

Precipitation Method for Determination of Carbon and Oxygen Isotopes to Detect Groundwater Contamination Near a Municipal Landfill

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Abstract

The paper emphasizes the importance of isotope studies as a unique tool for detecting groundwater contamination with the landfill leachate. The aim of the study was to present an additional and useful method for detecting groundwater contamination, based on stable isotope analysis. The proposed method relies on the interpretation of measured $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}$ levels (in precipitated carbonates during preparation of a water sample). According to this method, two zones with different isotope composition of groundwater were identified: the first zone with natural groundwater and with low $\delta^{13}\text{C}_{\text{DIC}}$ levels (from -20.6 to -12.4‰) and high $\delta^{18}\text{O}$ levels (from -13.6 to -8.0‰), and the second zone with leachate-contaminated groundwater rich in $\delta^{13}\text{C}_{\text{DIC}}$ (from -10.9 to $+3.6\text{‰}$) and high level of $\delta^{18}\text{O}$ (from -9.8 to -7.1‰). Measuring the isotopic composition of oxygen alone, is insufficient to delimit the contaminated zone due a partial overlap of natural levels with those of the contaminated with groundwater leachates. Determination of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}$ in the landfill leachate-contaminated water can provide an effective tool to detect groundwater contamination near municipal landfills, and it can help to minimize the number of samples collected for the analysis of conventional parameters. This proven method may offer an easy-to-use solution for detecting groundwater contamination.

Keywords

landfill, carbon isotope, oxygen isotope, groundwater contamination

1 Introduction

A reliable method to determine the impact zone of a landfill is of great importance to prevent possible contamination from spreading in the aquifer, or to avoid possible claims resulting from environmental pollution [1]. Depending on many natural factors (e.g. climate, hydrogeological conditions, (such as hydraulic conductivity of the aquifer) and the type of landfill (its size and age of the landfill, type of waste stored), the leachates can migrate in a porous aquifer even up to 2 km from the landfill, and the contamination zone may cover large areas [2, 3]. The load of contamination and its concentration in groundwater depends on several factors, such as:

1. the amount and type of waste and the age of the landfill,
2. dilution of the leachate with uncontaminated groundwater,
3. mixing of the anaerobic leachate with oxygenated water that facilitates the decomposition of organic matter and precipitation of metals, and

4. interaction of contaminants with aquifer minerals and organic matter.

Problems with assessing the condition of the soil and water environment around the landfill area may result from the fact that the contaminants migrating in the groundwater environment undergo many processes (e.g. biodegradation, biotransformation), and they can also be impulse-released from the landfill as a result of increased infiltration after rainfall, especially those old, technically unprepared for storage waste. Studies on municipal landfills non-isolated or poorly isolated from the bedrock showed that the composition of the landfill leachate from the same source as well as from different sources, is extremely variable.

Groundwater can be contaminated with various compounds of natural or anthropogenic origin. The analysis of chemicals (CO_2 , CH_4 , CO , H_2 , N_2 , and O_2) and isotopic composition ($\delta^{13}\text{C}_{(\text{CO}_2)}$ and $\delta^{13}\text{C}_{(\text{CH}_4)}$) of landfill gas and

chemical (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , NH_4^+ , NO_3^- , NO_2^- , B, Fe, Mn, As, Cr, Ni, Cu, Zn, Cd, Pb, and Hg), stable and radioactive isotopes (δD , $\delta^{18}\text{O}$, tritium, $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{34}\text{S}_{\text{SO}_4}$), synthetic chemicals (benzene, toluene, ethylbenzene, xylene (BTEX)), pesticides) and other parameters (chemical oxygen demand (COD), biochemical oxygen demand (BOD)) of leachate, groundwater, and surface waters has been the subject numerous studies. Researchers have been investigating this topic for decades and new methods are still being developed. This knowledge is crucial for a consistent interpretation the results of environmental analyses especially from polluted sites, and pollution source characterization and tracking, where there is often substantial heterogeneity of the environmental samples. Usefulness of isotope studies to assess the impact of municipal landfills on groundwater is widely discussed by many authors [4–14]. The stable isotopic methods are highly trusted and commonly uses to distinguish reaction mechanisms within the degrading compounds. Laboratory and field experiments based on stable isotope methods are employed to assess the reaction mechanisms and transformations in different hydrogeochemical environments. The application of stable isotopes ($\delta^{13}\text{C}$) for the identification of zones with different hydrogeochemical conditions is commonly known, however, testing $\delta^{18}\text{O}$ in laboratory precipitated carbonates is unusual.

