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ASSESSMENT OF PHYSICOCHEMICAL QUALITY OF THE POLLUTING LOAD OF LEACHATES FROM THE WILD DUMP OF EL HAJEB CITY (MOROCCO)

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Abstract

The dump in the town of El Hajeb (Morocco) is devoid of a collection and treatment system of the generated brownish effluents known as leachates. In a permeable soil and of a water table circulating in shallow depth, these percolate, after their generation, accumulate at the bottom of the waste and can infiltrate through the ground to reach the underlying water table, thus causing its contamination. Leachate would require, therefore, a specific treatment before their rejection in the receiving environment. This study aims to make a physicochemical characterization of these leachates. To do this, we conducted a series of sampling, from May 2015 to January 2017. During this period, the physicochemical analysis revealed, on the one hand, that it is discharge juice in the acidogenesis phase, conveying a significant pollutant load rich in organic and inorganic matter (COD = 23597.5 ± 595.61 $mgO_2\ L^{-1}$), in mineral salts (EC = 17.55 ± 0.72 mS cm^{-1}) and in nutrient salts (TKN = 888.54 ± 13.53 mg-N L^{-1} and TP = 139.65 ± 48.89 mg-P L^{-1}), concentrations exceed the values allowed by Moroccan and international standards, what makes these effluents toxic to the surrounding environment. By the present study, we incite decision-makers to manage well effectively the discharges taking into account the risks of the leachates generated.

Keywords: Leachate; Physicochemical; Analysis; Dump; Pollution.

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1. Introduction

Storage is one of the treatment methods of the most used non-hazardous waste in the world. Liquids generated by percolation of water in the massif of waste (leachate) contain high levels of pollutants (dissolved organic matter, inorganic macro-components, trace elements and xenobiotics organic compounds) [1]. The main risk associated with storage activity is the contamination of the subsoil, groundwater and surface water by migration of leachates outside the storage area [2]. The temperature and the rain are determining factors in the generation of leachates. Indeed, inside the landfill, through the waste, rain water load in pathogens and in organic and mineral pollutants. With the initial water content of the waste, the rainfall is the main contribution in the water balance, while the temperature has a role in waste oxidation and hydrolysis processes and also influences the speed of degradation, by affecting the development of bacteria and the chemical reactions [3]. Incorrectly secured and improperly operated municipal solid waste (MSW) landfills pose a serious threat to the environment, mainly to surface and ground waters. The need to protect ground waters as a valuable source of pure water for human use resulted in the 1960s in the introduction of the obligation to dump wastes on landfills with leak-tight bases. The elimination of the hazard related to the pollution of ground and surface waters is closely tied to the piping, storage and disposal of leachates generated during the exploitation of landfills and frequently also after their closure. The scale of this threat depends on the quantity and composition of the leachates and the distance of a landfill from waters [4, 5]. Knowledge of the quantity and composition of leachates is necessary when designing treatment facilities and is important in determining raw leachate pollution effect on the environment. MSW Landfill leachates can be considered as highly concentrated complex effluents which may contain mineral and organic compounds (humic substances, fatty acids and aromatic compounds), heavy metals and many other hazardous chemicals. Among mineral compounds, chlorides that are usually not attenuated by the soil and are extremely mobile under all conditions; they have a special meaning as tracer of the plume of leachate linking groundwater [6]. Total suspended solids (TSS) and total dissolved solids (TDS) have a significant effect on leachate (Modification of the turbidity and reduction of the penetration of the light therefore of the photosynthesis). The increase of TDS is an indicator of the increase in salinity, of the electrical conductivity and of inorganic matter in leachate. TDS is one of the parameters taken into consideration for licensing discharge of landfill leachate in many countries such as the U.K. Indeed, studies carried out on the ground by Brune et al. [7], by Rowe [8] and by Koerner et al. [9] have demonstrated that the effectiveness of drainage equipment in collection systems decreases rapidly with time due to "clogging" under the effect of the high mass loading of leachate constituents (volatile fatty acids, suspended solids, and dissolved inorganic constituents like calcium). Electrical conductivity (EC) is also a characteristic parameter of effluent quality. It provides information on the quantity of ionic species dissolved in leachates and evaluates their mineralization. The redox potential (Eh) and dissolved oxygen are two highly related parameters, indeed more the medium is reducing more Eh is low, and conversely, more the medium is oxidizing more Eh is strong. In addition, the amount of oxygen available determines the type of degradation, aerobic or anaerobic. The chemical oxygen demand (COD) of leachates is a measure of all oxidizable matter in the leachate and the biological oxygen demand (BOD_5) is a measure of the biodegradable organic mass. In addition, the BOD_5/COD-ratio can be considered as a measure of the biodegradability of the organic matter, and hence of the maturity of the leachate and the landfill, which typically decreases with time. Kruse [10] investigated 33 landfills in Northern Germany, the leachate concentrations mainly derive from the late eighties and early nineties. He defined three characteristic periods according to the BOD_5/COD-ratio (Table 1).

