GEOLOGIJA 66/2, 285-299, Ljubljana 2023
https://doi.org/10.5474/geologija.2023.014

Impact assessment of the Gajke and Brstje landfills on groundwater status using stable and radioactive isotopes

Ocena vpliva odlagališč Gajke in Brstje na stanje podzemne vode z uporabo stabilnih in radioaktivnih izotopov

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Prejeto / Received 17. 11. 2023; Sprejeto / Accepted 20. 12. 2023; Objavljeno na spletu / Published online 21. 12. 2023

Key words: groundwater, monitoring, landfill, stable isotopes, tritium, Gajke, Brstje
Ključne besede: podzemna voda, monitoring, odlagališče odpadkov, stabilni izotopi, tritij, Gajke, Brstje

Abstract

Waste disposal in landfills represents a severe threat to aquatic environments on the local, regional, and global levels. In Slovenia, there are 69 registered landfills where groundwater is regularly monitored. However, isotope techniques are not regularly employed. Therefore, we employed isotope analysis of hydrogen, carbon, and oxygen in combination with total alkalinity to assess the impact of the selected landfill on groundwater and to evaluate the biogeochemical processes at work. The $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, ^{3}H activity and total alkalinity were determined in October 2020 at 12 sampling points from the surrounding area of the Gajke and Brstje landfills and leachate from the Gajke landfill. The $\delta^{18}O$ (-9.24 ± 0.3 ‰) and $\delta^{2}H$ (-64.9 ± 2.7 ‰) in groundwater indicate that the main water source consists in direct infiltration of precipitation, with no significant isotopic fractionation. Total alkalinity in the investigated area ranges from 5.45 to 73 mM and $\delta^{13}C_{DIC}$ from –14.9 to +6.1 ‰, respectively. Higher values of total alkalinity (up to 73 mM), $\delta^{13}C_{DIC}$ (up to +6.1 ‰), $\delta^{18}O$ (-7.64 ‰) and ^{3}H (209.8 TU) are detected in the leachate, indicating biogeochemical process related to CO_2 reduction or methanogenesis. Methanogenesis could be present at locations GAP-10/13 (Brstje landfill) and G-2 (Gajke landfill) with $\delta^{13}C_{DIC}$ values ranging from –8.2 to –7.6 ‰ and with dissolved oxygen values around 0 % and elevated ^{3}H values (from 16 to 18 TU). This study demonstrates the effectiveness of isotopic analysis as a valuable tool for monitoring landfills, revealing shifts in biogeochemical processes within the groundwater there.

Izvleček

Odlaganje odpadkov na odlagališčih predstavlja resno grožnjo za vodna okolja na lokalni, regionalni in globalni ravni. V Sloveniji je 69 registriranih odlagališč, kjer se redno izvajajo obratovalni monitoringi kemijskega stanja podzemne vode. Kljub temu izotopske tehnike niso rutinsko uporabljene. Zato smo uporabili analizo izotopov vodika, ogljika in kisika v kombinaciji s skupno alkalnostjo, da bi ocenili vpliv izbranega odlagališča na podzemno vodo in ovrednotili biogeokemične procese. $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, aktivnost ^{3}H in skupna alkalnost so bile določene v oktobru 2020 v 12 vodnjakih v okolici odlagališč Gajke in Brstje in v izcedni vodi iz odlagališča Gajke. Vrednosti $\delta^{18}O$ (-9,24 ± 0,3 ‰) in $\delta^{2}H$ (-64,9 ± 2,7 ‰) v podzemni vodi kažejo, da je glavni vir vode neposredna infiltracija padavin, brez bistvene izotopske frakcionacije. Totalna alkalnost na preiskanem območju se spreminja od 5.45 do 73 mM, $\delta^{13}C_{DIC}$ od –14.9 do +6.1 ‰. Višje vrednosti totalne alkalnosti (do 73 mM), $\delta^{13}C_{DIC}$ (do +6.1 ‰), $\delta^{18}O$ (-7.64 ‰) in ^{3}H z 209.8 TU so zaznane v izcedni vodi CERO Gajke (kanal), kar kaže na biogeokemijski proces redukcije CO_2 ali metanogeneze. Metanogeneza bi lahko bila prisotna tudi na lokacijah GAP-10/13 (odlagališče Brstje) in G-2 (odlagališče Gajke) z $\delta^{13}C_{DIC}$ vrednostima od -8.2 do -7.6 ‰ in z vrednostjo raztopljenega kisika okrog 0 % ter povišano vrednostjo ^{3}H (od 16 do 18.2 TU). V tej raziskavi smo dokazali, da so izotopi koristna orodja v monitoring raziskavah odlagališč in kažejo na spremembe biogeokemičnih procesov v podzemni vodi.

Introduction

Economic development, population growth, and technological developments are resulting in ever-increasing amounts of deposited waste, making the importance of ecological waste management and environmental protection ever more apparent. Landfills, which are potential local sources of pollution, are generally considered minor local inconveniences and can also pose problems in larger areas, especially if the pollution spreads from the landfill to the groundwater and surface waters (Bhalla et al., 2013; Abiriga et al., 2020, 2021). Depending on the nature of the contaminants and their chemical properties, they may remain or decompose in groundwater for decades or even centuries. Once a waste facility is closed, proper functioning of landfill systems must be ensured, so operational monitoring of groundwater status and, in some cases, surface water status monitoring must be conducted to determine the status of groundwater during and after landfill operations have concluded. Operational monitoring of groundwater status is likely to be conducted in the area of the hydrogeologic target zone, which is a lithostratigraphic unit where contamination could be expected due to indirect or direct discharge of contaminants from a source of contamination to groundwater. Operational monitoring includes measurements of hydrogeological and chemical parameters, which we use to assess the impact of a landfill on the status of groundwater. An environmental permit is required to operate the landfill, which specifies the scope and content of monitoring; the content and scope are explained in more detail in the groundwater monitoring programme. In the event that the landfill is determined to have an impact on the status of groundwater based on the chemical analyses performed, it is also necessary to prepare a programme of measures that must include, among other things, an estimate of the discharge of pollutants from the landfill to groundwater and an assessment of the magnitude of the impact on the recipients (Serianz et al., 2017; Cerar et al., 2022).

In recent years, several studies have been published on the determination of chemical parameters in landfill leachate (Hussein et al., 2019; Ančić et al., 2020; Baettker, et al., 2020) and their impact on groundwater quality (Kapelewska et al., 2019; Chidichimo et al., 2020). Groundwater quality is usually assessed by defining chemical parameters and comparing the data with standards set in legislation. Such an approach provides information only on specific contaminants and provides little information on overall water quality. As different materials or wastes are introduced into the disposal body, the leachate also has a different chemical composition. As a result, there are also differences in the formation of a groundwater pollution plume along the length of the groundwater stream. An important factor in understanding the occurrence of contaminants in groundwater is also their zonation, which is due to the fact that landfill leachate alters the physicochemical properties of groundwater by creating reduction conditions that affect the behaviour of individual contaminants in groundwater (Abiriga et al., 2021).

Hackley et al. (1996) already suggested using the isotopes of hydrogen (δ^{2}H), carbon (δ^{13}C), and oxygen (δ^{18}O) of the major landfill constituents of landfill gas and leachate to identify landfill leachate contamination. Landfill gases (CO_2 and CH_4) and landfill leached products (water and dissolved inorganic carbon) have a characteristic isotope composition with respect to the surrounding environment (Hackley et al., 1996; Kerfoot et al., 2003, Bakkaloglu et al., 2021, Vavilin & Lokshina, 2023). Recently, several studies (Adeolu et al., 2011; Castañeda et al., 2012; Wimer et al., 2013; Negrel et al., 2017; Lee et al., 2020; Andrei et al., 2021) have observed that stable isotopes found in landfill leachates, such as δ^{13}C, δ^{2}H and δ^{18}O, are influenced by processes within municipal solid waste (MSW) landfills, mainly on the methanogenesis phase of the landfill. In addition, δ^{13}C has frequently been used in environmental monitoring studies of landfills and in the determination of the origin of dissolved inorganic carbon in groundwater (DIC) (North et al., 2006; Porowska, 2015; Nigro et al., 2017; de Medeiros Engelmann et al., 2018). Several studies included tritium (^{3}H) analysis as a tool to assess leachate contamination (Nigro et al., 2017; Raco & Battaglini, 2022; Gupta & Raju, 2023).

In Slovenia, there are 69 registered landfills where the chemical parameters of groundwater in the area of the landfill is monitored as part of the larger operational monitoring of the status of groundwater, while isotopic studies are not routinely performed. The only known case study in Slovenia applying the stable isotope analysis of oxygen (δ^{18}O) and hydrogen (δ^{2}H) in water and carbon in the dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in combination with ^{3}H activity concentrations were conducted at the Puconci landfill (Brenčič et. al., 2013). The combination of techniques used in the investigation of groundwater, surface water, and leakage water proved to be useful in identifying the influence of leakage water on surface and groundwater, the complexity of

contamination below the landfill, and also provided a picture of the methane-forming conditions in the landfill. One operational landfill in Slovenia is the Gajke landfill, where in the recharge area about 500 m upstream, there is also the closed Brstje landfill for non-hazardous waste. The results of the operational monitoring of groundwater status at the Brstje landfill showed that it has an impact on groundwater status, as warning levels for pollutants have been exceeded for several years (Cerar et al., 2019). When analysing the spatial distribution of pollutants in groundwater, it should be considered that pollutants in groundwater in the area of the Gajke landfill may originate from leachate or may be the result of contact between groundwater and waste or may already flow into the area of the landfill via groundwater from the Brstje landfill upstream. In such cases, it may be very difficult or even impossible to isolate the individual impacts on the condition of the groundwater. It is therefore essential to consider both landfills simultaneously when analysing pollutants in space and time.

