Application of $^2$H and $^{18}$O Isotopes for Tracing Municipal Solid Waste Landfill Contamination of Groundwater: Two Italian Case Histories

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Abstract: Groundwater contamination due to municipal solid waste landfills leachate is a serious environmental threat. During recent years, the use of stable isotopes as environmental tracers to identify groundwater contamination phenomena has found application to environmental engineering. Deuterium ($^2$H) and oxygen ($^{18}$O) isotopes have successfully used to identify groundwater contamination phenomena if submitted to interactions with municipal solid waste landfills leachate, with a significant organic amount. The paper shows two case studies, in central and southern Italy, where potential contamination phenomenon of groundwater under municipal solid waste landfills occurred. In both cases, isotope compositions referred to $^2$H and $^{18}$O highlight a $\delta^2$H enrichment for some groundwater samples taken in wells, located near leachate storage wells. The $\delta^2$H enrichment is probably caused by methanogenesis phenomena, during which the bacteria use preferentially the hydrogen “lighter” isotope ($^1$H), and the remaining enriched the “heavier” isotope ($^2$H). The study of the isotope composition variation, combined with the spatial trend of some analytes (Fe, Mn, Ni) concentrations, allowed to identify interaction phenomena between the municipal solid waste landfills leachate and groundwater in both case histories. Therefore, these results confirm the effectiveness of $^2$H isotopes application as environmental tracer of groundwater contamination phenomena due to mixing with municipal solid waste landfills leachate.

Keywords: environmental isotope; $\delta^2$H; municipal solid waste; leachate contamination; natural tracers

1. Introduction

Municipal solid waste landfills leachate can cause serious environmental problems for groundwater quality, due to the organic and inorganic pollutants of the leachate plumes [1]. Landfill leachate is defined as a liquid effluent containing contamination materials percolating through deposited waste and released within a landfill [2]. It is one of the most complex waste liquids to manage because it contains many organic and inorganic compounds such as nutrients, chlorinated organics, dissolved organic matter, inorganic compounds (e.g., ammonium, calcium, magnesium, sodium, potassium, iron, sulfates, chlorides) and heavy metals (e.g., cadmium, chromium, copper, lead, zinc, nickel) [3–7]. In fact, leachate coming from biological and physico-chemical decomposition of waste can cause damage to the environment when it percolates to the surrounding groundwater and stream water systems [3,7,8]. The leachate composition, in terms of chemical and microbiological matters, varies among different landfill types and depends on the characteristics of the solid wastes, age of the landfill, climate, environmental conditions, landfill operational mode and decomposition mechanism of the organic matter [3,7,9,10]. The spatial distribution and variation of the landfill leachate depend on the nature and partitioning of the waste properties (contouring degree and solid wastes compacting), moisture content, temperature, pH, oxygen level, microbial activity, groundwater inflow, surface water runoff, local rainfall regime,
hydrogeological settings and characteristics of landfill (age, design, such as size, depth and lining system) [6].

Generally, waste decomposing processes by bacteria in landfill involve four stages: (i) hydrolysis, (ii) acid fermentation, (iii) acetogenesis and methanogenesis and (iv) settlement phase. This entire system is dynamic, and every phase create a suitable environment by the preceding stage, leading directly towards the gas and leachate production [6,11]. The first phase of waste decomposition depends on the oxygen amount of organic matter and this phase continue until the available oxygen is deplete. This phase is followed by reactions such as oxidation, hydrolysis and anaerobic acidification. In particular, the third phase, acetogenesis and methanogenesis, produces a decrease in acetic acid (CH₃COOH) and determines the production of methane (CH₄) and carbon dioxide (CO₂). CH₄ and CO₂ are the major landfill gases and their formation is influenced by bacterial decomposition, waste composition, organic matter availability, moisture content, pH, temperature and possible chemical reactions in landfill [7,11].

Therefore, it is fundamental the assessment of environmental risks associated with landfill leachate going to water resources, specially to groundwater. These phenomena need environmental monitoring programs that have to detect the potential leachate influence in groundwater near to the landfill area. The monitoring is important for the leachate characterization and to avoid or mitigate environmental damages [12]. Several studies [1,7,8,13–16] have proposed multidisciplinary approaches to supply information about landfill environmental impacts. In order to assess the landfill leachate environmental impact, in addition to conventional parameters such as total dissolved solids (TDS), total suspended solids (TSS), hardness, alkalinity, chloride, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), and common inorganic ions, the use of additional tools such as stable isotopes can provide more information.

