation of the observed phenomenon can be given. A fleeting appearance of the injected tracer is possible, while another possible explanation is contamination in the vicinity of the spring.

Fig. 2 Rainfall at the Godnje station, discharge of the Timava/Timavo and the Reka, tracer breakthrough curves and uranine recovery curve for the Timava/Timavo spring, and tracer breakthrough curves for the Brojnica pri Nabrežini/Aurisina spring

Table 1 Distance between the injection point and the spring (D), maximum measured concentration of uranine (C_{max}) , time of the first detection of uranine (t_{min}) , apparent maximum flow velocity (v_{max}) ,

time of the maximum concentration of uranine (t_{dom}) , apparent dominant flow velocity (v_{dom}) and tracer recovery (R)

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Sampling point	D (km)	C_{max} (mg/m ³)	$t_{\rm min}$ (day)	v_{max} (m/h)	t_{dom} (day)	v_{dom} (m/h)	$R(\%)$
Timava/Timavo	27.0	0.21			30	38	68
Brojnica pri Nabrežini/Aurisina	20.4	0.18		34		<u>_</u>	0.2

The phenomenon will require the detailed taking of samples in future tracer tests.

Calculation of the recovered quantity of uranine on the basis of daily discharge measurements and measurements of uranine concentration showed that by the end of February 2014 (322 days after injection) almost 68% of the injected uranine had been discharged through the Timava/ Timavo spring (Fig. 2). This somewhat smaller than expected percentage is probably connected with the longer retention in the borehole area, which was shown by still present tracer in water of the borehole a year after injection.

The concentration of amidorhodamine G injected on the surface in Sela na Krasu for the most part fluctuated around the limit of detection. The small increases in concentration detected almost 9 months after injection (Fig. 2) are not

Fig. 3 Comparison of tracer breakthrough curves for the Timava/Timavo spring, water levels in the Gabranca Cave (in July 2013 the water level was below the measurement probe) and discharges of the Timava/Timavo and the Reka

Fig. 4 Comparison of uranine concentrations determined by analysis of samples in the laboratory (LS 45) and with the field fluorometer (LLF-M)

sufficient to confirm a connection of the Timava/Timavo spring with the injection point. Owing to the small quantity of injected tracer and the discharge of the Timava/Timavo, confirmation of this most likely direction of flow was not expected.

Brojnica pri Nabrežini/Aurisina spring

The rapid appearance of uranine in the Timava/Timavo was followed after a further 10 days by its appearance in the Brojnica pri Nabrežini/Aurisina spring (Fig. [2](#page-5-0)). In this case, too, the first tracer pulse had two peaks but only lasted a fortnight. In comparison with the Timava/Timavo, the velocities of flow towards this spring were slower. The apparent dominant velocity was 25 m/h (Table [1](#page-5-0)), and in particular the apparent maximum velocity was more than two times slower (just 34 m/h). As in the Timava/Timavo,

a second tracer pulse also developed, but owing to difficulties with sampling, it was not monitored in full. A field fluorometer was installed later, which recorded a few more slight increases in uranine concentration, coinciding with the increases in uranine in the Timava/Timavo.

The concentration of amidorhodamine G remained constantly below the limit of detection throughout the three-month period of observation.

When estimating the percentage of recovered tracer in the Brojnica pri Nabrežini/Aurisina spring, for the second tracer pulse uranine concentration values in the period without samples were interpolated from the tracer breakthrough curve for the Timava/Timavo. According to this estimate, only approximately 0.2% of the injected uranine flowed out through the Brojnica pri Nabrežini/Aurisina spring in 11 months.

Klariči pumping station

The LLF-M field fluorometer at the Klariči pumping station showed minimal fluctuations in the concentration of amidorhodamine G and uranine at the detection limit 6 months after injection (this was also confirmed by analyses of the samples taken in the period 2 months after injection). This was then followed by clear, non-continuous, bigger fluctuations of amidorhodamine G over a period of more than 2 months and of uranine over a period of 1 week (Fig. [5\)](#page-7-0). A detailed examination of the probes revealed that they were contaminated (a metallic particle adhering to the probe for amidorhodamine G which corroded and also later contaminated the probe for uranine), since from 20 November 2013 onwards, following

Fig. 5 Precipitation at the Godnje station and amidorhodamine G and uranine concentrations at the Klariči pumping station measured with an LLF-M field fluorometer

cleaning, they once again recorded low values for both parameters.