In this case study, we hypothesise that a multi-parameter isotope approach could be applied to separate the potential impact of two landfills, Gajke and Brstje on the groundwater in the municipality of Ptuj. By applying in-situ measurements in combination with determination of $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, and ^{3}H in groundwater at all available sampling points and in leachate from Gajke before treatment we characterised the spatial changes of measured parameters in autumn 2020. The results will be useful for improving the management of the landfills and could in future serve as example of improved water monitoring programme, incorporating isotope measurements, for other landfills in Slovenia.

Case study area characteristics

Gajke landfill

The active Gajke landfill for non-hazardous waste is located in an abandoned gravel pit north of the settlement of Spuhija, in the municipality of Ptuj (Fig. 1). The landfill, including the accompanying areas, currently covers 7.5 ha. It is surrounded by agricultural land on all sides. Waste disposal at the Gajke landfill started in 2003. In total, 572.886 t of waste were deposited from 2003 through 2018. Mixed municipal waste was no longer landfilled with the adoption of new regulations in 2016, as the regulations stipulated the need for post-treatment of this waste. Currently, all municipal waste is transported to Ormož for treatment and disposal. According to the environmental permit, the Gajke landfill still has the status of an active repository.

The bottom of the landfill is sealed with three layers of mineral clay (each layer 25 cm thick) and a 2.5 mm thick PEHD plastic film on top. A protective layer of geotextile is laid on the ground above the PEHD film, on top of which a 40 cm thick drainage layer of gravel is placed. A separating drainage felt is laid over the drainage layer. The collection and discharge of leachate and precipitation water is regulated. Leachate is collected in the leachate basin, then cleaned by a reverse osmosis treatment plant and discharged into the sewage system to the wastewater treatment plant in Ptuj. Precipitation from road and work areas is collected and discharged into the soil collection basin (lagoon), from where it is pumped into the sewer system to the wastewater treatment plant in Ptuj. Clean precipitation and backwater collect in the earth ditches and canals, from where they lead to subsidence chambers and sink into the ground.

Brstje landfill

The closed Brstje landfill for non-hazardous waste is located in the municipality of Ptuj, approx. 500 m north-west of the Gajke landfill (Fig. 1). The nearest residential houses are 100 m away from the landfill and are located in the Brstje district. The landfill, including the accompanying areas, covers 6.8 ha. The Brstje landfill consists of the older northern part of the deposition fields and the younger southern part of the deposition fields. The area was filled in several phases and subphases, which employed different ways of disposing of the waste and protection measures used to reduce negative environmental impacts. The exact geometry and area of the deposited waste is not known, nor is the volume and mass of the deposited waste.

The beginnings of waste disposal in the area of the Brstje landfill date back to the 1970s. Exact information on the earliest days of waste disposal there is not known. Data on the amount of waste deposited is only available for the southern landfill. Thus, the actual amount of waste deposited in the entire landfill is far higher. A total of 66,818 t of mixed municipal waste was deposited at the southern landfill. The youngest part of the landfill, where waste was deposited between 1996 and 2001, is the southernmost landfill.

The landfill is special because it is not located on the embankment, but rather the waste is deposited in the former gravel pit at a depth of 5 to 7 m below the surface. On the eastern side, the gravel

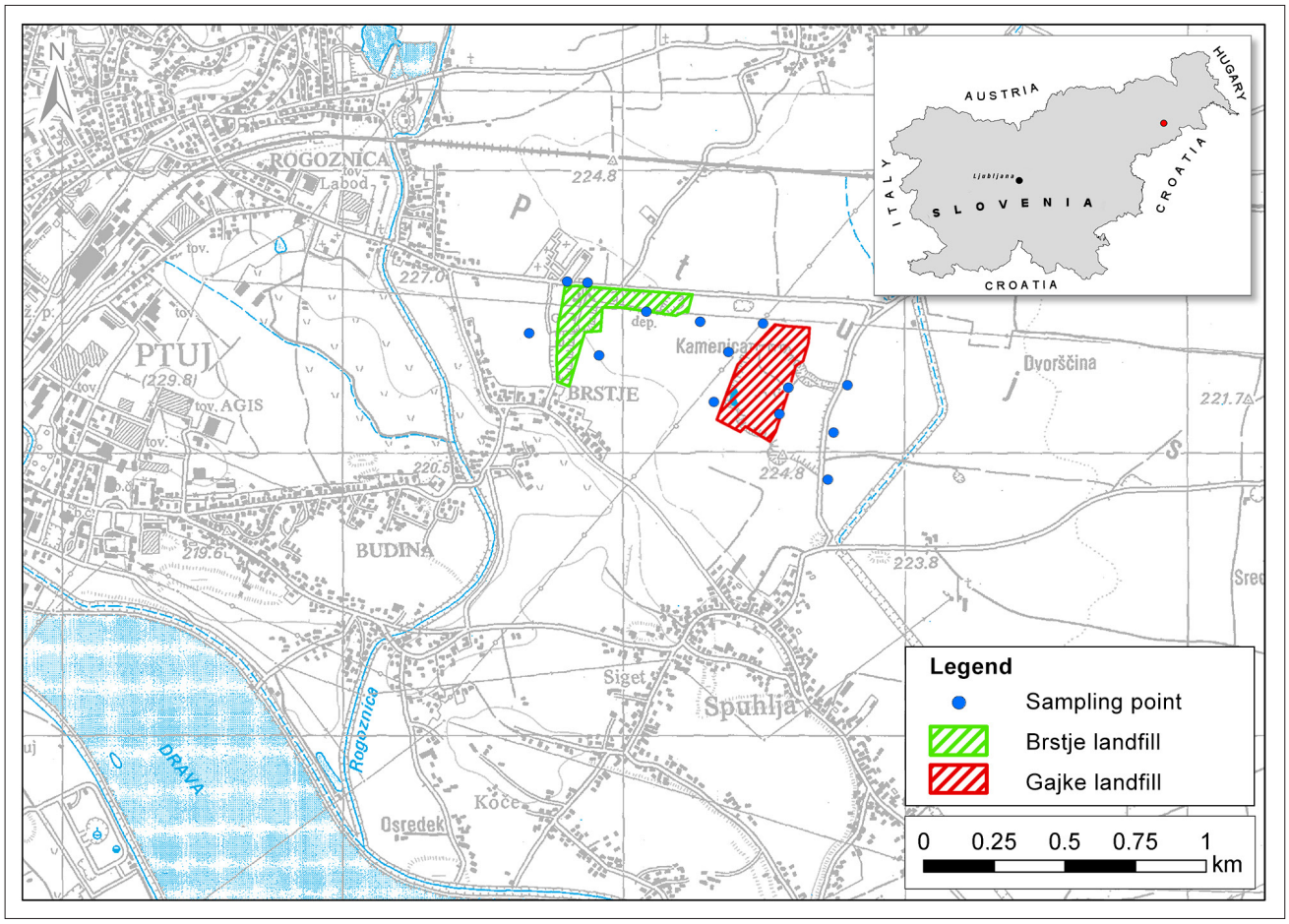

Fig. 1. Overview map of the area of the Gajke and Brstje landfills.

pit is recultivated with a poplar plantation. The old and new parts of the landfill are covered with a less permeable top layer of clay, geocomposite and a layer of soil and humus.

In the bottom of the new part, an impermeable PEHD foil with a drainage system with suction pipes for pumping out the leachate was installed, which is also a special feature of this landfill. In older deposit fields, the leachate drainage system is not regulated. All water drains gravitationally into the groundwater. Precipitation water is drained through the cover layer into the peripheral subsidence ditch.

Geographical and hydrological characteristics of the area

The Gajke and Brstje landfills are located in Ptujsko polje, which from the morphological point of view consists of two Drava terraces and is surrounded on all sides by agricultural land. The largest part of the field is occupied by a high terrace with an elevation of 222–224 m, where there are also landfills. In the western part of the field, the terrace is 7–8 m high, in the central part 4.5 m high, and in the eastern part it 2–3 m high.

About 500 m upstream northwest of the Gajke landfill is the closed Brstje landfill. The nearest surface water is the Rogoznica stream, which flows into the Drava River southeast of the landfill (Fig. 1) (Cerar et al., 2019).

Geological and hydrogeological features in the area of the landfills

The Gajke and Brstje landfills are located on the Quaternary aquifer of the Ptujsko polje, which consists in the upper part of alluvial deposits from the Drava, Pesnica, and Rogoznica rivers. These are mainly sediments of medium-grained sandy gravel, between which there are lenses of silt and clay with limited extension. The lower part is dominated by fine- and medium-grained gravels with more sand and silt, as well as sand layers with silt. The base of the Quaternary sediments is formed by fine-grained sediments of Pliocene age (Fig. 2).

The first hydrogeological unit in the landfill area is represented by a slightly permeable ($K=10^{-3}$ m/s), open Quaternary aquifer, with groundwater at a depth of about 8–9 m below the surface, freely fluctuating in the range between 2.5 and 3.2 m, depending on the hydrologic conditions.

