

Identification of groundwater contamination zone around a reclaimed landfill using carbon isotopes

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ABSTRACT

Chemical and isotopic analyses of groundwater from piezometers localized around a reclaimed landfill were performed in order to identify the boundaries of groundwater contamination zone. Spatial distribution of dissolved inorganic carbon (DIC) concentration and stable carbon isotopes in the groundwater was used to distinguish the piezometers localized within the contaminated aquifer. Background groundwater was characterized by low DIC concentration (from 1.8 to 5.0 mmol/L) and negative values of $\delta^{13}\text{C}_{\text{DIC}}$ (from -20.6‰ to -12.4‰). Higher DIC concentrations (from 6.0 to 12.5 mmol/L) and higher values of $\delta^{13}\text{C}_{\text{DIC}}$ (from -10.9 to $+3.6\text{‰}$) were determined in groundwater contaminated by landfill leachate. The study confirmed that $\delta^{13}\text{C}_{\text{DIC}}$ value in the groundwater was a useful tracer in determining the extent of the contamination zone around the landfill. In general, upgradient from the landfill, carbon isotopic composition of groundwater depended on natural sources of carbon and $\delta^{13}\text{C}_{\text{DIC}}$ values were negative. Downgradient from the landfill, where groundwater was contaminated by the landfill leachate, $\delta^{13}\text{C}_{\text{DIC}}$ values were higher, sometimes even positive.

Key words | carbon isotopic composition, dissolved inorganic carbon, landfill site, leachate

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INTRODUCTION

Numerous papers have investigated surface water and groundwater contaminated by landfill leachates. Interactions between landfills and groundwater in the aspect of the biogeochemical processes, evolution of the landfill leachate plume and attenuation of the contaminants have been widely documented by many researchers (Christensen & Kjeldsen 1989; Christensen *et al.* 1994, 2000a, 2000b, 2001; Fatta *et al.* 1999; van Breukelen *et al.* 2003; Mor *et al.* 2006; Oman & Junestedt 2008; Aelion *et al.* 2009; Kale *et al.* 2010; Cozzarelli *et al.* 2011; Iqbal *et al.* 2015). Isotopic aspects of carbon cycling have been studied in several landfills, indicating the impact of landfill carbon in groundwater from these sites (Walsh *et al.* 1993; Hackley *et al.* 1996; Kjeldsen & Christophersen 2001; Kerfoot *et al.* 2003; van Breukelen *et al.* 2003; Atekwana & Krishnamurthy 2004; North *et al.* 2004; Mohammadzadeh *et al.* 2005; North & Frew 2008; Cozzarelli *et al.* 2011; Mohammadzadeh & Clark 2011; Andrews *et al.* 2012; Haarstad & Mæhlum 2013; Wimmer *et al.* 2013). The usefulness of carbon isotope determination on demonstration of the landfill impact on environment was reported by North *et al.* (2006). The stable carbon

isotopes of groundwater provides a valuable insight into the carbon genesis in the natural and leachate impacted environments (Hatzinger *et al.* 2013), because $\delta^{13}\text{C}_{\text{DIC}}$ reflects the contributions of dissolved inorganic carbon (DIC) from different sources with distinct isotopic compositions. In a natural environment, the range of $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater is very wide, from approximately -30 to 0‰ , but usually the values range from -25 to -10‰ (Button 1991; Clark & Fritz 1997). The carbon isotopes composition reaches significantly higher value in leachate compared to most other environment. Due to enrichment of ^{13}C during the methanogenesis, and due to out-gassing of CO_2 , $\delta^{13}\text{C}_{\text{DIC}}$ of leachates is reported up to $+10\text{‰}$ (Wimmer *et al.* 2013) and even up to $+38\text{‰}$ (Grossman 1997). Heavy carbon isotope ratios ($\delta^{13}\text{C}_{\text{DIC}}$) can be used to diagnose the landfill contamination. The natural intrusion of oxygen starting at the end of the methanogenic phase (old landfills) will shift the isotopic signature to more negatives values.

Hydrogeochemical conditions in the vicinity of the reclaimed landfill in Otwock are complex and the stable carbon isotopes were used to identify the groundwater

contamination zone. Hydrogeological studies showed that despite its small area (approximately 2.8 ha) and performed reclamation, the landfill still exerted a negative impact on the environment. Even though the waste storage was finished in 1991 and the landfill was reclaimed, the groundwater quality was significantly affected by the leachate percolation downgradient from the landfill. The variations in the concentration of reactive and conservative solutes strongly correlated with climatic conditions (precipitation), hydrologic conditions (the water table position of the surface water – the Vistula and the Świder rivers), and hydrogeological conditions (highly permeable aeration zone, shallow groundwater position). These conditions played a key role in the groundwater chemistry in the vicinity of the landfill in Otwock; however, in other landfills, the quality of water may depend on many other parameters than those mentioned in this work. The load of contamination and its concentration in the groundwater differ spatially and temporarily. Identification of the boundaries of groundwater contamination zone based on the chemical analysis alone was difficult, which is why the measurements of carbon isotopic composition were performed. Carbon isotope analysis of groundwater was used to assess the extent of the contamination zone around the landfill site.

The aim of this study was to demonstrate that the method based on determination of carbon isotope composition of groundwater is a useful tool for identification of the contaminated area and for delineating the leachate plume under complex hydrogeochemical conditions, where the conventional methods are insufficient. The data from the Otwock research field were used to verify whether the method can be successfully used in other contaminated areas.

MATERIALS AND METHODS

The study was conducted around the reclaimed municipal landfill, located in the suburbs of Otwock, near Warsaw, Poland (Figure 1). Otwock landfill covers an area of 2.8 ha and was active in the period 1961–1991. It is estimated that it contains about 300,000 m³ of municipal waste (not sorted). The landfill was started as an uncontrolled site, thus the type of waste stored there is not well known. Generally, it received all types of municipal waste from the nearest community of Otwock. After closing, the landfill was covered with a layer of soil, consisting of approximately 30–50 cm of compost and planted with grass. The landfill leachate is formed from the infiltration and passage of

