Periodica Polytechnica
Chemical Engineering

61(3), pp. 156-162, 2017
https://doi.org/10.3311/PPch.9667

RESEARCH ARTICLE

A Simple Method for Delineation of Leachate Plumes

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Received 26 June 2016; accepted after revision 10 October 2016

Abstract
Measurement and calculation of the carbon isotopic composition of groundwater from piezometers located around a reclaimed landfill were performed in order to test the method to distinguish the piezometers localized within the contaminated area and to identify the boundaries of the leachate plume. In order to select the best method for delineation of the leachate plume it was analyzed: chemical composition, the stable carbon isotopic composition in groundwater, and the calculation of carbon isotopic composition in groundwater. Comparison of the different methods for delineation of the leachate plume indicate, that the best method appear to be method based on the measurement and calculation of the carbon isotopic composition in groundwater. The proposed method has been tested using the data from Otwock landfill (Poland), but it can also be used in other contaminated areas.

Keywords
landfill, groundwater, contaminated area, measured carbon isotope composition, calculated carbon isotope composition

1 Introduction

Landfill leachates contain a wide range of contaminants and when they mix with natural groundwater, significant changes in groundwater quality are observed [1-6]. In most cases, leachate plumes are relatively small, less than a thousand meters long [7]. However, the delineation of a leachate plume around a municipal landfill may be sometimes complicated and may present significant challenges. Leachate composition varies significantly among landfills, depending on waste composition, volume, age and landfilling technology. The intensity of groundwater contamination by a leachate depends on hydrogeological conditions, climate and the engineering of the landfill [8]. Landfill leachate can create groundwater contaminant plumes that may last for decades to centuries [9, 10]. The load of contamination and its concentration in the groundwater are often spatially and temporarily variable, thus making identification of the boundaries of groundwater contamination zone complicated. Due to complexity of hydrogeological conditions and biochemical processes in a landfill, the assessment of the leachate plume extent requires detailed and unconventional measurements. The observation of the biogas emissions and lateral gas transport in soil adjacent to a landfill is a supplementary tool to demonstrate landfill impact on the environment [11-13]. Usually, the assessment of a leachate-contaminated area is based on the physical and chemical composition of groundwater, biochemical oxygen demand, chemical oxygen demand, total organic carbon, and heavy metals [2, 14-18]. Becker [19] estimated the vertical and horizontal extent of a leachate plume by performing a series of specific conductance measurements in monitoring wells located upgradient and downgradient of the landfill. Standard methods like chemical analysis of groundwater, hydrological description, and geophysical studies (vertical electrical sounding and ground penetrating radar) were used for the identification and delineation of a contaminant plume in the shallow aquifer in Guadalupe Victoria landfill in Mexico [20]. Xenobiotic organic compounds (aromatic hydrocarbons, halogenated hydrocarbons and phenols), originating from household or industrial chemicals are also good indicators of a landfill contamination [7, 21]. Observation of microbial communities in polluted

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and natural groundwater revealed that a long-term monitoring of the changes in their structure, together with monitoring of the changes in environmental conditions and alterations in groundwater hydrochemistry, might be a useful set of tools for identifying a contaminated area [22, 23]. Moreover, these observations facilitate the understanding of natural attenuation processes in the aquifer around the landfill.

Another method for detecting a contaminated area involves a delineation of the leachate plume based on stable carbon isotope composition in groundwater. The usefulness of carbon isotope determination in demonstrating landfill environmental impact was reported by North et al. [24]. Findings were supported by Haarstad and Mæhlum [25], who concluded that $\delta^{13}C_{DIC}$ is a more sensitive tracer than the content of organic matter, salts, nutrients and heavy metals in the leachate. Roslanzairi Mostapa et al. [26] compared the conventional and stable isotope techniques and found out that the isotope technique was more accurate in determining the distribution of landfill leachate in the groundwater and surface water, but it should be coupled with the conventional technique.