On the basis of fluctuations of amidorhodamine G and uranine concentrations at Klariči at the limit of detection (if we attribute the interference to contamination), it was concluded that there is no connection with the injection points. Nevertheless, additional studies will be required in this area in order to definitively resolve the doubt arising from the difficulties in the implementation of measurements mentioned above, or to show the origin of the water flowing into the pumping station.

Other springs

In all the other observed springs, boreholes and caves, the measured concentrations of the two tracers fluctuated around the limit of detection. Therefore, underground water connections with the injection points cannot be confirmed.

Comparison with results of earlier tracer tests

In order to assess the characteristics of water flow and solute transport through the Classical Karst aquifer towards the spring of the Timava/Timavo, the results of the tracer test presented above were compared with the results of three selected older tracer tests. Uranine was used as a tracer in all the tests, but the hydrological conditions and tracer injection methods differed. The results are collected in Table [2](#page-8-0) and shown in Fig. [6](#page-9-0) together with precipitation and hydrological characteristics at the time of the tests.

Tracer was injected into the Reka sinking stream twice: in July 1962 and in September 2006. On 3 July 1962, in an experiment involving various organisations from Slovenia and Italy, 100 kg of uranine and 200 curies of tritium were simultaneously injected into the Reka in the Skocjan Caves (Mosetti [1965](#page-11-0); Bidovec [1967\)](#page-11-0). Injection took place at a time when the water level was low, but 85 mm of rain fell over the next 2 days and discharges increased rapidly. A clear flood pulse formed and pushed the injected tracer through the underground karst system. Difficulties occurred in the analysis of uranine breakthrough in the Timava/ Timavo spring because of high turbidity, as a result of which excessive fluorescence was measured in the samples. Accordingly, for the needs of comparison in this article, these values of uranine concentrations were corrected in accordance with the results of the tracing with tritium and an estimate of the quantity of recovered tracer. An apparent dominant flow velocity of 86 m/h was established for the underground connection with the springs of the Timava/ Timavo.

Tracing of the Reka sinking stream using 5 kg of uranine on 4 September 2006, when the water level was very low and there were no marked increases in discharge for the entire duration of the test, established an apparent velocity of flow of 47 m/h towards the Timava/Timavo spring (Peric [2012\)](#page-11-0).

A different method of injecting tracer was used on 20 April 2005, with 38 kg of uranine injected into a highly permeable fracture on the karst surface near Sežana. This permitted an assessment of the characteristics of authigenic recharge and the influence of the vadose zone on water flow and solute transport in the karst aquifer (Kogovšek and Petrič 2007). The water level was higher than during the previously described tracings of the Reka, and injection was followed by several successive precipitation events which enabled the faster transport of tracer through the approximately 200 m thick vadose zone and on into the system of conduits of the phreatic zone towards the springs. Apparent dominant flow velocity of 39 m/h to the Timava/ Timavo spring was established.

Type of injection	Date of injection	Mass (kg)	Distance (km)	Time to C_{max} (day)	v_{dom} (m/h)	Recovery in 5 months $(\%)$
Sinking river	3/7/1962	100	34	16	86	81
Sinking river	4/9/2006		39	35	47	69
Surface-fissure	20/4/2005	38	21.4	23	39	47
Borehole	10/4/2013	48	27	30	38	53

Table 2 Comparison of the modes and results of four selected tracer tests (for tracer breakthrough in the Timava/Timavo spring)

For the purposes of easier comparison, the calculation of the percentage of recovered tracer is limited for all tests to a period of 5 months (a period in which the greater part of the injected tracer was discharged in all the tracer tests); Distance refers to the distance between the injection point and the Timava/Timavo spring

In the tracer test in 2013, on the other hand, tracer was injected into a borehole in the central part of the Classical Karst aquifer, where the degree of karstification is lower than in the area of the underground flow of the Reka. Discharges of the Timava/Timavo spring were higher at this time than in any of the other tests included in the comparison, although declining. One characteristic of this test is the lengthy duration of tracer discharge and the formation of two large tracer pulses over a period of 4 months. Increased tracer transport occurred after rainfall, which drove the tracer from the area of the borehole and pushed it towards the main underground flow in the direction of the Timava/Timavo. Characteristic transport is only possible when hydraulic pressure falls in the main karst conduits. The highest tracer concentrations appear when the discharges of the Reka sinking stream are smallest and autogenous recharge predominates (Fig. [2](#page-5-0)).