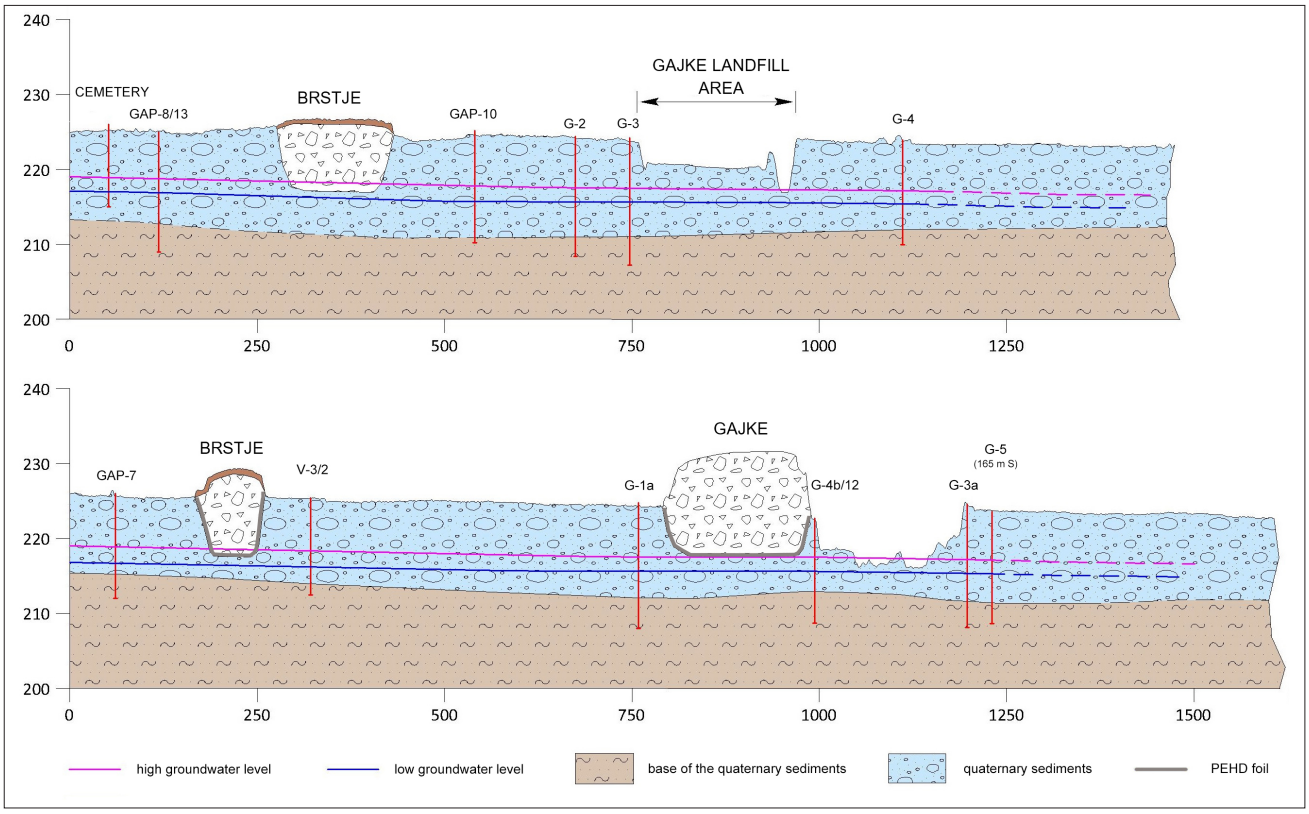

Fig. 2. Simplified hydrogeological cross-section through Gajke and Brstje landfills.

Groundwater flows in the Quaternary aquifer in the NW–SE direction to the Drava River, into which it discharges at 4 to 10 km (Fig. 3). The direction of groundwater flow is approximately the same with respect to the different hydrological conditions, with the largest deviations observed mainly in the south-eastern part of the Gajke deposit, where the flow is directed further to the northeast during floods. The groundwater flow gradient is 0.002 and depends on the intensity of recharge from precipitation. Groundwater velocity is estimated to be 2 to 3 m/day.

Depending on the depth of the deposited waste and the groundwater table, it is an indirect input of pollutants since the landfill is in or above the unsaturated zone. During the flood period, the bottom of the deposit body (the outside of the liner system) is occasionally in contact with groundwater (Cerar et al., 2019).

Methods and materials

Sampling

Sampling for isotope analysis was conducted in 27–28 October, 2020, by Javne službe Ptuj d.o.o. in collaboration with the NLZOH (National Laboratory of Health and Food, Maribor), following the prescribed instructions outlined below. Water samples for $\delta^{18}O$ and $\delta^{2}H$ analysis were gathered in 60 mL HDPE bottles, which were prewashed twice with the sample and had no headspace. Samples for $\delta^{13}C_{DIC}$ and total alkalinity (TA) analysis were filtered through a 0.45 µm membrane filter and transferred into two glass ampoules, each with a volume of 12 ml and no headspace, using gas-tight syringes. For ^{3}H analysis, 1 L of unfiltered water was collected in an HDPE container. Prior to stable isotope analysis, the samples were stored in the refrigerator at temperatures ranging from 4 to 6 °C, while samples for ^{3}H analysis were stored at room temperature. Sampling was conducted at a total of 13 locations (Table 1). Groundwater was collected from 12 wells in the Gajke and Brstje landfill areas and leachate was collected from a channel from the Gajke landfill (Fig. 3, Table 1). Sampling of groundwater from seven wells was performed by the NLZOH concurrently with the regular operational monitoring of groundwater conditions in accordance with SIST ISO 5667-11:2010 (referred to as “monitoring” in Table 1). Five other wells and leachate were sampled by the Javne službe Ptuj d.o.o. only for TA and isotope analysis (referred to as “other” in Table 1) and in situ measurements were not conducted.

Table 1. Locations of sampling points and time and type of sampling.

Sampling point	Date and time of sampling		Location*	N (D96)	E (D96)	Z_{ground} (m)	Z_{well} (m)	Type of sampling
G-1a	26.10.2020	08:00	upstream	142665	569926	224.70	224.79	monitoring
G-2	26.10.2020	08:35	upstream	142842	569978	224.28	224.38	other
G-3	26.10.2020	09:00	upstream	142944	570102	224.38	224.23	other
G-3a	26.10.2020	10:30	downstream	142556	570352	224.39	224.58	monitoring
G-4	26.10.2020	10:00	downstream	142724	570403	223.80	223.97	other
G-4b/12	26.10.2020	11:05	downstream	142622	570160	222.48	222.70	monitoring
G-5	26.10.2020	09:25	downstream	142388	570332	223.58	223.62	monitoring
GAP-7	26.10.2020	13:15	upstream	142911	569273	225.86	226.01	monitoring
GAP -8/13	26.10.2020	13:45	upstream	143090	569480	225.69	226.14	other
GAP -10/13	26.10.2020	11:45	upstream	142952	569880	224.66	225.19	monitoring
V-3/2	26.10.2020	12:15	upstream	142832	569521	225.44	225.44	monitoring
cemetery	26.10.2020	12:40	upstream	143094	569409	/	226.03	other
leachate	27.10.2020	07:30	laterally	142716	570192	218.30	/	other

* - according to the direction of groundwater flow in the Gajke landfill area

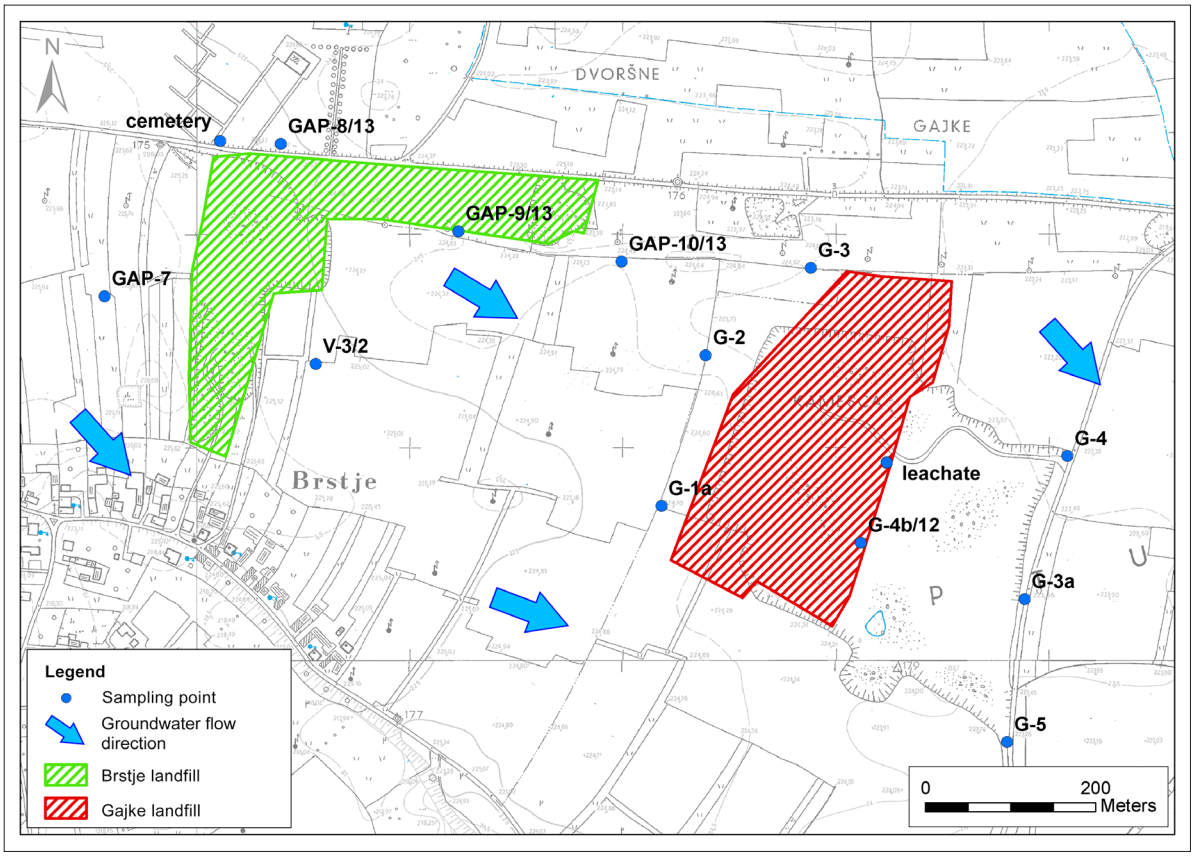

Fig. 3. Sampling points of groundwater and leachate in the Gajke and Brstje landfill area.

Analysis

All water samples received were analysed for isotope analysis at the Jožef Stefan Institute laboratories using the procedures described below. Since leachate analysis is not routinely performed, we anticipated problems with the analysis of this water. Ultimately, the only difficulties encountered were in determining the δ^2H, which could not be eliminated despite repeated analyses, so the result is not reported for this parameter.