Sometimes it is difficult to delineate the leachate plume using conventional methods, as physicochemical composition of the groundwater. In the groundwater around the Otwock landfill blurs a clear division into two zones, especially in the case of sulfates [27]. The leachate-contaminated area may be more effectively identified by measurement of stable carbon isotope composition. When the leachates are only to small extent mixed with groundwater, the measured values alone are not enough to conclude whether the isotopic composition of groundwater results from the landfill impact or from natural changes in the environment, and additional interpretation is necessary. The aim of this study is to present a new method to apply and evaluate an unconventional method to select piezometers with leachate-contaminated groundwater and delineate the leachate plume. This method is based on a comparison of measured and calculated values of $\delta^{13}C_{DIC}$ in groundwater and leachate. Carbon isotope composition may be calculated using $\delta^{13}C_{DIC}$ mass balance, assuming an appropriate isotopic fractionation, and taking into account physicochemical composition of groundwater [28-30]. The proposed method has been tested using the data from Otwock landfill, however is suitable for wider application. The method can also be successfully used in other contaminated areas.

2 Materials and methods

2.1 Site description

The study was conducted around a reclaimed municipal landfill, located in the suburbs of Otwock, about 25 km southwest of Warsaw (Poland) (Fig. 1). The landfill covers an area of 2.8 ha. It received municipal waste from the community of Otwock from 1961 to 1991. After closing, the landfill was covered with a layer of soil, consisting of approximately 30-50 cm of compost and planted with grass. The contamination of groundwater by leachate is from the infiltration and passage of water through the solid waste into the aquifer, because the landfill has no bottom liner.

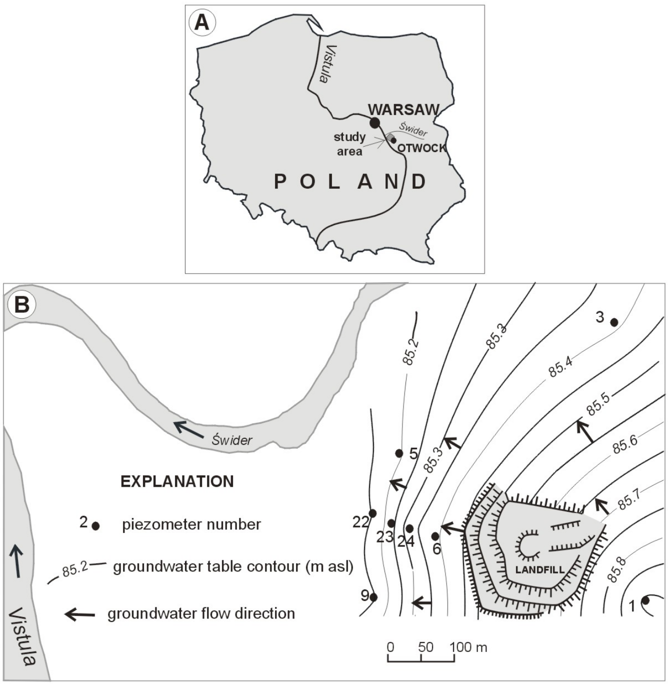

Fig. 1 Location of the study area (A), arrangement of the piezometers and groundwater table contour (B)

The geological profile includes highly permeable river deposits composed of gravels and varigrained sands, with occasional organic matter or peat layers distributed within the aquifer. The hydraulic conductivity of the aquifer ranged between $6.5 \cdot 10^{-4}$ m/s and $1.6 \cdot 10^{-3}$ m/s, depending on the clay content. The general groundwater flow direction is northwest, towards the Vistula and Świder (Fig. 1). During the study period, the groundwater table in the measured piezometers ranged from ~1.5 m below ground (bg) to ~2.7 m bg (from spring to autumn), and from ~1.0 m bg to ~1.7 m bg (in winter).

2.2 Sampling and analytical procedures

Field and laboratory research were conducted quarterly from May 2006 to March, using the same research equipment and analytical procedures. Groundwater samples for chemical analyses were collected from piezometers around the landfill (Fig. 1). Water temperature and pH were measured in the field using the pH-meter 330i (WTW). Bicarbonate (HCO_3^-) was measured on site by HCl titrating. Laboratory analyses included determination of the cations Mg^{2+}, Ca^{2+}, $K^{+,}$ and Na^+ (in filtered and acidified samples) by Perkin Elmer atomic absorption spectrometry, and the anions SO_4^{2-}, Cl^-, NO_3^- were determined by high-performance liquid chromatography (HPLC). The analyses were performed at the Central Chemical Laboratory of the Polish Geological Institute - National Research Institute in Warsaw and at the Laboratory of Institute of Hydrogeology and Engineering Geology, Faculty of Geology in Warsaw.