Generally, environmental tracers can be defined as physical properties and chemical components of water, whose spatial and temporal differentiation can be used to give information about pathways and dynamics of water through the environment [17]. The feature of environmental tracers (physical, chemical and isotopic) is that they are part of environmental e not must be artificially introduced [18]. The traditional isotope ratios of hydrogen (²H) and oxygen (¹⁸O) are recognizable tracers related to the water cycle and have widely used in hydrology [19]. In particular, the ²H and ¹⁸O isotopes are used in environmental hydrogeology not only because they are the main constituents of the water molecule but, also, they are stable isotopes with a nuclear composition not changed over time.

However, they can be subjected to isotopic fractionation phenomena. The isotopic fractionation is defined as the partitioning of heavy isotopes versus light isotopes in exchange reactions. This phenomenon will be more evident if the mass difference between the isotopes is sensitive. In environmental hydrogeology, evaporation and condensation processes highly influence the isotopic content: the “lighter” molecules tend to evaporate more quickly than the “heavier” ones. Instead, the opposite phenomenon is noted during the condensation processes [20–23].

Several studies [4,8,15,22] have observed that stable isotopes by landfill leachates, such as δ¹³C, δ²H and δ¹⁸O, are influenced by processes within municipal solid waste (MSW) landfills, mainly on methanogenesis phase of the landfill. Landfill gases (CO₂ and CH₄) and landfill leached products (water and inorganic carbon) have a characteristic isotopic, in terms of δ²H e δ¹⁸O, respect to the surrounding environment [24,25].

Methanogenesis is the process that determines the production of methane (CH₄) and carbon dioxide (CO₂) in a landfill by some microorganisms, known as methanogens. They, under anaerobic conditions, use organic and inorganic compounds to produce CH₄ and CO₂ [26–28]. The first two phases of the waste decomposing processes, hydrolysis and acid fermentation, cause a substantial reduction in the oxygen quantity in the landfill [11]. It is necessary to consider that isotope fractionation is a phenomenon strongly influenced by state change, such as condensation and evaporation processes [20–23]. Therefore, the changes in oxygen quantity due to hydrolysis and acid fermentation processes may not
necessarily cause also variations in the 18-oxygen isotopic content. However, there aren’t yet solidified scientific results that allow to prove the hydrolysis and acid fermentation influence on the isotopic content, in terms of δ²H e δ¹⁸O. On the contrary, several studies [29–31] have shown that the methanogenesis phase is the cause of the enrichment of the dissolved inorganic carbon (δ¹³C) and hydrogen (δ²H) stable isotopes in the leachate.

During the oxidation of the organic substance under anoxic environment, the methanogens can follow two metabolic pathways, are shown below [32]:

i. \[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \ (\text{CO}_2 \text{ reduction}); \]

ii. \[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \ (\text{acetate fermentation}). \]

In case of CO₂ reduction (i), microorganisms first use the “lighter” molecule of carbon dioxide (¹²C) to produce CH₄, leaving the remaining CO₂ enriched in the “heavier” one (¹³C). When acetate fermentation occurs (ii), CH₄ produced by the reaction is isotopically depleted in ¹³C, and, on the contrary, CO₂ produced by the reaction (ii) is isotopically enriched in ¹³C [23,32]. During the acetate fermentation process (ii), the hydrogen comes partly (¾) from CH₃COOH and partly (¾) from water present in the leachate. On the contrary, during CO₂ reduction process (i), the hydrogen is assumed to come completely from leaching water and therefore water is significantly more enriched in the “heavier” isotopes (²H). Therefore, isotopic fractionation occurring is due to the preferential use of “lighter” hydrogen (¹H) isotope with the gas phase, CH₄, leaving the “heavier” isotope (²H) in the liquid phase [8]. Due to the methane production, δ²H ratios can be located outside of the traditional ranges associated with natural waters of direct meteoric origin meteoric water line, undergoing a shift to positive range. The δ²H enrichment in groundwater surrounding landfill sites can be used as an indicator of leachate migration from landfill to groundwater and other activities near the study area [22].

Moreover, studies [2,15,24] have demonstrated that the landfill leachate is highly enriched in δ²H respect to local average precipitation values (by δ²H: +30‰ to 60‰) due to the production of microbial methane within the reservoir of a landfill. Another factor that can determine the variation of δ²H content in the leachate produced by landfills is the alternation between dry and wet seasons. Some studies [8] have also shown that δ²H in leachate is equal to +16‰ in dry season and +6‰ in wet season. This variation between dry and wet seasons is plausibly caused by the rainwater dilution, making less evident the isotopic signature of leachate [8]. On the contrary, it has also been observed that methanogenesis does not affect the ¹⁸O isotopic composition [8,33]. Studies highlight [24,34] that ¹⁸O isotopic composition variations in leachate are due to seasonal variations of precipitation, reflecting a rapid movement of water through the pile with minimal storage in the waste. In fact, Hackley et al. (1996) [24] have showed that δ¹⁸O was depleted in seepage water, related to local precipitation value (by δ¹⁸O: −1‰ to −3‰) [15].