Table 1: Leachates phases

BOD_5/COD ratio	Significance
≥ 0.4	Acid phase
0.4 – 0.2	Transient phase
≤ 0.2	Methanogenic phase

The first phases of anaerobic degradation of organic matter are characterized by significant mobilization of volatile fatty acids (VFA) from the early stages of biodegradation (hydrolysis and acidogenesis). During these first two phases, the VFA are the majority and can constitute 95% of the organic load of the young leachates. PH and VFA are good indicators to distinguish the acidogenesis phase (high VFA content and pH <7) from the methanogenesis phase during which the leachate is characterized by a low VFA content and a pH greater than 7 [11].

Other parameters that may characterize leachates are nitrate, nitrite, ammonia nitrogen and phosphate. Nitrites come either from nitrates reduction or from incomplete oxidation of ions ammoniums [12]; they are the intermediates between ammonia nitrogen and nitrates and are found to be toxic to aquatic biocenoses and fish fauna. Because of its stability in anaerobic conditions, ammonia nitrogen (NH_4–N) seems to be the constituent that lasts longer in landfill leachate and may be used to determine pollution potential in the landfill. Total Kjeldahl Nitrogen (TKN) represents the reduced forms of nitrogen; it is the sum of organic nitrogen and ammonia nitrogen. Total nitrogen (TN) includes all organic and inorganic nitrogen species (NH_4-N, NO_3-N, NO_2-N, TKN and Org-N). The sulfate elements also appear to be a good indicator of the methanogenic phase because their reduction in sulfides is significant during this phase. Calcium (Ca) and magnesium (Mg) can also be considered as indicators of anthropogenic water pollution. Iron (Fe), the most abundant metal in landfills initially in the form of ferric compounds in soils and wastes, is reduced to ferrous state (Fe^{2+}) by anaerobic bacteria; the latter can also form directly in the soil by inorganic reactions from the waste. The dark brown color of the leachate is mainly attributed to the oxidation of the ferrous form to the ferric form and to the formation of ferric hydroxide colloids and complexes with humic acid [13]. The objective of this work is to determine the physicochemical parameters of leachates from the wild dump of El Hajeb city (Morocco) and to assess their degree of pollution in order to study in the next work, the influence on the neighbouring groundwater.

2. Materials and Methods

2.1. Presentation of the Study Area

El Hajeb city is a part of a strategic region (Photo 1). Its altitude above sea level is 1054 m, and its total population is of 36.491inhabitants. It is characterized by intensive agricultural development where all the land is cultivated. The average annual rainfall in the study area is 520 mm. The average annual temperature is 15.2 °C. The average monthly humidity is 31.41%, while the ratio of evapotranspiration to annual mean precipitation ETR/P can reach 90%. The subsoil of the study area contains, at a depth of 5 m, the underground water. The limestone covers this water table. The geotechnical study carried out revealed the presence of sands having a high permeability (from $3.7.10^{-3}$ to $5.4.10^{-2}$ cm/s).

The municipal dump, which serves this city, is located to the west and about 12 km from this town. Its geographical coordinates in degrees are: latitude 33°39'55.7 "North; Longitude 5°27'29.1 "West.

Photo 1: Satellite image of the location of the wild dump of El Hajeb city (Morocco)

The average amount of household waste produced is estimated at 11.000 tons per year, at the rate of a daily ratio of about 1 Kg/day/capita. The main components of this discharge are household garbage with a share of 90% (Fig. 1). Their examination showed that they contain a high rate of organic matter of about 78.1% (Fig. 2).

