



Research article

Hydrogeochemistry and groundwater quality assessment in a municipal solid waste landfill (central Italy)

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Abstract: Municipal solid waste landfills leachate can cause serious environmental issues for groundwater quality. Therefore, the application of environmental tracing methods to identify groundwater contamination by municipal solid waste landfills leachate is significant. Hydrogeochemical evaluations to trace municipal solid waste landfills leachate are usually carried out. The study was carried out at a landfill in central Italy (Umbria). Samples of leachate and groundwater have been analyzed to evaluate the impact of leachates on groundwater through the comparison of their hydrogeochemical nature. Parameters like pH, Temperature (T), Electrical Conductivity (EC), redox potential (Eh) and Chemical Oxygen Demand (COD) were also measured in situ using digital instruments. Hydrogeochemical data (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , HCO_3^- , Cl^- , NO_3^-), ionic ratios and geochemical correlations were used to confirm the processes that govern the chemistry of the spring water and to identify leachate contamination phenomena. In fact, the main geochemical diagrams (Langelier-Ludwig, Piper, Schoeller) confirm the leachate contamination in a groundwater sample. In particular, the Piper diagram shows that a sample is in $\text{Na}^+ - \text{Cl}^- - \text{HCO}_3^-$ mixing zone, indicating a possible influence of the leachate on groundwater chemistry. As a matter of fact, some correlations between major elements, such as Cl^- versus Na^+ and Cl^- versus HCO_3^- , confirm that the leachate in this study area is highly enriched in Cl^- and HCO_3^- due to wastes dissolution and degradation

processes. Further, the assessment of K^+/Mg^{2+} ratio also confirms the presence of a sample heavily impacted from leachate contamination. These results indicate that also one basic hydrogeochemical study can be useful for fingerprinting the leachate pollution for groundwater samples.

Keywords: hydrogeochemistry; environmental tracers; major ions; municipal solid waste; leachates; hydrogeochemical evaluation; groundwater quality

1. Introduction

Landfill leachate is a serious source of groundwater pollution [1,2]. It can form by interaction between rainfall percolating and municipal solid wastes, thorough a range of biodegradation and leaching reactions [2,3]. The leachate contains 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) [4–8]. 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 [4,8,9]. Therefore, it is fundamental the assessment of environmental risks due to landfill leachate going to water resources, specially to groundwater. So, it is necessary to perform environmental monitoring programs, in order to detect the potential leachate influence on groundwater near to the landfill area. Pollution levels from landfill leachate plumes in groundwater can be assessed using hydrogeochemical and isotopic signatures of the landfill leachate. This kind of information can be used to provide proper measures for the remediation of landfill-impacted groundwater systems [1,9–11]. In fact, several studies [1,8,12,13] have proposed multidisciplinary approaches to supply information about landfill environmental impacts. Landfill leachates can undergo several bio-geochemical reactions, if they are set into surrounding groundwater. Therefore, these bio-geochemical reactions must be traced using parameters as signatures of the leachates and surrounding groundwater [1,14]. In literature, several hydrogeochemical and isotopic approaches have been proposed to study the biogeochemical processes occurring during organic waste degradation to control the leachate impacted aquifers [1,8,13–20]. 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 can provide more information about landfill environmental impacts. A study of hydrogeochemical processes in groundwater in this area of a landfill location, in Umbria (central Italy), has been carried out to understand the impact of the landfill leachates on groundwater quality, in order to distinguish between the rock-water interactions and anthropogenic influences. According to interaction with aquifer minerals or internal mixing of different groundwater along subsurface flow-paths, groundwater can chemically evolve [21]. A basic hydrogeochemical study has been proposed, applied to an aquifer near a landfill in Umbria, such as to consider the evaluation of the chemical-physical parameters (pH, Temperature—T, Electrical Conductivity—EC, redox potential—Eh and Chemical Oxygen Demand—COD) and of groundwater major elements (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , HCO_3^- , Cl^- , NO_3^-), in order to verify the suitability as fingerprinting tracers of

the leachate pollution. The ratios of major ions provide critical clues to explain different hydrogeochemical processes of water resource [22]. The aim is to assess the impact of the landfill on groundwater quality, to identify the hydrogeochemical processes related to groundwater quality, to carry on a hydrogeochemical evaluation of the aquifer system and to delineate the various factors controlling the water chemistry.

1.1. Study area

The study area (Figure 1) is characterized by a hilly morphology, with altitude ranging between 500 and 600 m a.s.l. According to Geological Map of Italy (scale 1:100.000), it is possible to identify the presence of two outcropping deposits: upper sandy conglomerate deposits and marly arenaceous formation (Figure 1). 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. The landfill plant, designed in the 80s, covers an area of approximately 0.12 km². Actually, it is used for the storage of municipal solid waste (MSW). In the study area, there is a debris layer, as shown in Figure 1, which has been therefore caused the design of an impermeable layer at the landfill bottom, capable of ensuring a perfect water seal of the landfill bottom. Moreover, an embankment has been located at downstream of the landfill. It is consisting of variable dimensions soil, with lithoid elements of sandstone and marl. On the embankment downstream of the landfill, a series of sub-horizontal drains have been drilled to drain most part of the landfill percolation water. These drains have been made with a slope, such as to drain the percolation water to the downstream of the embankment, towards the drains channels of the shallow waters. During the executive phase, in order to reduce the connection between rainwater and embanked waste and to avoid the production of leachate, drainage channels have been created. They are due to discharge the surface water into the canal at downstream of the embankment. In the end, a final covering with waterproofing layers has been located.

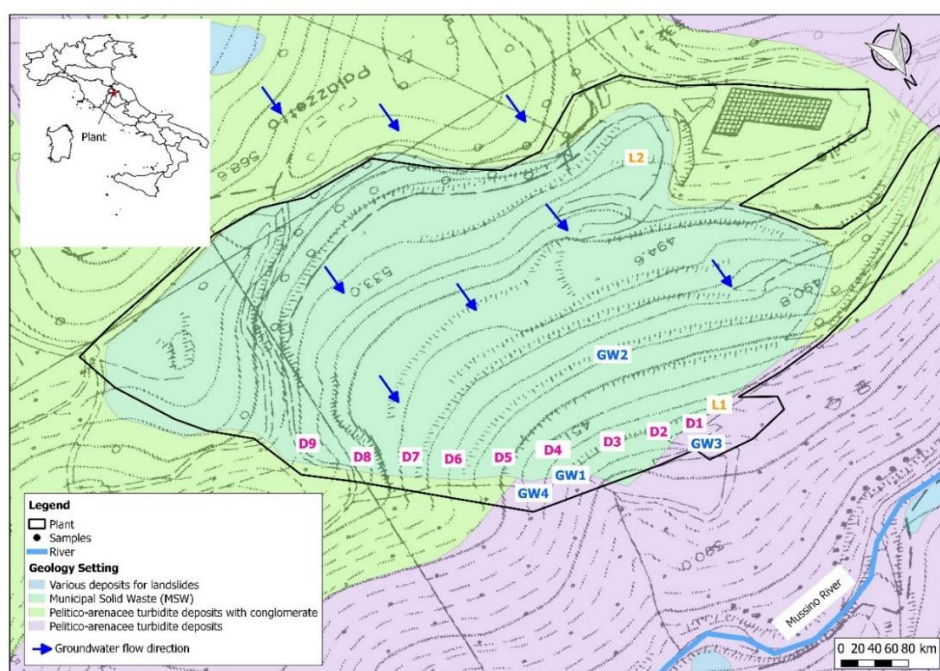


Figure 1. Geological Setting.

