TRACER TESTS AS A TOOL FOR PLANNING THE MONITORING OF NEGATIVE IMPACTS OF THE MOZELJ LANDFILL (SE SLOVENIA) ON KARST WATERS

SLEDILNI POSKUSI KOT ORODJE ZA NAČRTOVANJE MONITORINGA NEGATIVNIH VPLIVOV ODLAGALIŠČA ODPADKOV MOZELJ (JV SLOVENIJA) NA KRAŠKE VODE

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Abstract
Janja Kogovšek & Metka Petrič: Tracer tests as a tool for planning the monitoring of negative impacts of the Mozelj landfill (SE Slovenia) on karst waters

Tracer tests are one of the most useful research methods in karst hydrogeology and they have proved a valuable tool in various applied projects. In recent years we carried out a series of tracer tests, and their results were used as the bases for planning the monitoring of water quality in the influence areas of various pollution sources. In this paper, a case study of tracing at the landfill near Mozelj in southeastern Slovenia is described. The first goal was testing of the functioning of three monitoring boreholes, which were drilled at the margins of the landfill. As often happens in heterogeneous karst systems, they did not intersect the main flow paths from the landfill and are not suitable as monitoring points. On the other hand, the findings about the characteristics of tracer transport in the karst system and outflow through the karst springs were used for identifying the most suitable springs for monitoring and preparing an adequate sampling plan, which should be adapted to hydrological conditions.

Keywords: karst water, tracer test, monitoring, landfill, Mozelj, Slovenia.

INTRODUCTION

Karst aquifers are vulnerable to pollution. Due to strong fissuring and high permeability, the rainwater together with harmful substances enters quickly into the aquifer, and flows through karst channels or open fissures in different directions and toward distant springs. The capacity of natural filtration in karst is low and the possible negative influences very likely. In the case of landfills, more dangerous than the wastes themselves is the percolation of wastewater into the karst underground. Due to various contents of refuse, the resulting leachates are

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Characteristics of the Study Area

The landfill (19,120 m$^2$) is situated near the village Mozelj in southeastern Slovenia on the karst area between the valleys of the Kolpa and Krka Rivers. Since 1973 it has been used as a landfill of non-hazardous wastes of the Kočevje Municipality with approximately 17,000 inhabitants. Based on the existing data, it was not possible to define the position of the water divide between the two rivers, and the drainage pathways of the landfill were not known. Three monitoring boreholes were drilled at the margins of the landfill. The aim of the tracer test was to characterise the groundwater flow in the area and to verify whether the boreholes are representative for monitoring.

Hydrogeological Characteristics

The area (Fig. 1) is mainly composed of carbonate rock, and is dissected with the faults in NW-SE, NE-SW, and N-S directions. Jurassic limestone with the inliers of dolomite is dominant in the southern part, while in the northern part Cretaceous limestone with inliers of dolomite prevails. Between the two, Upper Triassic dolomite and Permian clastic rocks are to be found in a narrow belt southeast of Mozelj.

The Rinža River sinks at various locations (depending on hydrological conditions) southeast of Kočevje and flows underground toward the springs in the Kolpa valley. The last ponors, which are reached only during the highest waters, are less than 1 km distant from the landfill.

In the upper part of the Kolpa valley there are several springs on the left bank (Fig. 1). Larger and permanent are the Bilpa (Fig. 2), Dolski potok, Šumetac, and Kotnica springs. In the Krka valley, the most important are the Radešica and Obrh springs. In the past, the Dolski potok and Radešica springs were captured for water supply, but due to a deterioration of water quality they were replaced by other sources.

Tab. 1: Characteristic discharges of the springs (Habič et al. 1990).