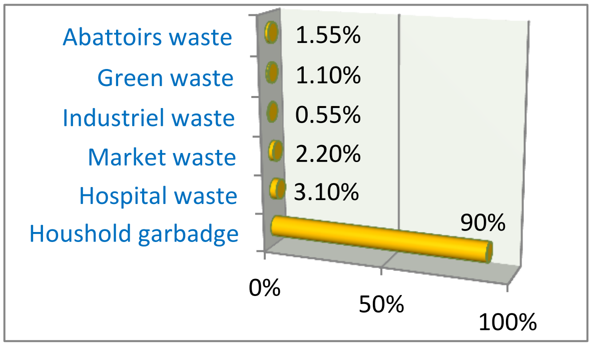

Figure 1: Waste source of landfill and her rates.

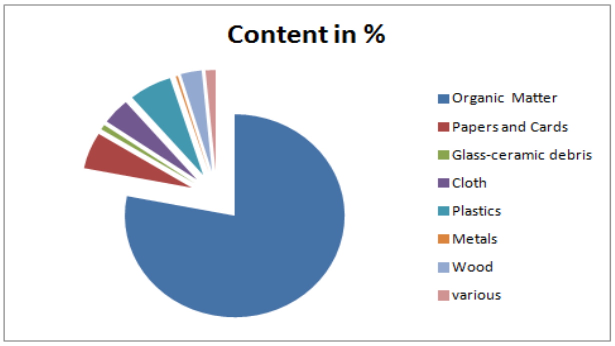

Figure 2: Types and rates of landfill waste.

2.2. Leachate Sampling for Analysis

Monthly, samples were taken in the sixteen places available within the landfill during the whole period which extends from May 2015 to January 2017, totaling 336 samples. The samples were collected in labeled clean bottles and were rinsed thrice before sample collection. Temperature (T), Hydrogen potential (pH), Conductivity Electrical (CE), the Total Dissolved Solids (TDS) and Redox potential (Eh) were measured in situ using a portable graphic Multiparameter (PH+ Cond HI5521 - Hanna Instruments). Dissolved Oxygen (DO) was measured in situ by means of a portable oximeter (HI 9146-10 - Hanna Instruments). The samples were then transported in ice cooler at a temperature below 5 °C immediately to the laboratory where they were stored in a refrigerator at 4 °C before proceeding with the analysis. In laboratory, the turbidity was determined by means of Turbidimeter (EUTCH TN-100) and the fluorides were determined using an Ionometer (G-0-08 N° series 08450495). The Na^+ and K^+ contents were measured using a flame photometer (BWB-XP). The chlorides were measured by the titrimetric method with mercuric nitrate. The Ca^{2+} and Mg^{2+} ions were assayed by the EDTA titrimetric method. BOD_5 was determined by the OxiTop method, COD by oxidation with potassium dichromate and sulfates by turbidimetry method. Total Suspended Solid (TSS) was measured by filtration and gravimetry. Total iron, Boron, Nitrates, Nitrites, Ammonia nitrogen and Phosphates were determined by molecular absorption spectrometry method. Total Kjeldahl Nitrogen (TKN) was assayed by mineralization and alkalimetry.

2.3. Statistical Analysis

Descriptive statistical analysis presented below was performed using the IBM SPSS Amos 21.0 software. The results of analysis were presented in the form of mean ± SE. The level of statistical significance was estimated at the significance threshold Alpha = 0.050 (Shapiro-Wilk statistical test). At this threshold, most statistical results are satisfactory and significant.

3. Results and Discussions

The temperature variations within the leachates were largely dependent on those of the outside. During the study period, the values of the leachate temperature varied in the standards with an average of 14.05 ± 0.31 °C (Table 2). The pH in the present study has varied in the standard between 6.21 and 7.48 with an average of 6.65 ± 0.05 (Table 2), this value suggested the existence of a slightly acidic medium in the early stages of anaerobic degradation of organic matter.

The TDS of the leachate in study have fluctuated between 4761.35 and 12564.1 mg L^{-1} with an average of 8329.75± 170.35 mg L^{-1}. Examination of TSS results showed an average of 940.9 ± 22.19 mg L^{-1}, value which widely exceeded the Moroccan standard [14] fixed to 30 mg L^{-1}. Turbidity recorded an average of 2289.42 ± 271.62 NTU (Table 1). Therefore leachates in study accused a strong mineral and organic load which can pose major problems during treatment and /or drainage.

