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Isotope-Based Early-Warning Model for Monitoring Groundwater–Leachate Contamination Phenomena: First Quantitative Assessments

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Abstract: Groundwater contamination due to municipal solid waste landfills' leachate is a serious environmental threat. Deuterium (^{2}H) and oxygen (^{18}O) isotopes have been successfully applied to identify groundwater contamination processes, due to interactions with municipal solid waste landfills' leachate, including significant organic amounts. A parameter influencing the isotope content of deuterium and oxygen18 is the deuterium excess (d or d-excess). This paper presents a d-isotope-based model, defined early-warning model, depending on the assessment of the deuterium excess variations in groundwater samples. The isotopic results are corroborated with the trace elements' concentrations (Fe, Mn, Ni, Co and Zn), suggesting that the methanogenic activity diminished under trace element limitation. This model provides the determination of an index, ***F***, as the percentage variation of d-excess, which makes it possible to define an alert level system to assess and check groundwater contamination by leachate. The procedure shows that values of ***F*** index higher than 1.1 highlight possible contamination phenomena of groundwater due to leachate and, therefore, actions by the municipal solid waste landfill management are required. This early-warning model is presented by the application to a case study in Central Italy in order to evaluate innovative aspects and opportunities to optimize the model. The application of the procedure to the case study highlighted anomalous values of the ***F*** index for the samples AD16 (F_{max} = 2.069) and AD13 (F_{max} = 1.366) in January, April, July and October surveys as well as the boundary values ($1 \leq F \leq 1.1$) for samples AD73 (***F*** = 1.229) and AD68 (***F*** = 1.219) in the April survey. The proposed model can be a useful management tool for monitoring the potential contamination process of groundwater due to the presence of landfills with municipal solid waste, including a significant organic component.

Keywords: deuterium excess; environmental isotopes; municipal solid landfill; leachate contamination; early-warning model

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1. Introduction

Effective municipal solid waste (MSW) management is crucial for preserving ecosystems. As the landfill is the primary method of MSW management, factors impacting groundwater contamination near MSW landfill sites generally must be studied based on field investigations, environmental impact assessment and geochemical and hydrogeological analyses.

Early warning systems (EWS) represent a relevant choice within the landfill risk management framework, primarily when structural measures cannot fully guarantee the safety of the areas of interest for contamination phenomena. Some of the several benefits linked to EWS comprise their fast, simple, low-cost implementation and environmental friendliness.

Several studies selected standard hydrogeological and hydrogeochemical tools that should be included in EWS design and implementation [1–6]. These tools can be summarized as follows:

- The field monitoring system can acquire physical and geochemical quantities related to the phenomenon and share them with the monitoring system;
- Analysis and forecasting methods describe the landfill evolution, predict its behavior and identify critical events based on alert thresholds (if available);
- The warnings and dissemination of alert messages to notify the relevant authorities about the forecasted critical event;
- Action plans and measures are to be activated based on the forecasting results obtained by applying the numerical model.

Among these actions, suggesting a correct definition, calibration and validation of the predictive model is essential. This issue is rigorously related to the choice of the monitoring system, which best suits the forecasting model implemented. In particular, innovative monitoring tools that reach high sampling frequencies with low-cost procedures or analyses represent a significant improvement likened to traditional approaches.

This paper presents a d-isotope-based model, defined early-warning model, depending on the assessment of deuterium excess variations in groundwater samples. The isotopic results are corroborated with the trace elements' concentrations (Fe, Mn, Ni, Co and Zn), suggesting that the methanogenic activity diminished under trace element limitation. This d-isotope-based model represents a faster and low-cost implementation to describe the ongoing phenomenon accurately and would be applied to the study of municipal solid waste (MSW) compared to the other geochemical and hydrogeochemical traditional approaches.

As isotope analysis of ^{2}H and ^{18}O can be carried out monthly, at an affordable cost, the proposed method can be defined as "early-warning", as it allows a prompt intervention in the case of certain values of d-isotope determination.

The presence of ^{2}H and ^{18}O stable isotopes in the water cycle is conditioned by meteorological processes, which give it a typical footprint that is useful, also, for groundwater contamination characterization: the source, the path, the residence times in the subsoil and any phenomena to which groundwater may have been subjected [1]. These isotopes are generally defined as conservative tracers, as they "retain" their features over the whole path of the groundwater [2,3]. Additionally, these environmental isotopes have been extensively used to assess the hydro-environmental issues associated with groundwater contamination by municipal solid landfill [1,4–6]. While oxygen-18 (^{18}O) and deuterium (^{2}H) generally correlate with the temperature at middle-to-high latitudes, the deuterium excess (d-excess, d) is correlated with the physical conditions (humidity, air temperature, evaporation during precipitation and sea surface temperature) of the oceanic source area of the precipitation [7]. The d-excess can be used to identify processes occurring under non-equilibrium conditions.

Among the phenomena shown in Figure 1, methanogenesis represents one of the phases of the decomposition process of municipal solid waste (MSW), with a significant organic component, due to the redox conditions of the system and the bacteria catalytic effect in landfill [8–14]. Several studies have shown that this process can cause a deuterium increase [4,12,13,15–18] because the bacteria use, preferentially, the "lighter" isotope, hydrogen (^{1}H), due to the methane production; thus, the remaining hydrogen is enriched in deuterium (^{2}H), that is, the "heavier" isotope [4,18,19], without producing a proportional increase in ^{18}O [4,19–21]. This process seems to increase the d-excess without a proportional increase in ^{18}O, producing a shift of the points from ideal conditions, represented by the reference meteoric water line [10,11].