<table>
<thead>
<tr>
<th>Spring</th>
<th>Period</th>
<th>Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilpa</td>
<td>April to June, 1988</td>
<td>0.8 to 5 m$^3$/s</td>
</tr>
<tr>
<td></td>
<td>28.9.2005 – 24.8.2007*</td>
<td>0.1 to 35.7 m$^3$/s</td>
</tr>
<tr>
<td>Dolski potok</td>
<td>April to June, 1988</td>
<td>1 to 3 m$^3$/s</td>
</tr>
<tr>
<td>Radešica</td>
<td>April to June, 1988</td>
<td>0.5 to 23 m$^3$/s</td>
</tr>
<tr>
<td>Obrh</td>
<td>April to June, 1988</td>
<td>0.5 to 2.5 m$^3$/s</td>
</tr>
</tbody>
</table>

* measured by the Environmental Agency

Several tracer tests were carried out in the past (Tab. 2, Fig. 1). As they were done at low waters, the assessed velocities are relatively low, and higher values are to be expected at high waters. Additionally, the tests were carried out almost twenty years ago, so we should be cautious in making the conclusions based on them. The main underground connections were confirmed, while for a more detailed assessment of the characteristics of the water flow from the landfill the results are not sufficient. Namely, in all previous tests the tracers were injected in the sinking streams, while for landfill a diffuse leakage from the surface is characteristic. Perculation through the vadose zone has an important...
influence on the flow and transport of pollutants. Due to the above facts, an additional tracer test was carried out with the injection of tracers at the surface near the landfill.

**HYDROGEOLOGICAL CHARACTERISTICS OF THE LANDFILL AREA**

Three monitoring boreholes were drilled at the margins of the landfill (Fig. 3); each of them in a different lithostratigraphic unit (Pregl et al. 2004). The northern part (borehole Mo-1) is composed of well karstified, bedded Upper Cretaceous limestone. Toward the southeast it is in a tectonic contact with thick-bedded to massive Lower Cretaceous limestone (borehole Mo-3), which dips gently toward southwest and west. The limestone is tectonically crushed and well karstified. The area south of the landfill is composed of well karstified, thick-bedded to massive Norian-Rhaetian dolomite (borehole Mo-2), which dips toward southwest and west. Below this dolomite lies low-permeable marly and sandy dolomite of

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**Tab. 2: Results of previous tracer tests (Gams 1965; Habič et al. 1990; Novak & Rogelj 1993).**

<table>
<thead>
<tr>
<th>Injection point (sinking stream)</th>
<th>Date of injection</th>
<th>Tracer</th>
<th>Proved connection (spring)</th>
<th>Apparent flow velocity (m/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rinža</td>
<td>30.8.1956</td>
<td>Uranine</td>
<td>Bilpa</td>
<td>18.0</td>
</tr>
<tr>
<td>Koprivnik</td>
<td>8.4.1988</td>
<td>Rhodamine</td>
<td>Dolski potok</td>
<td>33.8</td>
</tr>
<tr>
<td>Rinža</td>
<td>12.4.1988</td>
<td>Uranine</td>
<td>Bilpa</td>
<td>28.4</td>
</tr>
<tr>
<td>Kačji potok</td>
<td>12.4.1988</td>
<td>Phages</td>
<td>Radešica</td>
<td>42.5</td>
</tr>
<tr>
<td>Željnski potok</td>
<td>12.4.1988</td>
<td>Eosin</td>
<td>Radešica</td>
<td>29.5</td>
</tr>
<tr>
<td>Jame</td>
<td>12.11.1990</td>
<td>Uranine</td>
<td>Šumetac</td>
<td>?</td>
</tr>
<tr>
<td>Knežja Lipa</td>
<td>8.4.1991</td>
<td>Rhodamine</td>
<td>Šumetac</td>
<td>?</td>
</tr>
</tbody>
</table>
On April 5, 2006, we installed a rain-gauge Onset RG2-M in the village Zajčje polje (Fig. 1) to measure precipitation at 15-minute intervals (Fig. 8). On September 28, 2005 (data from June 24 to October 4, 2006, are missing due to technical trouble), an automatic gauging station for the measurement of water levels of the Bilpa spring was installed by the Environmental Agency. They provide us with the data on hourly discharges (Fig. 8).