Moreover the results of table 2 show that conductivity electrical (CE) have ranged around an average of 17.55 ± 0.72 mS cm^{-1} and far exceeded the Moroccan standards [14] indicating that the leachate is rich in inorganic substances. Chlorides in the present study showed an average of

Table 2: Physicochemical quality of leachate and descriptive statistical analysis.

Leachate samples (n = 336)									
Parameters	**Unit**	**Mean ± SE**	**Min**	**Max**	**CV**	**CS**	**CK**	***p-Value***	**Standards**
T	°C	14.05 ± 0.31	7.00	23.00	0.392	0.333	-1.226	< .0001	30*
pH	-	6.65 ± 0.05	6.21	7.48	0.073	0.971	-0.794	< .0001	5.5 – 8.5*
EC	mS cm^{-1}	17.55 ± 0.72	8.64	27.19	0.374	0.152	-1.008	< .0001	2.70*
DO	$mgO_2 L^{-1}$	1 ± 0.03	0.65	1.49	0.496	1.086	-0.724	< .0001	>3.8***
TSS	mg L^{-1}	940.9 ± 22,19	671.56	1238.54	0.216	0.213	-1.078	< .0001	30 *
Turbidity	NTU	2289.42 ± 271.62	1983.67	2678.31	0.119	0.213	-1.078	< .0001	-
TDS	mg L^{-1}	8329.75 ± 170,35	4761.35	12564.1	0.375	0.18	-1.633	< .0001	-
Eh	mV	-48.11 ± 0.67	-66.32	-35.84	-0.255	-0.439	-1.419	< .0001	-
BOD_5	$mgO_2 L^{-1}$	14448.67 ± 211,13	12000	17000	0.134	0.053	-1.55	< .0001	30**
COD	$mgO_2 L^{-1}$	23597.5 ± 595,61	17000	32000	0.231	0.456	-1.057	< .0001	125**
BOD_5/COD	-	0.62 ± 0.006	0.53	0.7	0.098	-0.352	-1.034	< .0001	-
NO_3^-	mg-N L^{-1}	68.24 ± 9.07	54.71	78.09	0.132	-0.594	-1.196	< .0001	20**
NO_2^-	mg-N L^{-1}	1.44 ± 0.06	0.65	3.21	0.73	-0.005	-1.36	< .0001	0.3**
TKN	mg-N L^{-1}	888.54 ± 13.53	673.54	968.11	0.14	-1.143	-0.686	< .0001	3**
NH_4^+	mg-N L^{-1}	392.21 ± 5.29	263.56	529.02	0.247	0.088	-1.23	< .0001	15**
TN	mg-N L^{-1}	956.82 ± 9.45	805.41	1005.67	0.091	-1.149	-0.681	< .0001	30**
PO_4^{3-}	mg-P L^{-1}	118.28 ± 28.72	94.73	132.84	0.121	-0.887	-0.834	< .0001	1**
TP	mg-P L^{-1}	139.65 ± 48.89	98.35	157.12	0.174	-1.086	-0.736	< .0001	10**
SO_4^{2-}	mg L^{-1}	1279.83 ± 177,78	993.56	1453.19	0.139	-0.734	-1.049	< .0001	500 *
Ca^{2+}	mg L^{-1}	1161.21 ± 21.15	589.31	1643.12	0.334	-0.305	-1.204	< .0001	-
Mg^{2+}	mg L^{-1}	483.27 ± 9.5	201.34	653.27	0.36	-0.777	-0.996	< .0001	-
Na^+	mg L^{-1}	879.32 ± 12.9	567.12	1194.23	0.269	0.008	-1.427	< .0001	200****
K^+	mg L^{-1}	1639.7 ± 33.95	1091.66	2693.52	0.38	1.009	-0.773	< .0001	-
Bore	mg L^{-1}	23.46 ± 0.54	9.14	36.77	-0.148	-0.16	-1.026	< .0001	5****
Cl^-	mg-Cl L^{-1}	1989.07 ± 320,32	1543.76	2387.18	0.161	-0.166	-1.434	< .0001	250***
F^-	mg L^{-1}	22.57 ± 0.46	10.92	34.66	0.375	0.088	-1.041	< .0001	15**
Total iron.	mg L^{-1}	807.15 ± 11.15	518.29	1069.54	0.253	-0.176	-1.304	< .0001	5*