Unfiltered samples of groundwater from the aquifer were collected to determine $\delta^{13}C_{DIC}$. The samples were conserved with $SrCl_2$-NH_4OH. The measurement of carbon isotopic composition was determined 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. $\delta^{13}C$ values of the dissolved inorganic carbon samples were reproducible to ±0.1‰. The results were expressed with reference to the VPDB standard. Routine $\delta^{13}C_{DIC}$ measurements had an overall precision exceeding 0.1‰.

Numerous groundwater components were analyzed for the Otwock landfill, but this paper presents only the parameters which are useful to the calculation of the carbon isotope composition of groundwater.

3 Theoretical considerations

The content of $\delta^{13}C$ in organic matter ranges from -34 to -24‰ [31], with average about -28‰ [32], and soil gas $CO_{2(g)}$ average concentration is about -23‰ [28]. During conversion of soil gas $CO_{2(g)}$ into dissolved carbon dioxide $CO_{2(aq)}$, an isotopic fractionation occurs and this enriches $CO_{2(aq)}$ with ^{13}C by approximately -1.1‰, relative to the $CO_{2(g)}$. Therefore, $\delta^{13}C$ of dissolved carbon dioxide $CO_{2(aq)}$ amounts to ca. -24.1‰. During conversion of dissolved carbon dioxide $CO_{2(aq)}$ into bicarbonate, the isotopic fractionation enriches HCO_3^- with ^{13}C by approximately 9‰, relative to $CO_{2(aq).}$ Therefore, $\delta^{13}C$ of bicarbonate is -15.1‰. However, the values of $\delta^{13}C$ in the leachates and leachate contaminated groundwater may also be positive, even up to +38‰ [33]. This simplified assessment of $\delta^{13}C$ concentration is not adequate when other sources of carbon is considered. The assessment is more accurate when carbon isotope composition is calculated using $\delta^{13}C_{DIC}$ mass balance equation (Eq. (1)) [28-30].

$$\begin{aligned}\delta^{13}C_{DIC-calc.} = \Big[& mCO_{2(aq)}\left(\delta^{13}C_{CO2(g)} + \varepsilon^{13}C_{CO2(aq)-CO2(g)}\right) \\ & + mHCO_3^-\left(\delta^{13}C_{CO2(g)} + \varepsilon^{13}C_{HCO3-CO2(g)}\right) \\ & + mCO_3^{2-}\left(\delta^{13}C_{CO2(g)} + \varepsilon^{13}C_{CO3-CO2(g)}\right)\Big] \Big/ \left(mCO_{2(aq)} + mHCO_3^- + mCO_3^{2-}\right)\end{aligned} \tag{1}$$

where:

$mCO_{2(aq)}$, $mHCO_3^-$, mCO_3^{2-} - molalities of the DIC species: $CO_{2(aq)}$, HCO_3^-, and CO_3^{2-}, respectively

$\delta^{13}C_{CO2(g)}$ - carbon isotopic composition of soil gas $CO_{2(g)}$

$\varepsilon^{13}C_{CO2(aq)-CO2(g),}$ $\varepsilon^{13}C_{HCO3-CO2(g)}$, $\varepsilon^{13}C_{CO3-CO2(g)}$ - equilibrium fractionations.

This equation was used to calculate carbon isotopic composition in groundwater. The values of equilibrium fractionation (ε) were adopted from Mook (ed.) [29] and Darling et al. [30], and are listed in Table 1 (temperatures appropriate for the groundwater in Otwock). Equilibrium fractionation between the carbonate ion (CO_3^{2-}) and carbon dioxide ($CO_{2(g)}$) were also determined by Zhang et al. [34], Hałas et al. [35], Szaran [36], and Leśniak and Zawidzki [37]. Molalities of DIC species and other calculations were based on physicochemical composition of groundwater, i.e. water temperature, pH, and the concentration of HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ [28].