TA was measured using Gran titration (Gieskes, 1974) with a precision of ±1 % within 24 hours of sample collection. Approximately 8–10 g of the sample was weighted in a plastic HDPE bottle with a magnetic stirrer. The pH electrode of the Mettler toledo Seven compact pH meter S220 was

calibrated using certificate buffers with values of 7.00 and 4.00 ±0.02. With this method we determined the change in pH depending on the volume of added acid with a known concentration, which is added to a solution of unknown concentration (Vreča et al., 2020).

$\delta^{13}C_{DIC}$ was determined using the Europa-Scientific 20-20 with TG preparation module. Approximately 200 µL of phosphoric acid (Sigma-Aldrich p.a., ≥85 %) was added to a 12 mL vial and purged with helium (He). Subsequently, the water sample (0.5 –5 mL, depending on total alkalinity) was injected into the ampoule, and CO_2 was measured from headspace. For one point normalization of samples, a Carlo Erba solution (8 mg/12mL) with a known value of –10.8 ±0.2 was used to calibrate $\delta^{13}C_{DIC}$ measurements (Spötl, 2005; Vreča et al., 2020).

$\delta^{2}H$ and $\delta^{18}O$ were determined using the H_2-H_2O (Coplen et al., 1991) and CO_2-H_2O (Epstein & Mayeda, 1953; Avak & Brand, 1995) equilibration technique. Measurements were performed on a dual inlet isotope ratio mass spectrometer (DI IRMS, Finnigan MAT DELTA plus, Finnigan MAT GmbH, Bremen, Germany) with an automated H_2-H_2O and CO_2-H_2O HDOeq 48 Equilibration Unit (custom built by M. Jaklitsch). All measurements were performed together with laboratory reference materials (LRM) calibrated periodically against primary IAEA calibration standards to VSMOW/SLAP scale. Samples were measured as independent duplicates and results were normalized to the VSMOW/SLAP scale using the Laboratory Information Management System for Light Stable Isotopes (LIMS) programme (https://water.usgs.gov/water-resources/software/RSIL-LIMS/). For independent quality control, we used internal LRM and USGS commercial reference materials. The overall measurement uncertainties are estimated to be less than 1 ‰ and 0.05 ‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively (Vreča et al., 2020).

The results for $\delta^{13}C_{DIC}$, $\delta^{2}H$ and $\delta^{18}O$ are expressed in a standard δ notation in per mil (‰) relative to international standards (Coplen et al., 1991; Coplen, 1994; IAEA, 2018).

For ^{3}H analysis, the samples were distilled prior to tritium enrichment in order to remove dissolved solids and other possible interferences. The ^{3}H was enriched using electrolysis. After electrolysis, the sample was transferred to stainless steel distillation flasks for a second distillation. Then 10 g of sample solution was mixed with 12 mL of Ultima Gold LLT scintillation cocktail and measured in Quantulus 1220 (Perkin Elmer) liquid scintillation counter for 5 h, together with a tritium-free water sample (dead water) to correct for detector noise and background and according to standards used to determine ^{3}H detection efficiency. In the STC 131/20 analytical report (Štrok & Svetek, 2020; Appendix 2), results for ^{3}H activity (As) are expressed in $Bqkg^{-1}$. Tritium units (TU = tritium unit) are commonly used in isotope hydrology, where 1 TU represents 1 ^{3}H atom per 10^{18} ^{1}H atoms. Therefore, the results were converted to TU for interpretation of the results, considering 1 TU = 0.118 BqL^{-1} (Ingraham, 1998; Gat et al., 2001) and 1 kg = 1 L.

Spatial analysis

The spatial distribution of individual parameters was carried out using GIS software ESRI® ArcMap™ (v. 10.5.) using the interpolation method of natural neighbours, which uses Thiessen polygons or Voronoi diagrams and weighted averages of neighbouring values to arrive at the most appropriate values. Experientially, this method is most suitable for the given spatial data density.

Results and discussion

The results of the in-situ measurements (temperature (T), pH, electrical conductivity (EC), redox potential (Eh) and dissolved oxygen (DO)) received from the client and performed by NLZOH, of isotope analysis ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, ^{3}H) and TA are presented in Table 2.

To assess the potential impact of the Gajke and Brstje landfills on groundwater quality status, maps illustrating the spatial distribution of $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, TA, and ^{3}H in groundwater were created for the entire study area. To separate the impacts of the two landfills, isotope groundwater data were compared with analytical results from additional sampling of leachate prior to reverse osmosis at the Gajke landfill. Leachate from the Brstje landfill was not analysed due to the unregulated drainage system. These leachates are collected at the bottom of the protected deposit field through pipes to the leachate where no changes have been observed for years, as leachate has not been detected since 2005. Monthly inspections of the leachate shaft and meter inventory are carried out, which is also performed several times a year by a representative of the Javne službe Ptuj d.o.o. Only the older parts of the landfill, where there are poplars and plateau, have no soil protection, although there is upper protection in the form of asphalt and poplars.

Table 2. Results of in-situ measurements (T, pH, EC, Eh, DO), isotope analysis ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, ^{3}H) and TA from 27–28 October, 2020 are summarised from Vreča et al. (2020) and Štrok & Svetek (2020).

Sampling point	T (°C)	pH	EC (µS/cm)	Eh (mV)	DO (mg/L)	DO (%)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{13}C_{DIC}$ (‰)	TA (mM)	^{3}H (TU)
G-1a	13.9	7.1	788	342	6.59	65.9	-9.57	-67.0	-14.9	7.72	5.9
G-2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-9.22	-65.3	-8.2	7.12	18.8
G-3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-9.30	-65.1	-10.6	7.70	11.8
G-3a	16.3	7.1	778	309	0.12	1.3	-8.87	-62.1	-14.3	7.85	5.9
G-4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-9.60	-67.5	-13.4	7.83	7.3
G-4b/12	19	7.0	790	335	5.51	61.3	-9.69	-68.6	-14.4	7.74	4.6
G-5	13.6	7.1	752	343	7.16	71.1	-9.47	-66.5	-13.4	8.11	4.4
GAP-7	14.9	7.1	794	426	7.63	77.8	-9.17	-65.1	-14.7	7.84	5.2
GAP -8/13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-8.81	-61.3	-14.8	5.5	6.0
GAP -10/13	14.4	6.9	977	329	0.06	0.6	-9.24	-65.2	-7.6	9.84	16.2
V- 3/2	14.2	7.1	750	331	1.73	17.4	-9.37	-65.9	-14.6	7.08	6.6
cemetery	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-8.56	-59.3	-14.4	6.07	7.5
leachate CERO Gajke (canal)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-7.64	n.d.	+6.1	73	209.8

n.d. - not determined

Field measurements

Groundwater temperatures at the Brstje landfill are lower compared to the measured groundwater temperatures in the Gajke area. The groundwater temperature in the Brstje landfill area is between 13.9 °C and 14.9 °C, while in the Gajke landfill area it is between 13.6 °C and 19 °C (Table 2). The G-3a (16.3 °C) and G-4b/12 (19 °C), which are located downstream (Fig. 3) of the Gajke landfill, are outstanding. Variable temperatures are result of different thickness and position of wastes which influences the heat-generating (exothermic) reactions.

The pH of the groundwater in the area of the Gajke landfill is constant at all sampling points (between 7.0 and 7.1). In the area of the Brstje landfill, the pH value varies between 6.9 and 7.1, and the pH value of the groundwater is comparable to that of the groundwater in the area of the Gajke landfill.

EC values in the entire study area fall in the interval from 750 to 977 µS/cm, deviating from the sampling point GAP-10/13 (977 µS/cm), which is located on the eastern edge (downstream) of the old deposition field of the Brstje landfill and about 200 m northwest (upstream) of the Gajke landfill (Fig. 3). The reason for the deviating values of the electrical conductivity on GAP-10/13 are the additional pressures on the groundwater caused by the Brstje landfill, which were already identified in the study by Cerar et al. (2019).

According to the measured contents of DO in the groundwater in the area of the Gajke and Brstje landfills, constant suboxic conditions prevail at the G-3a and GAP-10/13 sampling points. The measured DO content at these two sites is below the lower limit of quantification (LOQ = 0.5 mg/L). Somewhat higher values were obtained at V-3/2, where they are 1.73 mg/L. At the other monitoring points, DO values are higher, ranging from 5.51 to 7.63 mg/L (Table 2).

The Eh indicates the prevailing oxidation to transient oxidation-reduction conditions, expressed as values of 309–343 mV, with the upstream monitoring point GAP-7 standing out with a value of 426 mV, indicating higher aeration of the groundwater (7.63 mg/L), which is also confirmed by the highest concentration of DO.

Isotope composition of oxygen and hydrogen

Values for $\delta^{18}O$ in groundwater in the vicinity of the two landfills vary from -9.69 to -8.56 ‰ (Fig. 4). The lowest $\delta^{18}O$ values are observed at locations around the Gajke landfill, while the highest values were detected at locations northwest of Brstje and at G-3a in the south-eastern part of the study area downstream from the Gajke landfill. In leachate, the measured value for $\delta^{18}O$ is -7.64 ‰ and is slightly higher than in groundwater samples, indicating the influence of secondary processes on the $\delta^{18}O$ (Tazioli, 2011), as confirmed by positive $\delta^{13}C_{DIC}$ and higher TA values (Table 2).

The values for δ^2H in groundwater in the two landfills follow the changes in δ^{18}O and vary between -68.6 and -59.3 ‰ (Table 2, Fig. 5). In the leachate, δ^2H was not measured due to technical problems.