Min: Minimal value; Max: Maximal value; Mean: Average value; SE: Standard Error; CV: Coefficient of Variation; CS: Coefficient of Skewness; CK: Coefficient of Kurtosis

** Moroccan standards [14]. ** French standards [15]. *** Belgian standards [16]. **** Quebec Standards [17]*

1989.07 ± 320.32 mg-Cl L^{-1} (Table 2), such value far exceeded the Quebec standard [17] set at 1500 mg-Cl L^{-1} decreed by the council of the city of Quebec (Canada) for spills of sewage into sewer systems and the streams of the city. The high chloride value (2387.18 mS cm^{-1}) was recorded during the summer where the temperature and the contribution in waste were maximal. As for fluorides, the mean value detected was of the order of 22.57 ± 0.46 mg L^{-1} (Table 2), value greater than the French standards [15] set at 15 mg L^{-1}.

On the other hand, concentrations of dissolved oxygen (Table 2) were low and ranged from a minimum of 0.65 to a maximum of 1.49 mgO_2 L^{-1} with an average of 1 ± 0.03 mgO_2 L^{-1}, such values were lower than a Belgian standards [16] set at 3.8 mgO_2 L^{-1}, thus allowing the leachate to be classified as an almost anoxic environment lacking free oxygen and tends to be reducing under the effect of the significant oxidizable organic load. The maximum value (1.49 mgO2 L^{-1}) was recorded during the rainy seasons; in fact, in winter the permanent rainfall and the decrease in bacterial activity ensure a strong and continuous oxygenation of the leachates. The redox potential (Eh) showed an average of -48.11 ± 0.67 mV (Table 2), this result demonstrated that the juice of the discharge was in the reducing conditions (decrease of the oxygen). The absence of dissolved oxygen in the leachates and the low values of the redox potential indicate that the anaerobiosis phenomenon is predominant.

The results obtained for the COD showed an average of 23597.5 ± 595.61 mgO_2 L^{-1} and the BOD_5 varied around an average of 14448.67 ± 211.13 mgO_2 L^{-1} (Table 2). These two parameters varied in the time with values which widely exceeded the French standards [15], fixed to 30 mgO$_2$ L^{-1} for BOD$_5$ and 125 mgO$_2$ L^{-1} for COD. For this study this BOD$_5$/COD-ratio varied around 0.62 ± 0.006 (Table 2). According to Kruse [12], this average indicated that the discharge was unstable producing leachate in the acid phase of young class, rich in organic matter of good biodegradability. As organic intake has not been interrupted (active discharge) the increase in the biodegradability of leachates cannot come only of leachate generated by fresh waste.

Nitrate (NO$_3$-N) were worth on average 68.24 ± 9.07 mg-N L^{-1} (Table 2), high value as most Moroccan landfills. It is explained by the increase, year after year, of sources of contamination by nitrogen pollution, such as wastes from agricultural activities (out-of-date Nitrogen fertilizers and phytosanitary, livestock farming) and slaughterhouse waste. In the study, nitrites (NO$_2$-N) represented a negligible proportion of nitrogen compounds, with an average concentration of 1.44 ± 0.06 mg-N L^{-1} (Table 2). Given that this leachate was anoxic and highly reductive, the presence of nitrites cannot have as origin that the reduction of some of the nitrates by anaerobic bacteria. The mean of ammonia nitrogen (NH$_4$–N) recorded in the study site varied around 392.21 ± 5.29 mg-N L^{-1} (Table 2); it was present in high concentrations, probably due to the deamination of amino acids during the decomposition of organic compounds and precisely due to the decomposition of the natural proteins in microorganisms and phytoplankton. It can also be derived from the feeding of refined urban effluents, domestic, industrial or agricultural waste. The mean value of Total Kjeldahl Nitrogen (TKN) recorded was 888.54 ± 13.53 mg-N L^{-1}, it can be deduced that the organic nitrogen represented approximately 66% of the Kjeldahl nitrogen evidenced through the Org-N/TKN-ratio which ranged from 0.61 to 0.7; the mean concentration of Total Nitrogen (TN) was of the order of 956.82 ± 9.45 mg-N L^{-1} (Table 2). In the present study the TKN represented 93% of the NT; this allows us to deduce that total Kjeldahl nitrogen is then the dominant species.