Sampling in the boreholes was done before and during the tracer test by the co-workers of the Institute for Mining, Geotechnology and Environment, who used special sampling bottles. For chemical analysis the water samples were taken at all three boreholes on March 28, 2006, and on April 5, 2006, only in borehole Mo-1. In borehole Mo-3 additional 8 samples were taken during the tracer test. Additionally, we obtained the results of monitoring on September 6, 2005, which were made by order of the landfill manager.

According to the suggestions in the previous hydrogeological report (Pregl et al. 2004) and provisions of the contract with the landfill manager, two different injection points and two different tracers, uranine and eosin, were applied. On April 5, 2006, between 10:30 a.m. and 10:45 a.m., the solution of 18 kg of eosin was injected at point T1 at the southwestern border of the landfill and washed off with 5 m$^3$ of water. At the same time, the solution of 18 kg of uranine was injected at the point T2 at the northern border and washed off with the same amount of water (Figs. 3 and 6).

Water from the boreholes was sampled in the first three days after the injection, and then additionally on two days after the precipitation event on April 13. In the Bilpa and Radešica springs the samples were taken first at 12-hour intervals, and later once per day with automatic samplers (ISCO 6700). In the Bilpa spring, the fluorescence of the two tracers was additionally measured in situ by a two-channel Fiber-optic Fluorometer.

Cordevolian age. The carbonate rocks are covered with thin, often interrupted layers of soil, which have low protection function.

All three boreholes with a depth of approximately 120 m reached the saturated zone (Pregl et al. 2008). Water levels in them were measured occasionally (8 measurements in the period from 2005 to 2008), therefore only some approximate assessments of their characteristics can be done. The water level is the highest in the borehole Mo-2 (between 411 and 435 m asl), similar in the borehole Mo-1 (between 413 and 420 m asl), and the lowest in the borehole Mo-3 (between 389 and 395 m asl). Based on the comparison of the water levels, the groundwater flow direction toward the east and southeast respectively can be defined. The depth of the vadose zone below the landfill can be assessed at 35 to 70 m. As all measurements were carried out during low or medium waters, the water table is even closer to the surface at high waters.
LLF-M Gotschy Optotechnik at 30-minute intervals. The Dolski potok and Šumetac springs were sampled manually once per day, and later once in each two days. The Kotnica and Obrh springs were sampled only occasionally during weekly control visits. We ended the sampling in May 2007.

Fluorescences of uranine (\(E_{ex}=491\) nm, \(E_{em}=512\) nm) and eosin (\(E_{ex}=516\) nm, \(E_{em}=538\) nm) were measured in our laboratory by a Luminescence Spectrometer LS 30, Perkin Elmer. Detection limit for uranine was 0.01 mg/m³ and for eosin 0.05 mg/m³. First measurements were carried out immediately after the sampling and then later when possible suspended particles in the samples were decanted.

Both tracers were detected in the Bilpa spring practically simultaneously; therefore during the analysis some interactions between them occurred. The quantities of the two injected tracers were the same. As in the solutions of equal concentrations the fluorescence of uranine is significantly higher than that of eosin, the impact of uranine on eosin is high, while the impact of eosin on uranine is low. The easiest way to recognize the two tracers is to run a synchronized wavelength change of the excitation and fluorescence monochromators through the spectrum of interest with a constant wavelength distance \(\Delta\lambda\) (Kass 2004). However, we were not able to use this method with the Luminescence Spectrometer LS 30, so for the assessment of concentrations a combination of calculations and measurements at lower pH value, at which the total amount of present eosin and only a small part of uranine can be detected (Kass 2004), was used. For additional verification of the impact of uranine on eosin, we tested several solutions with various concentrations of eosin in the presence of uranine, and vice versa. Measured and calculated values were checked by the fluorescence measurements of the mixture of both tracers in various concentrations. Based on the calculations and comparisons the concentrations of the two tracers were evaluated. We are aware of the fact that such approach generates a bigger error.