Table 1 The values of equilibrium fractionations (ε) used in the calculation

Water temperature	$\varepsilon\ ^{13}C_{CO2(aq)-CO2(g)}$	$\varepsilon\ ^{13}C_{HCO3-CO2(g)}$	$\varepsilon\ ^{13}C_{CO3-CO2(g)}$
1	-1.2	10.1	10.2
6	-1.1	9.6	9.6
7	-1.1	9.5	9.5
8	-1.1	9.4	9.4
9	-1.1	9.3	9.3
10	-1.1	9.2	9.2
11	-1.1	9.1	9.1
12	-1.1	9.0	8.9
13	-1.1	8.9	8.8
14	-1.1	8.8	8.7

4 Results and discussion

In order to select the best method for delineation of the leachate plume was analyzed, i.e: the concentration of major ions, the stable carbon isotopic composition in groundwater, and the calculation of carbon isotopic composition in groundwater.

4.1 Delineation of the leachate plume using the chemical composition in groundwater

Separating between the zone of natural conditions and leachate-contaminated area resulting from an analysis of the major ions was not clear (Fig. 2). Unequivocal delineation of the contaminated area around the Otwock landfill is difficult due to gradual changes in the chemistry between the adjacent piezometers e.g. for bicarbonates or sulfates independent of the sampling site [27, 38]. Chemical composition of the groundwater changed gradually, and so the method of dividing the groundwater into zones depending on the concentration of the major ions is not appropriate in this case.

Similar concentration of sulfates, from 36.2 mg/dm^3 to 106 mg/dm^3, was found in the groundwater around the landfill (Fig. 3). According to the above-discussed division into two zones, sulfate concentration in the natural groundwater ranged from 36.2 mg/dm^3 to 110 mg/dm^3, and in the leachate-contaminated water from 56 mg/dm^3 to 106 mg/dm^3. Therefore, sulfate concentration, as the concentration of other major ions, was unsuitable for assessing the extent of the leachate plume.

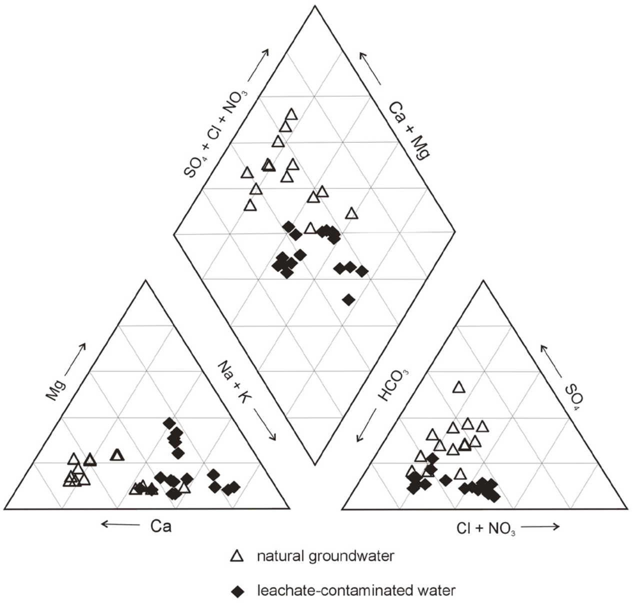

Fig. 2 Chemical composition of groundwater around the Otwock landfill

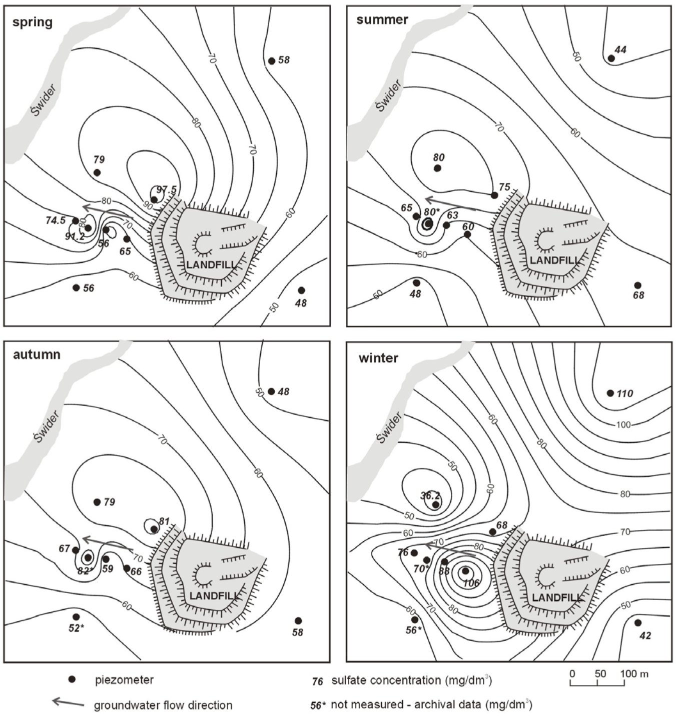

Fig. 3 Distribution of sulfate concentration in groundwater around the Otwock landfill