Orthophosphates (PO$_4^{3-}$) showed concentrations that varied between a minimum of 94.73 mg L^{-1} and a maximum of 132.84 mg L^{-1} with the mean of 118.28 ± 28.72 mg-P L^{-1}. As for Total Phosphorus (PT), it revealed a minimum content of 98.35 mg L^{-1} and a maximum content of 157.12 mg L^{-1} with an average of 139.65 ± 48.89 mg-P L^{-1} (Table 2). The PO$_4^{3-}$ represented 85% of the TP; this would suggest that phosphate leached by the discharge was mainly in the orthophosphate form. The phosphate compounds are largely derived from detergents, phosphate and organic fertilizers and the decomposition of the skeletons of animal corpses. Besides, the results (Table 2) indicate that all the nutrients of leachates of El Hajeb landfill, with the exception of nitrites, showed average values that exceed the French standards [15].

The average content of Sodium (Na$^+$) found was 879.32 ± 12.9 mg L^{-1}, a result on the one hand that exceeded the limit value 200 mg L^{-1} set by the Quebec standards [17] relative to the rejection of leachates susceptible to reach subterranean waters. Whereas the Potassium (K$^+$) content found on average was of the order of 1639.7 ± 33.95 mg L^{-1} (Table 2) and can come from outdated chemical fertilizers rejected in the discharge. As for Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) ions, the ionic balance of the leachate (Table 2) showed variable contents of Ca^{2+} around the mean of 1161.21 ± 21.15 mg L^{-1}, it can come from the bones and teeth of the carcasses and skeletons of animals, that of Mg^{2+} was 483.27 ± 9.5 mg L^{-1}. Concerning Ca^{2+}, Mg^{2+} and K$^+$, leachates rejection standards are non-existent, however they exceeded the standards EECS [18] relative to the drinking water which limit these concentrations to 100 mg L$^-$

^{1} in Ca^{2+}, to 50 mg L^{-1} in Mg^{2+}, and to 12 mg L^{-1} in K^{+}. Therefore these leachates too loaded by these ions constituted a major danger if they reach the surface water or groundwater.

Sulfates showed an average of 1279.83 ± 177.78 mg L^{-1} (Table 2), value was excessive and far exceeded the Moroccan standard [14] set at 500 mg L^{-1}. In present study, sulfate could result from the decomposition proteins. Moreover, the low sulfate levels could be explained by the sulfates reduction to sulfides (H_2S) who are among the gases responsible for the bad odors released by landfills. The mean concentration of total iron recorded was of the order of 807.15 ± 11.15 mg L^{-1} (Table 2); such value was significantly higher to the Moroccan standard [14] set at 5 mg L^{-1}. The Boron content in the study site was about 23.46 ± 0.54 mg L^{-1} (Table 2). Such value exceeded the limit value (5 mg L^{-1}) set by the Quebec standards [17] relative to the rejection of leachates susceptible to reach subterranean waters. It may be derived from borates and perborates which are used in the manufacture of mild antiseptic products, cosmetics, medicines, antioxidants for soldering, cleansers, detergents, and agricultural fertilizers.

4. Conclusions & Recommendations

In the light of the physicochemical results if leachate is allowed to flow directly into surface water and consequently the groundwater, it can cause serious damage. It can destroy life in a water resource by covering the bottom sediments so that feeding by the animal population is excluded, iron is an excellent example.

Moreover, following to the high TDS and TSS content, which characterizes the leachates, the problem of clogging can occur at any time due in case of adoption of drainage or pumping system of leachates. On the other hand, the good biodegradability and the high organic composition of waste give the advantage to the success of a composting project which can benefit from substantial profits for the region such as reduced leachate volume, the production of compost (natural fertilizer) and the generation of biogas (natural energy). Furthermore the completion of the study by developing a validation map of physicochemical analysis of samples of groundwater and of surfaces around the discharge will be a very important tool for the diagnosis of the quality of water resources. The resulting data of the affected areas and / or risk of pollution are a very important tool to help protect the aquifer and also for good water management and soil in the region.

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