The aim of this study was to indicate an additional and useful method for detecting contamination of groundwater based on isotope analysis. The novelty of this approach is the application of two isotopes: carbon and oxygen in strontium carbonate precipitate (obtained during precipitation from water) to detect contamination of groundwater near municipal landfills. The method yields reliable results and does not require additional field tests apart from isotopic determinations of oxygen in a laboratory. The sample preparation is performed simultaneously with carbon isotope determinations. Groundwater samples around the Otwock landfill (Poland) were collected in order to identify suitable tracers and develop a convenient technique for monitoring groundwater contamination from the landfill leachate. The landfill, covering an area of 2.8 ha was operational for 30 years (1961–1991), without proper technical preparation. It is localized on highly permeable gravels and sands with hydraulic conductivity of the aquifer ranging from $6.5 \cdot 10^{-4}$ m/s to $1.6 \cdot 10^{-3}$ m/s. The results of this study might provide important information for the design of reclaimed municipal landfills and the surrounding area. They can also be helpful in identifying potential pollution sources in other areas.

2 Review of methods for identifying groundwater contamination

There are many known methods that can be used to identify groundwater contamination in the vicinity of municipal landfills. One of them is the assessment of the physicochemical or isotopic composition of water. An important group of methods that is independent of water testing are geophysical surveys.

2.1 Methods based on physicochemical composition of the water

One of suitable methods that can be used to identify groundwater contamination in the vicinity of municipal landfills is the assessment of physicochemical composition of the water, i.e. its specific electrical conductivity (SEC) (or mineralization) [15], concentration of major ions, such as HCO_3^- , Cl^- , NO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ (or other components e.g. heavy metals [16, 17], some minor and trace elements (NH_4^+ , NO_2^- , Br^-) [18], dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), and comparing them with the hydrogeochemical background range [15] or with the quality standards for groundwater [19, 20]. Such a comparison indicates differences between background water and leachate-contaminated water and helps to delineate the area of contaminated groundwater. A good solution seems to be to compare the concentration of calcium and bicarbonates concentrations in the groundwater around the landfill [10]. Generally, this relationship indicates the areas not impacted by the landfill contamination. As discussed previously, sometimes this method is not appropriate [10]. Assuming that the landfill leachate contains high concentrations of dissolved organic matter (as a result of organic matter biodegradation), which might contaminate the groundwater, BOD/COD ratio can be used to assess the spread of the leachate plume in the aquifer [21, 22]. As the biodegradable organic compounds may also be of natural origin (peatlands), this method can be unreliable [21]. It is commonly known, that BTEX, PAHs, pesticides, microplastics, and other components not formed in the natural environment are clearly indicative of contamination [22–26]. On the other hand, biodegradation of synthetic polymers, recognized as environmental pollutants, is difficult to assess, as it depends on both the environment in which they are placed and the chemical properties of the polymers.

Assessment of water aggressiveness based on the estimation of saturation indices (SIs) or laboratory determinations is also a useful method to identify groundwater contamination around a landfill [27]. Depending on the organic and inorganic constituents of the leachates, carbonate

precipitation may occur and the landfill leachate collection systems may be clogged [28–34]. Sometimes microbiological tests are performed simultaneously with physicochemical measurements [24, 34–36]. Combined chemical and isotope analysis is a good method to assess the landfill and leachate effects on groundwater [5, 8, 12, 16, 24, 37].

2.2 Methods based on carbon isotope data

The application of isotopic techniques to trace the range of groundwater contamination is described by many authors [e.g. 11, 12, 18, 38], who used both stable or radioactive isotope tests to identify contaminants [18]. Stable isotopes and radiocarbon are used to identify carbon sources in various environments [39]. Raco and Battaglini [15] confirmed that tritium content is an effective leachate tracer, both due to large differences in its level between the groundwater and the leachate, and its conservative properties. Nigro et al. [40] used boron and tritium isotopes for tracing landfill contamination in groundwater.

2.2.1 Relationship between measured and calculated $\delta^{13}\text{C}_{\text{DIC}}$

By focusing on carbon isotopes, we can trace the usefulness of a method based on the comparison of their measured and calculated composition (Fig. 1) [10]. Knowing the chemical composition of groundwater, the equilibrium fractionation, and the results of $\delta^{13}\text{C}_{\text{DIC}}$ mass balance, it is possible to calculate the carbon isotopic composition of groundwater. The theoretical considerations on this method are presented in detail in the previous publication [10].