For a more objective comparison of tracer breakthrough curves and the percentage of recovered tracer, the values were normalised according to the differences in the quantity of injected tracer and distances between injection points and the spring of the Timava/Timavo. On the Y-axis measured tracer concentrations were divided by the tracer mass injected, while on the X-axis the times after injection were divided by the factor of distance (Fig. [7\)](#page-10-0). The factor of distance was determined by dividing, for each individual test, the distance between the injection point and the sampling point by the shortest such distance in the tracer tests considered: 21.35 km for the 2005 test. The factors were thus $F_{2013} = 27$ km/21.4 km = 1.26 for the 2013 test, $F_{2006} = 39 \text{ km}/21.4 \text{ km} = 1.82 \text{ for the } 2006 \text{ test}$, $F_{1962} = 34$ km/21.4 km = 1.59 for the 1962 test and $F_{2005} = 21.4$ km/21.4 km = 1 for the 2005 test.

Discussion

The results of the tracer test in 2013 reflect the characteristics of water flow and solute transport from the central part of the Classical Karst aquifer, which is outside the area of the main conduits of underground flow. Roughly a quarter of the injected tracer discharged, with an apparent dominant velocity of 38 m/h, through the Timava/Timavo spring in a period of one month (first tracer pulse), when the discharge of the spring reduced below $45 \text{ m}^3\text{/s}$ and of the Reka sinking stream below $4 \text{ m}^3\text{/s}$ (Fig. [2\)](#page-5-0). With higher water levels, concentrations of tracer were correspondingly lower. With the next clear decline in discharge to the minimum values, a second tracer pulse developed, lasting 2 months and with roughly the same concentrations as the first pulse. The percentage of recovered tracer reached 53% in this period. In view of the increased concentration of uranine recorded in the Storje-1/12 borehole a year after injection (1.1 mg/L), it can be concluded that part of the tracer was retained in the borehole and in the less permeable parts of the surrounding rock. Subsequent precipitation events gradually pushed it towards the main drainage conduits, and in conditions of low water levels, it then reappeared in the springs in perceptible concentrations.

On the other hand, both tests involving injection in the Reka sinking stream were carried out at low water levels. The apparent dominant velocities of 86 m/h in 1962 and 47 m/h in 2006 are significantly lower than the maximum measured during tracing at high water level in 1907, when velocity was estimated at 162 m/h (Timeus [1928\)](#page-12-0). Since the water level was extremely low during the tracer test in 2006, a velocity of 47 m/h may be considered as the lowest possible velocity for the main underground flow of the Reka in the system of large karst conduits.

The flow velocity is significantly affected by hydrological conditions in the period directly before and after injection, when a characteristic water pulse can push tracer from the ponor towards the springs (1962 test). Such concentrated transport of the tracer cloud in a closed flow along the underground conduit is also confirmed by the high concentrations and the high percentage of recovered tracer (81%) during the first tracer pulse. In the 2006 test, with the water level very low, the velocity of transport and percentage of recovered tracer in the first pulse (only around 20%) are significantly lower. Part of the tracer was Fig. 6 Comparison of precipitation (P), discharges of the Timava/Timavo (Q) and the Reka (Q_R), tracer breakthrough curves (C) and recovery curves (R) for the selected tracer tests in the first 5 months of tracing. (Note that concentrations for the 1962 test are presented on the secondary Y-axis.)

retained for a long time in the less permeable parts of the karst conduit system but discharged relatively uniformly at the spring after a certain delay and in lower concentrations. The continuity of discharge is also reflected in the uniform growth of the tracer recovery curve, which after 3 months reached 69%.