However, the degradation of organic matter is not constant, during the landfill operational time. In fact, the burial of wastes in a landfill has been developed, depending on some complex series of chemical and biological reactions. During the methanogenesis, the accumulated acids are converted to CH₄ and CO₂ by bacteria, and the methane production rate will increase. During this phase, the methane production rate will reach its maximum, and decrease thereafter as the pool of soluble substrate (carboxylic acids) decreases [35,36]. Therefore, this behavior could affect the ²H isotopic contents, but, on the contrary, it doesn’t involve ¹⁸O, at all. Despite experimental results [37] showing that the δ²H isotopic content increases continuously from the waste deposition [15], even if there aren’t yet consolidated scientific results that can confirm this phenomenon.

This paper purpose is to show the effectiveness of the application of the hydrogen (²H) as tracer of the leachate presence in groundwater near to municipal solid waste landfills, when it is present a significant organic amount. As a matter of fact, here it is shown as the leachate presence in groundwater can influence δ²H ratios without determining an δ¹⁸O enrichment. Two case studies are presented: the former in Sardinia, southern Italy, and the latter in Umbria, central Italy. The two case histories show how the use of the hydrogen
(δ²H) and oxygen (δ¹⁸O) isotopes, combined with other investigation tools, can highlight leachate contamination phenomena in groundwater.

2. Geological and Hydrogeological Setting

2.1. Case History I in Sardinia (Southern Italy)

The study area is located in Sardinia, in the province of Cagliari, on the border between two different municipalities (Figure 1). The landfill plant is part of a complex geological setting, characterized by the presence of the Nurallao deposits, consisting mainly of sandstones (Serra Longa sandstones) (Geological Map of Sardinia (1:25,000.00)). However, on the north-west side of the plant, it is also possible to check for the presence of alluvial deposits, dates to the Holocene epoch, and the anthropic deposits. The anthropic deposits are from both the landfill and the quarries near the study area.

![Geological Map of Case History I](image_url)

**Figure 1.** Geological (above) and Permeability (below) Map of Case History I.

The geological setting (above in Figure 1) is confirmed by the hydrogeological framework (below in Figure 1), with permeability ranging from medium for fracturing, in correspondence with the Nurallao deposits, up to high levels for porosity, in alluvial deposits, in west part of the study area (Permeability Map of Sardinia (1:25,000.00)).

The study area is characterized by two artesian aquifers, as shown in Figure 2:
- Aquifer 1 (shallow): represented by conglomerates and sand of the Nurallao deposits;
- Aquifer 2 (deep): characterized by conglomerates and gravels of the Nurallao deposits.

Aquifer 1 is represented by conglomerates and sand of the Nurallao deposits, while Aquifer 2 is characterized by conglomerates and gravels of the Nurallao deposits.
Aquifer 2 (deep): characterized by conglomerates and gravels of the Nurallao deposits.

Figure 2. Water table map of Case History I.

The supply area of two aquifers is mainly represented by the fractured schist and granite settings of the Nurallao deposits, which dates to the Miocene epoch. In fact, both aquifers are characterized by a North-East supply, coming from the Miocene sediments of the Nurallao deposits, with groundwater flow direction from east to the west.

The landfill plant covers an area of approximately 0.4 km$^2$ and consists of 6 slots, set up partly for municipal solid waste (MSW) storage and partly for industrial waste one. In Table 1 it is shown the distinction between the slots of landfill plant based on the type of waste stored. Only Slot 6, for industrial wastes, is in operation, while the other slots have been closed.

Table 1. Municipal solid waste (MSW) and industrial waste.

| Municipal Solid Waste (MSW) | Industrial Waste |
|-----------------------------|------------------|
| Slot 2                      | Slot 1           |
| Slot 3                      | Slot 5           |
| Slot 4                      | Slot 6           |

2.2. Case History II in Umbria (Central Italy)

The study area is located in the province of Perugia in Umbria. The area is characterized by a hilly morphology, with altitude ranging between 500 and 600 m a.s.l., and it is located in the upper part of stream basin. Generally, the outcropping deposits are mainly formed by flysh, with marly, arenaceous and calcarenitic layers. By the Geological Map of Italy (scale 1:100,000.00), it is possible to identify the presence of two outcropping deposits (Figure 3):

- Upper sandy conglomerate deposits;
- Marly arenaceous formation.
- Upper sandy conglomerate deposits;
- Marly arenaceous formation.