For parallel measurements with the LLF-M fluorometer we used Em 1 special filter for measurements of uranine in combination with eosin. We made calibrations of the two channels with both tracers and calculated interdependence. In this way measured and corrected values coincide well with the corrected measurements of LS 30 (Fig. 4). The main flow of both tracers toward the Bilpa spring is also confirmed by their very low concentrations in the other observed springs.

RESULTS

CHEMICAL ANALYSIS OF WATER FROM THE BOREHOLES

The Ca/Mg ratio (normal concentrations of Ca and Mg) was highest in borehole Mo-1 (between 10 and 40), stable around 1.5 in borehole Mo-2, and constant at nearly 3 in borehole Mo-3. We can infer that borehole Mo-1 is mainly recharged from limestone, especially during increased inflow after rainfall. Borehole Mo-2 is located in a dolomite area, and for borehole Mo-3 various inflows from the areas of the two other boreholes are indicated.
nia, and higher concentrations of nitrates indicate the presence of oxidation processes, which can take place at favourable conditions in this part of the vadose zone (Kogovšek 1987). This indicates differences in short distances within the vadose zone.

In the samples from March, 2006, after a precipitation event, the highest concentrations of nitrates (18.8 mg/l NO$_3$) and chemical oxygen demand-COD

the electrical conductivity-EC was up to 9000 µS/cm, and concentrations of chlorides (450 mg/l), ferrous iron (9.7 mg/l), zinc (0.36 mg/l), and copper (11.8 µg/l) were high. Only slightly increased concentrations of contaminants in the boreholes indicate a weak connection of the main flow of leachates from the Mozelj landfill and the monitoring boreholes.

DETECTION OF TRACERS IN THE BOREHOLES

In borehole Mo-1 the concentrations of tracers remained around the detection limit. In borehole Mo-2 the uranine concentrations oscillated only slightly above the detection limit, which excludes any connection with the injection point T2 (Fig. 7). The first increase of the eosin concentration on April 5, 2006 at 5 p.m. was probably a reaction to the washing off of the injected eosin with water. A higher concentration was detected on April 6, 2006 at 3 p.m. after rainfall which pushed injected eosin through less permeable fissures toward the borehole Mo-2. In the following period until April 14, 2006, after the appearance of peak concentrations in the Bilpa spring, the eosin concentrations in borehole Mo-2 were below 0.15 mg/m$^3$. We can infer that by this time most of the injected eosin was washed out of the upper, less permeable part of the vadose zone through well permeable fissures which do not intersect borehole Mo-2.

In borehole Mo-3, increased uranine concentrations were detected on April 5 (Fig. 7), probably as a result of washing off with water. The calculated apparent flow velocity of 85 m/h is comparable with the fast flow through the most permeable fissures in the vadose zone above the Postojna Cave in southwestern Slovenia in similar hydrological conditi-

Fig. 5: Concentrations of contaminants in the boreholes (COD-chemical oxygen demand, NH-ammonia, NO-nitrates, SO-sulphates, Cl-chlorides, TOC-total organic carbon, o-PO-o-phosphates). Samples were taken on September 6, 2005, and March 28, 2006 (note that some parameters were measured only for one sampling).

Fig. 6: Injections of eosin (left) and uranine (right) on April 5, 2006 (Photo: M. Petrič).
ions (Kogovšek 1997). Such high velocities were possible due to the fact that many of the fissures in the vadose zone were temporarily filled with water and hydraulically connected.

Eosin was detected in borehole Mo-3 on April 7, 2006 at 8:35 a.m. following a precipitation event. A similar breakthrough curve with the peak 18 hours before was measured in borehole Mo-2. Considering that the distance between boreholes Mo-2 and Mo-3 is 463 m, the apparent velocity of flow between them was 25.2 m/h. This indicates that the underground water connection between the two boreholes is better than between the injection point T1 and borehole Mo-2 ($v_{dom}=6.7$ m/h).

At the time of increased concentration of eosin in Mo-3 measured lower Ca/Mg ratio (Ca/Mg=1.4) indicates a more intensive inflow to the boreholes, especially from the dolomite area (Fig. 7).