Based on this method, two groups differing in the

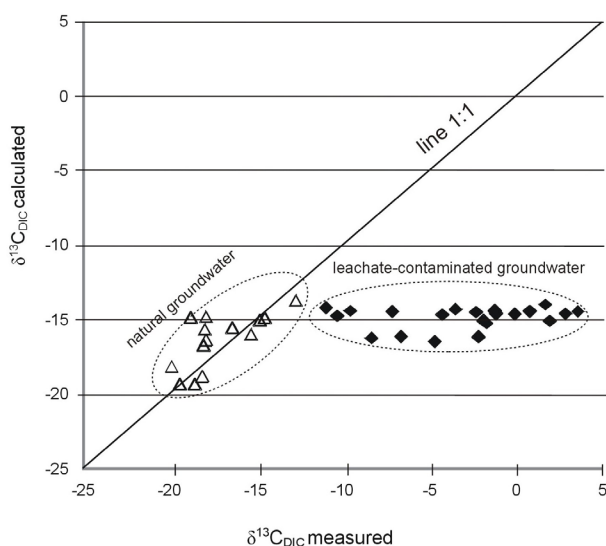


Fig. 1 Relationship between measured and calculated $\delta^{13}\text{C}_{\text{DIC}}$ [10].

calculated and measured concentrations of $\delta^{13}\text{C}_{\text{DIC}}$, could be identified around the landfill. In the natural groundwater, the points were arranged along 1:1 line, whereas in the leachate-contaminated groundwater they were placed below this line (Fig. 1). This suggested that other sources of carbon (coming from the landfill leachate) were very important in the leachate-contaminated area. Due to enrichment with ^{13}C during methanogenesis, $\delta^{13}\text{C}_{\text{DIC}}$ of the leachate may increase even up to +38‰ [41]. In landfills, methanogenesis can trigger methane production. Due to the activity of specific microorganisms and their preference for the lighter ^{12}C isotope, the residual CO_2 of the leachate pool is enriched with the heavier ^{13}C isotope. Therefore, $\delta^{13}\text{C}_{\text{DIC}}$ of the leachate-contaminated groundwater is very rich in ^{13}C isotope.

2.2.2 Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and concentration of dissolved inorganic carbon

Comparison of the relationships between $\delta^{13}\text{C}_{\text{DIC}}$ and concentration of dissolved inorganic carbon in groundwater provides a powerful tool for identification of groundwater contaminated with the landfill leachate Fig. 2 [8, 9, 11].

The leachate-contaminated groundwater is isotopically distinct from the natural groundwater. The carbon isotope composition reaches the highest values in

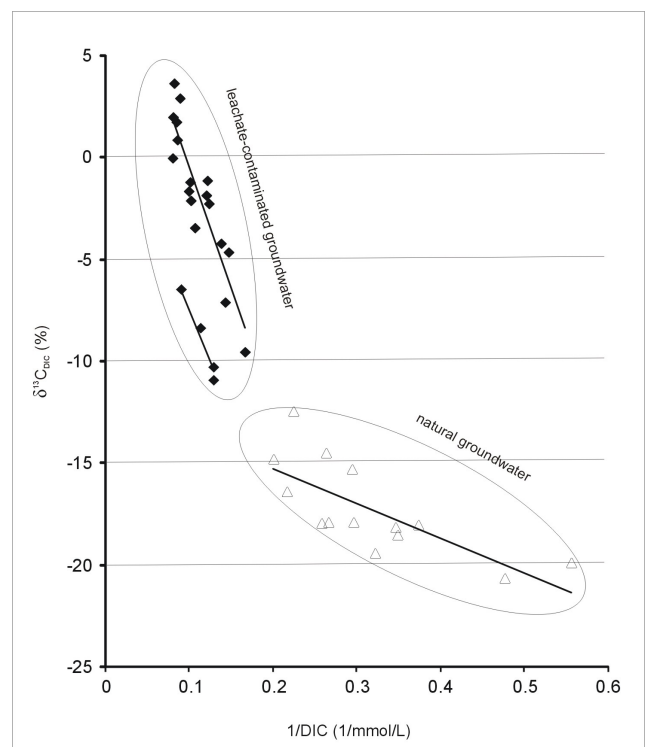


Fig. 2 Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and 1/DIC [8, 9, 11]

leachate-contaminated groundwater and heavy carbon isotope ratios $\delta^{13}\text{C}_{\text{DIC}}$ can be used to diagnose the landfill contamination. Leachate-contaminated groundwater was characterized by high values of $\delta^{13}\text{C}_{\text{DIC}}$ (from -10.9 to $+3.6\text{‰}$) and high DIC concentration (from 6.0 to 12.5 mmol/L) [8, 9, 11]. Lower values of $\delta^{13}\text{C}_{\text{DIC}}$ (from -20.6 to -12.4‰) and lower DIC concentration (from 1.8 to 5.0 mmol/L) were determined in the natural groundwater. These values were comparable with the results reported by Lee [13] for a Korean municipal landfill, where $\delta^{13}\text{C}_{\text{DIC}}$ of groundwater ranged from -18.7 to $+11.6$ (DIC concentration from 0.6 to 11.5 mmol/L) depending on the contamination size. The $\delta^{13}\text{C}_{\text{DIC}}$ values of the leachate ranged from $+16.5$ to $+21.2\text{‰}$ at this landfill (DIC concentration from 6.5 to 22.1 mmol/L) [13].