Figure 3. Geological Setting Case History II.

The marly arenaceous formation outcrops all over the area and is made of marly and arenaceous layers, alternated with clay and limestone lenses. In fact, the landfill substrate consists of flysch with compact marly and arenaceous layers.

The landfill plant, actually in operation, covers an area of approximately 0.12 km$^2$. Moreover, the study area is characterized by a series of marly and arenaceous layers, with low permeability, alternated with limestone lenses which, if fractured, can host suspended aquifers.

3. Material and Methods

In July 2020, eleven samples are collected for Case History I. The samples location is shown in Figure 1. Instead, for Case History II, during groundwater sampling in July 2020, nine samples are collected. Samples location is shown in Figure 3.

Table 2 shows the results of the chemical-physical parameters (pH, Eh, temperature and electrical conductivity), the Iron (Fe) concentrations (Legislative Decree 152/06 threshold equal to 200 µg/L), the Manganese (Mn) concentrations (Legislative Decree 152/06 threshold equal to 50 µg/L), the Nickel (Ni) concentrations (Legislative Decree 152/06 threshold equal to 20 µg/L) and isotopic data ($\delta^2$H and $\delta^{18}$O) for Case History I (Table 2a) and Case History II (Table 2b). All results refer to the July 2020 sampling survey.
Table 2. Summary of chemical-physical parameters, Fe, Mn and Ni concentrations and isotopic data for groundwater and leachate samples: (a) Case History I, (b) Case History II.

### Case History I (July 2020)

| Samples | pH | T  | Eh  | Electric Conductivity | Fe  | Mn  | Ni  | δ²H—1‰ (VSMOW) | δ¹⁸O—0.05‰ (VSMOW) |
|---------|----|----|-----|-----------------------|-----|-----|-----|----------------|-------------------|
| P1      | 6.91 | 32.07 | 107.6 | 6127 | 18.2 | 197 | 11.5 | −32          | −5.86             |
| P3      | 7.45 | 21.61 | 65.8  | 1100 | 8.7  | 1.3 | 1.7  | −36          | −6.37             |
| P4      | 7.25 | 22.26 | 113.5 | 2228 | 3    | 1.3 | 1.6  | −33          | −5.82             |
| P5      | 7.38 | 24.22 | −104.7 | 1487 | 10.9 | 85.9 | 1.6  | −35          | −6.23             |
| P12     | 6.48 | 26.66 | 50.1  | 3396 | 89   | 1271 | 53.9 | −31          | −6.13             |
| P12BIS  | 6.96 | 28.14 | −171.7 | 8020 | 8022 | 2941 | 221  | −18          | −6.03             |
| Slot 1  | na  | na  | na   | na   | na   | na  | na   | −16          | −2.65             |
| Slot 2  | na  | na  | na   | na   | na   | na  | na   | −8           | −6.36             |
| Slot 6  | na  | na  | na   | na   | 100  | 26  | 28   | −11          | −1.91             |

For Case History I, the Table 2a shows eight groundwater samples (identified by “P”) and three samples by leachate tanks (identified by “Leach_Slot”). The samples with the same number, but “bis”, are in the same point, but they track the shallowest aquifer. Instead, for Case History II, the Table 2b shows five groundwater samples (identified by “P” and “PM”), two samples by leachate tanks (identified by “PE”) and two drainage water samples (identified by “AD”). In fact, to drain enough the landfill infiltration water, a series of sub-horizontal drains have been drilled on the embankment downstream of the landfill.

Concentrations of minor elements (Fe, Mn and Ni) were measured using an ICP-MS by a certified (Accredia) Italian laboratory. The analytical accuracy of these methods is equal to 5%. Ultrapure water (Millipore, Milli-Q, 16 MΩ cm) was used in preparing blanks, standard solutions, and sample dilutions.

The δ²H and δ¹⁸O contents of groundwater and leachate samples were analyzed by the Isotope Geochemistry Laboratory of the University of Parma (Italy) using the IRMS (isotope-ratio mass spectrometry) continuous flow-equilibration method with CO₂.
Isotopic abundance ratios are expressed as parts per million of their deviations, as given by the Vienna Standard Mean Ocean Water (VSMOW) (Equation (1)) [38]:

$$\delta = \left( \frac{R_{\text{sample}}}{R_{\text{SMOW}}} - 1 \right) \times 10^3$$

(1)

where:

- $R_{\text{sample}}$ is the abundance ratio of the isotopic species, respectively $^2\text{H}/^1\text{H}$ for hydrogen and $^{18}\text{O}/^{16}\text{O}$ for oxygen, for each sample;
- $R_{\text{SMOW}}$ is the isotopic ratio of the standard (Standard Mean Ocean Water), accepted for the isotopes in water [39].