Figure 1 shows groundwater sampling points (identified by “GW” annotation), leachate tanks sampling points (identified by “L” annotation), and drainage water sampling points (identified by “D” annotation). Moreover, for the study a rainfall sample (identified by “RW” annotation) has been considered.

2. Materials and methods

The water sampling survey was carried out during the groundwater monitoring sampling in the rainy season (January 2020) to include any possible dilution phenomena. Two monitoring sampling surveys have been carried out: the first one on January 9th, 2020 (in this study identified as case A), for a total of 12 samples, and the second one on January 27th, 2020 (in this study identified as case B), for a total of 8 samples. They are referred to the same rainy season and this fact makes more sound the output of the elaborations and interpretations of data, here presented. Groundwater sampling has been carried out according to the low flow sampling procedure, established by Environmental Protection Agency [23] for groundwater samples collection from monitoring wells. The sampling procedure provides [23] that, prior to sampling, each well was purged of approximately one to two well volumes until stabilization of temperature (T), electrical conductivity (EC), and pH values in order to ensure the removal of stagnant water and the sampling of water from the aquifer. In fact, for the study case, the monitoring wells purging was accomplished by using a submersible pump, with a pumping rate ranging from 1 to 5 l/min. Moreover, according to the sampling procedure provides [23], the samples were collected in high-density polyethylene (HDPE) bottles and include, for each well, (i) one filtered and unacidified aliquot for alkalinity determination and anion analysis and (ii) one filtered aliquot acidified with ultrapure nitric acid (1% v/v) for analysis of major cations. Filtration was performed in the field with 0.45- μm membrane filters using disposable plastic syringes. The chemical-physical parameters were measured in the field using a multiparameter probe (WTW, 3320). Once collected in HDPE bottles, the samples were stored in ice until delivery to the laboratory and stored at 4 °C until analysis. The chemical composition has been determined using standard analytical methods [24]. Bicarbonate was determined on site by titration with 0.1 N HCl using color turning method with methyl orange. According to guidelines [25,26] element concentrations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , HCO_3^- , Cl^- , NO_3^-) were determined at the Geochemistry Laboratory of Sapienza University in Rome with a Dionex ICS5000 ion chromatograph (gradient proportioning accuracy and precision $\pm 0.5\%$ at 2 mL/min, analytical only) using a Dionex AS9-SC column for anions (eluent—1.8 mM sodium carbonate, 1.7 mM sodium bicarbonate; flow rate—2.0 mL/min; injection volume—50 μL ; detection suppressed conductivity, ASRS® ULTRA 4-mm, AutoSuppression®, recycle mode) and a Dionex ICS 1100 ion chromatograph (precision $\pm 5\%$ at 0.25 mL/min, analytical only) using a Dionex CS-12 column for cations. Sigma-Aldrich PRIMUS-Primary Multi-Ion Standards for Ion Chromatography (10 mg/kg of each anion and cation solutions) were used for calibration.

3. Results

This paragraph shows the results of the chemical-physical parameters (Table 1) and the concentrations of the major elements (Tables 2 and 3), anions and cations, determined with the ion

chromatograph. Table 1 shows the results of the chemical-physical parameters (pH, Temperature—T, Electrical Conductivity—EC, redox potential—Eh and Chemical Oxygen Demand—COD).

Table 1. Chemical-physical parameters. Case A: January 9th, 2020; Case B: January 27th, 2020. D: drainage; GW: groundwater; L: leachate; RW: rainwater.

Case A					
Sample	pH	EC μS/cm	T °C	COD mg/L O ₂	Eh mV
D1	7.73	1630	10.8	19	162
D2	7.44	5690	10.7	449	167
D3	8.23	1310	10.5	35	171
D4	7.86	1100	7.86	21	175
D5	8.04	1210	10.9	17	171
L1	8.35	11100	–	2060	–
L2	8.45	15200	–	4590	–
GW1	8.12	1070	9.8	28	133
GW2	8.32	850	8.32	11	172
GW3	8.25	840	9.7	21	151
GW4	7.75	1380	7.75	34	177
RW	6.55	11	12.3	11	190
Case B					
Sample	pH	EC μS/cm	T °C	COD mg/L O ₂	Eh mV
D2	7.37	5790	10.3	479	199
D6	7.94	1710	10.5	22	187
D3	8.01	1430	10.1	29	189
D4	7.96	1240	10.4	11	192
D7	8.03	1390	10.7	10	195
D5	7.91	1250	10.5	9	197
D8	8.05	1080	10.8	9	194
D9	7.65	1200	10.2	11	203

Table 1 shows that the D2 sample has high EC, i.e., 5690 μS/cm for case A and 5790 μS/cm for case B. In fact, the L1 sample by leachate tanks showed also comparatively high EC values, i.e., 11,100 μS/cm for case A (Table 1). D2 is a sub-horizontal drain positioned at the embankment downstream of the landfill and it is near L1, a tank used for the leachate storage. Table 2 shows the major elements results. The chemical composition has been determined using standard analytical methods [24]. Bicarbonate was determined on site by titration with 0.1 N HCl using color turning method with methyl orange.

The major elements are expressed in milligrams per liter (mg/L) in Table 2. However, thanks to the conversion factors, the major elements concentrations have been converted in milliequivalents per liter (meq/L) in Table 3.

Table 2. Major elements concentrations in mg/l. Case A: January 9th, 2020; Case B: January 27th, 2020. D: drainage; GW: groundwater; L: leachate; RW: rainwater.

Case A								
Sample	Cations				Anions			
	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	Cl ⁻ mg/l	SO ₄ ²⁻ mg/l	HCO ₃ ⁻ mg/l	NO ₃ ⁻ mg/l
<i>Detention</i>	0.5	0.5	0.5	0.1	0.1	0.1	6	0.1
<i>Limit</i>								
D1	281	47.7	43.8	4.0	234	50.5	683	5.3
D2	306	72.4	419	174	980	16	720	0.1
D3	235	29.9	68.2	10.4	210	60.8	510	12.8
D4	199	23.2	65.4	1.6	107	67.2	543	3.3
D5	259	27.9	48.9	1.1	120	57.4	670	0.8
L1	133	38.2	869	660	1230	80.3	6470	0.1
L2	57.7	29.7	1350	1210	2200	299	8400	0.1
GW1	175	26.7	37.8	1.53	91.1	127	458	5.6
GW2	129	39	12.1	2.61	12.9	111	485	0.84
GW3	132	25.9	16.9	2.86	28.8	101	421	2.19
GW4	223	25.1	41.3	15.8	45.4	146	695	28.8
RW	1.1	0.5	0.7	0.4	1.53	0.9	18	0.1
Case B								
Sample	Cations				Anions			
	Ca ²⁺ mg/l	Mg ²⁺ mg/l	Na ⁺ mg/l	K ⁺ mg/l	Cl ⁻ mg/l	SO ₄ ²⁻ mg/l	HCO ₃ ⁻ mg/l	NO ₃ ⁻ mg/l
D2	299.0	70.4	476.0	196.0	950	8.4	1500	0.1
D6	365.0	20.2	48.7	4.2	241	27.6	800	0.1
D3	215.0	29.4	81.1	10.8	230	64	430	19.8
D4	204.0	27.0	69.2	1.8	127	67.5	540	2.64
D7	272.0	26.0	54.3	1.2	143	58.5	670	0.1
D5	236.0	30.5	46.2	1.2	140	54.3	630	0.66
D8	206.0	25.0	30.1	0.7	76.7	28.9	610	0.1
D9	228.0	24.6	47.9	1.2	84.2	68.5	653	5.45

The analytical precision of the data has been measured using the normalized inorganic charge balance, which is defined as $[(\sum cat - \sum an)/(\sum cat + \sum an)] \times 100$ and represents the fractional difference between the total cations ($\sum cat$) and total anions ($\sum an$), considering both case A and case B. According to the standard method 1030E “checking analyses correctness” [24], the charge balance percentage between anions and cations concentrations sum in meq/L was assessed and analyses were accepted for deviations of $< \pm 5\%$.