Nine days after the injection the concentrations of both tracers in all three boreholes were at the detection limit.

DETECTION OF TRACERS IN THE SPRINGS

The main flow toward the Bilpa spring was proven. By the installed equipment, the uranine was first detected on April 12, 2006 at 10 a.m., and the eosin on the same day at 3 p.m. (Fig. 8). These first appearances were induced by 40 mm of rain in the conditions when many of the fissures in the vadose zone were temporarily filled with water. The discharge of the spring was in recession, and after the rainfall it increased only slightly. The maximum concentrations of uranine (19 mg/m$^3$) and eosin (12 mg/m$^3$) were detected practically simultaneously on April 14, 2006 at 8 a.m. (Fig. 9). Then they decreased quickly, and persisted at the values slightly above 1 mg/m$^3$ until the end of April. The peak discharge of 12 m$^3$/s was reached after rain (45 mm) at the end of April. The concentrations of both tracers decreased, while the amount of recovered tracers increased (Fig. 9). We infer that in this
to the discharge of the Bilpa spring was increased. Calculated apparent flow velocities toward the Bilpa spring were practically the same for both tracers (Tab. 3).

Intensive rain during the last week of May (altogether almost 100 mm) induced increased outflow of tracers, but parallel with the increase of discharge up to 36 m³/s the concentrations decreased. At the end of June, the uranine concentrations dropped below the detection limit, and the eosin oscillated around 0.05 mg/m³.

In the other observed springs the tracers appeared only in low concentrations. In the Dolski potok and Šumetac springs a more significant increase was detected parallel with the discharge increase on May 30, 2006 (Tab. 3). Continuous appearances of eosin (up to 0.1 mg/m³) and uranine (up to 0.03 mg/m³) were detected in the Radešica spring from the beginning of May 2006 to January 2007 after each more intensive precipitation event (Tab. 3). We can conclude that underground water connections between the landfill and these three springs are possible but weak.

In the period of one week after the appearance of tracers in the Bilpa spring, the main wave of the breakthrough curve was formed in the conditions of discharge recession. Within this interval approximately 70% of injected uranine and 55% of eosin were recovered. The main transport of uranine (90%) and eosin (almost 74%) was registered in the period from April 13 to May 6 (23 days), when al-
together 230 mm of rain of various intensities were recorded after the injection (Fig. 9). Until the end of July 2006, approximately 92% of uranine and 79% of eosin were recovered. The calculation of recovery for other springs was not possible because the discharge data were not measured. However, low concentrations of tracers indicate relatively low share of recovery through these springs.

DISCUSSION

In the monitoring boreholes no significant negative impacts from the landfill were detected by previous chemical analysis of water. No tracers in borehole Mo-1, the appearance of both tracers in borehole Mo-3 in relatively low concentrations, and the absence of uranine in borehole Mo-2 indicate that the majority of injected tracers flowed mainly along the paths which are not intersected by the boreholes. For the uranine calculated apparent flow velocity toward borehole Mo-3 was more than 8-times higher than the one for the eosin. Washing off with 5 m$^3$ of water after the injection was sufficient to induce the transport of uranine, while for the transport of eosin some additional rainfall was needed. Low flow velocities of eosin from the injection point T1 toward the nearby borehole Mo-2 indicate that this borehole was drilled in a local low-permeability zone and is out of the main groundwater flow south of the landfill. The results indicate that the three boreholes are not representative for monitoring. This confirms a general finding that in karst monitoring in boreholes is unsuitable in the majority of cases due to the high heterogeneity of karst aquifers.

A preliminary test with injections of water at various locations around the landfill was carried out to compare the capacity of infiltration and to select the injection points. This capacity was low, so we expected longer retention and adsorption of the injected tracers, and even decided to increase the amount of used tracers. However, the tracer test resulted in one high, continuous breakthrough curve in the Bilpa spring without significant oscillations, even though the precipitation inducing this wave was relatively moderate. This indicates high permeability of the karst system observed, but the importance of abundant previous precipitation (and consequently the conditions when a major part of pores and fissures in the soil and vadose zone is temporarily filled with water and hydraulically connected) for a rapid transport of tracers toward the Bilpa spring should be emphasised too. Such conclusion is comparable with the results of detailed researches of hydrodynamics of drippwater and tracer tests on some other test sites on the Slovene karst (Kogovšek 1997; Trček 2007; Kogovšek & Petrič 2006).