The analytical error is 0.05‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$.

4. Results and Discussion

Several studies [14,29–31] have highlighted how methanogenesis processes can affect leachate enrichment in $\delta^2\text{H}$. As a matter of fact, the methanogenic bacteria, during the methane production, use first the “lighter” isotope of hydrogen ($^1\text{H}$), therefore leaving enriched the “heavier” isotope of hydrogen in leachate ($^2\text{H}$) [8,22,23,32].

This paper is referred to two case histories in Italy, dealing with groundwater interaction with leachate from municipal solid waste landfills. The aim is to show how the $^2\text{H}$ enrichment is an index of the groundwater contamination, due to interaction with leachate in some piezometers.

Isotope composition data, reported in Table 2, have been graphed with the main isotope diagrams. For a suitable assessment, the isotope composition data for both history cases are compared with the main meteoric lines:

- Global Meteoric Water Line (GMWL) [39], described by Equation (2):

$$\delta^2\text{H} = 8 \delta^{18}\text{O}‰ + 10$$

(2)

- Mediterranean Meteoric Water Line (MMWL) [40,41], defined as follow (Equation (3)):

$$\delta^2\text{H} = 8 \delta^{18}\text{O}‰ + 22$$

(3)

The deviation from meteoric lines, GMWL (Equation (2)) and MMWL (Equation (3)), shows alteration phenomena due to processes occurred in the soil: mixing with marine waters of ancient or recent origin or contamination fluids leaching from soil to groundwater. In particular, the variation by meteoric lines highlights mixing phenomena of groundwater with leachate, coming from landfills of municipal solid waste consisting of a significant organic part.

4.1. Case History I in Sardinia (Southern Italy)

Figure 4 shows deuterium $\delta^2\text{H}$ and oxygen $\delta^{18}\text{O}$ isotope composition for groundwater sampled under Sardinia landfill site (Table 2a). The Figure 4 shows also the GMWL (Equation (2)), MMWL (Equation (3)) and Local Meteoric Water Line (LMWL) for southern Italy [42], described by Equation (4):

$$\delta^2\text{H} = 6.94 \delta^{18}\text{O}‰ \ (\pm 0.45) + 6.41 \mid (\pm 2.65)‰$$

(4)
Figure 4. δ²H vs. δ¹⁸O values for Case History I: all samples (a) and Slot 2 & P12bis (b).

In addition, the Capo Caccia gauge station, located north-west of the plant (Figure 1), is identified and the isotope data δ¹⁸O e δ²H, there sampled, and analyzed by the International Atomic Energy Agency (IAEA), is reported in Figure 4. This figure shows that samples coming from Capo Caccia station are very close to the LMWL, proposed by Giustini et al., 2016 [42] for southern Italy and identified by Equation (4), which, as a consequence of it, is a good reference of isotope composition for precipitations in this area.

The isotope diagram in Figure 4a represents that the groundwater sampled in P1, P3, P4, P5, P12, P13 and P13bis is very close to meteoric lines, showing they are groundwater completely belonging to the natural hydrological cycle. In contrast, samples coming from leachate collecting tanks, located downstream of Slot 1 and Slot 6, used for the storage of industrial waste, are below the range of the reference meteoric lines. Therefore, it is possible to say that the variation of the isotope composition for deuterium δ²H and oxygen δ¹⁸O is not influenced by contamination of the leachate, as they come from industrial waste storage. On the contrary, the sample coming from the leachate collecting tank downstream Slot 2 presents anomalous values, equal to −8‰ for δ²H and −6.36‰ for δ¹⁸O, positioning itself in the isotope diagram, beyond the reference meteoric lines (Figure 4b). Slot 2 has been used for the municipal solid waste storage, which were enriched by organic component (Table 1). In particular, the isotope enrichment in deuterium δ²H content (−8‰) for leachate well downstream of Slot 2, seems to be linked with methanogenesis phenomena. As a matter of fact, in municipal solid waste landfills, where the organic part in wastes is significant, the methanogenic bacteria use, preferentially, the “lighter” isotope hydrogen (¹H) due to the methane production. Therefore, the remaining hydrogen is enriched in deuterium (²H), the “heavier” isotope [8,22]. The P12bis groundwater sample presents, as well, anomalous value for δ²H (−18‰), and it is placed in the diagram close to the sample taken downstream of Slot 2 (Figure 4b). These results show contamination phenomena for groundwater sampled in P12bis point due to the mixing with leachate from Slot 2 and sampled in the collecting tank located downstream of it. The ²H enrichment for P12bis point, due to interaction with the leachate by collection tank downstream of lot 2, does not cause an equal ¹⁸O enrichment (−6.03‰). This is due to methanogenesis phenomena,
during which bacteria use the “lighter” isotope hydrogen ($^1$H), than the remaining the “heavier” isotope ($^2$H), which doesn’t involve oxygen [8,22].