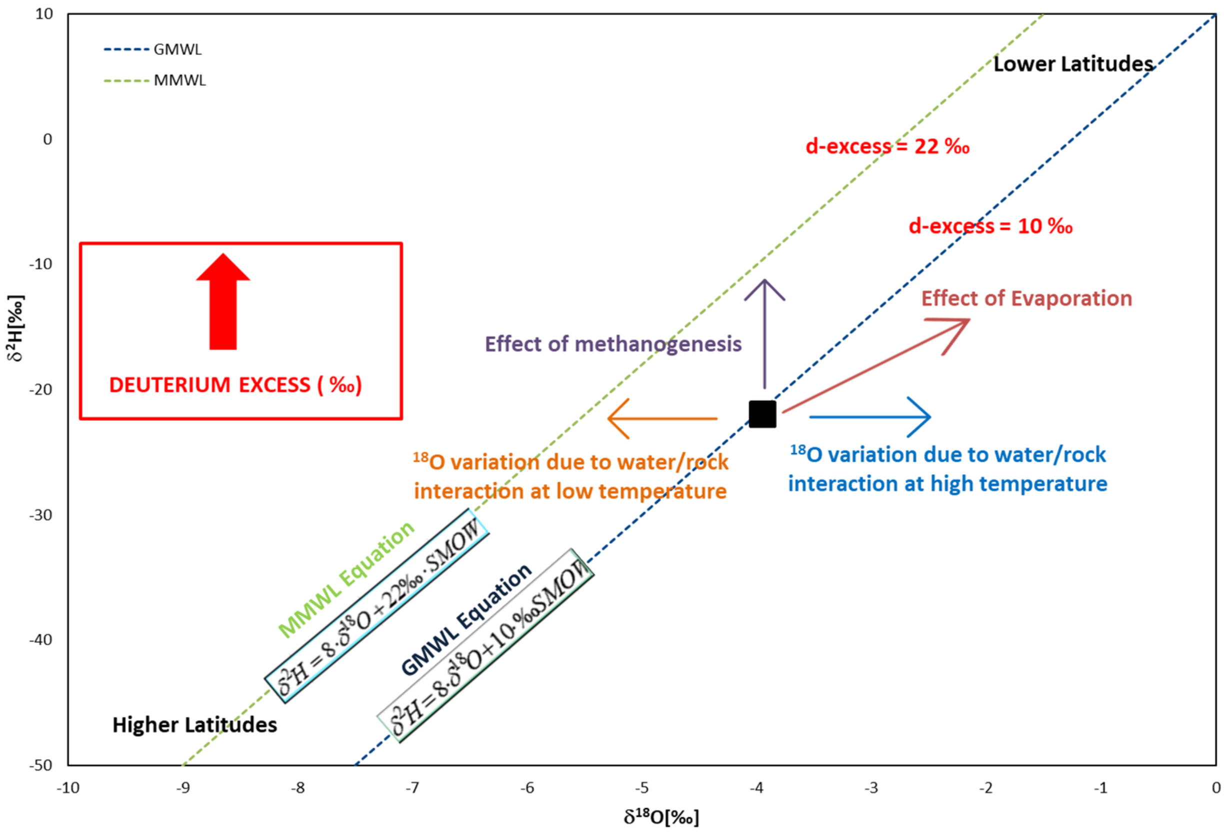


Figure 1. Schematic of the main processes that may alter ^{18}O and ^{2}H isotopic compositions of groundwaters. Adapted from Hackley et al., 1996 [12] and Jasechko, S. 2019 [13].

However, in this paper, building on similar examples [22–33] from the literature, using d-excess as a marker of groundwater pollution, an early-warning model is proposed for the management of groundwater leachate contamination phenomena resorting from municipal solid waste landfills, based on the assessment of deuterium excess variations, which can occur after precipitation infiltration inside the subsoil.

2. Materials and Methods

This paper presents an isotope-based, defined early-warning model for assessing d-excess variations (‰). The model has been proposed for managing groundwater contamination phenomena in municipal solid waste landfills with solid wastes caused by a significant organic component. The procedure and the isotope data (^{2}H and ^{18}O) used to apply the proposed model are reported in the following paragraphs, referring to some surveys performed in an area in central Italy.

2.1. The Model

The proposed model is based on the d-excess assessment in groundwater samples. The d-excess reflects the deviation of a sample from the "ideal" condition (evaporation in equilibrium conditions at 25 °C), represented by the meteoric water line. An increase in the d-excess, without a proportional increase in ^{18}O, causes the points' shift from ideal conditions, represented by the reference meteoric water line (Figure 1). Figure 2 shows the flowchart of the proposed procedure. In the area under study, the local precipitation regression line is very close to the Local Meteoric Water Line for Pian dell'Elmo station, as the reference value of the d-excess, whose intercept value is equal to +18.15‰ (d-$_{REFtheo}$).

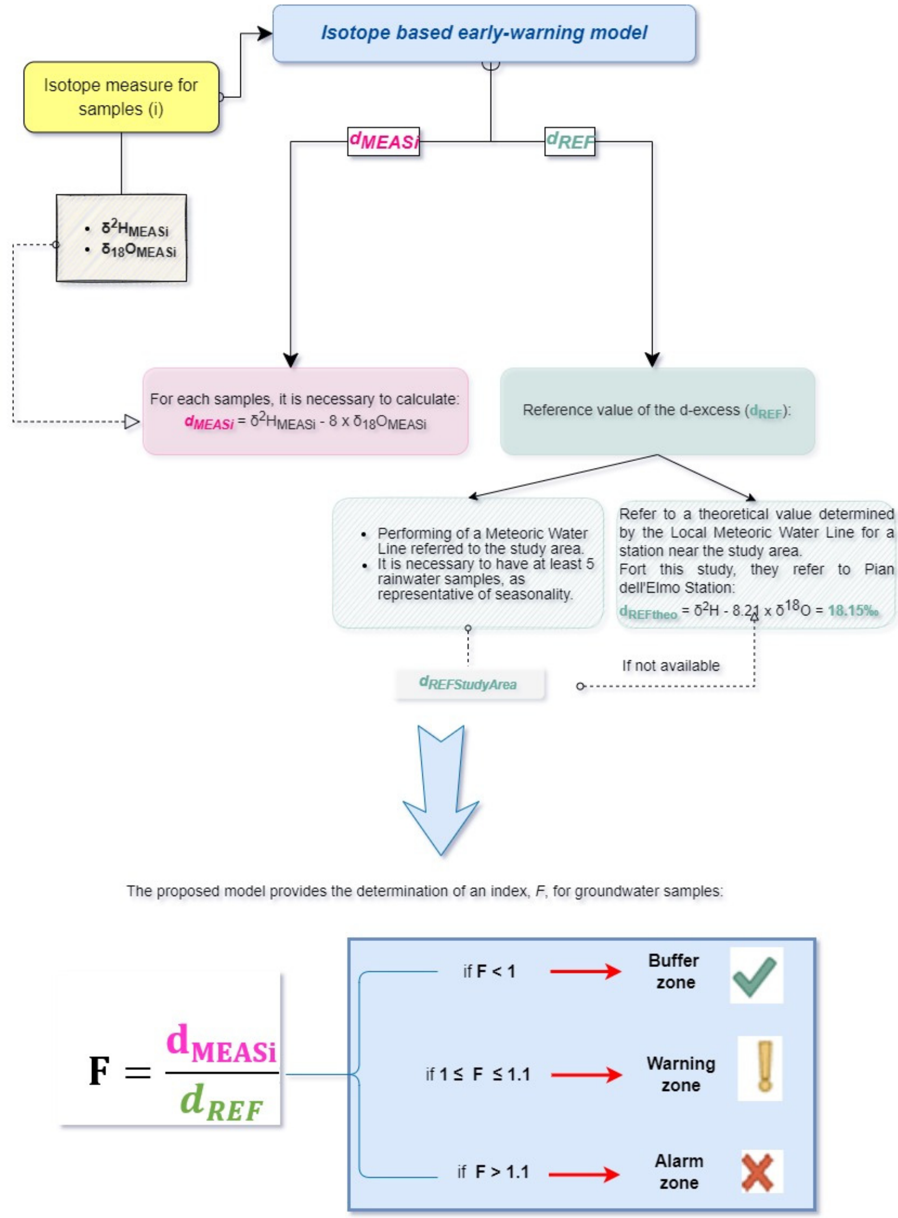


Figure 2. Flowchart of proposed procedure for ***F*** index determination.

The proposed procedure (Figure 2) provides the determination of an index, ***F***, for groundwater samples, as follows (3):

$$\boldsymbol{F} = \frac{d_{\text{MEASi}}}{d_{REF}} \tag{1}$$

where:

d_{MEASi} is referred to the isotope determination in the i-sample according to equation

$$d_{\text{MEASi}} = d^2H_{\text{MEASi}} - 8d^{18}O_{\text{MEASi}} \text{ measured in groundwater samples (i)} \tag{2}$$

$$\begin{gathered} d^2H = 8.21d^{18}O + 18.15‰ \\ d_{\text{REF}} = d^2H - 8.21d^{18}O = 18.15‰ \ (d\text{-}_{\text{REFtheo}}) \text{ for reference of d-excess (Pian dell'Elmo station)} \end{gathered} \tag{3}$$

The Pian dell' Elmo (MC) station has been identified as a reference of precipitations' isotope composition in this area, and its isotopic data are provided by the International

Atomic Energy Agency (IAEA). In fact, Equation (3) is defined by the isotopic data for the 2002 year.