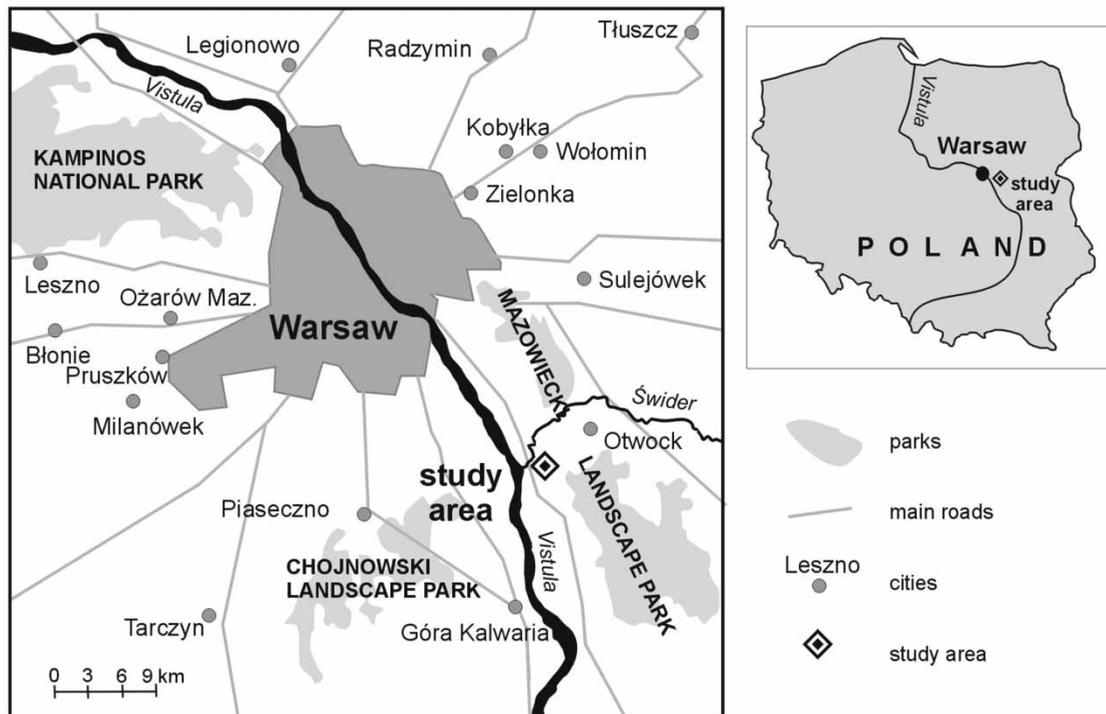


Figure 1 | Location of the study area.

water through solid waste into the aquifer. The landfill has no bottom liner. The site history and landfill gas composition, as well as hydrogeochemical conditions, were investigated in a previous study (Porowska & Gruszczyński 2006, 2013; Porowska 2015). Archival data and field research revealed no other pollution sources within the study area.

The Otwock landfill is located on alluvial deposits of the Vistula river, close to the Świder river. The landfill and the majority of the piezometers are located on the floodplain terrace (Holocene), and just a few piezometers are on the meadow terrace of Praski (Vistula glaciation) (Małecki 2006). Despite the geomorphological differences, granulometric composition is similar for all the piezometers (Figure 2).

The geology of the landfill is represented by highly permeable river deposits composed of gravels and varigrained sands, with spots of organic matter or peat layers distributed within the aquifer. The full extent of the peat deposits is not known, but some of them are in the northern area, where piezometer No. 2 is located. The hydraulic conductivity of the aquifer, is between 6.5×10^{-4} m/s and 1.6×10^{-3} m/s (Małecki 2006). Highly permeable, sandy aquifer provides favorable conditions for the transportation of the contamination.

According to the groundwater table contour shown in Figure 2, the general flow direction is northwest, towards the rivers. The groundwater is drained from the landfill area by the Świder river to the north, and by the Vistula river to the west. Groundwater flow velocity, determined by Małecki (2006) is expected to be about 70 m per year.

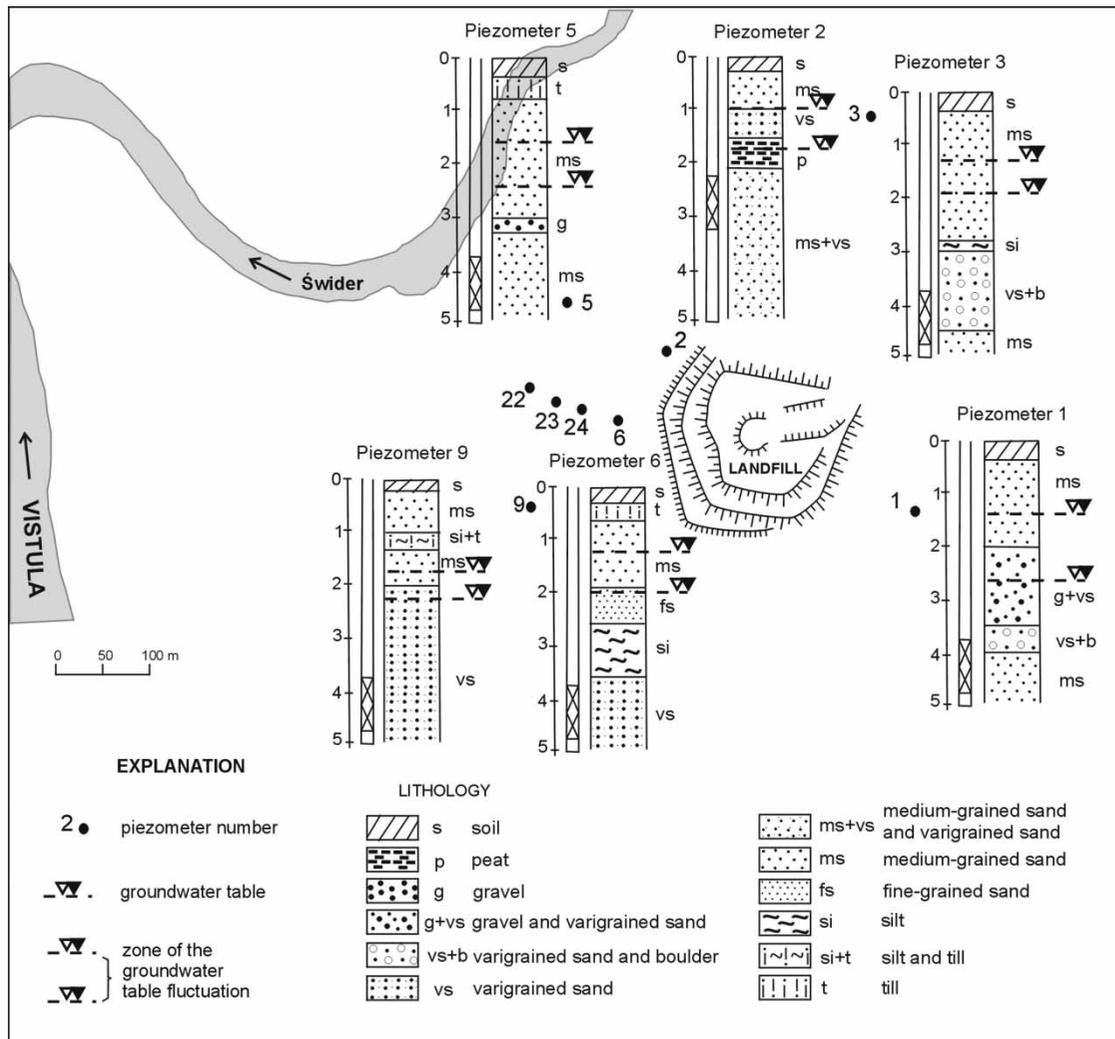


Figure 2 | Selected lithological profiles within the study area.