All measured δ^{18}O and δ^2H values in groundwater indicate that the main water source consists in direct infiltration of local precipitation and does not indicate the considerable influence of evaporation or other secondary processes. The isotope composition was monitored in the period 2016–2018 at Murska Sobota and Sv. Urban, i.e., locations NE and SW of the investigated area (Vreča et al., 2022). The average δ^{18}O and δ^2H values amounted –9.28 ‰ and –65.8 ‰ for Murska Sobota and –8.53 ‰ and –59.2 ‰ for Sv. Urban.

The δ^{18}O values vary as a function of temperature and are lowest at sites where temperatures are lowest. Unfortunately, water temperature was not measured at all sites where samples were collected. Only G-4b/12 deviates, where water temperature was relatively high (19 °C) and δ^{18}O was lowest (-9.69 ‰). The result indicates different water properties at this site (δ^2H and ^{3}H activity are also the lowest) and is due to the location of G-4b/12, which is at the edge of the storage field and has a higher temperature compared to the other points.

Values for δ^{18}O and δ^2H in groundwater indicate that the main source of water is direct infiltration of precipitation, with no significant isotopic fractionation, and that the isotope composition depends on water temperature, which was determined at only 7 sampling points. It is estimated that the δ^{18}O and δ^2H values in groundwater downstream of the Brstje landfill decrease, while they increase again slightly at the G-3a. This indicates that the impact of the Gajke landfill cannot be completely excluded.

Total alkalinity

The TA values in groundwater around the two landfills range from 5.45 to 8.11 mM, deviating GAP-10/13 with slightly higher values of 9.84 mM (Fig. 6). In the leachate the measured value is 73 mM. The spatial distribution shows that the highest values (9.84 mM) appear at the downstream sampling point of GAP-10/13 and then decrease at sampling points: G-1a and G-4b/12 (around 7.7 mM) downstream of the Gajke landfill. The lowest values (5.45 mM) are located upstream (GAP-8/13) from the Brstje landfill.

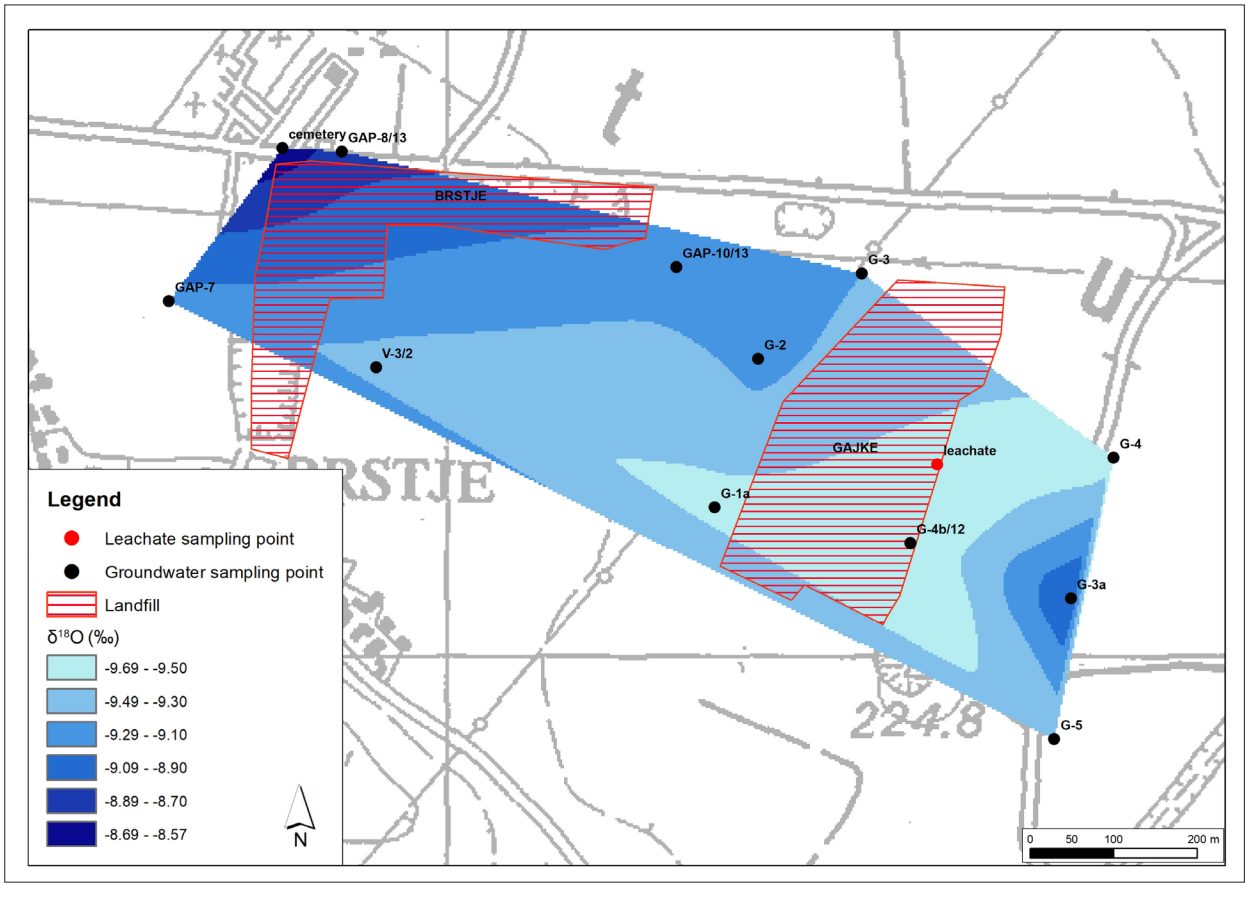

Fig. 4. Spatial distribution of δ^{18}O (‰) in groundwater in the Gajke and Brstje landfill area.

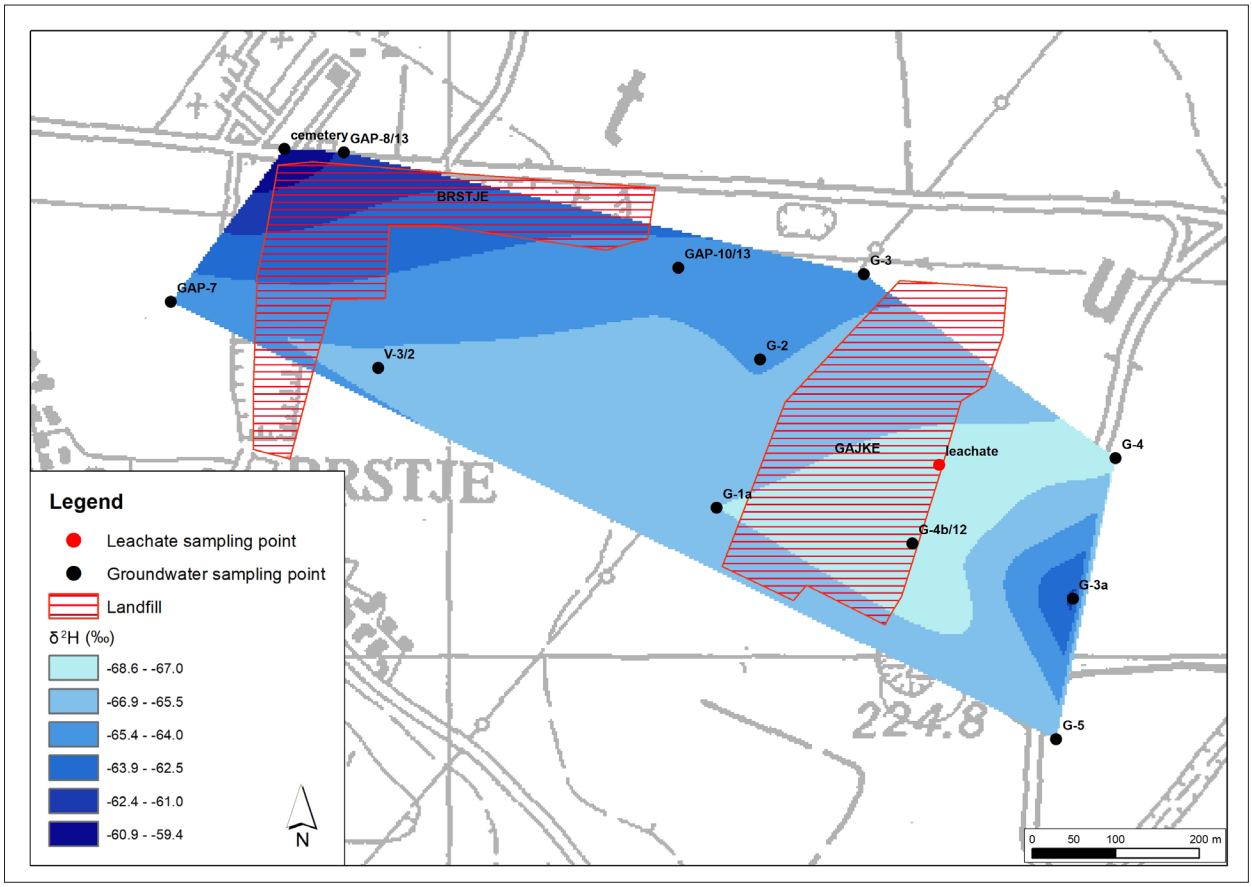

Fig. 5. Spatial distribution of δ^2H (‰) in groundwater in the Gajke and Brstje landfill area.