Isotope composition results, which show anomalies for the P12bis sample, are confirmed by the concentrations of some analytes, such as iron, manganese and nickel, whose spatial trends are represented in Figure 5.

Figure 5. Cont.
Figure 5 shows high values from upstream to downstream of the plant, especially for the P12bis piezometer. In particular, there are concentrations equal to 8022 μg/L for Iron (Figure 5a), 2941 μg/L for Manganese (Figure 5b) and 221 μg/L for Nickel (Figure 5c), significantly higher than the threshold by Legislative Decree 152/06. Figure 5 shows very high concentrations, sometimes higher than the Legislative Decree 152/06 threshold for the Iron (200 μg/L), Manganese (50 μg/L) and Nickel (20 μg/L), also in P12, P13 and P13b is groundwater samples. This behavior is not detected by the isotope diagram in Figure 5, which is however a good indicator to verify possible interactions between groundwater and leachate.

The Pearson correlation matrix (Table 3) is used to determine the relationship between isotopic composition (δ²H and δ¹⁸O) and iron, manganese and nickel concentrations. The correlation is considered significant if greater than 0.5 [4].

|     | pH  | T   | Eh  | Fe   | Mn   | Ni   | δ²H  | δ¹⁸O |
|-----|-----|-----|-----|------|------|------|------|------|
| pH  | 1   | 1   | 1   | 1    | 1    | 1    | 1    | 1    |
| T   | −0.567 | 1   |     |      |      |      |      |      |
| Eh  | −0.194 | 0.018 | 1   |      |      |      |      |      |
| Fe  | −0.078 | 0.197 | −0.753 | 1   |      |      |      |      |
| Mn  | −0.393 | 0.286 | −0.692 | 0.919 | 1    |      |      |      |
| Ni  | −0.274 | 0.544 | −0.260 | 0.500 | 0.515 | 1    |      |      |
| δ²H | −0.428 | 0.504 | −0.451 | 0.836 | 0.833 | 0.791 | 1    | 1    |
| δ¹⁸O| −0.433 | 0.444 | 0.463 | −0.047 | −0.077 | 0.214 | 0.352 | 1    |

The Pearson correlation matrix in Table 3 does not consider the sampling points by the leachate collection tanks because the data are incomplete (Table 2a). Pearson matrix shows high correlations between δ²H and Fe (0.836), Mn (0.833) and Ni (0.791). On the contrary, Table 3 highlights fair correlations between δ¹⁸O and Fe (−0.047), Mn (−0.077)
and a moderate correlation with Ni (0.214). In fact, some scatter plots are graphed in Figure 6.

Figure 6. Scatter plot (a) Fe and δ²H, (b) Fe and δ¹⁸O, (c) Mn and δ²H, (d) Mn and δ¹⁸O, (e) Ni and δ²H and (f) Ni and δ¹⁸O.

Figure 6 supports what it is showed in isotope diagram of Figure 4, as it presents not only values over the legal threshold for Iron (Figure 6a), Manganese (Figure 6c) and Nickel (Figure 6e) in P12bis groundwater sample, but also a δ²H enrichment. Other groundwater samples, such as P12, P13 and P13bis, have concentrations above the legal threshold,
as already showed in Figure 5, without however having a $\delta^2$H enrichment. As regards the relationships between $\delta^{18}$O and concentrations of Iron (Figure 6b), Manganese (Figure 6d) and Nickel (Figure 6e), no enrichments are highlighted. Nevertheless, the Legislative Decree 152/06 thresholds are over for three analytes in P12, P12bis, P13 and P13bis points. The leachate sampled in Slot 6, used for the industrial waste storage, shows different behavior for the three analytes in relation to $\delta^2$H and $\delta^{18}$O, confirming different sources of water, with respect to the groundwater samples. Therefore, this processing confirms that the methanogenesis phenomena cause a deuterium enrichment, due to bacteria use the “lighter” isotope hydrogen ($^1$H), without generating variations for $^{18}$O isotope. Moreover, the presented comparison between $\delta^2$H enrichment and other metals let us outline as, when there is a $\delta^2$H enrichment and one metal high concentration values, these latter values are due to contamination process, and they can’t be referred to a natural background level.