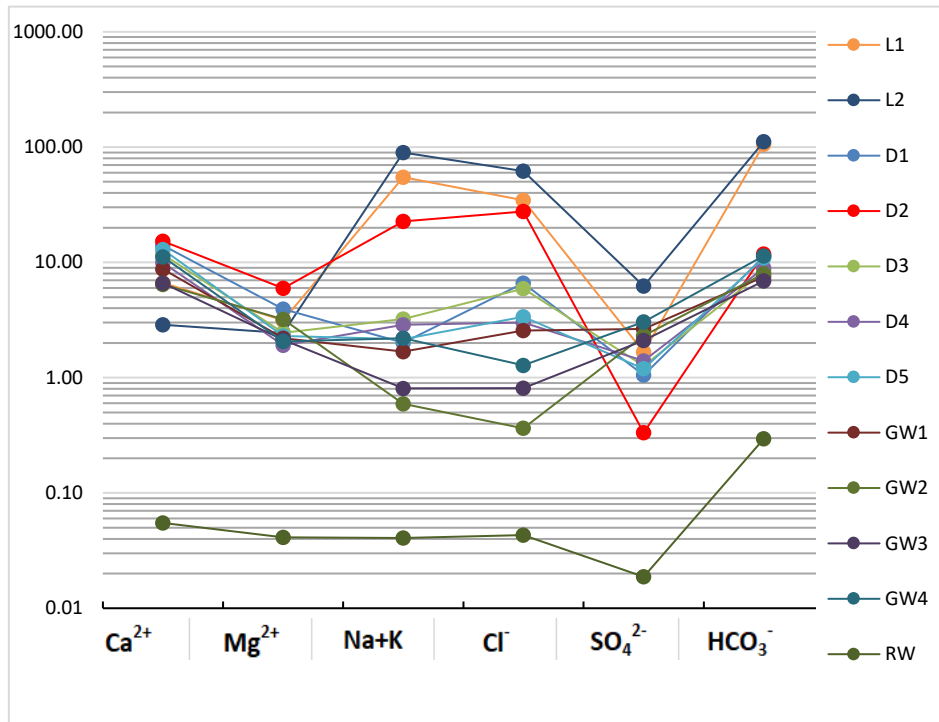
Table 3. Major elements concentrations in meq/l. Case A: January 9th, 2020; Case B: January 27th, 2020. D: drainage; GW: groundwater; L: leachate; RW: rainwater.

Case A									Δ (%)
Sample	Cations				Anions				
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	
	meq/l	meq/l	meq/l	meq/l	meq/l	meq/l	meq/l	meq/l	
D1	14.02	3.92	1.90	0.10	6.60	1.05	11.19	0.09	3%
D2	15.27	5.95	18.22	4.45	27.64	0.33	11.80	0.00	5%
D3	11.73	2.46	2.97	0.27	5.92	1.27	8.359	0.21	5%
D4	9.93	1.91	2.84	0.04	3.02	1.40	8.90	0.05	5%
D5	12.92	2.29	2.13	0.03	3.38	1.20	10.98	0.01	5%
L1	6.64	3.14	37.78	16.88	34.69	1.67	106.04	0.00	-2%
L2	2.88	2.44	58.70	30.95	62.04	6.23	137.68	0.00	-1%
GW1	8.73	2.196	1.64	0.04	2.57	2.64	7.51	0.09	-1%
GW2	6.44	3.21	0.53	0.07	0.36	2.31	7.95	0.01	-2%
GW3	6.59	2.13	0.73	0.07	0.81	2.10	6.90	0.04	-2%
GW4	11.13	2.06	1.80	0.40	1.28	3.04	11.39	0.46	-3%
RW	0.0549	0.0411	0.0304	0.0102	0.0431	0.0187	0.2950	0.0016	-
Case B									Δ (%)
Sample	Cations				Anions				
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	
	meq/l	meq/l	meq/l	meq/l	meq/l	meq/l	meq/l	meq/l	
D2	14.92	5.79	20.70	5.01	26.790	0.175	24.58	0.002	-5%
D6	18.21	1.66	2.12	0.11	6.796	0.575	13.11	0.002	4%
D3	10.73	2.42	3.53	0.28	6.486	1.332	7.04	0.319	5%
D4	10.18	2.22	3.01	0.05	3.581	1.405	8.85	0.043	5%
D7	13.57	2.14	2.36	0.03	4.033	1.218	10.98	0.002	5%
D5	11.78	2.51	2.01	0.03	3.948	1.131	10.32	0.011	3%
D8	10.28	2.06	1.31	0.02	2.163	0.602	9.99	0.002	3%
D9	11.38	2.02	2.08	0.03	2.374	1.426	10.70	0.088	3%

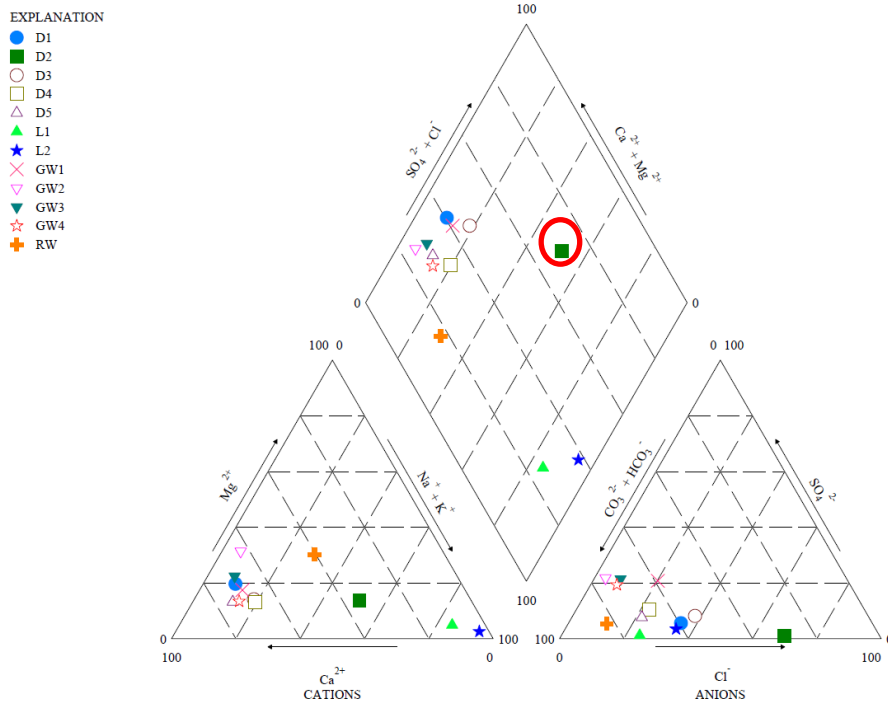
4. Discussions

4.1. Graphical representation of water quality data

Analysis results of the groundwater major elements have been plotted with the main geochemistry diagrams: Schoeller, Langelier-Ludwig and Piper. These graphical methods are designed to simultaneously represent the Total Dissolved Solid concentration (TDS) and the relative proportions of certain major ionic species [21,27–30]. Figure 2 shows the Schoeller's (Figure 2a) and Piper's (Figure 2b) diagram for the case A and Figure 3 shows the Schoeller's (Figure 2 a) and Piper's (Figure 2b) diagram for the case B.