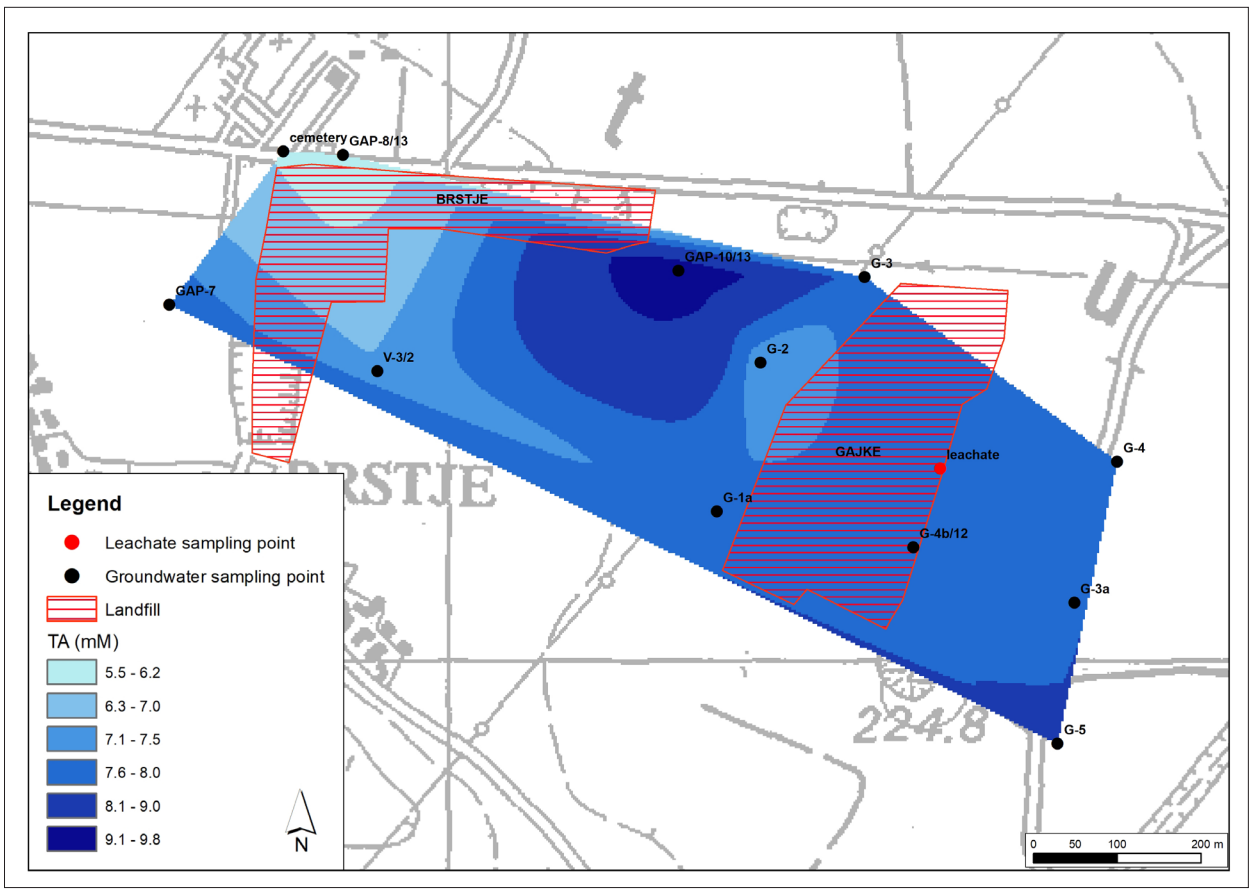

Fig. 6. Spatial distribution of TA (mM) in groundwater in the area of the Gajke and Brstje landfill area.

Isotope composition of carbon from dissolved inorganic carbon

The $\delta^{13}C_{DIC}$ values in groundwater in the two landfills vary from -14.9 to -8.2 ‰ (Table 2, Figs. 7 and 8). The spatial distribution of $\delta^{13}C_{DIC}$ shows that the lowest values were measured upstream of the Brstje landfill at GAP-8/13 (-14.8 ‰), where the impact of the landfill leachate is not expected. Slightly higher $\delta^{13}C_{DIC}$ values are observed at downstream monitoring point G-4 (-13.4 ‰) and G-5 (-13.4 ‰) from Gajke landfill compared to G-4b/12 with $\delta^{13}C_{DIC}$ of –14.4 ‰. To confirm the influence of leachate, measurements should be repeated several times during the hydrological year.

The measured $\delta^{13}C_{DIC}$ value in the leachate from the Gajke landfill is +6.1 ‰ (Table 2, Figs. 7 and 8). This value characterizes degradation of organic matter, including methanogenesis under anoxic conditions in landfills. Leachate becomes enriched with a heavier carbon isotope (^{13}C) during this process (Fig. 8).

The highest positive $\delta^{13}C_{DIC}$ values in groundwater at locations GAP-10/13 (-7.6 ‰) and G-2 (-8.2 ‰) indicate a significant impact on the carbon cycle in groundwater (see Table 2, Figs. 7 and 8). Furthermore, at GAP-10/13, recorded dissolved oxygen concentrations around 0 % (Table 2) could suggest the presence of methanogenesis in groundwater (North et al., 2006). However, this presence isn't as pronounced as in the leachate. North et al. in 2006 found $\delta^{13}C_{DIC}$ ranged from +2.8 to +15.8 ‰ in all analysed leachate samples, indicating the presence of methanogenesis.

The maximum values of $\delta^{13}C_{DIC}$, TA, and ^{3}H were detected at monitoring points GAP-10/13 (-7.6 ‰, 9.84 mM, 16.2 TU) and G-2 (-8.2 ‰, 7.12 mM, 18.8 TU) and gradually decreased toward monitoring points G-4b/12 and G-4 downstream of the Gajke landfill. This indicates that no significant impact is expected downstream of the Gajke landfill but occurs in the north-central part of the Gajke landfill. Similar results have already been observed during "benchmarking".

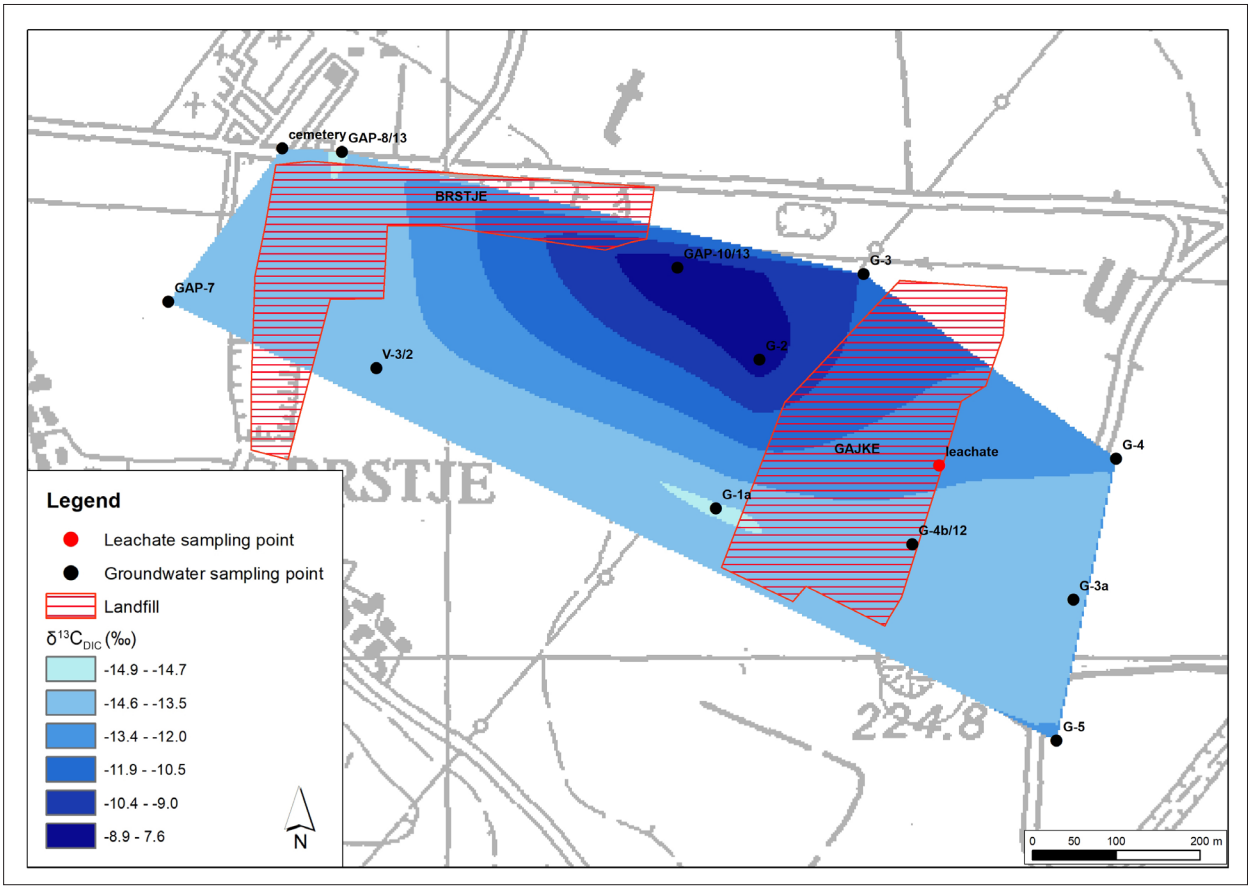

Fig. 7. Spatial distribution of $\delta^{13}C_{DIC}$ (‰) in groundwater in the Gajke and Brstje landfill area.