The proposed model provides the determination of ***F*** index (Equation (1), given by the ratio between the d-excess for the i-sample (d_{MEASi}) and the d-excess reference value (d_{REF}). Since the latitude influences the d-excess trend, it would be better to consider a meteoric water line reference for the study area in order to define an appropriate reference for d-excess ($d_{REFStudyArea}$). To perform a meteoric water line of the study area, it would need at least 4 rainwater samples collected in the study area, all over one year, to represent the seasonality. If this hydrological information is not available, it is possible to refer to other Local Meteoric Water Lines, available in the literature. The application of the proposed model considers the Local Meteoric Water Line for Pian dell'Elmo station (3), as the reference value of the d-excess, whose intercept value is equal to +18.15‰ ($d\text{-}_{REFtheo}$).

This procedure provides the determination of a coverage index, as usually found in geochemical prospecting, *F*, as the d-excess percentage variation, which makes it possible to define an alert level system in monitoring the groundwater's potential contamination due to leachate from municipal solid waste landfills. Depending on the value assumed by the ***F*** index, it is possible to hypothesize three zones (Table 1).

Table 1. Zones for ***F*** index: values assumed by index ***F***.

Values	Zones
$\boldsymbol{F} > 1.1$ (+10%)	Alarm zone—✗
1 (+1%) $\leq \boldsymbol{F} \leq$ 1.1 (+10%)	Warning zone—!
$\boldsymbol{F} < 1$ (+1%)	Buffer zone—✓

The methanogenesis phenomena can cause an exclusive enrichment of the deuterium isotope (d^2H) and, therefore, an increase of d-excess.

The choice of 1.1 as a threshold value for the alarm zone of ***F*** is because, in environmental monitoring processes, it is mandatory to apply a caution criterion. This means that, as a contamination process could occur, the management of the landfill must be alerted as soon as possible. On the other hand, 10% is the maximum variation we can have, usually for δ^2H and $\delta^{18}O$ contents in rainwater [8,9,34,35]

2.2. Study Area and Sampling Data

The study area is located in central Italy and is characterized by a hilly morphology, with altitude ranging between 500 and 600 m a.s.l. The landfill plant, designed in the 1980s, covers an area of approximately 0.12 km^2. It is used for the storage of municipal solid waste (MSW). The study area, where the landfill plant is located, is characterized by two outcropping deposits: upper sandy conglomerate deposits and marly arenaceous formation. The latter outcrops all over the area, and it is made of marly and arenaceous layers, alternated with clay and limestone lenses.

Moreover, the study area is characterized by marly and arenaceous layers with low permeability, alternated with limestone lenses which, if fractured, can host suspended aquifers. In the study area, there is a debris layer, which has, therefore, caused the design of an impermeable layer at the landfill bottom, capable of ensuring a perfect water seal of the landfill bottom. Downstream of the landfill, a barrier has been located. It consists of variable dimensions soil, with sandstone and marl lithoid elements. On the barrier downstream of the landfill, a series of sub-horizontal drains have been drilled to drain most of the landfill percolation water. These drains have been made with a slope such as to drain the percolation water downstream of the barrier towards the drain's channels of the shallow waters. During the executive phase, drainage channels have been created to reduce the connection between rainwater and embanked waste and to avoid the production of leachate. They are due to the discharge of the surface water into the canal downstream of the embankment. In the end, a final covering with waterproofing layers has been located.

Figure 3 shows (i) groundwater samples identified with "P" and "PM" that are related to piezometers that cross all sediments until the impermeable layer, (ii) rainwater samples identified with "AP", (iii) samples by leachate tanks, identified with "PE", and (iv) drainage water samples used to catch percolation water, identified with "AD".

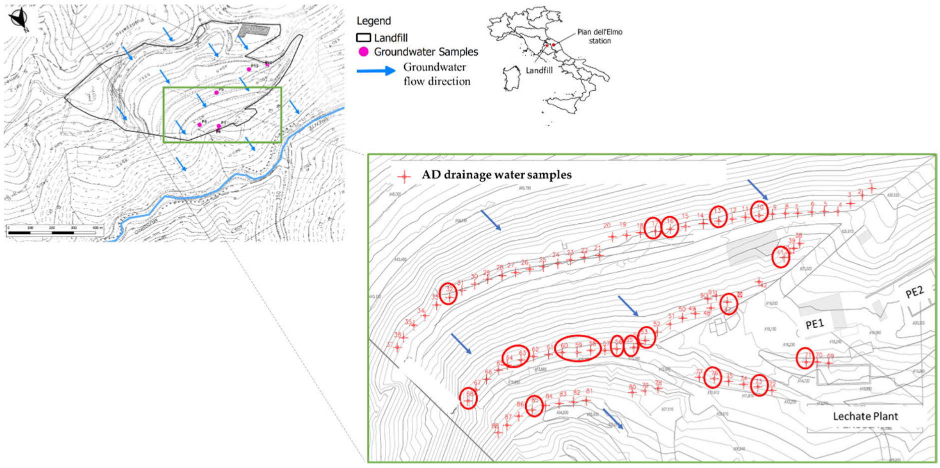


Figure 3. Municipal solid waste landfill map with sampling points (the red circles identify the drainage water samples).

2.2.1. d^2H and $d^{18}O$ Isotopes

Table 2 presents the isotope data (d^2H and $d^{18}O$) considered for the proposed model implementation. The data refer to some monitoring surveys performed at a municipal solid waste landfill in central Italy (Figure 3). The isotope data of four monitoring surveys, carried on in 2020, have been considered: January, April, July and October. In fact, the four monitoring surveys can properly represent a whole hydrological year: January and April for the wet season, July and October for the dry season. The δ^2H and $\delta^{18}O$ 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 CO_2. Isotopic abundance ratios are expressed as parts per million of their deviations, as given by the Vienna Standard Mean Ocean Water (VSMOW).

Table 2. Isotopes (d^2H and $d^{18}O$) data for monitoring surveys: January, April, July and October.

January			April		
Samples	**‰d(^{2}H) ± 1 ‰ (VSMOW)**	**‰d(^{18}O) ± 0.05 ‰ (VSMOW)**	**Samples**	**‰d(^{2}H) ± 1 ‰ (VSMOW)**	**‰d(^{18}O) ± 0.05 ‰ (VSMOW)**
AD16	−22.7	−7.5	AD16	−28.2	−8.22
AD17	−36.6	−6.92	AD13	−37.6	−7.8
AD47	−36.5	−7.29	AD47	−40.1	−7.69
AD63	−40.8	−6.85	AD68	−41.8	−7.99
AD60	−39.8	−7.178	AD73	−44.1	−8.3
AD32	−40.3	−6.9	AP	−7.8	−2.69
AD64	−41.2	−6.778			
AD85	−38.56	−6.287			
AP	−8.73	−3.37			
PE1	−17.2	−5.85			
PE2	−2	−4.52			
P1	−40.4	−5.9			
P6	−41.1	−6.3			
PM1	−42.1	−6.28			
P5	−44.55	−6.92			