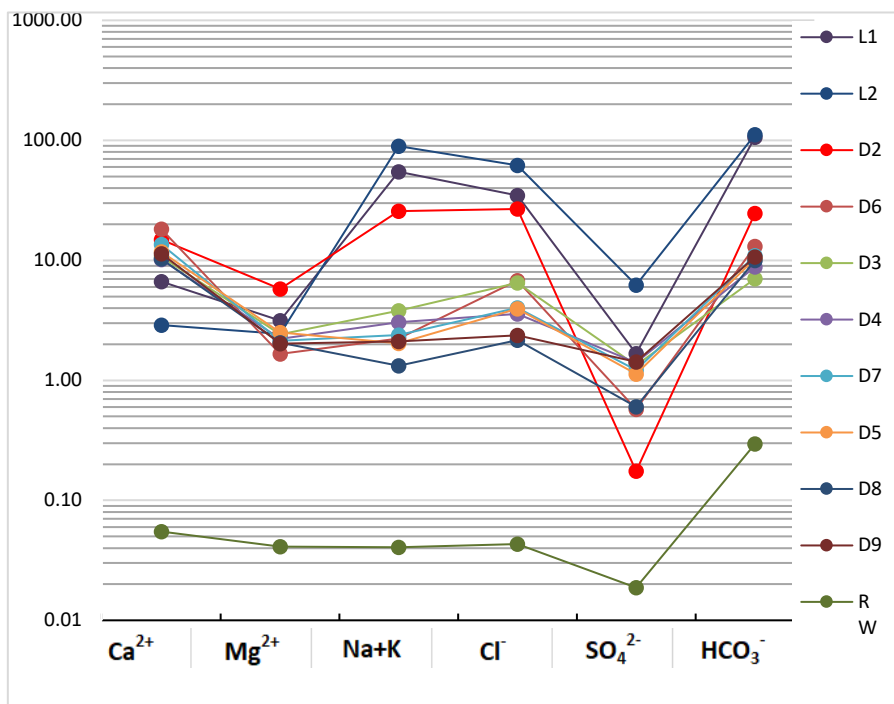


a)

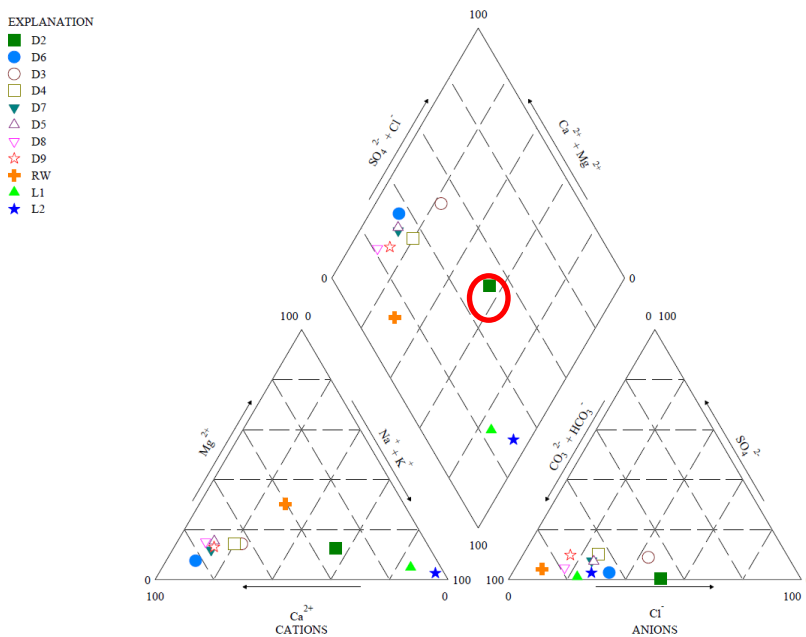


b)

Figure 2. Case A geochemical representation: a) Schoeller's and b) Piper's diagram.



a)



b)

Figure 3. Case B geochemical representation: a) Schoeller's and b) Piper's diagram.

For case B, the diagrams of the groundwater major elements show also the rainfall sample RW and the two leachate samples L1 and L2 of case A in order to perform some comparisons. The geochemical results show that D2 sample has strange geochemical behaviour with respect to the other groundwater samples. In fact, the Schoeller diagram, for case A (Figure 2a) and case B (Figure 3a), shows that for sample D2 (in red in the Figure 2a and Figure 3a) the main cation is Na^+ , with abundance order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$, while the anions are dominated by Cl^- , with abundance order of $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. The geochemical behaviour, in fact, is more similar to leachate samples L1 (in orange in Figure 2a) and L2 (in purple in Figure 3a), thus showing a possible phenomenon of groundwater contamination for D2 sample. At the same time, the Piper diagram (Figure 2b and Figure 3b) shows that these groundwater samples (GW1 – GW4) are characterized by a prevalence of magnesium bicarbonate facies. On the contrary, sample D2 is located in the $\text{Na}^+ - \text{Cl}^- - \text{HCO}_3^-$ mixing zone (Figure 2b and Figure 3b). Leachate samples L1 and L2, as well as sample D2, in the study area are highly enriched in Na^+ , Cl^- , and HCO_3^- due to waste dissolution and degradation processes [1]. The groundwater chemistry has evolved from $\text{Ca}^{2+} - \text{HCO}_3^-$ association to $\text{Na}^+ - \text{Cl}^- - \text{HCO}_3^-$ association, due to the presence of leachate on groundwater chemistry (Figure 2b and Figure 3b). Moreover, Figure 4 shows the Langelier-Ludwig diagram.