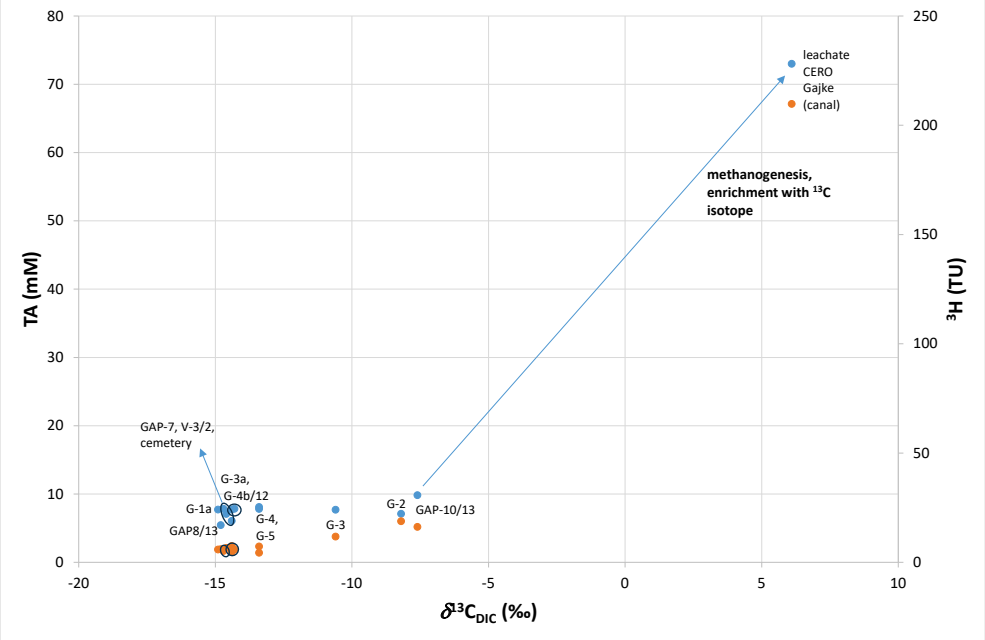

Fig. 8. TA and ^{3}H versus $\delta^{13}C_{DIC}$ with associated locations.

Tritium

Groundwater ^{3}H activities in the surrounding area of two landfills range from 4.4 to 18.7 TU (Figs. 8 and 9). The highest activities of ^{3}H occur in wells GAP-10/13 (16.2 TU), G-2 (18.8 TU), and G-3 (11.8 TU), all of which are upstream of the Gajke landfill and may be attributed to the influence of the Brstje landfill, whose leachate was not sampled. The lowest activities were found upstream of the Brstje landfill and downstream of the Gajke landfill. Downstream of Gajke, ^{3}H deviates at G-4 (7.3 TU), and the southward changes show the same trend as the change in boron concentration (Cerar et al., 2019). The spatial distribution of ^{3}H in groundwater shows similar characteristics to TA and $\delta^{13}C_{DIC}$ (Figs. 6, 7 and 8).

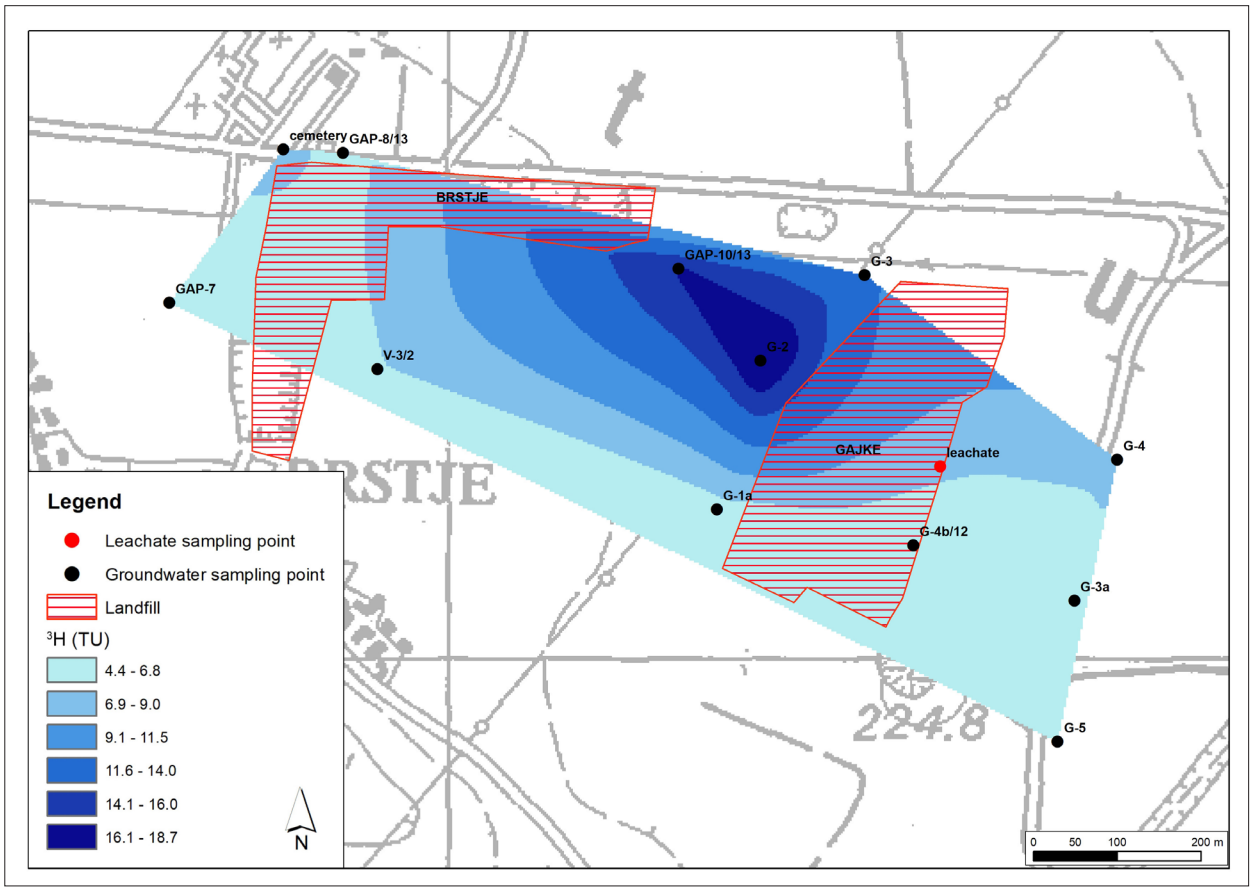

Fig. 9. Spatial distribution of ^{3}H (TU) in groundwater in the Gajke and Brstje landfill area.

In the leachate of the Gajke landfill, the measured activity is significantly higher than in the groundwater and is 209.8 TU (Fig. 8). High ^{3}H activities are characteristic of leachate and can be as high as 1,000 TU (Tazioli, 2011). In monthly precipitation over Slovenia, ^{3}H activity rarely exceeds 20 TU (Internet 1) and amounts to an annual average of less than 10 TU over the past decade (Kern et al., 2020; Vreča et al., 2022), making the ^{3}H parameter a very good indicator of pollution from landfills. Raco and Battaglini (2022) found ^{3}H values in leachate ranging from 55 to 923 TU, while Gupta and Raju (2023) found in their study of landfill leachate and groundwater sample ^{3}H value from 8.11 TU and 3.03 TU, respectively. We could conclude that higher measured activity in GAP-10/13 is the result of pollution from the Brstje landfill.

Conclusions

The results of the present study show that isotope analysis is a valuable tool for monitoring landfills, revealing shifts in biogeochemical processes within groundwater and allowing prediction of contamination plumes in the potential impact area. The results will further improve the picture of the spatial distribution of conservative contaminants, while also identifying possible scenarios for the input of leachate from the Gajke Landfill into the aquifer. Tritium, which demonstrates high activity in leachate, proved to be the most reliable parameter for such a prediction. The analyses performed proved to be an effective method to determine the dispersion of loads from landfills, especially in terms of predicting the spatial distribution of the loads and possible scenarios of the load of the aquifer by leachate.

However, it should be noted that this paper summarises the results of a single sampling. For a more reliable assessment, we suggest repeating the same analyses in different water conditions (low, medium, high) or establishing monthly monitoring of $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, and ^{3}H in the groundwater at all 12 sampling points in order to allow for adequate isotopic characterization of the water. In addition, we propose including sampling of the Rogoznica stream upstream and downstream of the Brstje landfill in the monitoring, as knowledge of surface water infiltration and surface/groundwater interactions are also important in any evaluation of the results. Further, systematic research is necessary due to climate extremes that can significantly impact the flow of groundwater, thus affecting the spread of pollution clouds.

Acknowledgments

This research was funded by Javne službe Ptuj d.o.o., the Slovenian Research Agency, and Innovation (ARIS), under the Research Programmes Groundwater and Geochemistry (No. P1-0020) and Cycling of Substances in the Environment, Mass Balances, Modelling of Environmental Processes, and Risk Assessment (No. P1-0143). The authors would also like to express gratitude to Barbara Svetek, Klara Žagar, and Stojan Žigon for their valuable help with isotope analysis.

References

Abiriga, D., Vestgarden, L.S. & Klempe, H. 2020: Groundwater contamination from a municipal landfill: Effect of age, landfill closure, and season on groundwater chemistry. Science of The Total Environment, 737: 140307. https://doi.org/10.1016/j.scitotenv.2020.140307

Abiriga, D., Vestgarden, L.S. & Klempe, H. 2021: Long-term redox conditions in a landfill-leachate-contaminated groundwater. Science of The Total Environment, 755: 143725. https://doi.org/10.1016/j.scitotenv.2020.143725

Adeolu, A.O., Ada, O.V., Gbenga, A.A. & Adebayo, O.A. 2011: Assessment of groundwater contamination by leachate near a municipal solid waste landfill. African Journal of Environmental Science and Technology, 5/11: 933-940.

Andrei, F., Barbieri, M. & Sappa, G. 2021: Application of ^{2}H and ^{18}O isotopes for tracing municipal solid waste landfill contamination of groundwater: Two Italian case histories. Water, 13/8: 1065. https://doi.org/10.3390/w13081065

Ančić, M., Huđek, A., Rihtarić, I., Cazar, M., Bačun-Družina, V., Kopjar, N. & Durgo, K. 2020: PHYSICO chemical properties and toxicological effect of landfill groundwaters and leachates. Chemosphere, 238: 124574. https://doi.org/10.1016/j.chemosphere.2019.124574

Avak, H. & Brand, W.A. 1995: The Finning MAT HDO-Equilibration—A fully automated HO/gas phase equilibration system for hydrogen and oxygen isotope analyses. Thermo Electron. Corp. Appl. News, 11: 1–13.