A similar arrangement of groundwater table contour was found throughout the year, despite the differences in the depths of the water table. In the research period, the groundwater table position depended on the study site and it ranged from ~1.5 m bgl to ~2.7 m bgl (from spring to autumn), and from ~1.0 m bgl to ~1.7 m bgl (in winter) (Figure 1). The annual water table fluctuation was 0.64–0.99 m, but the general groundwater flow direction did not change (Figure 3). The water table position around the landfill correlates with rainfall and river levels (Małecki 2006). During periods of high recharge (after intense rainfall) and high river levels (during flood peaks), the position of the groundwater table increases. During the periods of high groundwater table elevation, large part of the landfill is below the groundwater table, within the aquifer.

This way, the leachate is formed and the load of the contamination is released from the landfill, moved into the aquifer and is further transported according to the groundwater flow direction. These conditions play a key role in the groundwater chemistry in the vicinity of the landfill.

To identify the zone of groundwater contamination within the study area, field and laboratory research were conducted quarterly from May 2006 to March 2007, using the same research equipment and analytical procedures. Water samples for chemical analysis were collected within the same aquifer (from similar depth – 3.8 to 4.8 m bgl) using the PVC

piezometers that were installed in a series along the main groundwater flow direction (seven piezometers) and above the landfill (two piezometers) covering an area of 0.25 km² (Figure 2). Sampling points for carbon isotope analysis were thoroughly selected on the basis of archival data on water chemistry from 20 piezometers located around the landfill. The measurement of carbon isotopes were performed in nine sampling point (four in the area considered as natural and five in leachate-contaminated area). The field studies included also measurements of the water table and water sampling. A flow-through cell (Eijkelkamp Corp.) was used to improve the measurement precision of on-line parameters such as water temperature, oxidation-reduction potential (ORP), content of dissolved oxygen (DO), pH and specific electrical conductivity (SEC) of the water. Water quality characteristics were measured using the following portable instruments for field analysis – water temperature and pH – pH-meter 330i (WTW), ORP – pH-meter 330i (WTW) with redox electrode PolyPlast ORP, SEC – conductivity-meter CC-401 (Elmetron Corp.), DO – oxygen meter of the ProfiLine Oxi 197 (WTW). Field measured ORP was corrected to the standard hydrogen electrode (Weight & Sonderegger 2000). Dissolved carbon dioxide (CO_{2aq}) and bicarbonate (HCO₃⁻) were measured on site by titrating against NaOH and HCl, respectively. Water samples were collected for laboratory tests according to the updated sampling procedures described by Weight &

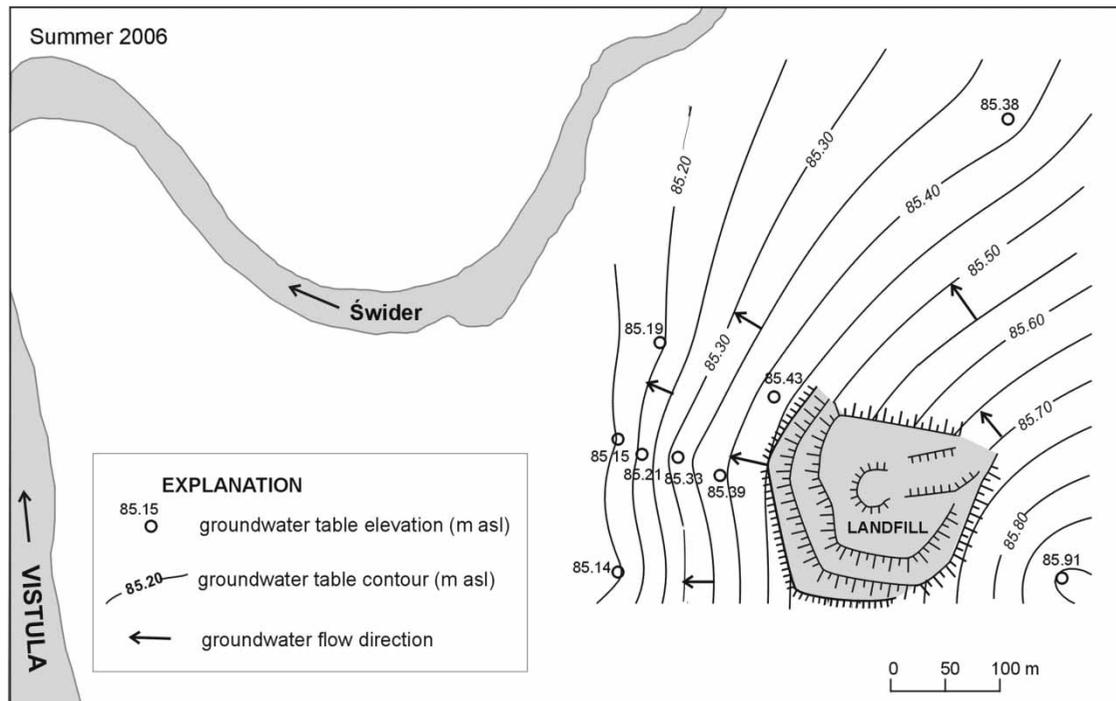


Figure 3 | Groundwater table contour around the Otwock landfill.

Sonderegger (2000), Witczak *et al.* (2013), and Polish Standards. Laboratory tests included determination of the following ions: HCO_3^- , SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ and K^+ . The analyses were performed at the Central Chemical Laboratory of Polish Geological Institute – National Research Institute in Warsaw and at the Laboratory of the Institute of Hydrogeology and Engineering Geology, Faculty of Geology in Warsaw. Only the dissolved carbon dioxide ($\text{CO}_{2\text{aq}}$) and bicarbonate ion (HCO_3^-) data will be discussed in details. DIC was calculated as the sum of HCO_3^- and dissolved carbon dioxide ($\text{CO}_{2\text{aq}}$) determined analytically.