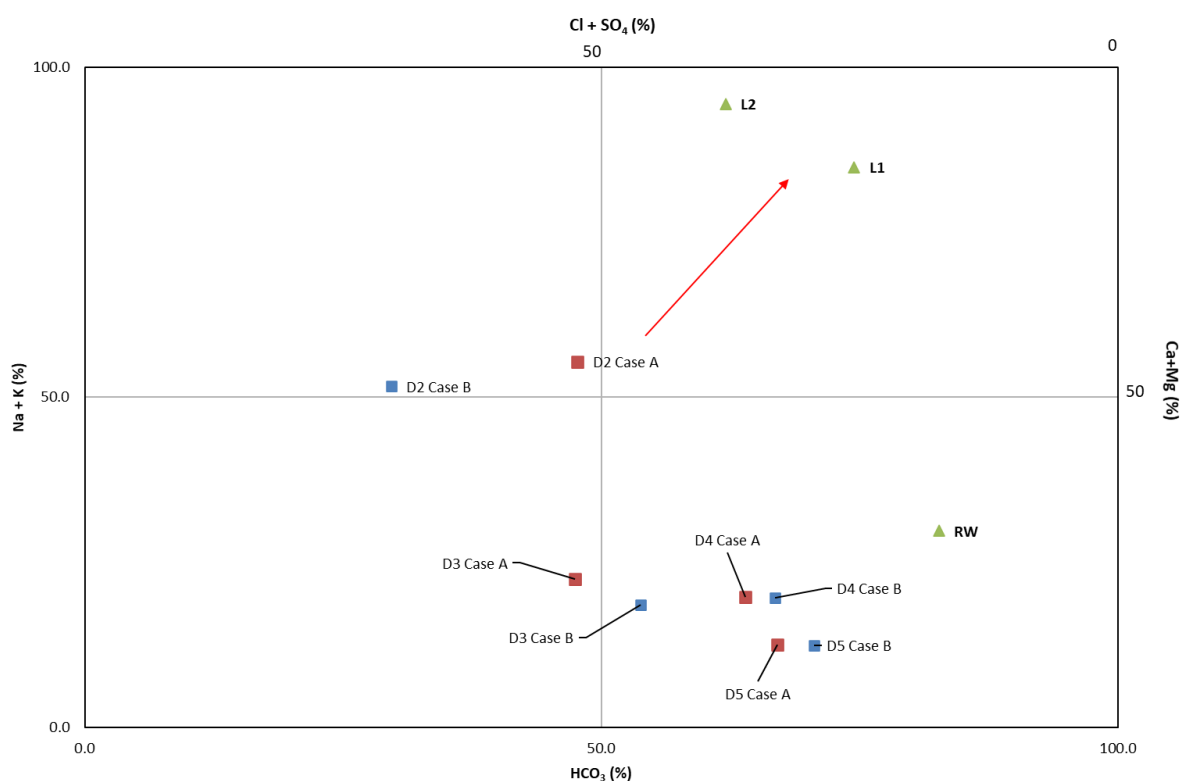


Figure 4. Langelier-Ludwig diagram.

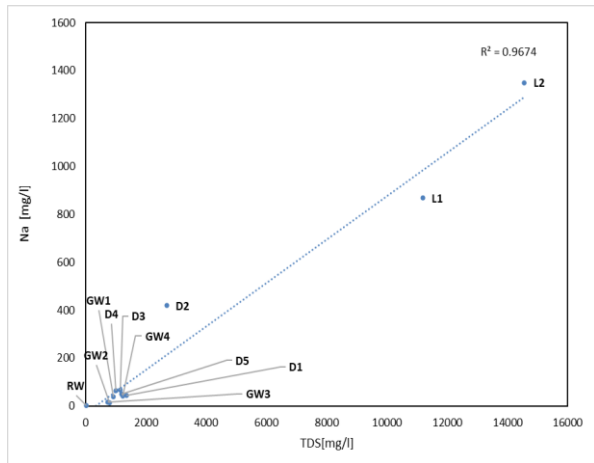
Figure 4 shows only the samples carried out during both monitoring sampling surveys. The drainage water samples D3, D4, D5 and the rainfall sample RW show a prevalence of the bicarbonate (HCO_3^-) ions, thus proving a magnesium bicarbonate facies. The sample D2 shows a prevalence of the $\text{Na}^+ + \text{K}^+$ cationic association and bicarbonate, as well as samples L1 and L2.

4.2. Hydrogeochemical evaluation

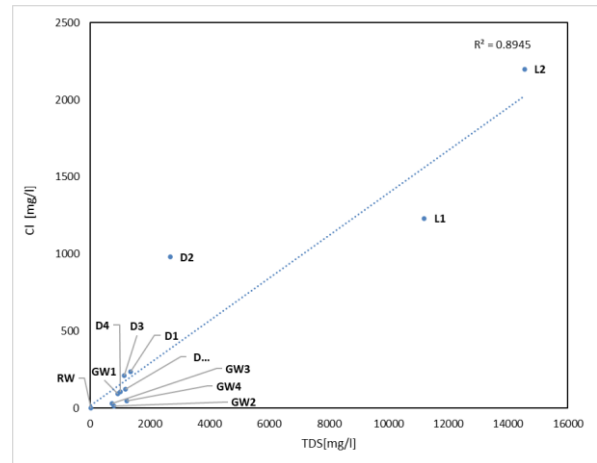
Bivariate major element versus TDS diagrams (Figure 5 and Figure 6) are, usually, applied to assess the geochemical processes, and in particular to identify possible contamination between leachate and groundwater [15–17,30]. In the following elaborations, for case B, the chemical results of the groundwater samples and leachate samples L1 and L2 of the case A have been considered, due to lack of data.

Figure 5 (a–c) shows a statistically significant linear trend ($R^2 \geq 0.9$, $N = 12$) between TDS and Na^+ (Figure 5a), Cl^- (Figure 5b) and HCO_3^- (Figure 5c) for the case A. However, sample D2 has an anomalous geochemical behaviour, closer to L1 and L2 leachate samples, in comparison with the other samples, which in fact are closer to the origin where the rainfall sample RW is present. On the contrary, sample D2 has very high concentrations of Na^+ (419 mg/L) and Cl^- (980 mg/L) and HCO_3^- (720 mg/L), as well as a high TDS content (2690.52 mg/L), closer to the behaviour to L1 and L2 leachate samples. This is also highlighted by Case B, in Figure 6 (a–c), verifying a statistically significant linear trend ($R^2 = 0.9$, $N = 15$). In fact, for case B, the sample D2 shows a geochemical behaviour as well as the leachate samples L1 and L2, with very high concentrations of Na^+ (476 mg/L), Cl^- (950 mg/L), HCO_3^- (1500 mg/L). Moreover, Figure 7 (a and b) shows a bivariate SO_4^- versus TDS diagram for the two cases.

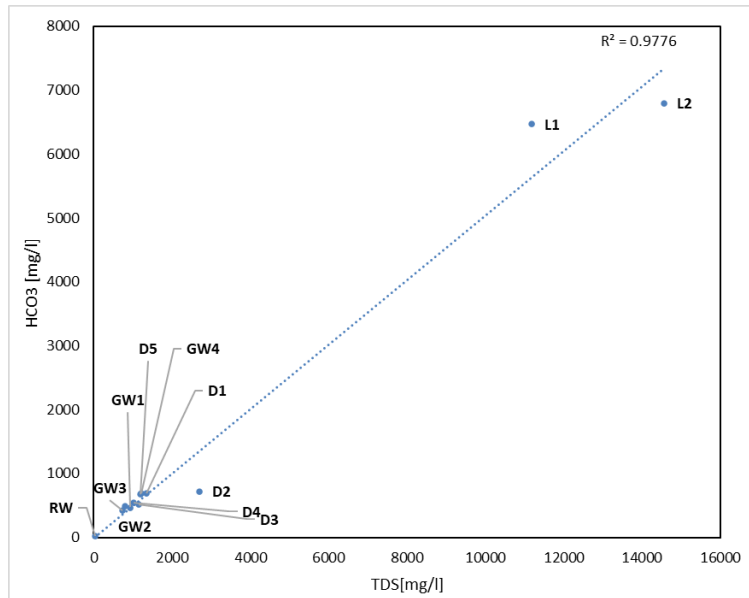
Figure 7 (a–b) shows geochemical trends for groundwater samples (GW) similar to each other, but nevertheless different from drainage water samples (D). However, sample D2 both in case A (Figure 7a) and in case B (Figure 7b) appears to have geochemical behaviours same as leachate samples L1 and L2, with high TDS values. However, the extent of landfill impact on groundwater has been assessed by comparing the chemistry of groundwater, drainage water and leachates, combining with the hydrogeological information about probable flow paths [30]. In fact, the geochemical variations in the ionic concentrations in groundwater and drainage water can easily be understood, when they are plotted along an X–Y coordinate [17,21,27]. Results from the chemical analyses were used to identify the geochemical processes and mechanisms in the groundwater aquifer system and to assess possible contamination phenomena (Figure 8 a–d).



a)