Table 2. *Cont.*

July			October		
Samples	**‰d(^{2}H) ± 1 ‰ (VSMOW)**	**‰d(^{18}O) ± 0.05 ‰ (VSMOW)**	**Samples**	**‰d(^{2}H) ± 1 ‰ (VSMOW)**	**‰d(^{18}O) ± 0.05 ‰ (VSMOW)**
AD13	−42.2	−7	AP	−30	−5.3
AD16	−24.3	−7.5	AD10	−40.6	−7.71
P1	−46.1	−7.6	AD16	−28	−8.2
P4	−43.3	−7.5	AD17	−41.3	−7.76
P5	−50.5	−7.9	AD41	−43.5	−7.8
P6	−40.9	−6.9	AD47	−41	−7.67
P12	−52.6	−8.3	AD53	−42.9	−7.68
PM1	−42.3	−6.9	AD68	−40	−7.2
P13	−49.5	−8	AD71	−43.9	−7.73
ADF	−49.2	−8	AD76	−44.4	−7.85
PE1	−21.3	−7.9	AD55	−41.6	−7.52
PE2	−4	−6.1	AD56	−41.6	−7.52
			AD58	−41.8	−7.56
			AD59	−41.4	−7.48
			AD73	−41.8	−7.52
			AD13	−45.3	−7.88
			ADF	−46.5	−8.19
			P1	−45.7	−7.96
			P4	−46.3	−8.18
			P5	−50	−8.49
			P6	−42.5	−7.49
			PM1	−40.7	−7.36
			P12	−49.3	−8.45
			P13	−47.7	−8.24
			PE1	−27.1	−7.78
			PE2	−19.9	−7.09

Table 2 presents the isotope data for (i) groundwater samples, identified with "P" and "PM", (ii) rainwater sample, identified with "AP", (iii) samples by leachate tanks, identified with "PE" and (iv) drainage water samples, identified with "AD". In fact, on the embankment downstream of the landfill, a series of sub-horizontal drains have been drilled to collect most of the landfill percolation water and to carry it outside the landfill. These drains have been made with a slope to drain the percolation water to the downstream of the embankment towards the drain channels of the shallow waters.

2.2.2. Trace Elements Concentration: d^{2}H and d^{18}O

Supplementary Materials (Table S1) shows the concentrations of the trace elements: Iron (Fe), Manganese (Mn), Nickel (Ni), Cobalt (Co) and Zinc (Zn). Trace element concentrations were determined for the samples used for the monitoring surveys. Laboratory analyses for the determination of concentrations of some trace elements were performed at the Laboratory of the Department of Earth Sciences of the University of Rome "La Sapienza". Concentrations of trace elements were measured using an ICP-MS (X Series 2, Thermo Fisher Scientific, Waltham, MA, USA) following filtration (0.45 µm) and acidification in the field (HNO3 1:1).

3. Results and Discussion

Several studies [4,30–33] have highlighted how methanogenesis processes can affect leachate enrichment in δ^{2}H. As a matter of fact, the methanogenic bacteria, during the methane production, use first the "lighter" isotope of hydrogen (^{1}H), therefore, leaving the enriched "heavier" isotope of hydrogen in the leachate (^{2}H) [20,21,36,37]. In the natural environment, the abundance and concentration of trace elements might enhance the rate of carbon source degradation by methanogens either directly or in a more indirect way. For example, it might increase the specific metabolic activity of bacterial groups such as primary or secondary fermenters whose products are the substrates for methanogens. Burgess et al. [38] reported that trace metals influence microbial waste degradation and species diversity within sewage sludge. By comparing enrichment cultures with and without trace element amendments (Fe, Ni, Co, Mo, Co, Zn, B, Mn), Unal et al. [39] not only have found a correlation between the increasing mcrA levels and elevated methane production but have also demonstrated a shift in the metabolically active methanogenic community from a M. formicicum-like group to a M. subterraneum-like. Figure 3 shows deuterium δ^2H and oxygen δ^{18}O isotopes composition for groundwater samples. Figure 4 shows also the GMWL, MMWL and Local Meteoric Water Line for Pian dell'Elmo station (2).

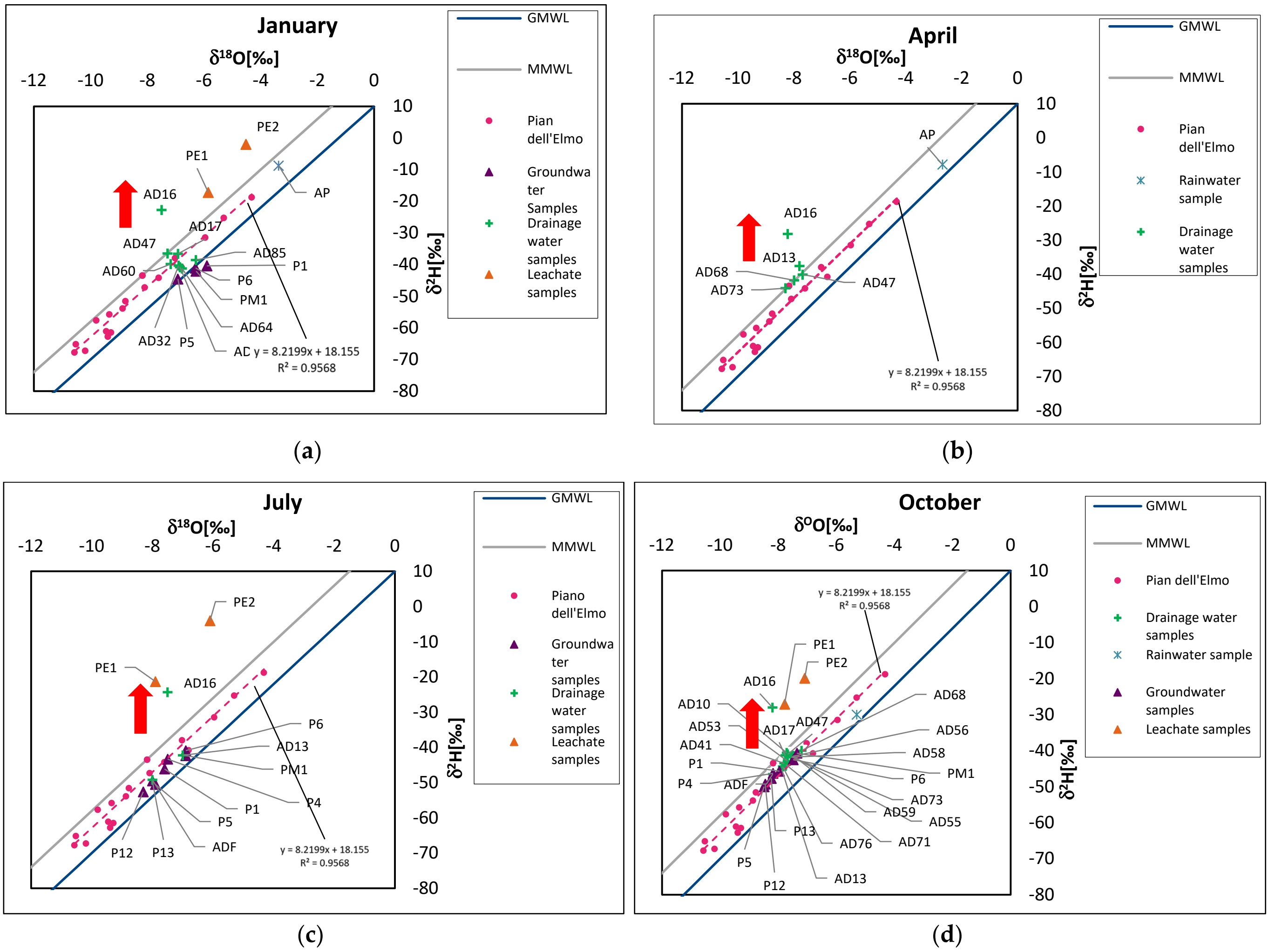


Figure 4. δ^2H vs. δ^{18}O values: (**a**) January, (**b**) April, (**c**) July and (**d**) October.