Regarding the time distribution, the transport of tracer in the 2005 test, when uranine was injected into a highly permeable fracture on the surface in the area above the underground flow of the Reka, shows similar characteristics to the transport of tracer in the 2006 test. With

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favourable hydrological conditions, the sufficiently permeable vadose zone enabled the continuous transport of approximately one-third of the injected tracer to the main underground flow, which then carried it onwards towards the spring at an apparent dominant velocity of 39 m/h. The shapes of the tracer recovery curves are also very similar during this first pulse. There is, however, a difference in the transport of the remainder of the tracer, which in the 2006 test was retained in the conduits of the underground Reka, and in the 2005 test in less permeable parts of the vadose zone. In the first case, continuous transport continues

Fig. 7 Comparison of tracer breakthrough curves and recovery curves: tracer concentrations normalised according to the mass injected, and time after injection adjusted to the factor of distance between injection and sampling points

relatively independently of precipitation conditions, while in the second case further transport of tracer only occurs during individual sufficiently intense precipitation events, when infiltrated rainwater drives part of the retained tracer from the fissures and pores of the vadose zone. In this second case, the percentage of tracer recovered during the five-month comparison period is also correspondingly lower (47%), since the period of discharge of tracer from the vadose zone is considerably longer and can even last for several years (Kogovšek and Petrič 2014).

Based on the comparison of the results of the all four above described tracer tests, it is possible to conclude that solute transport by the sinking stream and through the main drainage system of karst conduits means relatively high velocities (162–47 m/h), depending above all on hydrological conditions. Tracer recovery curves indicate uniform, continuous transport towards the springs even in periods without precipitation events, and a high percentage of tracer recovered in a relatively short period (1–2 months). In this sense there is a significant difference in the flow of water and the transport of tracer directly from the surface, which is tied above all to precipitation. In this case, part of the water and solutes are retained in the less permeable parts of the vadose zone and then gradually transported towards the springs, potentially even several years after pronounced precipitation events. The example described highlights the important role of the vadose zone. The influence of water flow dynamics in the vadose zone and of hydrological conditions on the transport of solutes through karst aquifers has been analysed in greater detail in a number of other studies (Perrin et al. [2004](#page-11-0); Flynn and Sinreich [2010](#page-11-0); Kogovšek [2010;](#page-11-0) Kogovsek and Petric [2014](#page-11-0)).

With the tracing via injection into a borehole in 2013, the influence of the vadose zone was reduced, but an assessment of the characteristics of water flow and solute transport from less permeable parts of the karst aquifer outside the primary drainage conduits is possible. Despite the water level being highest, the flow velocities established by this test were lowest (although similar to those in the 2005 test, which involved injection on the surface). Continuous discharge of the majority of tracer in greater concentrations lasted for as long as 4 months. Interim reductions of concentrations are the consequence of an increase in hydraulic pressure in the main karst conduits of the underground flow, which limited inflow from the broader area of the aquifer, while dilutions were also greater. At higher water levels, then, flow and transport via the primary drainage conduits of the karst system prevail, while at low water levels the recharge of these conduits from the less permeable parts of the aquifer is enabled to a greater extent.

Conclusions

Numerous tracer tests have been carried out in the Classical Karst area on the border between Slovenia and Italy in the past, but for the most part they have served to investigate main flow characteristics in the underground system of large karst conduits. In the recent years, the tracer tests with new modes of recharge in different parts of the aquifer were carried out at different hydrological conditions and the results revealed new information on the hitherto less well researched zones. A comparison of the results enabled a better understanding of the role of various aquifer recharge modes and the influence of the heterogeneity of aquifer structure on the characteristics of water flow and solute transport in complex karst aquifers.

The study confirmed the usefulness of the method of tracing using artificial tracers to understand solute transport processes in karst aquifers. An individual tracer test enables us to obtain basic information about directions of flow towards karst springs, while in order to understand the functioning of complex karst systems, multiple tracings and multi-tracer tests in different hydrological conditions are necessary, since this enables a comparison of the results of different modes of recharge and flow through the vadose and phreatic zones of a karst aquifer.

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