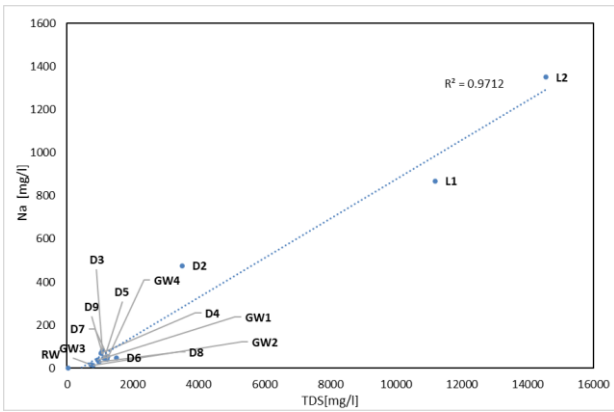


b)

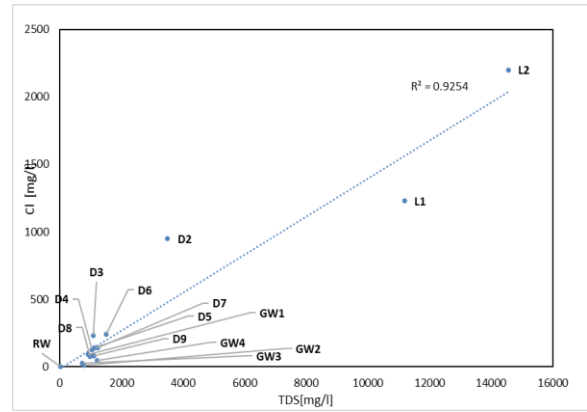


c)

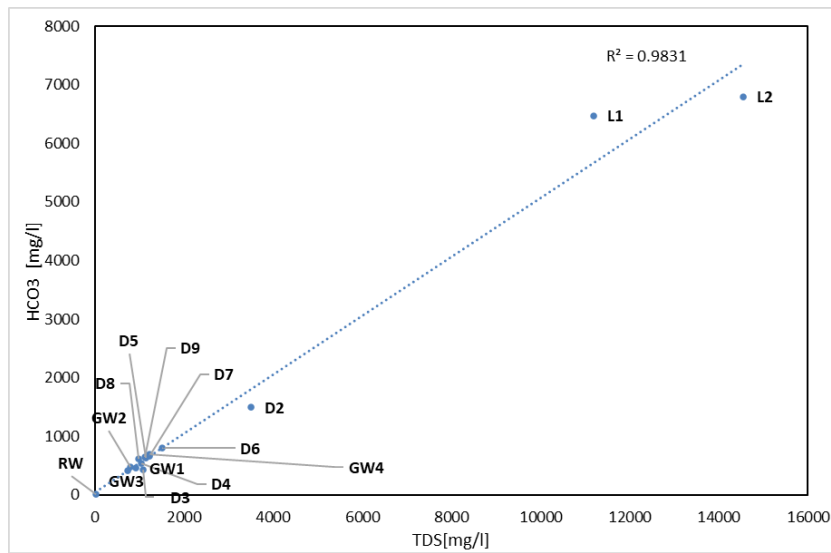
Figure 5. TDS versus major element concentrations (Case A): a) Na^+ , b) Cl^- , c) HCO_3^- .



a)

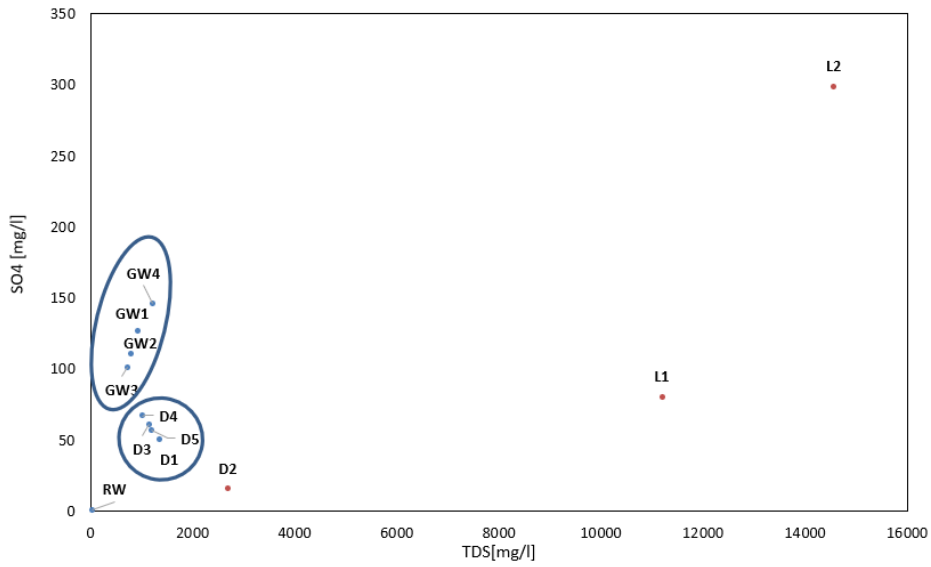


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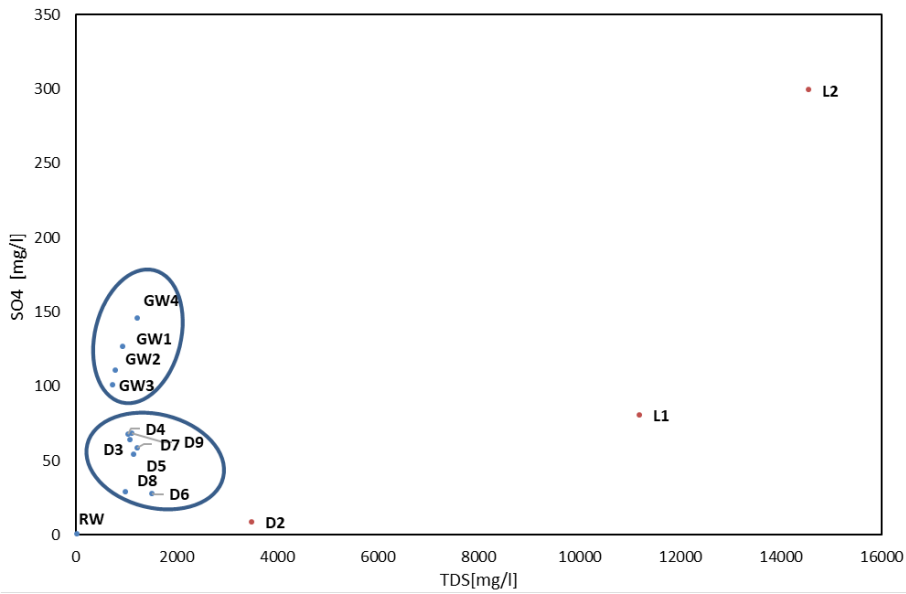


c)

Figure 6. TDS versus major element concentrations (Case B): a) Na^+ , b) Cl^- , c) HCO_3^- .



a)



b)

Figure 7. TDS versus SO₄⁻ : a) for Case A, b) for Case B.