A better method seems to be the comparison of calcium and bicarbonates concentrations in groundwater around the landfill (Fig. 4). This plot indicates which piezometers are not influenced by landfill contamination. The samples representing natural conditions are located along 1:1 line and suggest that chemical composition of groundwater (main ions: HCO_3^-, Ca^{2+}) is principally controlled by natural biogeochemical processes such as CO_2 generation in the soil and aquifer through the decay of natural organic matter and calcite dissolution. Groundwater samples collected from contaminated area located below 1:1 line manifest high HCO_3^- concentration in comparison to Ca^{2+} concentration caused by anthropogenic processes (activity of the landfill). This division in not so clear in the case of contaminated area, because sometimes the point may be located near the line 1:1, so this method is not appropriate in this case.

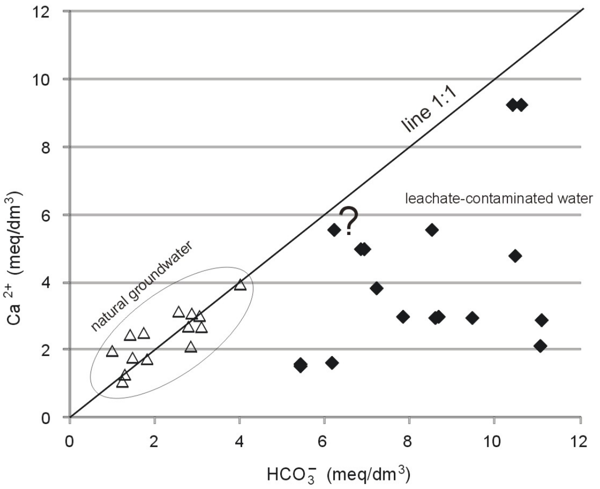

Fig. 4 Relationship between calcium and bicarbonates concentrations in groundwater around the Otwock landfill

4.2 Delineation of the leachate plume using the carbon isotopic composition in groundwater

The measured of carbon isotopic composition of groundwater ($\delta^{13}C_{DIC}$) varied widely, from -20.6‰ in piezometer No. 3 to +3.6‰ in piezometer No. 6 (Fig. 5). It could be expected that the groundwater downgradient from the landfill was contaminated and the results from piezometers No. 2, 6, 22, 23, and 24 confirmed this assumption. Piezometers No. 1 and 3 were both localized upgradient from the landfill (Fig. 5), and thus represents the natural groundwater. However, it is not clear whether the $\delta^{13}C_{DIC}$ of -12.4‰ detected in the piezometer No 1 in the winter indicates that the groundwater is contaminated by leachate. Similarly, it is not clear whether piezometer No. 9 belongs to the area of natural groundwater or the contaminated area, because $\delta^{13}C_{DIC}$ concentrations recorded there were -14.5‰ and -14.8‰, depending on the season. In general, natural groundwater is characterized by a wide range of $\delta^{13}C_{DIC}$ (from -30 to 0‰ but most commonly from -25 to -10‰) [28, 39], and a comparison of the results with the literature data does not provide answers to the question whether they represent the natural groundwater or the leachate-contaminated water.

Leachates are usually characterized by positive values of $\delta^{13}C_{DIC}$ (even up to +38‰) [33], but when they are only to small extent mixed with groundwater, it is difficult based on the measured values only, without additional interpretation to assess whether the isotopic composition of the groundwater is due to the landfill impact or to natural changes in the environment, e.g. increasing share of carbonate dissolution naturally occurring in the aquifer.