The deviation from meteoric lines shows alteration phenomena due to processes that occurred in the soil. In particular, the variation from meteoric lines highlights the mixing phenomena of groundwater with leachate, coming from landfills of municipal solid waste, made of a significant organic part [4]. PE1 and PE2 (red arrows, Figure 4) have been used to assess the leachate levels of isotope compositions; in fact, they confirm a sound enrichment in δ^2H (Figure 4), and they act as end-members of possible mixing processes. In addition to the leachate sampling points, Figure 4 shows deviations from the reference meteoric lines for the drainage water samples: AD16 and AD13. The former shows deuterium enrichment for all four monitoring surveys, with values ranging from a minimum of −28.20‰ in April and a maximum of −22.74‰ in January; on the contrary, the latter presents deuterium enrichment in April with a value equal to −37.6‰. At the same time, in April, the points AD68 and AD73 show isotopic connotations at the boundary with the reference meteoric lines, with deuterium values equal to −41.80‰ for AD68 and −44.10‰ for AD73. In particular, the AD16 sample presents a significant enrichment in deuterium isotopes in January and July related, respectively, to the beginning of the wet and dry seasons. Therefore, it seems evident that the methanogenesis processes, during which bacteria use the "lighter" isotope hydrogen (^1H) and leave the "heavier" isotope (^2H) in leachate, cause a deuterium isotope enrichment without involving ^{18}O [12,20,21]. The proposed isotope model considers the index, F, according to d-excess percentage variation. The ***F*** index (Equation (1)) is given by the ratio between the d-excess for the samples (d_{MEASi}) and the d-excess reference value, given by the Local Meteoric Water Line for Pian dell'Elmo station ($d\text{-}_{REFtheo}$ = +18.15‰). Figure 5 shows the results of the index F, calculated according to Equation (3).

	January		April		July		October	
Samples	d_{MEASi} [‰]	*F [-]*	d_{MEASi} [‰]	*F [-]*	d_{MEASi} [‰]	*F [-]*	d_{MEASi} [‰]	*F [-]*
AD16	37.260	✗ 2.053	37.560	✗ 2.069	35.700	✗ 1.967	37.600	✗ 2.072
AD17	18.760	! 1.034					20.780	✗ 1.145
AD13			24.800	✗ 1.366	13.800	✓ 0.760	17.740	✓ 0.977
AD47	21.830	✗ 1.203	21.420	✗ 1.180			20.360	✗ 1.122
AD63	13.970	✓ 0.770						
AD60	17.594	✓ 0.969						
AD32	14.890	✓ 0.820						
AD64	12.994	✓ 0.716						
AD85	11.736	✓ 0.647						
AD68			22.120	✗ 1.219			17.600	✓ 0.970
AD73			22.300	✗ 1.229			18.360	! 1.012
AP	18.230	! 1.004	13.720	✓ 0.756			12.400	✓ 0.683
PE1	29.600	✗ 1.631			41.900	✗ 2.309	35.140	✗ 1.936
PE2	34.160	✗ 1.882			44.800	✗ 2.468	36.820	✗ 2.029
P1	6.800	✓ 0.375			14.700	✓ 0.810	17.980	✓ 0.991
P6	9.300	✓ 0.512			14.300	✓ 0.788	17.420	✓ 0.960
PM1	8.140	✓ 0.448			12.900	✓ 0.711	18.180	! 1.002
P5	10.810	✓ 0.596			12.700	✓ 0.700	17.920	✓ 0.987
P4					16.700	✓ 0.920	19.140	✗ 1.055
P12					13.800	✓ 0.760	18.300	! 1.008
P13					14.500	✓ 0.799	18.220	! 1.004
ADF					14.800	✓ 0.815	19.020	! 1.048
AD10							21.080	✗ 1.161
AD41							18.900	! 1.041
AD53							18.540	! 1.021
AD71							17.940	✓ 0.988
AD76							18.400	! 1.014
AD56							18.560	! 1.023
AD58							18.680	! 1.029
AD59							18.440	! 1.016

Figure 5. Isotope-based early-warning model results.

The values of index ***F*** in Figure 5 shows how the exceeding of a value equal to 1.1, corresponding to an increase of 10% compared to the $d\text{-}_{REFtheo}$ (+18.15‰), confirms contamination phenomena due, probably, to mixing with leachate. The methanogenesis phenomena can cause an exclusive enrichment of the deuterium isotope (d^2H) and, therefore, an increase of d-excess. As shown in Table 1, three characterizing zones have been proposed, according to the results of index ***F*** related to the considered samples. Figure 5 shows that the AD16 sample presents an index ***F*** higher than 1.1 for the four monitoring surveys, with values in a range between 1.96 and 2.072. The AD13 sample also shows an anomalous d^{2}H in April such as to result in an index ***F*** equal to 1.36 (Figure 5). At the same time, the AD68 and AD73 samples have an index ***F*** equal to 1.21 and 1.22, respectively (Figure 5). Moreover, the October survey shows numerous samples in the warming zone. Therefore, according to ***F*** index results (Figure 5), Figure 6 shows a scatter plot between d^{2}H and ***F*** index for monitoring surveys.