Usefulness of carbon isotope studies to assess the impact of municipal landfills on groundwater is discussed by many authors [5–14]. Sometimes the researchers measure water content of $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{13}\text{C}_{\text{DIC}}$ to identify the leachate-contaminated groundwater near the landfills [13].

2.2.3 Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and saturation indices with respect to carbonates

An excess of dissolved inorganic carbon may drive in situ precipitation of calcium carbonate as authigenic carbonates resulting from early diagenesis mediated by microbes [28–34, 42]. Authigenic carbonates can be precipitated from the landfill leachate collection system. In leachate-contaminated zone, an excess of dissolved inorganic carbon may cause the precipitation of calcium carbonate in situ in the aquifer. The possibility of carbonate minerals precipitation in the impact zone of a landfill is confirmed by the analysis of saturation indices with respect to carbonates (calcite, aragonite, dolomite, magnesite and siderite) [27]. The leachate-contaminated groundwater is in equilibrium, or is supersaturated with calcite, aragonite, dolomite, and siderite, and a spontaneous precipitation of these minerals was possible, whereas in natural groundwater, carbonate minerals can be dissolved. Based on this regularity, it can be seen that the comparison of the relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and saturation indices with respect to carbonates is a useful tool for identifying groundwater contaminated with the landfill leachate (Fig. 3).

2.3 Other methods

Many approaches have been used to assess the contamination of groundwater. Other tools to detect contamination

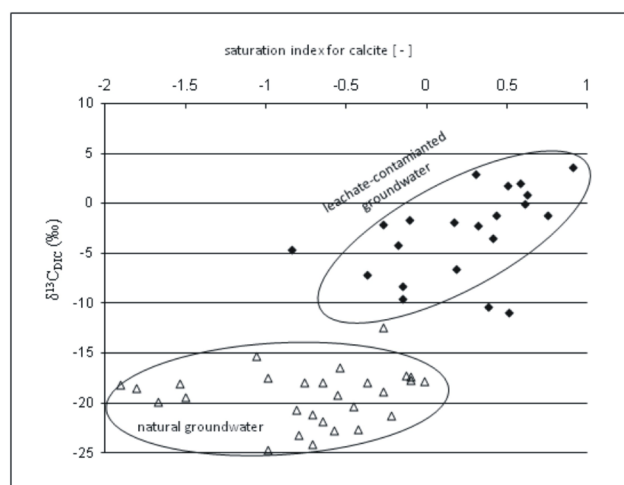


Fig. 3 Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and saturation index for calcite

around landfills (without the physicochemical and isotopic analysis of the water) are offered by geophysical methods (e.g. electrical resistivity tomography) [43–45]. The advantage of using geophysical methods is their ability to determine the extension of the leachate plume and its spatial variation, not a point variation. The best way to define the shape of the leachate contamination plume is a comparison of the information gained from geophysical measurements and hydrogeological modeling of the contaminated sites [46–48]. Two different geophysical techniques, a crosshole and multichannel analysis of surface waves, were applied by Abreu et al. [49] to investigate the properties of municipal solid waste and characterize a sanitary landfill.

3 Methodology

3.1 Theoretical considerations

An analysis of the results of not common laboratory experiments demonstrated that the theoretical basis of the used methodology needs to be clarified. Theoretical considerations, such as the mechanism of carbonate precipitation and the kinetic isotope effect were described by Chacko et al. [50] and Kim et al. [51]. There are many techniques for determining the carbon isotope composition of water samples [52–55] and water oxygen levels [56]. Of the four methods proposed by Atekwana and Krishnamurthy [57] for determination of the carbon isotope composition, the method of precipitation was chosen (Fig. 4). In this method, DIC is precipitated as carbonate (BaCO_3 or SrCO_3) by adding BaCl_2 or SrCl_2 to the sample and controlling pH with alkaline reagents. In this study SrCO_3 was precipitated from the solution. The precipitated carbonate was filtered and reacted with acid (usually H_3PO_4) to release CO_2 under a vacuum system. Apart from measuring the