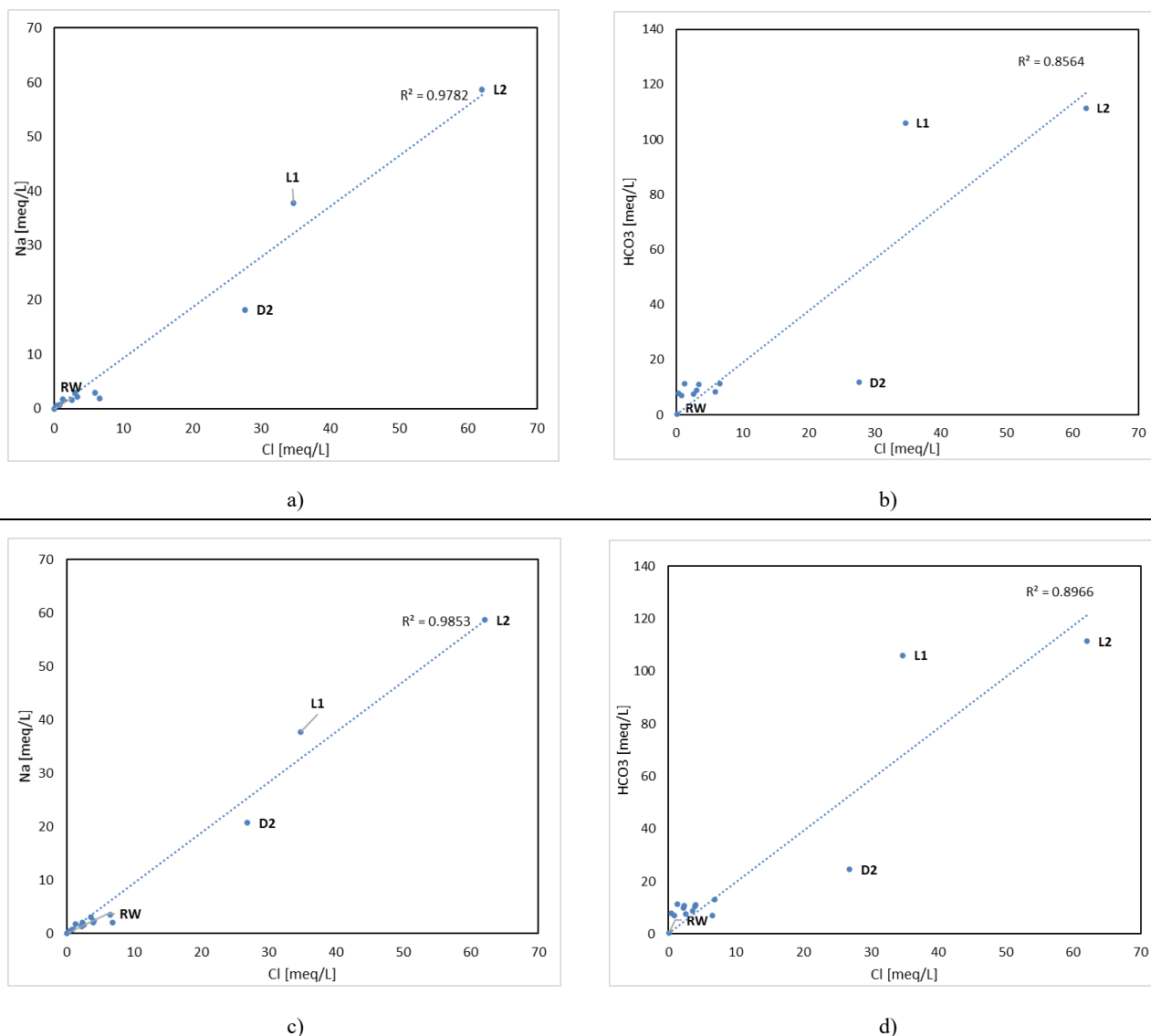
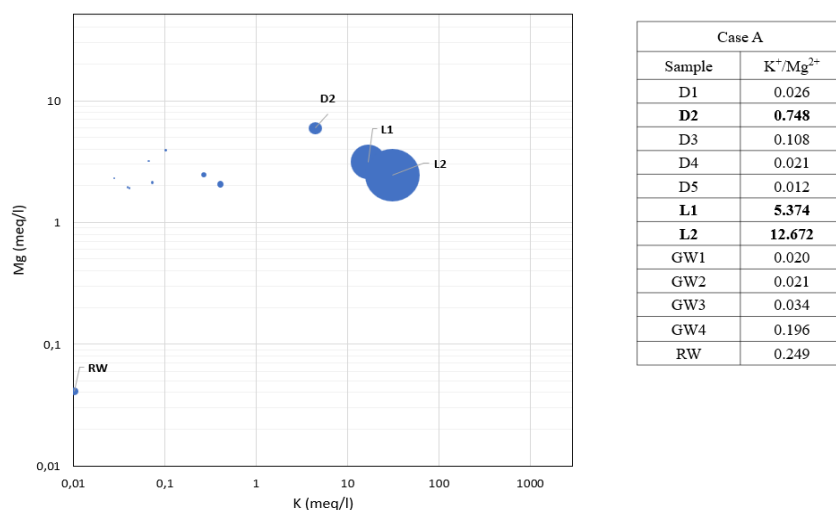


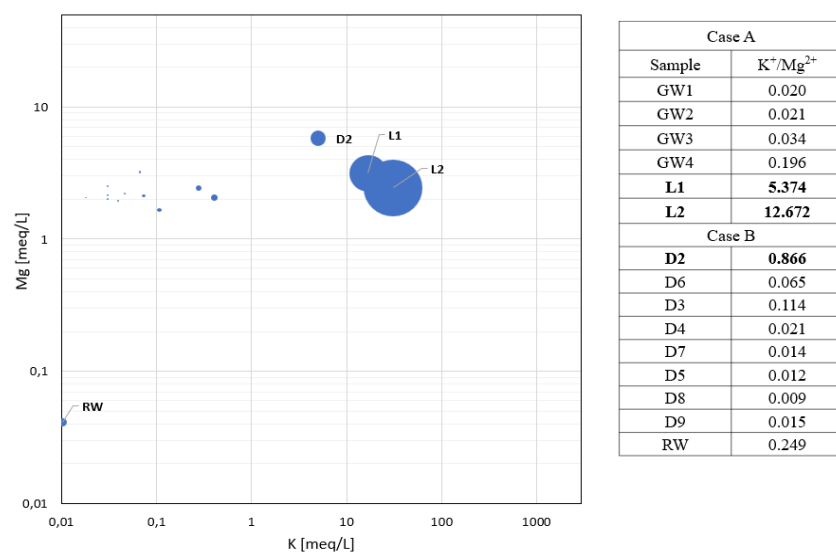
Figure 8. For case A: a) Plot of Cl^- versus Na^+ , b) plot Cl^- of versus HCO_3^- ; for case B: c) plot of Cl^- versus Na^+ , d) plot of Cl^- versus HCO_3^- .

Scatter plots have been performed between major elements: Cl^- versus Na^+ , for case A (Figure 8a) and for case B (Figure 8c), Cl^- versus HCO_3^- , for case A (Figure 8b) and for case B (Figure 8d). Na^+ concentrations is positively correlated with Cl^- content [1,31], with R^2 equal to 0.9782 for case A (Figure 8a) and equal to 0.9853 for case B (Figure 8c). However, the drainage water sample D2 and the leachate samples L1 and L2 show anomalous geochemical behaviour due to high content of chloride (Cl^-) concentrations. In fact, according to Olosson et al., 2005 [16], most composite landfills produce a leachate rich in chloride since chloride ions usually follow the water flow. In fact, Cl^- is a conservative tracer of the direct influence of landfill leachate [1] as high Cl^- concentrations can indicate an external input from the landfill, like leachate, as samples L1 shows, since there is no possible natural source of chloride in the study area. Moreover, the trend of chloride versus bicarbonates has been also represented, for case A in Figure 8b and for case B in Figure 8d. These scatter plots show high HCO_3^- concentrations for sample D2 and for leachate samples L1 and L2. In fact, the Piper diagram in Figure

2b and Figure 3b have been shown that the sample D2, as well as the leachate samples L1 and L2, are located in the $\text{Na}^+ - \text{Cl}^- - \text{HCO}_3^-$ mixing zone due to waste dissolution and degradation processes [1]. This is supported by the positive correlation between Cl^- and HCO_3^- concentrations, with $R^2 = 0.856$ for case A in Figure 8b and equal to 0.896 for case B in Figure 8d, indicating the influence of the leachate plumes [1]. Furthermore, to verify possible impacts of leachate on groundwater and drainage water samples, comparisons between magnesium (Mg^{2+}) and potassium (K^+) concentrations have been performed through a scatter plot on log scale (Figure 9 a, b).