In the phreatic zone the main flow from the landfill converges with the underground flow of the Rinža stream, which sinks east of the landfill. Its maximum discharge of several tens of m$^3$/s indicates the existence of large karst channels with high hydraulic gradient of 26‰ toward the Bilpa spring. Such concentrated flow is also proved by high recovery rates within the first week of sampling (70% of uranine, 55% of eosin) and within 23 days after the injection (90% of uranine, 74% of eosin) respectively.

Some differences were detected in the transport characteristics of uranine and eosin. In the first part of the breakthrough curve, the amount of detected eosin was lower, while its outflow lasted longer and its concentrations in later periods were higher (Fig. 9). The recovery curve of eosin converges in time with the one of uranine. The reason could be longer retention of eosin in the dolomite area south of the landfill, as well as different characteristics of the two tracers (higher sorption properties of eosin; Käss 2004).

A rapid flow toward the Bilpa spring and high concentrations of tracers confirmed that this spring is the most suitable monitoring point. However, the interpretation of the results of monitoring is difficult, because the Rinža sinking stream, polluted with various pollution sources in the Kočeje area, is also recharging the spring. To assess its influence, a simultaneous monitoring of Bilpa and Rinža is necessary. Furthermore, some characteristic contaminants have to be selected and the monitoring concentrated mainly on them. The monitoring plan should be supported by the measurements of precipitation, discharges and physical parameters of water.

This main underground flow toward the Bilpa spring gets an additional contribution by primary recharge of unpolluted water. It leads to a dilution of contaminants, which is highly influenced by precipitation and hydrological conditions. As a consequence, the water quality of Bilpa is better than that of Rinža. Therefore it is important to measure and compare the inflows from various contribution areas within this complex catchment to interpret properly the results of monitoring.
CONCLUSIONS

The described case study, as well as our previous experiences in the study of karst aquifers, shows that tracer tests are a valuable research tool for defining the characteristics of water flow and transport of pollutants in karst systems. Additional information can be gathered by simultaneous measurements of precipitation in the area of injection and physical parameters at springs, as well as by complementary chemical analysis of selected parameters.

Due to specific characteristics of karst aquifers and their high heterogeneity the boreholes are not representative for detecting the pollution of karst waters, and karst springs or other natural objects with water flow should be selected as monitoring points. However, as many karst springs have large catchment areas and complex structures, the overlapping of negative influences from various pollution sources is possible and a good understanding of the functioning of karst aquifers is necessary to interpret the monitoring results.

Based on the results of tracer tests, the most representative monitoring points can be selected, and the influence of various hydrological conditions considered in the construction of the monitoring plan. To increase the possibility of detecting the pollution, it is sensible to sample in the periods when the highest concentrations of pollutants can be expected. During wet periods already medium intensive rainfall would initiate such conditions, while during dry periods a more intensive precipitation is needed. In dry conditions rainwater is first used to saturate deposited waste and the soil; only then do leachates infiltrate into the vadose zone and then further on toward the spring. Especially during long summer droughts, when precipitation water is only stored in wastes, soil and vadose zone, the waste water from the landfill does not reach the springs. Only sufficiently intensive precipitation in the following period induces the leaching of contaminants out of the landfill and pushing of the previously stored contaminants from the vadose zone toward the phreatic zone. From there the transport to the springs is very rapid. As the conditions in karst aquifers change quickly, it seems the most efficient to take several samples in the time of a complete water wave: from the beginning of the increase of discharge, through the discharge peak, and in the recession phase back to the initial state. To avoid strong dilution, it is better not to sample in conditions of very high discharges.

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REFERENCES