Bakkaloglu S., Lowry D., Fisher R.E., France J.L. & Nisbet E.G. 2021: Carbon isotopic characterization and oxidation of UK landfill methane emissions by atmospheric measurements. Waste management, 132: 162–175. https://doi.org/10.1016/j.wasman.2021.07.012

Baettker, E.C., Kozak, C., Knapik, H.G. & Aisse, M.M. 2020: Applicability of conventional and non-conventional parameters for municipal landfill leachate characterization.

Chemosphere, 251: 126414. https://doi.org/10.1016/j.chemosphere.2020.126414

Bhalla, B., Saini, M.S. & Jha, M.K. 2013: Effect of age and seasonal variations on leachate characteristics of municipal solid waste landfill. International Journal of Research in Engineering and Technology, 2/8: 223–232. http://www.ijret.org

Brenčič, M., Ivanuša-Šket, H., Torkar, A. & Vreča, P. 2013: Influences of sanitary landfill on groundwater under the complex hydrogeological conditions. In: Cossu, R. (ed.): 14th International waste management and landfill symposium, 30 September - 4 October 2013, Forte Village, S. Margherita di Pula, Cagliari, Sardinia, Italy. Cagliari: CISA, cop. 2013. 10 p.

Castañeda, S.S., Sucgang, R.J., Almoneda, R.V., Mendoza, N.D. S. & David, C.P.C. 2012: Environmental isotopes and major ions for tracing leachate contamination from a municipal landfill in Metro Manila, Philippines. Journal of environmental radioactivity, 110, 30-37. https://doi.org/10.1016/j.jenvrad.2012.01.022

Cerar, S., Serianz, L., Koren, K. & Lapajne, S. 2019: Carrying out a comparative analysis of basic and indicative parameters in groundwater and water balance in the Gajke landfill area. Ljubljana: Geological Survey of Slovenia.

Cerar, S., Serianz, L., Koren, K., Prestor, J. & Mali, N. 2022: Synoptic Risk Assessment of Groundwater Contamination from Landfills. Energies, 15/14: 5150. https://doi.org/10.3390/en15145150

Chidichimo, F., De Biase, M. & Straface, S. 2020: Groundwater pollution assessment in landfill areas: Is it only about the leachate? Waste Management, 102: 655–666. https://doi.org/10.1016/j.wasman.2019.11.038

Coplen, T.B., Wildman, J.D. & Chen, J. 1991: Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope-ratio analysis. Analytical Chemistry, 63/9: 910–912. https://doi.org/10.1021/ac00009a014

Coplen, T.B. 1994: Reporting of stable hydrogen, carbon, and oxygen isotopic abundances (technical report). Pure and applied chemistry, 66/2: 273–276. https://doi.org/10.1351/pac199466020273

de Medeiros Engelmann, P., Dos Santos, V.H.J.M., Barbieri, C.B., Augustin, A.H., Ketzer, J.M.M. & Rodrigues, L.F. 2018: Environmental monitoring of a landfill area through the application of carbon stable isotopes, chemical parameters and multivariate analysis. Waste Management, 76/591–605. https://doi.org/10.1016/j.wasman.2018.02.027

Epstein, S. & Mayeda, T. 1953: Variation of ^{18}O content of waters from natural sources. Geochimica et cosmochimica acta, 4/5: 213–224. https://doi.org/10.1016/0016-7037(53)90051-9

Gat, J.R., Mook, W.G. & Meijer, H.A. 2001: Atmospheric water. In: Environmental Isotopes in the Hydrological cycle. Edited by W.G. Mook, IAEA and UNESCO, Technical documents in Hydrology, 39/II, UNESCO Paris: 63–74.

Gieskes, J.M. 1974: The alkalinity – tool carbon dioxide system in seawater. Marine chemistry, 5 (The Sea). Edited by Goldberg E.D. New York: John Wiley and Sons: 123–151.

Gupta, S. & Raju, N.J. 2023: Potential environmental pollution study by leachate generation and health risk assessment in the vicinity of bandhwari landfill disposal site, National Capital Region, India. Groundwater for sustainable development 23: 101032. https://doi.org/10.1016/j.gsd.2023.101032

Hackley, K.C., Liu, C.L. & Coleman, D.D. 1996: Environmental isotope characteristics of landfill leachates and gases. Groundwater, 34/5: 827-836. https://doi.org/10.1111/j.1745-6584.1996.tb02077.x

Hussein, M., Yoneda, K., Zaki, Z.M. & Amir, A. 2019: Leachate characterizations and pollution indices of active and closed unlined landfills in Malaysia. Environmental Nanotechnology, Monitoring & Management, 12: 100232. https://doi.org/10.1016/j.enmm.2019.100232

Ingraham, N.L. 1998: Isotopic variations in precipitation. In: Kendall C. & McDonnell, J.J. (eds.): Isotope tracers in catchment hydrology. Elsevier, 87–118.

IAEA - International Atomic Energy Agency 2018: Reference Sheet for VSMOW2 and SLAP2 International Measurement Standards. IAEA, Vienna, Austria: 8 p.

Lee, K.S., Ko, K.S. & Kim, E.Y. 2020: Application of stable isotopes and dissolved ions for monitoring landfill leachate contamination. Environmental geochemistry and health, 42: 1387–1399. https://doi.org/10.1007/s10653-019-00427-y

Kerfoot, H.B., Baker, J.A. & Burt, D.M. 2003: The use of isotopes to identify landfill gas effects on groundwater. Journal of Environmental Monitoring, 5/6: 896–901. https://doi.org/10.1039/B310351J

Kapelewska, J., Kotowska, U., Karpińska, J., Astel, A., Zieliński, P., Suchta, J. & Algrzym, K. 2019: Water pollution indicators and chemom-

etric expertise for the assessment of the impact of municipal solid waste landfills on groundwater located in their area. Chemical Engineering Journal, 359: 790–800. https://doi.org/10.1016/j.cej.2018.11.137

Kern, Z., Erdélyi, D., Vreča, P., Krajcar Bronić, I., Fórizs, I., Kanduč, T., Štrok, M., Palcsu, L., Süveges, M., Czuppon, G., Kohán, B. & Gábor Hatvani, I. 2020: Isoscape of amount-weighted annual mean precipitation tritium (^{3}H) activity from 1976 to 2017 for the Adriatic–Pannonian region – AP^{3}H_v1 database, Earth Syst. Sci. Data, 12, 2061–2073. https://doi.org/10.5194/essd-12-2061-2020

Negrel, P., Ollivier, P., Flehoc, C. & Hube, D. 2017: An innovative application of stable isotopes (δ^2H and δ^{18}O) for tracing pollutant plumes in groundwater. Science of the Total Environment, 578: 495–501. https://doi.org/10.1016/j.scitotenv.2016.10.214

Nigro, A., Sappa, G. & Barbieri, M. 2017: Application of boron and tritium isotopes for tracing landfill contamination in groundwater. Journal of geochemical exploration, 172: 101–108. https://doi.org/10.1016/j.gexplo.2016.10.011

North, J.C., Russel, D.F. & Van Hale, R. 2006: Can stable isotopes be used to monitor landfill leachate impact on surface waters? Journal of geochemical exploration, 88: 49–53. https://doi.org/10.1016/j.gexplo.2005.08.003

Porowska, D. 2015: Determination of the origin of dissolved inorganic carbon in groundwater around a reclaimed landfill in Otwock using stable carbon isotopes. Waste Management, 39: 216–225. https://doi.org/10.1016/j.wasman.2015.01.044

Raco, B. & Battaglini, R. 2022: Tritium as a tool to assess leachate contamination: An example from Conversano landfill (Southern Italy), Journal of geochemical exploration, 235: 106939. https://doi.org/10.1016/j.gexplo.2021.106939

Serianz, L., Cerar, S., Koren, K., Prestor, J., Mali, N. & Mladenović, B. 2017: Evaluation of the impact of landfills on groundwater status, Water Congress, Podčetrtek 19.–20. 4. 2017.

Spötl, C. 2005: A robust and fast method of sampling and analysis of δ^{13}C of dissolved inorganic carbon in ground waters. Isotopes in Environmental and Health Studies, 41/3: 217–221. https://doi.org/10.1080/10256010500230023

Štrok, M. & Svetek, B. 2020: Determination of tritium. AP STC 131/20: Client of Public Service Ptuj d.o.o. Ljubljana: Jožef Stefan Institute, Department of Environmental Sciences, 3 p.

Tazioli, A. 2011: Landfill investigation using tritium and isotopes as pollution tracers. Acquae Mundi, 18: 83–92.

Vavilin, V.A. & Lokshina, L.Y. 2023: Carbon and hydrogen dynamic isotope equations are used to describe the dominant processes of waste biodegradation: effect of aeration in methanogenic phase of landfill. Waste management, 166: 280–293. https://doi.org/10.1016/j.wasman.2023.04.027

Vreča, P., Kanduč, T., Žigon, S. & Nagode, K. 2020: Determination of the isotope composition of oxygen and hydrogen, carbon from dissolved inorganic carbon and total alkalinity according to Gran in water. AP GEO 25/2020: Client of Public Service Ptuj d.o.o. Ljubljana: Jožef Stefan Institute, Department of Environmental Sciences, 5 p.

Vreča, P., Pavšek, A. & Kocman, D. 2022: SLONIP–A Slovenian Web-Based Interactive Research Platform on Water Isotopes in Precipitation. Water, 14/13: 2127. https://doi.org/10.3390/w14132127

Wimmer, B., Hrad, M., Huber-Humer, M., Watzinger, A., Wyhlidal, S. & Reichenauer, T.G. 2013: Stable isotope signatures for characterising the biological stability of landfilled municipal solid waste. Waste Management, 33/10: 2083-2090. https://doi.org/10.1016/j.wasman.2013.02.017

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Internet 1. SLONIP: Slovenian Network of Isotopes in Precipitation. Jožef Stefan Institute. Available online: https://slonip.ijs.si/ (accessed on 13 November 2023).