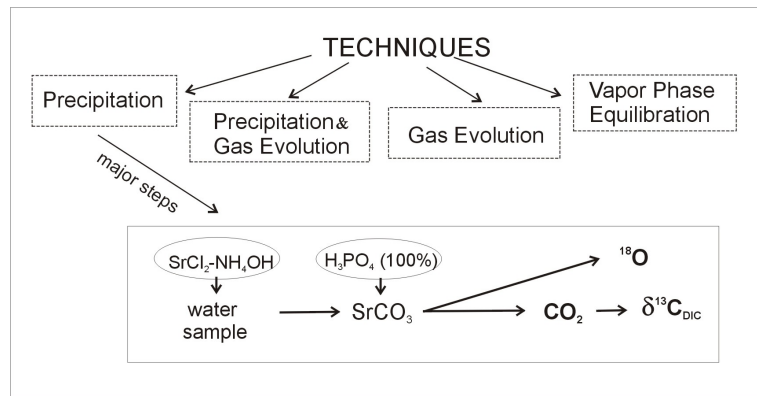


Fig. 4 Techniques and major steps involved in measurement of $\delta^{13}\text{C}_{\text{DIC}}$

isotopic composition of carbon, the isotopic composition of oxygen was also assessed in the evolved CO_2 .

Despite promising results, this method requires the precipitation technique for determination of the isotopic composition of carbon and oxygen. Currently other methods, such as gas evolution or vapor phase equilibration are also widely used [e.g. 52].

According to Szynekiewicz et al. [58], co-precipitation of other chemicals, as well as interaction of DIC with other substances dissolved in water may occur. To check for possible co-precipitation of other chemical compounds in the analyzed groundwater, selected sediment samples were subjected to X-Ray diffraction spectrometry at the Central Chemical Laboratory of the Polish Geological Institute – National Research Institute in Warsaw, and their content of carbon compounds was determined. The analysis showed that strontium carbonate (SrCO_3) was the only crystalline phase in the sediment, and one of the examples is shown in Fig. 5. Therefore the adopted methodology of carbon isotope determination in this aspect does not raise any objections.

Carbonates from the groundwater contaminated with the landfill leachate resulting from precipitation method used for carbon isotope measurement are the basis of the adopted research method.

3.2 Sampling and analytical procedures

Groundwater samples around the Otwock landfill (Poland) were collected in order to identify the suitable tracers and develop a convenient technique for monitoring groundwater contamination from the landfill leachate. To identify the zone of leachate-contaminated groundwater, the samples for chemical analysis were collected from similar depth of 3.8 to 4.8 m below ground level (bgl), using the same research equipment and analytical procedures. The groundwater table position depended on the study site and

it ranged from ~1.5 m bgl to ~2.7 m bgl. The sampling points were thoroughly selected on the basis of archival data on water chemistry from piezometers located around the landfill (along the main groundwater flow direction and above the landfill) [8, 9]. The measurements of carbon and oxygen isotopes were performed for 22 sampling points (14 in the area considered natural condition and 8 in the leachate-contaminated area). In the field, unfiltered samples of groundwater from the aquifer were collected into 1000 ml glass bottles and were poisoned with $\text{SrCl}_2\text{-NH}_4\text{OH}$. The water collected and analyzed for carbon isotopes was treated as described by Gleason et al. [59], Kusakabe [53], and Atekwana and Krishnamurthy [57]. The samples were acidified with phosphoric acid at 70 °C. The $^{13}\text{C}/^{12}\text{C}$ ratios of the resulting CO_2 were determined using a Finnigan MAT Delta+ mass spectrometer at the Isotope Dating and Environment Research Laboratory of the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. International standard NBS 19 was analyzed per every ten samples. The resulting values were expressed with reference to the VPDB standard. The difference in the ratio of the sample compared and with the standard was expressed as a δ value (Eq. (1)). The associated $^{18}\text{O}/^{16}\text{O}_{\text{DIC}}$ was reported with the δ notation, with respect to the SMOW international standard (Eq. (2)).

$$\delta^{13}\text{C} = \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}} - ^{13}\text{C}/^{12}\text{C}_{\text{standard}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} \times 1000 \quad (1)$$

$$\delta^{18}\text{O} = \frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{standard}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} \times 1000 \quad (2)$$

Accuracy of the measurement standard deviation is as follows: $(1 \sigma) \delta^{13}\text{C} \pm 0.03\%$ and $(1 \sigma) \delta^{18}\text{O} \pm 0.07\%$.