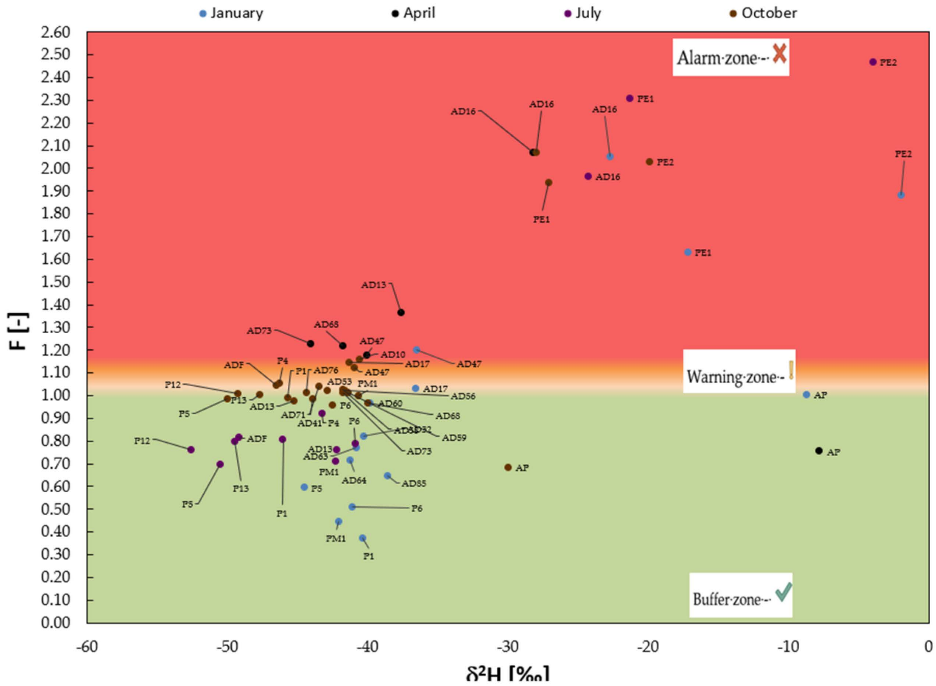
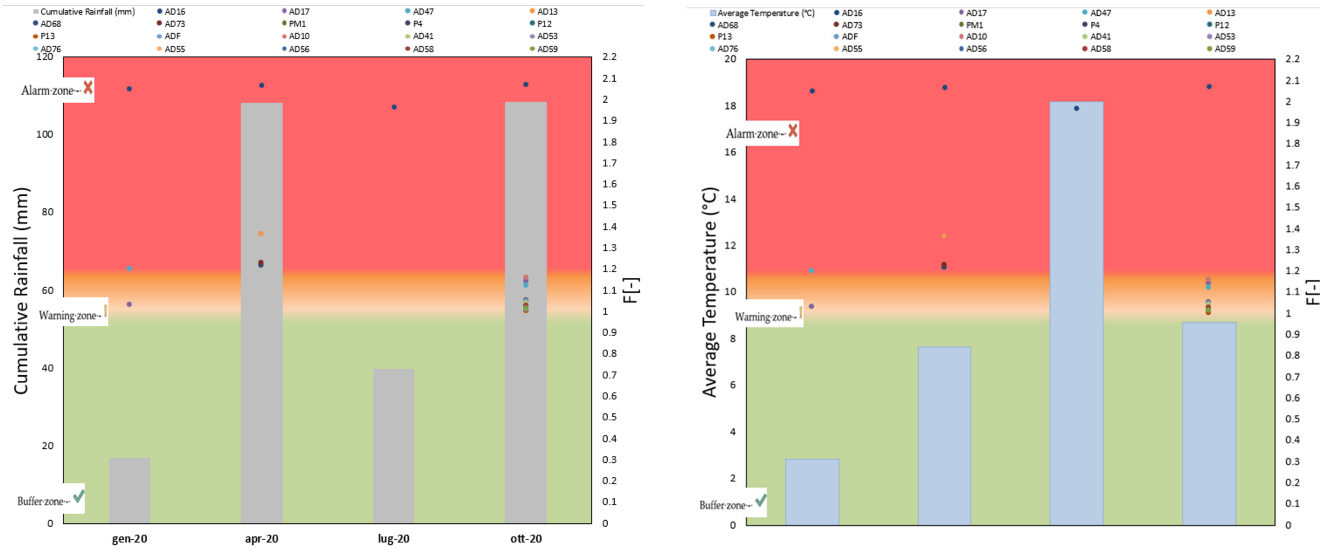


Figure 6. Scatter Plot between the d^{2}H and the ***F*** index for monitoring surveys.

Figure 6 shows that the leachate samples, PE1 and PE2, have values of ***F*** index which are all inside the alarm zone. At the same time, the AD16 sample shows values of the ***F*** index as being within the alarm zone (Figure 6), confirming contamination phenomena of drainage water by leachate. In the April monitoring survey, the AD13 sample shows an index value ***F*** > 1.1, which is, in fact, in the alarm zone (Figure 6). On the contrary, there are no anomalies in July and October surveys. At the same time, the AD73 and AD68 samples present ***F*** index values, such as being in the warning range (Figure 6). Therefore, the occurring value for AD13, AD73 and AD68 samples, resulting from the April monitoring survey, could be due to a seasonal anomaly. To assess the seasonality influence, Figure 7a,b shows a combined graph where the monthly cumulative rainfall (Figure 7a) and the monthly average temperatures (Figure 7b) are represented with the ***F*** index of AD16, AD13, AD73 and AD68 samples. As the thermo-pluviometric data by Pian dell' Elmo station for 2020 were not available, the data by Monte San Vicino (MC) station have been considered, which is located a few kilometers from Pian dell'Elmo. The thermo-pluviometric data have been provided by the Regional Meteorological-Hydrological Information System managed by the Civil Protection Service of Marche Region.



(**a**) (**b**)

Figure 7. Combined graph of monthly cumulative rainfall (**a**) and monthly average temperatures (**b**) with index ***F*** for samples AD16, AD13, AD73 and AD68.

Figure 7a,b shows that April 2020 is a month characterized by large precipitations (Figure 7a) and moderate average temperatures (Figure 7b). This process influences the ^{2}H enrichment in AD13, AD73 and AD68 samples, which, actually, show values of the ***F*** index greater than 1.1 for the AD13 sample and values in the range 1 and 1.1, for the AD73 and AD68 samples. However, for the months of July and October 2020 (Figure 7a,b), the ***F*** index is less than 1 for the AD13, AD73 and AD68 samples, thus confirming a seasonal anomaly. On the contrary, the AD16 sample does not seem to be influenced by seasonality (Figure 7a,b); in fact it shows values of ***F*** > 1.1 in all monitoring surveys. The results of the ***F*** index confirm leachate contamination in the AD16 sample, according to results by the main isotope diagrams in Figure 3, and, therefore, it confirms the validity of the proposed model as a useful management tool in the case of landfills with municipal solid waste with a significant organic component.

Furthermore, the correlations between the trace elements (Fe, Mn, Ni, Co e Zn), whose data are shown in Table S1 of Supplementary Materials, and the index ***F*** are shown in Figure 8.

Trace element concentrations (Table S1 of Supplementary Materials) highlight a higher content of Fe, Mn, Co and Zn in the drainage water samples (AD16, AD13, AD16, AD68 and AD63) affected by methanogenic processes as well as in the leachate samples (PE1 and PE2). Many unknowns exist regarding trace elements' effects due to their bioavailability, their optimal concentration on facilitated methanogenesis and their toxic concentrations for microbial growth and activity in coal bed basins in situ. The bioavailability and toxicity of trace elements in the environment are controlled by geochemical processes such as mineral dissolution, precipitation and ion adsorption/desorption. In this study, the abundance and concentration of trace elements might enhance the rate of carbon source degradation by methanogens either directly or indirectly. For example, it might increase the specific metabolic activity of bacterial groups such as primary or secondary fermenters whose products are methanogen substrates. Further investigation should focus on the effects of trace elements on bacterial activity in coal biodegradation pathways and their associated community compositions. Therefore, a better understanding of trace elements as a limiting factor for methanogenic activity in a coal bed basin will have a broader impact on our knowledge of the ecology and physiology of methanogens.