4.2. Case History II in Umbria (Central Italy)

Figure 7 represents isotope composition for deuterium $\delta^2$H and oxygen $\delta^{18}$O referred to the Umbria case history. According to Equation (2) for GMWL and Equation (3) for MMWL, the isotope composition (Table 2b) is graphed with the Local Meteoric Water Line (LMWL) for central Italy [42], described as follow:

$$\delta^2H = 7.46\delta^{18}O‰ (\pm 0.32) + 8.29 (\pm 2.33)‰$$ (5)
which outline $\delta^2$H isotope values respectively equal to $-21\%$ and $-4\%$. PE1 and PE2 have been used to assess the leachate levels of isotopes composition, in fact they confirm a sound enrichment in $\delta^2$H, due to methanogenesis processes. Anomalous behavior has been found for sampling coming from AD16 point, as it presents values equal to $-24\%$ for $\delta^2$H, showing a significant variation upwards respect to the reference meteoric lines (Figure 7b). AD16 is a sub-horizontal drain positioned at the embankment downstream of the landfill and it is near PE1, a tank used for the leachate storage (Figure 3). The $\delta^2$H enrichment for AD16 point, with values equal to $-24\%$, seems to be linked to mixing with leachate coming from solid waste landfill, which can disperse leachate, enriched in the “heavier” isotope [8,22], due to the methanogenesis processes. The results, therefore, prove an interaction between groundwater and leachate in the AD16 drain. As shown for Case History I, the $\delta^2$H enrichment for the AD16 groundwater sample, due to the bacteria during methanogenic processes, does not also induce a $\delta^{18}$O enrichment, with value equal to $-7.5\%$.

The concentrations spatial trend of some analytes was also represented for plant in Perugia: Iron (Figure 8a), Manganese (Figure 8b) and Nickel (Figure 8c).

Figure 8 shows anomalous concentrations for AD16 groundwater sample, higher than Legislative Decree 152/06 threshold values, whose concentrations are equal to 1150 µg/L for Iron, 383 µg/L for Manganese and 105 µg/L for Nickel. These high concentration values confirm results of the $\delta^2$H isotope composition for AD16 groundwater sample, thus highlighting a groundwater contamination phenomenon. Actually, Figure 8 shows elevated values, sometimes higher than the Legislative Decree 152/06 threshold for three analytes, also in AD13 and PM1 groundwater samples. This behavior is not detected by the isotope diagram in Figure 7, which is however a good indicator to verify possible interactions between groundwater and leachate.

![Figure 8. Cont.](image-url)
Figure 8. Concentrations spatial trend for the Case History II: (a) Iron, (b) Manganese, (c) Nickel.
As the Case History I, the Pearson correlation matrix (Table 4) is used to determine the relationship between isotopic composition (δ²H and δ¹⁸O) and Iron, Manganese and Nickel concentrations.

Table 4. Pearson correlation matrix for Case History II (in red fair correlation, in orange moderate correlation and in green high correlation).

|       | pH  | T    | Eh   | Fe   | Mn   | Ni   | δ²H  | δ¹⁸O  |
|-------|-----|------|------|------|------|------|------|-------|
| pH    | 1   | -0.741 | 1    | -0.184 | 0.206 | -0.921 | -0.359 | -0.625 |
| T     |     | 1    |      | -0.230 | 0.709 | -0.841 | -0.732 | -0.374 |
| Eh    |     |      | 1    | -0.184 | 1     | -0.087 | 0.288  | -0.047 |
| Fe    |     |      |      | 0.279 | 0.324 | 0.939 | 0.956  | 0.016  |
| Mn    |     |      |      | 0.324 | 1     | 0.396 | 0.484  | 0.747  |
| Ni    |     |      |      | -0.359 | 0.288 | 0.936 | 0.964  | 0.020  |
| δ²H   |     |      |      | -0.921 | 0.288 | 0.939 | 0.956  | 0.016  |
| δ¹⁸O  |     |      |      | -0.359 | 0.939 | 0.956 | 0.964  | 0.330  |

The Pearson matrix correlation in does not consider the sampling points PE1 and PE2, by the leachate collection tanks, because the data are incomplete (Table 2b). Pearson matrix shows high correlations between δ²H and Fe (0.936) and Mn (0.964) and a moderate correlation between with Ni (0.484). On the contrary, Table 4 indicates fair correlations between δ¹⁸O and Fe (0.016), Mn (0.280) and a high correlation with Ni (0.747).