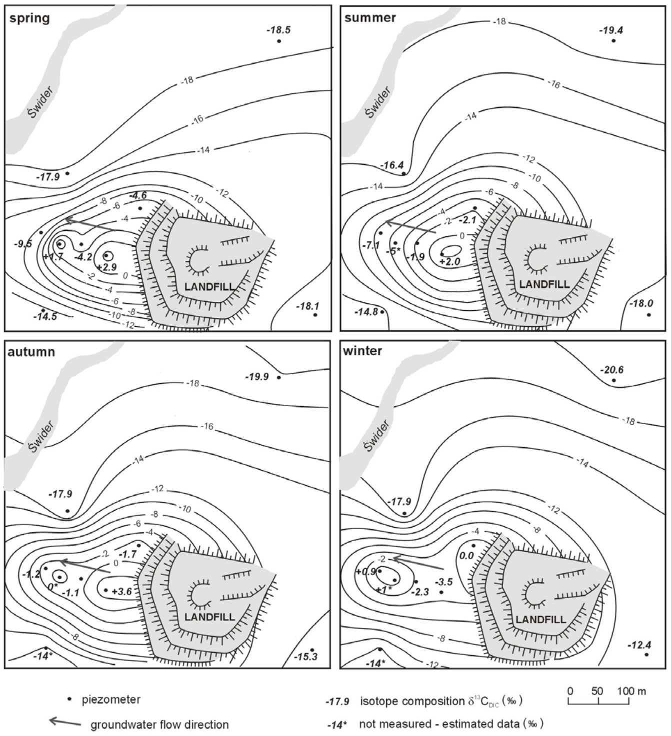

Fig. 5 Distribution of carbon isotope composition in groundwater around the Otwock landfill

4.3 Delineation of the leachate plume using the calculation of carbon isotopic composition in groundwater

$\delta^{13}C_{DIC}$ in the groundwater in Otwock was determined from the isotope mass balance equation (Eq. (1)), using equilibrium fractionation values (ε) from Table 1 and physicochemical composition parameters of the groundwater (water temperature, pH, HCO_3^-, SO_4^{2-}, Cl^-, Mg^{2+}, Ca^{2+}, Na^+, K^+). Measured $\delta^{13}C_{DIC}$ varied widely, from -20.6‰ to +3.6‰, and the calculated concentrations ranged from -19.3‰ to -13.7‰. Measured $\delta^{13}C_{DIC}$ were compared with respective calculated concentrations in Figure 6. Two groups, differing in the calculated and measured concentrations of $\delta^{13}C_{DIC}$, could be identified in the landfill area. The first one represents carbon isotope composition in the natural groundwater, and the second in the leachate-contaminated groundwater. In the natural groundwater, the points were arranged along 1:1 line, whereas in the leachate-contaminated groundwater they were placed below this line. This suggests that other sources of carbon were important in this type of groundwater and different processes have caused isotope fractionation.

The similar calculated and measured value of $\delta^{13}C_{DIC}$ in natural conditions indicates that isotopic fractionation takes place in a generally known manner, and the values of equilibrium fractionations used in calculations and listed in Table 1 show the real fractionation occurring in this environment. In the leachate-contaminated area higher measured than calculated value of $\delta^{13}C_{DIC}$ indicated, that the landfill activity was a significant source of carbon in this area, causing changes in carbon isotope fractionation. During anaerobic decomposition of organic matter in landfill occur high isotope fractionation. The values of equilibrium fractionations are different compared to natural conditions and individual in every landfill. This causes differences in the calculated and measured values $\delta^{13}C_{DIC}$ as well as differences between the natural groundwater and the leachate-contaminated groundwater. Due to enrichment of ^{13}C during methanogenesis, $\delta^{13}C_{DIC}$ of leachates may increase up to +10‰ [40] or even up to +38‰ [33], whereas in natural environment this value ranged from -25 to -10‰ [28].

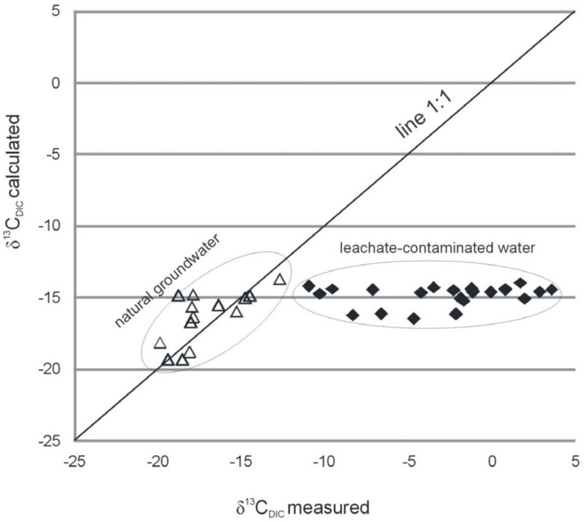

Fig. 6 Relationship between $\delta^{13}C_{DIC}$ measured and $\delta^{13}C_{DIC}$ calculated