The procedure for sample preparation and measurement of $\delta^{13}\text{C}$ followed the methods described by Gleason *et al.* (1969), Bishop (1990), Kusakabe (2001), and de Groot (2004). A conventional precipitation technique was used to estimate the precipitation of DIC as strontium carbonate SrCO_3 . A step-by-step procedure of sample preparation and performing the analysis is described by Singleton *et al.* (2012).

Unfiltered samples for measuring carbon isotopic composition $\delta^{13}\text{C}_{\text{DIC}}$ were collected in 1,000 mL glass bottles (Simax Corp.) and conserved with 20 mL of $\text{SrCl}_2\text{-NH}_3$ in the field. This amount of reagent was calculated to be sufficient to precipitate the carbonates from the water sample. The precipitate of SrCO_3 was subsequently filtered and dried in the laboratory in CO_2 -free atmosphere. A representative sample of the precipitate was reacted with phosphoric acid under closed system conditions. The evolved carbon dioxide was purified and its isotopic ratio $^{13}\text{C}/^{12}\text{C}$ was measured using a Finnigan MAT Delta+ mass spectrometer in a Dual Inlet system at the Isotope Dating and Environment Research Laboratory of the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. $\delta^{13}\text{C}$ values of the DIC samples were reproducible to $\pm 0.1\text{‰}$. They were expressed with reference to VPDB standard. Overall precision of routine $\delta^{13}\text{C}_{\text{DIC}}$ measurements exceeded 0.1‰. All of the samples are prepared and analyzed in triplicate. Samples of groundwater collected separately into three bottles from the same piezometer but individually prepared using the same methods, i.e. reagent and mass spectrometer.

A computer program Surfer 8.0 was used for the spatial interpretation of the isotopic composition of inorganic carbon in the groundwater around the landfill.

RESULTS AND DISCUSSION

The values of groundwater temperature, pH, SEC, ORP, and concentration of such ions as HCO_3^- , Cl^- ,

SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ and K^+ differed in the groundwater around the landfill site. Groundwater temperature was highest for piezometer No. 6, localized close to the landfill body (Figure 2 and Table 1). The piezometer location relative to the groundwater flow direction was also important. Groundwater temperature was higher close to the landfill and along the groundwater flow direction. This depended not only on high ambient air temperatures in the summer, but much more on the fermentation heat during decomposition of the organic waste (exothermic reactions). In winter, the differences in the groundwater temperatures were the most evident. The minimum temperature of 1.4 °C was observed in the piezometer No. 1, located upgradient from the landfill, while the temperature of the groundwater from the piezometer No. 2, located downgradient from the landfill, reached 6.3 °C.

SEC of groundwater increased from less than 275 $\mu\text{S}/\text{cm}$ in the piezometer No. 3 to over 2,550 $\mu\text{S}/\text{cm}$ in the piezometer No. 6 (Table 1). Regardless of the season, the lowest SEC values occurred in the piezometer No. 3, located upgradient from the landfill, whereas the highest SEC values were measured in the piezometer No. 6, located along the groundwater flow direction, close to the landfill (inside the leachate plume).

Considerable differences were found for the ORP in groundwater (from -33 mV to 288 mV) in Otwock (Table 1). Negative ORP values indicated anaerobic conditions and are characteristic only for the groundwater collected from the piezometers Nos. 22 and 23, located downgradient from the landfill. In the other parts of the aquifer, the minimum ORP values were positive. However, although field measurements of ORP may provide a relative indication of changing redox conditions within a groundwater system, they are not suitable for the determination of the specific redox processes occurring within the system (Baedecker & Cozzarelli 1992). ORP does not correlate well with the concentration of DO, but such a situation is described in the literature (Rose & Long 1988). Redox potentials cannot be used for adequate prediction of DO concentrations, nor can DO concentrations be used to calculate the redox potentials. Regardless of location and season, the concentration of DO was low and did not exceed 0.18 mg/dm^3 in the groundwater in Otwock.

The pH of the groundwater in Otwock varied from 6.36 to 7.88 (Table 1). The highest pH values were found in the groundwater downgradient from the landfill, within the area referred to as contaminated. However, no significant trend signifying pH changes was detected depending on the distance from the landfill.

Table 1 | Concentrations of selected constituents in groundwater around the Otwock landfill

No. piezometer		1	2	3	5	6	9	22	23	24
Temperature of water (°C)	spring	8.8	9.9	8.6	8.4	10.5	8.2	8.5	8.2	9.6
	summer	11.8	13.5	12.5	10.1	11.7	10.2	10.8	nm	10.8
	autumn	10.5	9.3	10.5	10.7	11.3	nm	10.8	nm	10.9
	winter	1.4	6.3	7.2	9.0	10.2	nm	9.6	nm	9.8
SEC (µS/cm)	spring	365	880	334	529	2,216	677	879	2,253	1,288
	summer	401	1,070	306	651	2,437	523	1,163	nm	1,475
	autumn	445	1,136	274	605	2,550	nm	1,795	nm	1,446
	winter	913	1,324	414	414	2,131	nm	2,214	nm	1,536
ORP (mV)	spring	251	205	192	288	29	246	-33	-2	81
	summer	136	170	229	144	68	125	-1	nm	68
	autumn	192	171	245	154	-16	nm	-20	nm	60
	winter	259	123	228	138	6	nm	-12	nm	58
O ₂ (mg/dm ³)	spring	nm	nm	nm	nm	nm	nm	0.11	0.13	nm
	summer	0.05	0.03	0.04	0.02	0.05	nm	0.03	nm	0.04
	autumn	0.16	0.05	0.05	0.05	0.07	nm	0.05	nm	0.07
	winter	0.09	0.09	0.18	0.09	0.11	nm	0.11	nm	0.08
Reaction pH (-)	spring	6.45	6.87	6.36	7.04	7.56	7.30	7.59	7.88	7.47
	summer	6.87	6.98	6.39	7.12	7.32	7.31	7.70	nm	7.31
	autumn	7.02	7.17	6.58	6.92	7.67	nm	7.75	nm	7.57
	winter	7.68	7.31	7.30	7.36	7.73	nm	7.63	nm	7.58
CO _{2aq} (mmol/L)	spring	1.6	1.4	1.4	1.0	1.8	0.7	0.6	0.8	1.1
	summer	1.4	2.0	1.4	1.6	1.8	1.0	0.8	nm	1.4
	autumn	1.6	1.4	0.8	1.2	1.8	nm	1.4	nm	1.4
	winter	1.6	1.4	0.7	0.6	0.8	nm	1.2	nm	0.9
HCO ₃ ⁻ (mmol/L)	spring	1.3	5.4	1.5	2.9	9.5	3.1	5.4	11.1	6.1
	summer	1.3	7.8	1.7	3.0	10.6	4.0	6.2	nm	6.9
	autumn	1.8	8.7	1.0	2.6	10.4	nm	8.5	nm	6.8
	winter	2.9	11.1	1.4	2.8	8.6	nm	10.5	nm	7.2
DIC (mmol/L)	spring	2.9	6.8	2.9	3.9	11.3	3.8	6.0	11.9	7.2
	summer	2.7	9.8	3.1	4.6	12.4	5.0	7.0	nm	8.3
	autumn	3.4	10.1	1.8	3.8	12.2	nm	9.9	nm	8.2
	winter	4.5	12.5	2.1	3.4	9.4	nm	11.7	nm	8.1

nm – not measured.