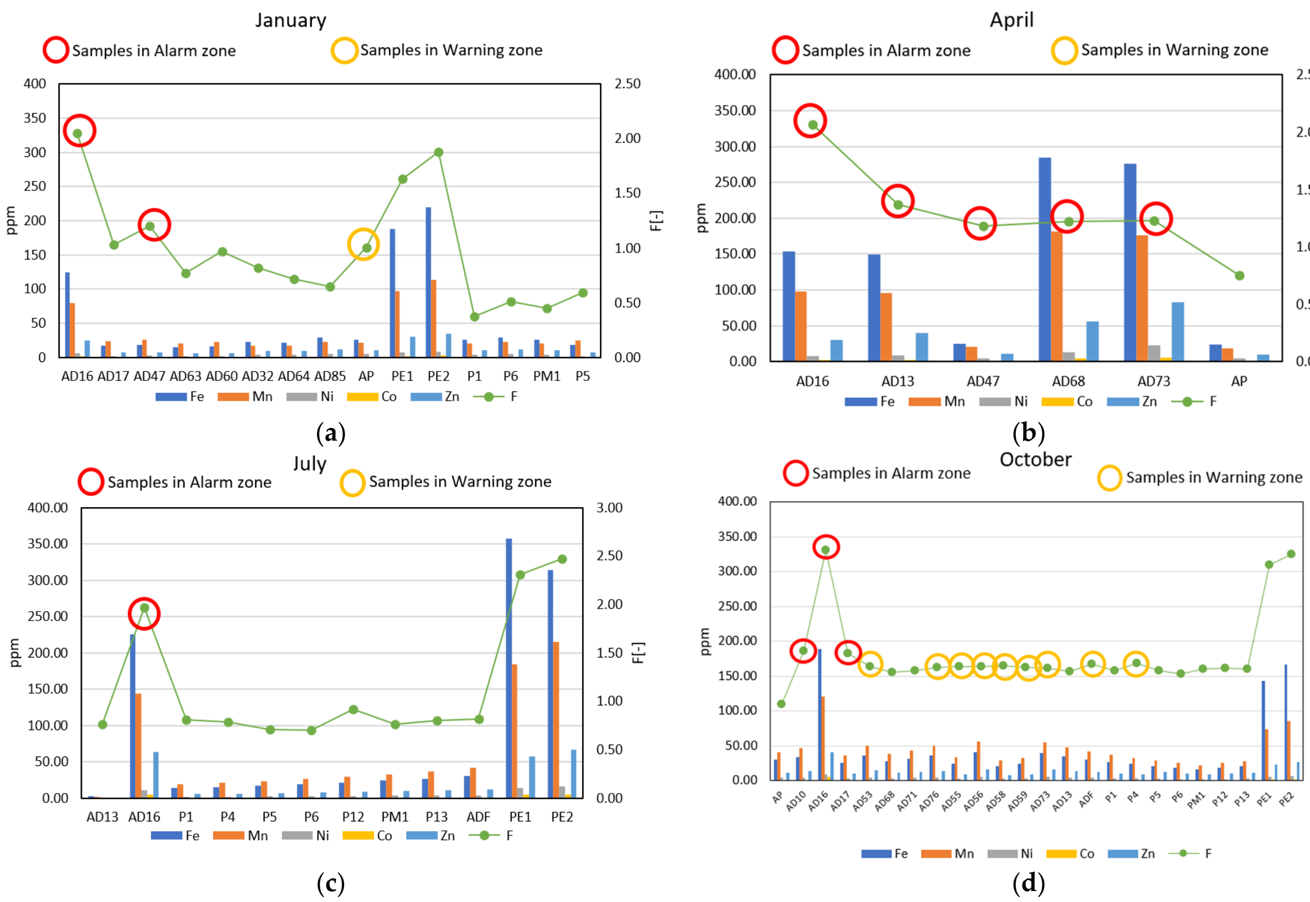


Figure 8. Combined graph of trace elements and index F: (**a**) January, (**b**) April, (**c**) July and (**d**) October.

4. Conclusions

This paper proposes an original procedure for the application of isotope-based early-warning model for monitoring the potential mixing phenomena between groundwater and leachate from municipal solid waste with a significant organic component. Several studies [4,14,15,18–22] have shown that methanogenesis can cause a deuterium increase because bacteria use, preferentially, the "lighter" isotope hydrogen (^{1}H) along the methane production; therefore, the remaining hydrogen is enriched in deuterium (^{2}H), that is, the "heavier" isotope, without causing a proportional increase in ^{18}O. The isotopic model is validated by the abundance and concentration of trace elements that seem to enhance the rate of carbon source degradation by methanogens.

The proposed isotopic model has assessed the d-excess variation for the management of groundwater leachate contamination phenomena. This seems to be an original application for d-excess, as it is generally used for the calibration of atmospheric general circulation models [7,8,21,35]. The proposed procedure (Figure 2) provides the determination of ***F*** index (Equation (1)), given by the ratio between the d-excess for the samples (d_{MEASi}) and the d-excess reference value (d_{REF}). Based on the values assumed by ***F*** index, the model proposes three zones (Table 1) with diverse warning levels for the management of mixing phenomena between leachate and groundwater. Values of ***F*** index higher than 1.1 (Table 1) confirm contamination phenomena between groundwater and leachate, and, therefore, actions by the municipal solid waste landfill manager are required. The results (Figures 5 and 6) of the application to a study case of the proposed procedure show that the ***F*** index can be used as a footprint for mixing phenomena between groundwater and lactate by the municipal solid waste landfill. Furthermore, these results (Figure 7a,b) also show how the seasonality is a parameter to consider in ***F*** index assessment, as it can affect the ^{2}H enrichment and, so, the d-excess in groundwater samples. Groundwater samples that are located in the warning zones must be monitored to verify the anomaly source, such as due to seasonality or leachate contamination, by carrying out samplings; if not for the whole hydrological year, they should at least be, in any case, representative of seasonality. According to the procedure of this proposed model (Figure 2), the determination and monitoring of the ***F*** index can be a useful tool to assess and manage possible mixing phenomena between groundwater and leachate from municipal solid waste landfills. The proposed isotope-based early-warning model is still in a first phase, as it would be better to consider a meteoric water line that refers to the study area for the ***F*** index determination, as the d-excess is highly affected by latitude trend. However, in the lack of other information and as a cautionary guide, the Mediterranean Meteoric Water Line has been considered as a reference. In fact, the value from an equation of a Local Meteoric Water Line could be lower.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w15142646/s1. Table S1: Trace elements concentrations. Data for monitoring surveys: January, April, July and October.

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References

1. Abu Jabal, M.S.; Abustan, I.; Rozaimy, M.R.; El Najar, H. The deuterium and oxygen-18 isotopic composition of the groundwater in Khan Younis City, southern Gaza Strip (Palestine). *Environ. Earth Sci.* **2018**, *77*, 155. [CrossRef]
2. Barbieri, M. Isotopes in hydrology and hydrogeology. *Water* **2019**, *11*, 291. [CrossRef]
3. Calligaris, C.; Mezga, K.; Slejko, F.F.; Urbanc, J.; Zini, L. Groundwater characterization by means of conservative (δ18O and δ2H) and non-conservative (87Sr/86Sr) isotopic values: The classical karst region aquifer case (Italy–Slovenia). *Geosciences* **2018**, *8*, 321. [CrossRef]
4. Andrei, F.; Barbieri, M.; Sappa, G. Application of 2H and18O isotopes for tracing municipal solid waste landfill contamination of groundwater: Two Italian case histories. *Water* **2021**, *13*, 1065. [CrossRef]
5. Sankoh, A.A.; Derkyi, N.S.A.; Frazer-Williams, R.A.D.; Laar, C.; Kamara, I. A review on the application of isotopic techniques to trace groundwater pollution sources within developing countries. *Water* **2022**, *14*, 35. [CrossRef]
6. Wijewardhana, R.; Senarathne, S.; Jayawardana, C.K.; Edirisinghe, V.; Wijesekara, H.; Mannapperuma, N. Evaluation of the effect of landfill leachate on surface and groundwater quality: A case study in tropical Sri Lanka using the evidence of stable isotopes. *Environ. Monit. Assess.* **2022**, *194*, 628. [CrossRef] [PubMed]
7. Froehlich, K.; Gibson, J.; Aggarwal, P. Deuterium excess in precipitation and its climatological significance. In Proceedings of the Study of Environmental Change Using Isotope Techniques, Vienna, Austria, 23–27 April 2001; pp. 54–66.
8. Craig, H. Isotopic variations in meteoric waters. *Science* **1961**, *133*, 1702–1703. [CrossRef] [PubMed]
9. Kopec, B.G.; Feng, X.; Posmentier, E.S.; Sonder, L.J. Seasonal Deuterium Excess Variations of Precipitation at Summit, Greenland, and their Climatological Significance. *J. Geophys. Res. Atmos.* **2019**, *124*, 72–91. [CrossRef]
10. Bershaw, J.; Hansen, D.D.; Schauer, A.J. Deuterium excess and 17O-excess variability in meteoric water across the Pacific Northwest, USA. *Tellus Ser. B Chem. Phys. Meteorol.* **2020**, *72*, 1–17. [CrossRef]
11. Gat, J.R.; Carmi, I. Evolution of the Isotopic Composition of Atmospheric Waters in the Mediterranean Sea Area. *J. Geophys. Res.* **1970**, *75*, 3039–3048. [CrossRef]
12. Gat, J.R.; Carmi, I. Effect of climate changes on the precipitation patterns and isotopic composition of water in a climate transition zone: Case of the Eastern Mediterranean Sea area. In *The Influence of Climate Change and Climatic Variability on the Hydrologic Regime and Water Resources*; International Association Hydrological Sciences Publication Vancouver: Wallingford, UK, 1987; pp. 513–524.
13. Bajjali, W. Spatial variability of environmental isotope and chemical content of precipitation in Jordan and evidence of slight change in climate. *Appl. Water Sci.* **2012**, *2*, 271–283. [CrossRef]