Mixing leachates and groundwater in the aquifer along the groundwater flow direction causes differentiation in carbon isotopic composition in the leachate plume. The concentration of $\delta^{13}C_{DIC}$ in the groundwater depends on the amount of the leachate and hydrogeochemical conditions within the aquifer. With this assumption in mind, it was possible to select the piezometers with natural groundwater and leachate-contaminated water. Piezometers No. 2, 6, 22, 23 and 24, located the closest to the landfill and along the groundwater flow direction shows contamination by the leachate (Fig. 7). Piezometers No. 1 and 3, located upgradient from the landfill belongs to the area of natural groundwater, as do piezometers No. 5 and 9, despite their location downgradient from the landfill.

The outcomes of $\delta^{13}C_{DIC}$ mass balance equation were consistent with earlier research using cross-plot of $\delta^{13}C_{DIC}$ versus 1/DIC.

According to the previous study [41], the research area is divided into two zones differing in the landfill activity. In the first, carbon is derived from the organic matter degradation and from carbonate dissolution in the natural groundwater. In the second, $\delta^{13}C_{DIC}$ concentration is controlled by the mixing ratio of organic matter degradation within the aquifer sediments and biodegradation of organic matter stored in the landfill.

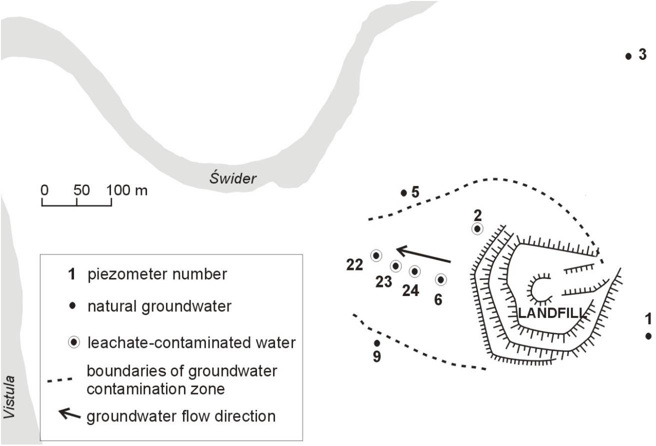

Fig. 7 Arrangement of the piezometers with natural groundwater and leachate-contaminated water

5 Conclusions

Delineation of the leachate plume using the calculation of carbon isotopic composition in groundwater seems to be a suitable and useful method. Knowing the chemical composition of groundwater, the equilibrium fractionation and the results of $\delta^{13}C_{DIC}$ mass balance, it is possible to calculate the carbon isotopic composition of groundwater. A comparison of the calculated and measured values of carbon isotopes $\delta^{13}C_{DIC}$ in the groundwater around the reclaimed landfill in Otwock unequivocally demonstrated that it is an effective method of selecting the piezometers with leachate-contaminated groundwater and delineating the leachate plume. The proposed method was tested in the research performed around the Otwock landfill, but it can be used in other areas, contaminated by leachate. According to this method, the piezometers No. 2, 6, 22, 23, and 24, located downgradient from the landfill, were impacted by the leachate. Water in the piezometers No. 1 and 3, located upgradient from the landfill, as well as the piezometers No. 5 and 9, despite their location downgradient from the landfill, could be classified as natural water.

The advantages of the proposed method compared with the other methods that are currently applied for delineating the area of contaminated groundwater are the following: 1) evident selection of the piezometers with leachate-contaminated groundwater 2) no additional cost 3) no additional laboratory tests, 4) easy to realize 5) suitable for wider application in other area contaminated by leachate.

Acknowledgement

The project presented in this article is supported by the State Committee for Scientific Research (project no. 4 T12B 061 28) and partly also by the Faculty of Geology, University of Warsaw.

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