In the pH of the groundwater in Otwock, the major dissolved species of DIC is HCO₃⁻, whereas CO_{2aq} is a less common species. Dissolved carbon dioxide (CO_{2aq}) ranged from 0.6 to 2.0 mmol/L (Table 1). Neither a spatial nor the seasonal variability of dissolved CO₂ was established. The spatial distribution of HCO₃⁻ showed that the highest values occurred downgradient from the landfill and exceeded 8 mmol/L in the spring and summer, and were up to 10 mmol/L in the autumn and winter (Table 1). Regardless of the season, two peaks of HCO₃⁻ were noticed, indicating a periodical (pulse) release of the load of contamination. HCO₃⁻ concentrations were variable depending on time and place. The load of contamination slowly moved downgradient from the landfill, depending on the climatic and hydrogeological conditions (precipitation, river levels

and groundwater table fluctuations). DIC concentration ranged from 1.8 to 12.5 mmol/L (Table 1) and showed a similar spatial variability as HCO₃⁻.

Chemical composition of groundwater was different within the research area, however, the division into the zone of uncontaminated groundwater and leachate-contaminated water based on the major ions concentration was not clear (Figure 4).

Unequivocal delineation of the contaminated area was difficult due to gradual changes in the chemistry between the adjacent piezometers (e.g. bicarbonates or SEC) or similar values (e.g. sulfates), independent of the sampling site. The piezometers No. 1 and 3 were both localized upgradient of the landfill (Figure 2), so they represented background groundwater (uncontaminated groundwater in natural condition).

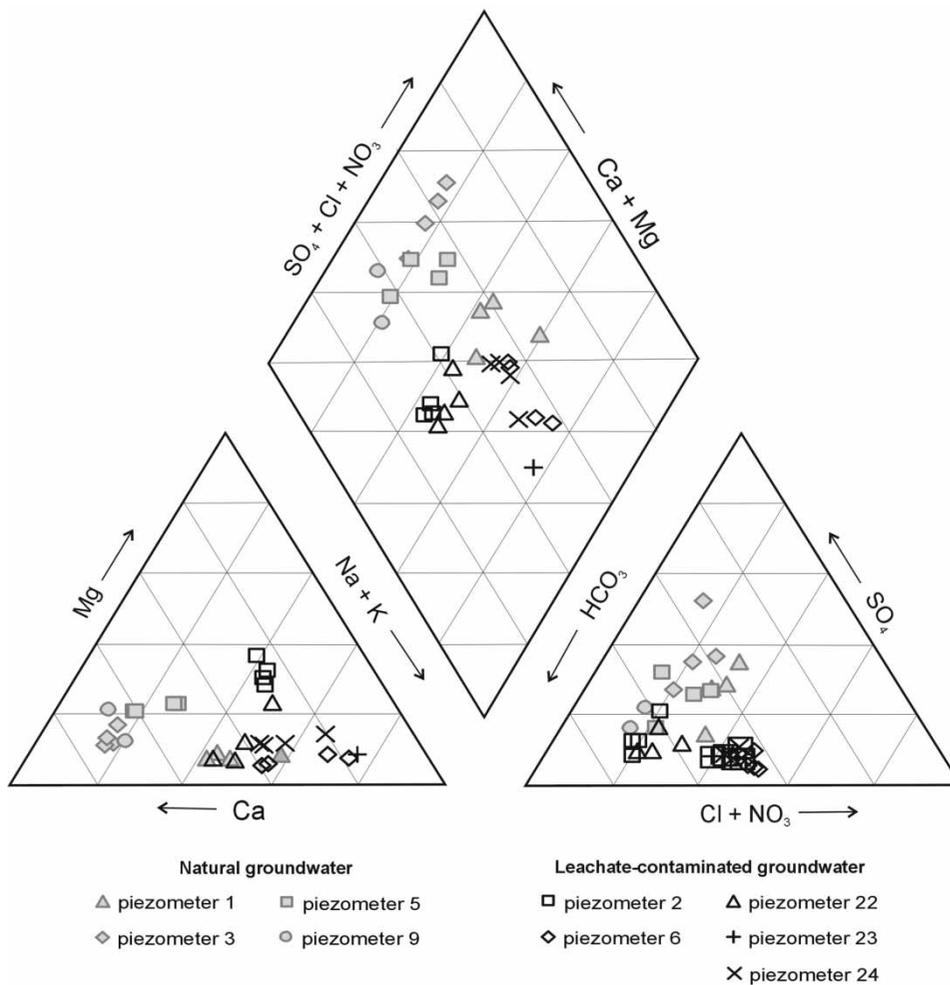


Figure 4 | Chemical composition of groundwater around the Otwock landfill.

Basically, it could be expected that the groundwater downgradient from the landfill was contaminated and the piezometers No. 2, 6, 22, 23, and 24 confirmed this assumption. However, it was not clear whether the piezometers No. 5 and 9 belonged to the area of natural groundwater or already contaminated area. The division into those two zones previously performed on the basis of the relationship between the concentration of bicarbonates and calcium (Porowska 2014) was not so clear. There was the necessity to apply another method, which allowed delineation of a contamination zone around the landfill and demonstrate the impact of the landfill on the groundwater quality. Stable carbon isotopes were used to achieve this aim. It was possible due to the diversity of the carbon isotopic composition in the natural groundwater and leachate-contaminated water. Huge variations in $\delta^{13}\text{C}_{\text{DIC}}$ values in the groundwater around the landfill reflected the contribution of different carbon sources to the DIC pool. $\delta^{13}\text{C}_{\text{DIC}}$ values

varied widely, between -20.6‰ in the piezometer No. 3 and $+3.6\text{‰}$ in the piezometer No. 6 (Figure 5). This diversity resulted from different sources of carbon in DIC pool. Downgradient from the landfill, the groundwater was enriched in ^{13}C , and often $\delta^{13}\text{C}_{\text{DIC}}$ values were positive. The highest value ($+3.6\text{‰}$) was found in the autumn in the piezometer No. 6.