14. Hackley, L.C.; Liu, C.I.; Coleman, D.D. Environmental Isotope Characteristics of Landfill Leachates and Gases. *Groundwater* **1996**, *34*, 827–836. [CrossRef]
15. Jasechko, S. Global Isotope Hydrogeology—Review. *Rev. Geophys.* **2019**, *57*, 835–965. [CrossRef]
16. de Medeiros Engelmann, P.; dos Santos, V.H.J.M.; Barbieri, C.B.; Augustin, A.H.; Ketzer, J.M.M.; Rodrigues, L.F. Environmental monitoring of a landfill area through the application of carbon stable isotopes, chemical parameters and multivariate analysis. *Waste Manag.* **2018**, *76*, 591–605. [CrossRef] [PubMed]
17. Varjani, S.; Gnansounou, E.; Baskar, G.; Pant, D. *Waste Bioremediation*; Springer: Berlin/Heidelberg, Germany, 2018; ISBN 9789811074127.
18. Mukherjee, S.; Mukhopadhyay, S.; Hashim, M.A.; Gupta, B. Sen Contemporary environmental issues of landfill leachate: Assessment and remedies. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 472–590. [CrossRef]
19. Wimmer, B.; Hrad, M.; Huber-Humer, M.; Watzinger, A.; Wyhlidal, S.; Reichenauer, T.G. Stable isotope signatures for characterising the biological stability of landfilled municipal solid waste. *Waste Manag.* **2013**, *33*, 2083–2090. [CrossRef]
20. Pujiindiyati, E.R. Application of deuterium and oxygen-18 to trace leachate movement in Bantar Gebang sanitary landfill. *Atom Indones.* **2011**, *37*, 76–82. [CrossRef]
21. Castañeda, S.S.; Sucgang, R.J.; Almoneda, R.V.; Mendoza, N.D.S.; David, C.P.C. Environmental isotopes and major ions for tracing leachate contamination from a municipal landfill in Metro Manila, Philippines. *J. Environ. Radioact.* **2012**, *110*, 30–37. [CrossRef]
22. Morasch, B.; Richnow, H.H.; Schink, B.; Vieth, A.; Meckenstock, R.U. Carbon and hydrogen stable isotope fractionation during aerobic bacterial degradation of aromatic hydrocarbons. *Appl. Environ. Microbiol.* **2002**, *68*, 5191–5194. [CrossRef]
23. Froehlich, K.; Kralik, M.; Papesch, W.; Rank, D.; Scheifinger, H.; Stichler, W. Deuterium excess in precipitation of Alpine regions—Moisture recycling. *Isot. Environ. Health Stud.* **2008**, *44*, 61–70. [CrossRef]
24. Gonfiantini, R. La composizione isotopica della precipitazioni. *Rend. Soc. Ital. Mineral. Petrol.* **1983**, *38*, 1175–1187.
25. Kerfoot, H.B.; Baker, J.A.; Burt, D.M. The use of isotopes to identify landfill gas effects on groundwater. *J. Environ. Monit.* **2003**, *5*, 896–901. [CrossRef]
26. Meckenstock, R.U.; Morasch, B.; Griebler, C.; Richnow, H.H. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated acquifers. *J. Contam. Hydrol.* **2004**, *75*, 215–255. [CrossRef] [PubMed]
27. Lee, K.S.; Ko, K.S.; Kim, E.Y. Application of stable isotopes and dissolved ions for monitoring landfill leachate contamination. *Environ. Geochem. Health* **2020**, *42*, 1387–1399. [CrossRef]
28. Aboyeji, O.S.; Eigbokhan, S.F. Evaluations of groundwater contamination by leachates around Olusosun open dumpsite in Lagos metropolis, southwest Nigeria. *Environ. Manag.* **2016**, *183*, 333–341. [CrossRef]
29. Nisi, B.; Raco, B.; Dotsika, E. Groundwater contamination studies by environmental isotopes: A review. *Handb. Environ. Chem.* **2016**, *40*, 115–150. [CrossRef]
30. Porowska, D. Identification of groundwater contamination zone around a reclaimed landfill using carbon isotopes. *Water Sci. Technol.* **2017**, *75*, 328–339. [CrossRef]
31. Teh, Y.A.; Silver, W.L.; Conrad, M.E.; Borglin, S.E.; Carlson, C.M. Carbon isotope fractionation by methane-oxidizing bacteria in tropical rain forest soils. *J. Geophys. Res. Biogeosci.* **2006**, *111*, 1–8. [CrossRef]
32. Grossman, E.L.; Cifuentes, L.A.; Cozzarelli, I.M. Anaerobic methane oxidation in a landfill-leachate plume. *Environ. Sci. Technol.* **2002**, *36*, 2436–2442. [CrossRef]
33. North, J.C.; Frew, R.D.; Van Hale, R. Can stable isotopes be used to monitor landfill leachate impact on surface waters? *J. Geochem. Explor.* **2006**, *88*, 49–53. [CrossRef]
34. Dansgaard, W. Stable isotopes in precipitation. *Tellus* **1964**, *16*, 436–468. [CrossRef]
35. Bershaw, J. Controls on deuterium excess across Asia. *Geosciences* **2018**, *8*, 257. [CrossRef]
36. Bates, B.L.; McIntosh, J.C.; Lohse, K.A.; Brooks, P.D. Influence of groundwater flowpaths, residence times and nutrients on the extent of microbial methanogenesis in coal beds: Powder River Basin, USA. *Chem. Geol.* **2011**, *284*, 45–61. [CrossRef]
37. Tazioli, A. Landfill investigation using tritium and isotopes as pollution tracers. *AQUA Mundi* **2011**, *18*, 83–92. [CrossRef]
38. Burgess, J.E.; Quarmby, J.; Stephenson, T. Role of micronutrients in activated sludge-based biotreatment of industrial effluents. *Biotechnol. Adv.* **1999**, *17*, 49–70. [CrossRef]
39. Ünal, B.; Perry, V.R.; Sheth, M.; Gomez-Alvarez, V.; Chin, K.J.; Nüsslein, K. Trace elements affect methanogenic activity and diversity in enrichments from subsurface coal bed produced water. *Front. Microbiol.* **2012**, *3*, 175. [CrossRef]