Figure 9, again, confirms what showed in the isotope diagram of Figure 7, as it shows not only values over the legal threshold for Iron (Figure 9a), Manganese (Figure 9c) and Nickel (Figure 9e) in AD16 groundwater sample, but also a δ²H enrichment. In fact, the AD16 groundwater sample shows trends closer to the sample by PE1, a tank used for the leachate storage. In fact, the leachate samples coming from points PE1 and PE2 show different behavior with respect to the groundwater samples. Moreover, the other groundwater samples, although they have concentrations over Legislative Decree 152/06 thresholds for the three analytes, do not show the same deuterium enrichment. In regards to the relationships between δ¹⁸O and Iron (Figure 9b), Manganese (Figure 9d) and Nickel (Figure 9e), no enrichments are highlighted. Therefore, this processing confirms that the methanogenesis phenomena cause a deuterium enrichment, due to bacteria use the “lighter” isotope hydrogen (¹H), without generating variations for 18 oxygen isotope.

Figure 9. Cont.
Further regarding to this case study, the presented comparison between δ²H enrichment and other metals, outlines that, when there is a δ²H enrichment and one metal high concentration values, these latter values are due to contamination process, and they can’t be referred to a natural background level. The same outline is not present for ¹⁸O, as this element one is not involved in such a process.

5. Conclusions

This paper aims to assess the effectiveness of deuterium and oxygen isotopes application as environmental traces for contamination phenomena, due to the leachate interaction with groundwater.

Two Italian case history are showed: Case History I is referred to a plant in Cagliari province of Sardinia region, and Case History II deals with a plant in Perugia province of Umbria Region. In both study areas, there are in operation landfills used for the storage of municipal solid waste (MSW), organic component of municipal solid wastes was not negligible. Results of the two presented Italian case histories show that isotope composition of groundwater samples is significantly influenced by interaction phenomena by leachate mixing, due to a δ²H enrichment. The case histories prove how δ²H enrichment determines a significant shift of the groundwater samples from the reference meteoric lines: Global Meteoric Water Line (GMWL) [39], Mediterranean Meteoric Water Line (MMWL) [40,41] and Local Meteoric Water Line (LMWL) [42].

The Case History I highlighted δ²H anomalous values for the P12bis groundwater sample (−18‰), located downstream of Slot 2, used for the municipal solid waste storage.
The δ²H enrichment confirms an interaction of the leachate from Slot 2 with groundwater, phenomenon therefore an index of contamination processes. This behavior is also confirmed by the concentration values of some analytes, such as Iron (8022 µg/L), Manganese (2941 µg/L) and Nickel (221 µg/L), validating the hypothesis of pollution for the P12bis groundwater sample. On the other side, Case History II anomalous values, referred to deuterium isotope have been highlighted in AD16 groundwater sample (−24‰). The AD16 point appears to be located near tank 1 (PE1), used for leachate collecting. The δ²H enrichment indicates a pollution phenomenon caused by interaction between leachate and groundwater. This phenomenon also is confirmed by the concentrations of some analytes, such as Iron (1150 µg/L), Manganese (383 µg/L) and Nickel (105 µg/L), with values over Legislative Decree 152/06 threshold. On the contrary, there are no significant variations for the 18-oxygen isotope content. In the Case History I, the point P12bis has a value of δ¹⁸O equal to −6.03‰ very close to the result of leachate Point 2 (−6.36‰). In the same way, for Case History II, the groundwater sampling point AD16 has a δ¹⁸O value equal to −7.5‰ very close to the result of point PE1 (−7.9‰). However, the δ²H enrichment does not lead to a following δ¹⁸O variation, confirming that the methanogenesis phenomena do not influence the oxygen isotope content.

Furthermore, for both case histories, a statistical approach was applied to study correlations between δ¹⁸O and δ²H isotopes and concentrations of Iron, Manganese and Nickel. The Pearson matrix, performed for both case histories, confirms a high relationship between δ²H and the concentrations of Iron, Manganese and Nickel. For Case History II, scatter plots showed a similar trend between the groundwater sample AD16 and PE1. On the contrary, regarding relationships between δ¹⁸O and the Iron, Manganese and Nickel concentrations, no enrichments are highlighted, as δ¹⁸O is not involved in such a process. On the other side, it has come out that the δ²H isotope excess, occurring at the meantime with high concentration values of metals, is a tracer that these latter ones can’t become from a natural background level, but they are due to contamination processes.

Therefore, the results of these case histories confirm that the δ²H isotope enrichment is a valid tracer to identify contamination processes between leachate, coming from municipal solid waste landfills and groundwater.

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