Except in wintertime, the groundwater at this piezometer exhibited positive values of $\delta^{13}\text{C}_{\text{DIC}}$. Outside the leachate plume, $\delta^{13}\text{C}_{\text{DIC}}$ values for the natural groundwater were negative and ranged from -20.6 to -12.4‰ . Carbon isotopic composition of the groundwater downgradient from the landfill affected by leachate contamination was significantly different as compared to uncontaminated groundwater. Therefore, it can be stated that carbon isotope analysis is a useful tool to identify the groundwater contamination zone around the landfill.

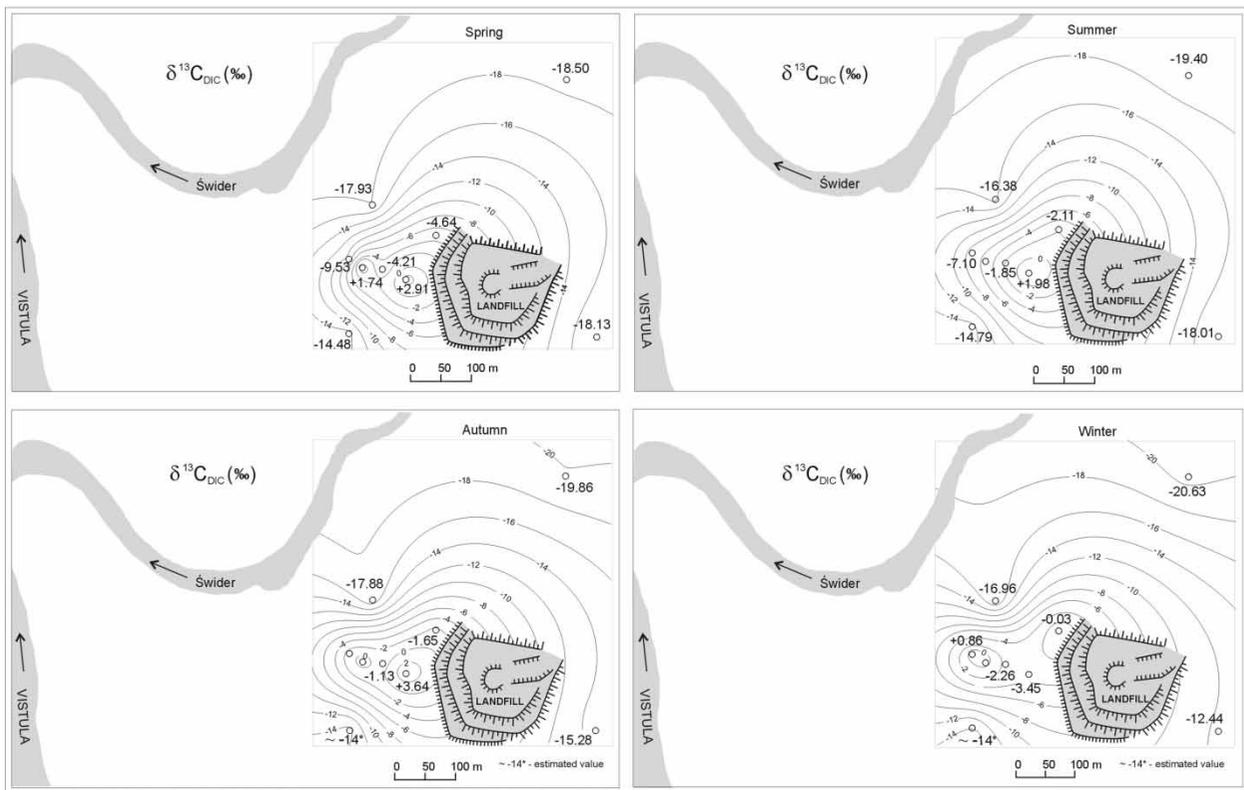


Figure 5 | Distribution of the carbon isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) in groundwater around the Otwock landfill.

The results of the present study showed that both, stable carbon isotopes and concentrations of DIC divided the groundwater samples into two groups (Figure 6). The leachate-contaminated groundwater below the landfill was isotopically distinct from the natural groundwater upgradient from the landfill. In the samples representing natural conditions, $\delta^{13}\text{C}_{\text{DIC}}$ values varied from -20.6‰ to -12.4‰ , and DIC content ranged from 1.8 to 5.0 mmol/L (1/DIC is from 0.20 to 0.56 1/mmol/L). The content of $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater samples collected from the contaminated area ranged between -10.94‰ and $+3.64\text{‰}$ and DIC concentration was between 6.0 and 12.5 mmol/L (1/DIC was from 0.08 to 0.166 1/mmol/L). To assess the mixing of the natural groundwater and the leachate-contaminated groundwater within the aquifer and to identify $\delta^{13}\text{C}_{\text{DIC}}$ of the source carbon, $\delta^{13}\text{C}_{\text{DIC}}$ was plotted against 1/DIC (Figure 6). A regression line through data points that included only uncontaminated water was described by: $\delta^{13}\text{C}_{\text{DIC}} = -17.038(1/\text{DIC}) - 11.852$ (Figure 6). The y intercept of this line gave $\delta^{13}\text{C}_{\text{DIC}}$ value of -11.852‰ for the natural groundwater component. According to this, contour lines of the value -12‰ was treated as a threshold distinguishing the natural groundwater and the groundwater

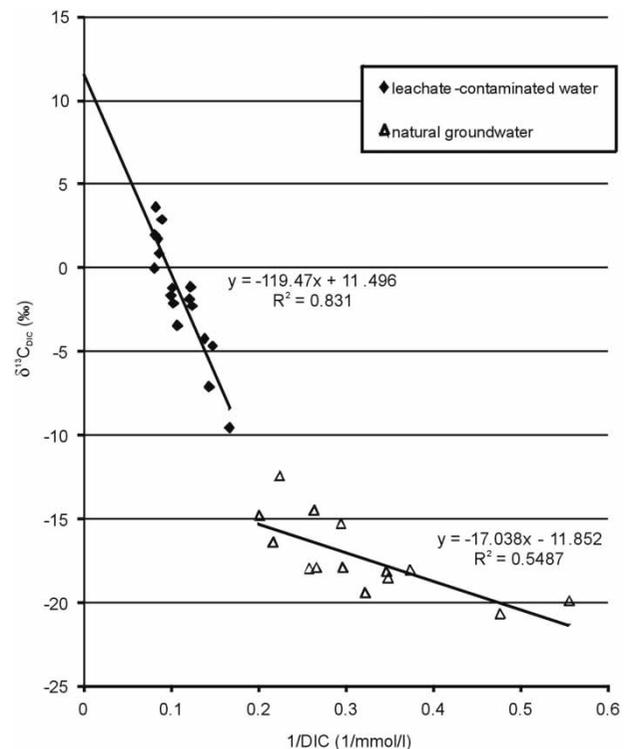


Figure 6 | Cross-plot of $\delta^{13}\text{C}_{\text{DIC}}$ versus 1/DIC for groundwater around the Otwock landfill.