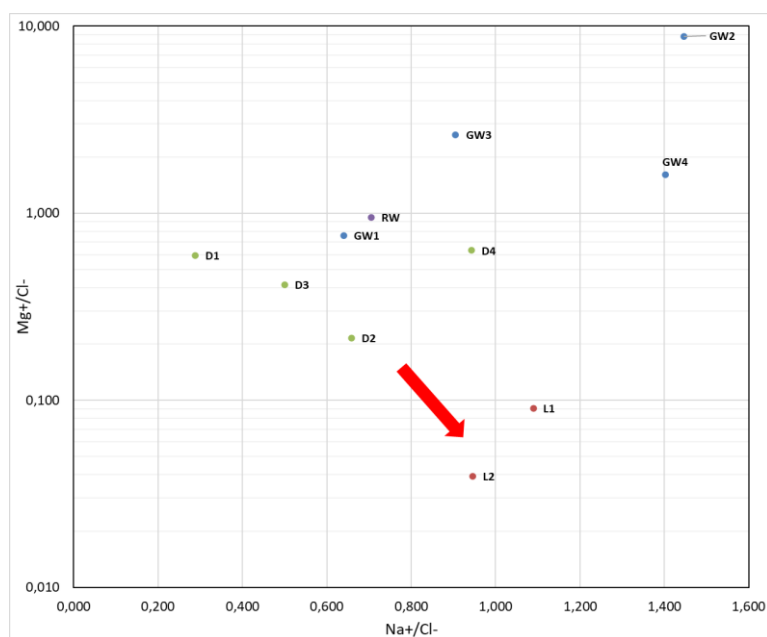


a)

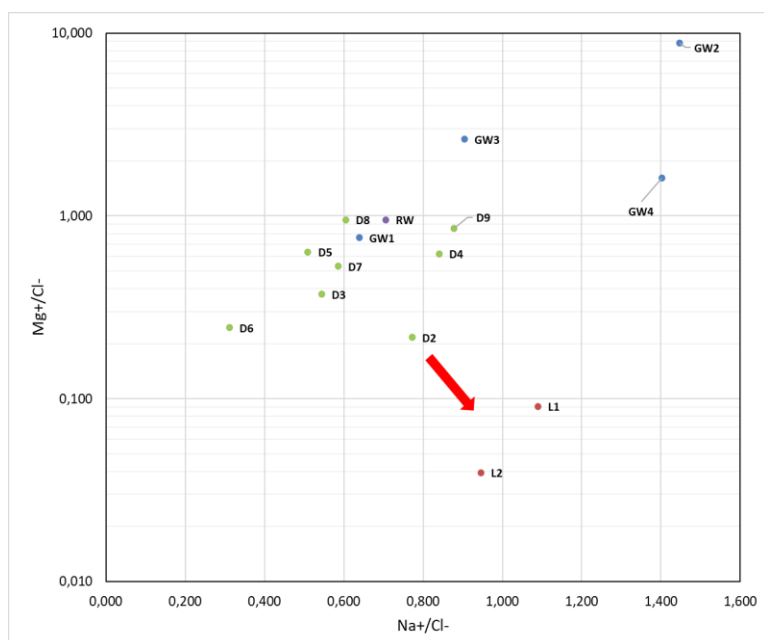


b)

Figure 9. Scatter plot of Mg^{2+} Versus K^+ with leachate samples to observe the impact on groundwater samples and drainage water samples: a) case A, b) case B (the size of the symbol indicates the $\text{K}^+/\text{Mg}^{2+}$).



a)



b)

Figure 10. The ion ratios of $\text{Mg}^{2+}/\text{Cl}^-$ versus Na^+/Cl^- : a) for case A, b) for case B.

The Mg^{2+} versus K^+ graph in Figure 9 on log scale highlights significant differences between the sample's compositions [30]. Figure 9 shows that leachate L1 and L2 has the highest $\text{K}^+/\text{Mg}^{2+}$ ratio (symbol size) [30], due to high values of potassium, as well as the drainage water sample D2, whose

geochemical characteristics are influenced by leachate contamination. For case A, the drainage water sample D2 shows a K^+/Mg^{2+} ratio equal to 0.748 (Figure 9a) and for case B the K^+/Mg^{2+} ratio is equal to 0.866 (Figure 9b). The leachate in the study site is highly enriched in Na^+ , K^+ and HCO_3^- due to waste dissolution and degradation processes [1,30]. Moreover, a plot of the ratio magnesium/chloride (Mg^{2+}/Cl^-) versus sodium/chloride (Na^+/Cl^-) [16] have been shown in Figure 10 (a, b).

Figure 10 (a, b) shows that the groundwater samples are characterized by high Mg^{2+}/Cl^- ratios, because they have high Mg^{2+} concentrations, according to magnesium bicarbonate facies of aquifer, shown in Piper diagram (Figure 2a and Figure 3b). On the contrary, the leachate samples L1 and L2 have high Na^+/Cl^- due to high Cl^- concentrations, produced by landfills [16]. In fact, D2 sample stretch along a line towards leachate, confirming contamination phenomena.

5. Conclusions

Groundwater is one of the most important naturale resource for different uses water supply, worldwide. This research indicates that the water-rock interaction affects, sensitively, groundwater quality, especially when the main groundwater flow system is local. The hydrogeochemical results confirm the leachate contamination in some drainage samples. This shows that the leachate samples are highly enriched in Na^+ , K^+ , HCO_3^- and Cl^- due to waste dissolution and degradation processes. The correlation between Cl^- versus Na^+ (for case A in Figure 8a and for case B in Figure 8c) e between Cl^- versus HCO_3^- (for case A in Figure 8b and for case B in Figure 8d) show that D2 are enriched in Cl^- , as well as in HCO_3^- . In fact, according to Olosson et al., 2005 [16], most composite landfills produce a leachate rich in chloride since chloride ions usually follow the water flow. The ion Cl^- is a conservative tracer that may indicate the direct influence of landfill leachate[1]. Therefore, the high Cl^- concentrations in D2 sample can indicate an external input from the landfill, maybe from leachate samples. At the same time, the correlation between Mg^{2+} and K^+ , shown on log scale graph in Figure 9 (a, b), confirms a contamination of D2 sample by leachate. The highest K^+/Mg^{2+} ratio for D2 sample, as well as for L1 and L2 leachate samples, shows high concentrations of potassium due to waste dissolution and degradation processes [1,30].

Therefore, performing monitoring programs of geochemical parameters, in correspondence with municipal solid waste landfills (MSW), is useful for assess and control possible contamination phenomena by leachate. In fact, a particular attention should be paid to the wells situated down gradient of the landfill and in the direction of groundwater flow.

Conflict of interest

The authors declare no conflict of interest.

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