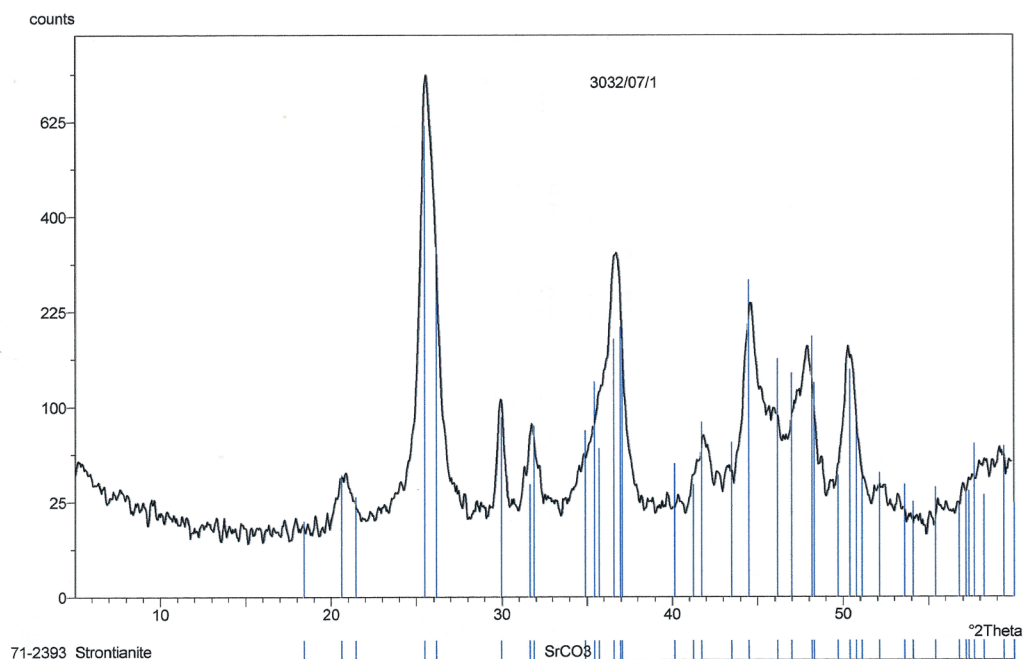


Fig. 5 Example X-Ray diffraction pattern of the selected sample

4 Results and discussion

Using the precipitation technique, the carbon and oxygen isotope composition were determined and the relations between them were assessed. Based on the proposed method, two zones with different isotope composition of groundwater were identified: a zone with natural groundwater, characterized by low $\delta^{13}\text{C}_{\text{DIC}}$ values (from -20.6 to -12.4 ‰) and high $\delta^{18}\text{O}$ values (from -13.6 to -8.0 ‰), and a zone with leachate-contaminated groundwater, characterized by both high values of $\delta^{13}\text{C}_{\text{DIC}}$ (from -10.9 to $+3.6$ ‰) and high values of $\delta^{18}\text{O}$ (from -9.8 to -7.1 ‰) (Fig. 6).

The comparison of the carbon and oxygen isotope composition in natural groundwater and in leachate-contaminated groundwater shows a significant differentiation of the carbon isotope composition, with a partially similar oxygen isotope composition. In order to explain the differences in the isotopic composition of carbon, it is necessary to consider the sources of carbon and the processes that take place in this environment. According to our previous study [8], the isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) in the natural groundwater in the analyzed areas has two sources: decomposition of organic matter and carbonate dissolution within the aquifer sediments, whereas in the leachate-contaminated groundwater, $\delta^{13}\text{C}_{\text{DIC}}$ values depend on the degradation of organic matter within the aquifer sediments and biodegradation of organic matter stored in the landfill under anaerobic conditions.

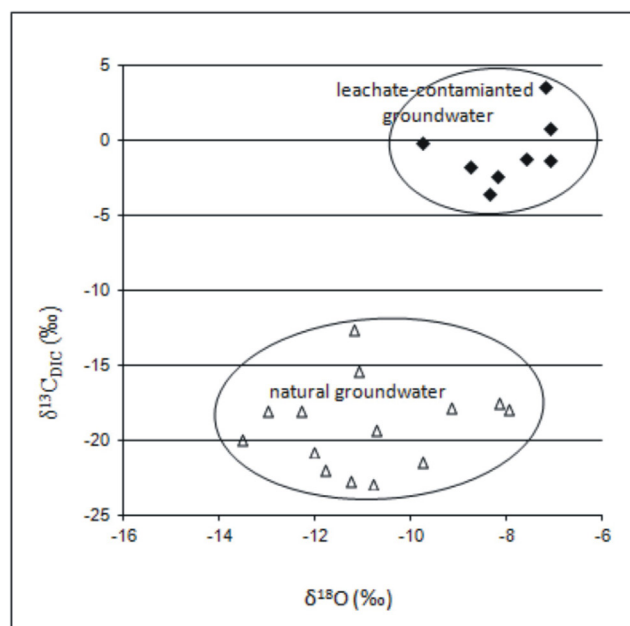
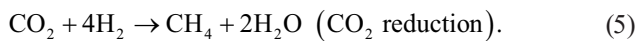
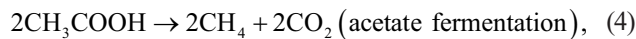