contaminated by the landfill leachate. $\delta^{13}\text{C}_{\text{DIC}}$ value of the natural groundwater was similar in many cases (Table 2). The range of $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater was very wide, from approximately -30 to 0‰ , but the most common values ranged from -25 to -10‰ (Button 1991; Clark & Fritz 1997). Generally, in natural groundwater DIC is a mixture of carbon released during decomposition of the organic matter in the soil and aquifer ($\delta^{13}\text{C}_{\text{DIC}} \sim -28\text{‰}$) (Deines 1980) and dissolution of carbonate material in the aquifer ($\delta^{13}\text{C}_{\text{DIC}} \sim -10.3 - +1.1\text{‰}$) (Cerling 1984). Less negative values of $\delta^{13}\text{C}_{\text{DIC}}$ indicate increased dissolution of calcite.

This is consistent with a saturation index (SI) with respect to calcite (Porowska 2010). SI calculated on the basis of current data, confirmed undersaturation with respect to calcite and the potential possibility dissolution of this mineral in the natural groundwater. This often was found in the natural groundwater. The calculated partial pressure of CO_2 was generally above the atmospheric pressure, hence the atmospheric CO_2 as a source of carbon in DIC pool was negligible.

In the leachate-contaminated groundwater, the $\delta^{13}\text{C}_{\text{DIC}}$ and $1/\text{DIC}$ correlation can be expressed as $\delta^{13}\text{C}_{\text{DIC}} = -119.47(1/\text{DIC}) + 11.496$ (Figure 6). The y intercept ($+11.496$) was consistent with landfill carbon contamination

and $\delta^{13}\text{C}_{\text{DIC}}$, as reported in the literature (Table 2). The more depleted isotopic values at Otwock landfill, as compared with other places listed in Table 2, were probably due to one of the following causes or their combination: (a) reduced methanogenic activity by gradual depletion of existing organic sources with no waste input since the closure almost 20 years ago; and (b) mixing of the leachate and natural groundwater within the aquifer. High values of $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater indicate a source of heavy carbon from the landfill. The biologically mediated methanogenic processes, associated with waste decomposition in the landfill, result in isotopic enrichment of carbon ($\delta^{13}\text{C}$) in DIC in the landfill leachate (Hackley *et al.* 1996; Atekwana & Krishnamurthy 2004; North *et al.* 2006). Thus, the measurement of $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater can be a useful indicator of methanogenesis in the environment. Enrichment of the leachate and groundwater around the landfill ($\delta^{13}\text{C}_{\text{DIC}}$) is caused by methanogenic bacteria that decompose carbon compounds to methane and prefer the use of a lighter carbon isotope (^{12}C) (Hackley *et al.* 1996; van Breukelen *et al.* 2003; North *et al.* 2004). There are two methanogenic pathways: acetate fermentation ($6\text{CH}_2\text{O} \rightarrow 3\text{CO}_2 + 3\text{CH}_4$) and CO_2 -reduction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) (Mohammadzadeh & Clark 2011). Both of them can lead to an increase in $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater.

Table 2 | The isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) in leachate and groundwater around the selected landfills

Location	$\delta^{13}\text{C}_{\text{DIC}}$ (‰) natural groundwater	$\delta^{13}\text{C}_{\text{DIC}}$ (‰) leachate-contaminated water	$\delta^{13}\text{C}_{\text{DIC}}$ (‰) leachate	References
Otwock, Poland	from -20.6 to -12.4	from -10.9 to $+3.6$	–	This study
New York City landfill	-23.1	–	from $+20.9$ to $+24.3$	Walsh <i>et al.</i> (1993)
Illinois (landfill 2)	–	–	from $+16$ to $+22$	Hackley <i>et al.</i> (1996)
Norman landfill, Oklahoma	from -17.8 to -12.5	$+11.9$ from -8.8 to $+10.3$	–	Cozzarelli <i>et al.</i> (2000, 2011) Grossman <i>et al.</i> (2002)
Southern California	-20.28	from -17.3 to -13.18	$+2.27$	Kerfoot <i>et al.</i> (2003)
Banisveld landfill, The Netherlands	-19.6	from $+9.6$ to $+13.1$	–	van Breukelen (2003)
Dunedin landfill, New Zealand	–	–	$+16.11 \pm 0.23$	North <i>et al.</i> (2004), North & Frew (2008)
New Zealand	–	–	from $+2.8$ to $+15.8$	North <i>et al.</i> (2006)
Kalamazoo landfill, Michigan	from -16.9 to -10.0	from -2.3 to $+5.7$	–	Atekwana & Krishnamurthy (2004)
Trail Road landfill, Ottawa	–	–	from $+7.0$ to $+15.4$	Mohammadzadeh <i>et al.</i> (2005)
Landfill	from -15 to -12	–	$\sim +10$	Wimmer <i>et al.</i> (2013)
Landfill	–	from -25.4 to $+14.7 \text{‰}$	from -5.5 to $+25.9$	Haarstad & Mæhlum (2013)

Taking into account high values of $\delta^{15}\text{C}_{\text{DIC}}$ in the groundwater downgradient from the Otwock landfill, it can be stated that the processes within the landfill are still active, methanogenesis proceeds into the deposited waste and the groundwater is affected by the landfill. In general, the inorganic carbon dissolved in the leachate-contaminated groundwater is a mixture of the carbon released during the decomposition of organic matter that occurs within the aquifer sediments ($\delta^{15}\text{C}_{\text{DIC}} \sim -28\text{‰}$), and the biodegradation of organic matter inside the landfill followed by methanogenesis ($\delta^{15}\text{C}_{\text{DIC}} \sim +10\text{‰}$ and even up to $+38\text{‰}$) (Grossman 1997; Wimmer *et al.* 2013). Gas measurements confirmed that methane was generated inside the landfill (Porowska & Gruszczyński 2006). The calculated partial pressure of CO_2 was generally above the atmospheric pressure, hence the atmospheric CO_2 as a source of carbon in DIC pool was negligible. The contribution of DIC derived from the dissolution of carbonates downgradient from the landfill was negligible, too, due to the carbonate mineral supersaturation and the possibility of their precipitation (Porowska 2010, 2015). The leachate-contaminated groundwater are supersaturated with respect to calcite and tend to spontaneous calcite precipitation (e.g. Manning 2001).