Fig. 6 Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}$

Assuming that in natural conditions the $\delta^{13}\text{C}_{\text{DIC}}$, released during decomposition of organic matter in the aquifer sediments was about -28 ‰ [60], and the $\delta^{13}\text{C}_{\text{DIC}}$ of carbonates was about -11.85 ‰, depending on the intensity of biogeochemical processes, it is possible that $\delta^{13}\text{C}_{\text{DIC}}$ values in natural groundwater range from -20.6 to -12.4 ‰. Such $\delta^{13}\text{C}_{\text{DIC}}$ values are typical for the natural groundwater and were similar to many cases described

in the literature [e.g., 57, 61, 62]. In leachate-contaminated areas, the amount of $\delta^{13}\text{C}_{\text{DIC}}$ released during decomposition of organic matter in the aquifer sediments was similar (about -28) whereas the $\delta^{13}\text{C}_{\text{DIC}}$ of organic matter stored in the landfill may reach up to $+38\%$ [41].

Groundwater contamination with leachate enriched with $\delta^{13}\text{C}$, depends on many processes but mainly on mixing natural water with the leachate within the aquifer. Leachate contains carbon from methane and carbon dioxide produced under anoxic environment by microorganisms (methanogens), which prefer to use the "lighter" molecule in metabolic pathways, according to the reactions shown below [55]:



The microorganisms tend to react more rapidly with "lighter" isotopes (^{12}C) of CH_4 leaving the "heavier" isotope (^{13}C) in the leachate. Methane produced during acetate fermentation (Eq. (4)) and CO_2 reduction (Eq. (5)) is isotopically depleted in ^{13}C , whereas carbon dioxide is isotopically enriched with ^{13}C (Fig. 7).

The isotopic composition of carbon in methane ($\delta^{13}\text{C}_{\text{CH}_4}$) ranges from -65 to -47% [62–66], and the values of $\delta^{13}\text{C}_{\text{CO}_2}$

in carbon dioxide generated in the reducing environment may be as high as $+20\%$ [67], but they are often positive.

It has been observed that methanogenesis does not affect the ^{18}O isotopic composition. This is because $\delta^{18}\text{O}$ isotope fractionation is only influenced by phase changes, such as evaporation and condensation, but is unaffected by biogeochemical reactions and transpiration [55]. Other studies confirm that methanogenesis does not affect the ^{18}O isotopic composition [7].

Summing up, the stated differentiation of carbon results from the microbial predisposition to use isotopically lighter particles in their vital processes, while the differences in the oxygen isotope composition result from increased evaporation. Carbon and oxygen isotope compositions indicate that carbon is derived mainly from the residual CO_2 after methanogenesis, and oxygen is predominantly derived from meteoric waters.

Measurements of the isotopic composition of oxygen alone, due to their partial overlap with natural values and those indicating groundwater contaminated with leachates, do not allow for unambiguous determination of the zones contaminated with leachate, but these data, combined with the isotopic composition of carbon, provide unambiguous results (Fig. 6).

As $\delta^{13}\text{C}$ content is elevated during methanogenesis but methanogenesis has no effect on $\delta^{18}\text{O}$ these parameters can be effectively combined to determine the leachate sources.

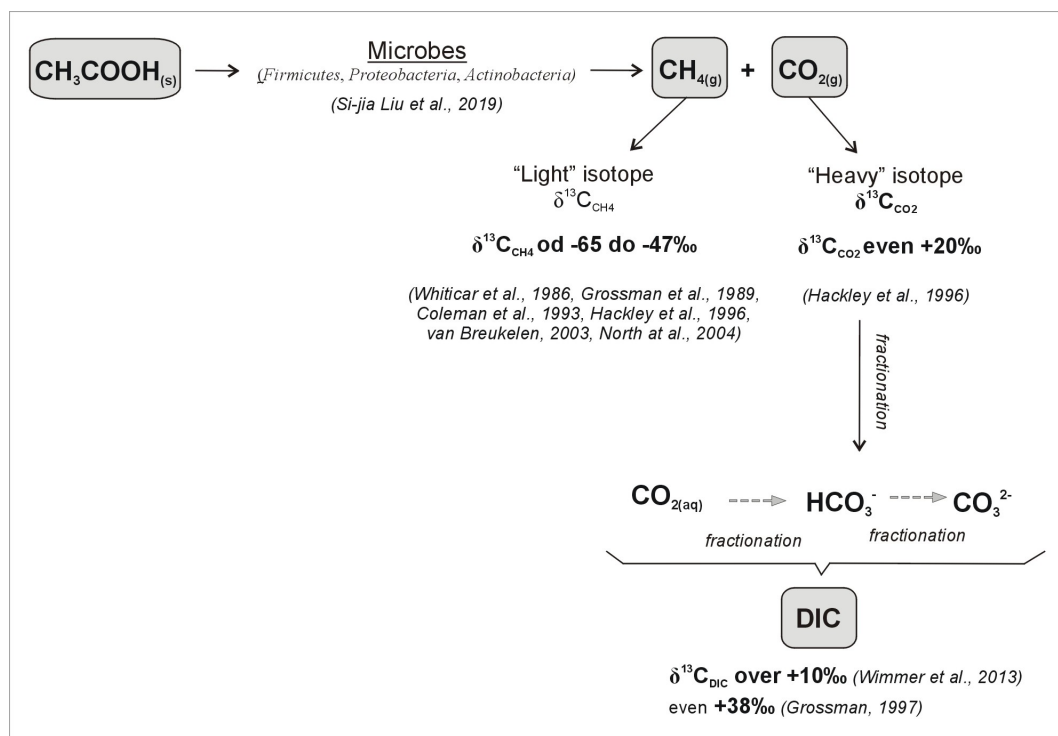


Fig. 7 A scheme of acetate fermentation in a landfill [41, 62–68]

Coupling the data on stable $\delta^{13}\text{C}$ isotopes with those on $\delta^{18}\text{O}$ has proved to be an effective tool for the assessment of groundwater contamination in the vicinity of municipal waste landfills.

5 Conclusion

The evaluation of groundwater quality near landfills should be an essential part of landfill management due to the possible risk to the natural environment over a large area. Reliable assessment of groundwater contamination around the landfill is essential for land development in the post-exploitation phase of the landfill. Landfills are important and difficult issues in terms of assessing their environmental impact and should be treated individually, with a specifically dedicated scope of research. Due to the specificity of a landfill (size, type of waste, age, climatic and hydrogeological conditions), and the need to adapt to individual cases, any method of contamination detection is valuable. The method tested at the landfill in Otwock yields reliable results and does not require additional field works apart from isotopic determinations of oxygen in the laboratory. Sample preparation is performed simultaneously with carbon isotope determinations. Determination of $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}$ can provide a powerful tool to identify the zone with natural and leachate-contaminated groundwater. Based on this method, it was stated that natural groundwater is characterized with low $\delta^{13}\text{C}_{\text{DIC}}$ values and high $\delta^{18}\text{O}$ values, whereas the leachate-contaminated groundwater is characterized with high values of $\delta^{13}\text{C}_{\text{DIC}}$ and high values of $\delta^{18}\text{O}$. In the study area these values were as follows: in natural groundwater $\delta^{13}\text{C}_{\text{DIC}}$ ranged from -13.6 to -8.0‰ , and $\delta^{18}\text{O}$ from -13.6 to -8.0‰ , and in the leachate-contaminated groundwater $\delta^{13}\text{C}_{\text{DIC}}$ ranged from -10.9 to $+3.6\text{‰}$ and $\delta^{18}\text{O}$ from -9.8 to -7.1‰ .

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The performed analysis showed that assessing the relationship between the measured $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{18}\text{O}$, as well as $\delta^{13}\text{C}_{\text{DIC}}$ and other parameters, such as:

1. calculated $\delta^{13}\text{C}_{\text{DIC}}$,
2. dissolved inorganic carbon concentration,
3. saturation indices with respect to carbonates is an appropriate method to detect groundwater contamination in the vicinity of municipal landfills and also suitable for other areas contaminated with organic compounds.

The outcomes based on the oxygen and carbon isotope measurements were consistent with those based on other methods, which confirms their usefulness for detecting groundwater contamination. The advantages of the proposed method, as compared with other solutions currently used to determine the area of contaminated groundwater are:

1. unambiguous identification of the piezometers with leachate-contaminated groundwater,
2. no additional field work,
3. no additional cost,
4. easy to implementation,
5. low number of samples collected for the analysis of conventional parameters,
6. suitability for wider use in another leachate contaminated area.

The study demonstrated that this kind of measurement provides additional information to get a detailed picture of the environmental state around landfill areas, and can be recommended in research on the migration of organic pollutants in the aquifer.

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