This study indicated that the processes within the investigated landfill were still active and that the groundwater downgradient from the landfill was affected by the landfill leachate (piezometers No. 2, 6, 22, 23, and 24) (Figure 7). Taking into account the spatial interpretation, it can be concluded that the piezometers No. 5 and 9 and 1 and 3 belonged to the area of natural groundwater.

The estimated zone of the investigated landfill impact on the groundwater was determined (Figure 7) based on the groundwater table contour distribution (Figure 3) and $\delta^{15}\text{C}_{\text{DIC}}$ contour lines of the value -12‰ (Figure 4). The analysis of $\delta^{15}\text{C}_{\text{DIC}}$ and $1/\text{DIC}$ relationship indicated that, in the investigated area, the value of -12‰ can be treated as a threshold distinguishing the natural groundwater and the groundwater contaminated by the landfill leachate.

The extent of the landfill impact on the groundwater located north from the landfill was determined on the basis of the landfill gas generation activity (Porowska & Gruszczyński 2006, 2013) and the position of groundwater table. The leachate plume extended northwest from the landfill, towards the Vistula river and the Świder river. Depending on the hydrodynamic conditions and the intensity of the processes occurring in the waste accumulated in the landfill, the boundary of the landfill impact might be slightly modified.

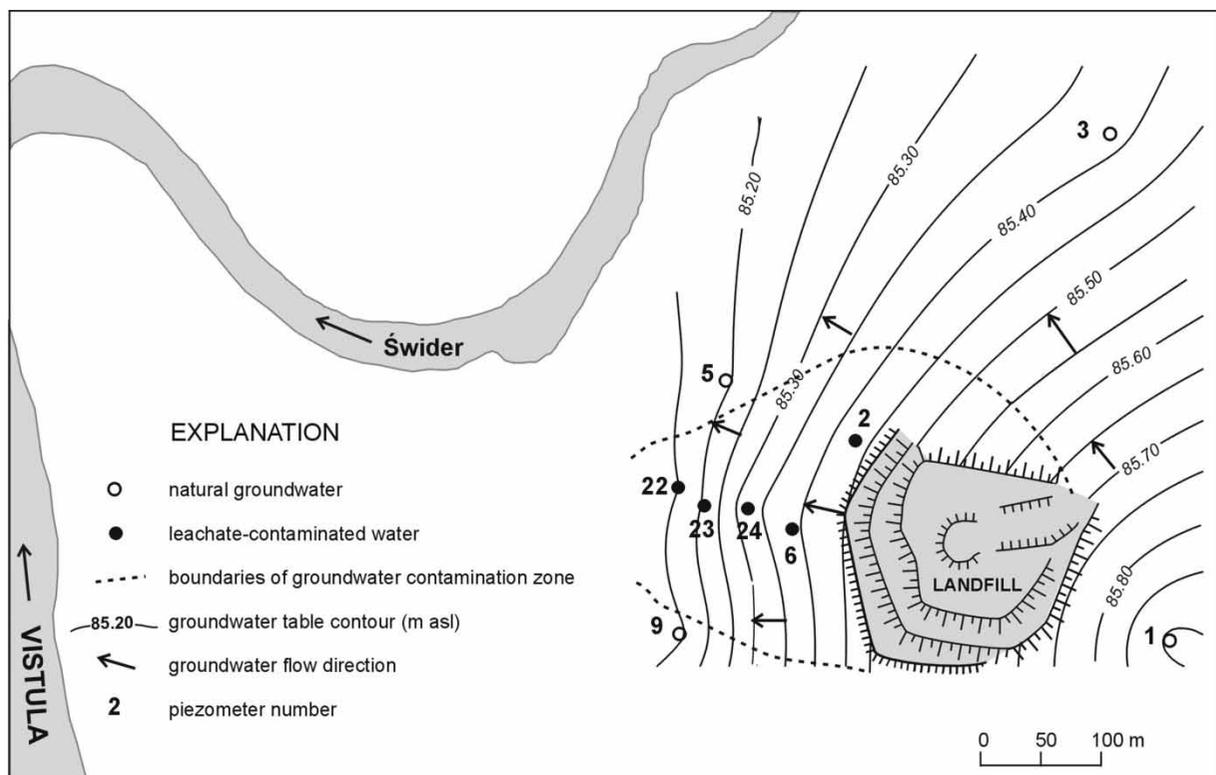


Figure 7 | Boundaries of groundwater contamination zone around the Otwock landfill.

CONCLUSIONS

The following conclusions can be drawn based on the results obtained for stable carbon isotopes and other groundwater parameters:

- DIC concentration and isotope composition $\delta^{13}\text{C}_{\text{DIC}}$ in the natural groundwater ranged from 1.8 to 5.0 mmol/L and from -20.6‰ to -12.4‰ , respectively. Higher values of $\delta^{13}\text{C}_{\text{DIC}}$ (from -10.9 to $+3.6\text{‰}$), as well as higher DIC concentration (from 6.0 to 12.5 mmol/L) can be attributed to the landfill impact. High values of $\delta^{13}\text{C}_{\text{DIC}}$ indicate that the groundwater is affected by the landfill leachate, where methanogenesis occurs. The changes of $\delta^{13}\text{C}_{\text{DIC}}$ values in the groundwater along the flow direction indicated a possibility of mixing the leachate-contaminated water and natural groundwater within the aquifer.
- The study demonstrated the possibility of identifying groundwater contamination with landfill leachate based on the concentration of DIC and carbon isotopic composition $\delta^{13}\text{C}_{\text{DIC}}$ in the groundwater. Data concerning the landfill gas generation, position of groundwater table, and archival analyses are useful in confirming the results of the isotopic data.
- The results of the study clearly indicate that carbon isotope composition and DIC concentration in the groundwater downgradient from the landfill affected by leachate contamination differ significantly from the uncontaminated groundwater (natural water), and thus the measurement of $\delta^{13}\text{C}_{\text{DIC}}$ in groundwater together with carbon concentration is a useful method to identify groundwater contamination around the landfill and to monitor the changes in groundwater chemistry due to anthropogenic inputs.

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