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RESEARCH PAPER

Temporal Monitoring and Effect of Precipitation on the Quality of Leachate from the Greater Casablanca Landfill in Morocco

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ABSTRACT

A monthly temporal monitoring of the physico-chemical parameters of the leachate from the Greater Casablanca "Mediouna" open-air landfill in Morocco over a period of 13 months was carried out to show their variability over time. This monitoring also highlights the effect of rainfall on leachate quality through fluctuations observed in wet and dry periods. Indeed, the leachate was sampled from a collector that drains a mixture of young and mature leachate. Several physico-chemical parameters were studied: pH, temperature, conductivity, organic matter (BOD_5 and COD), total matter (TS, TVS), nitrogen ($N\text{-}NO_2^-$, $N\text{-}NO_3^-$, $N\text{-}NH_4^+$, TKN), total phosphorus (Tp), salts (Cl^-, SO_4^{2-}) and metals (Cd, Co, Cr, Ca, Cu, Fe, K, Mg, Mn, Ni, Pb, Zn). As a result, significant concentrations were recorded throughout the monitoring for the majority of the parameters, showing a high aggressiveness of the leachate. Also, statistically significant relationships were observed between the different parameters. On the other hand, the leachate pollution index (LPI) was calculated to determine the overall potential of leachate pollution. The identification and study of the behaviour of the physico-chemical parameters is very useful for the design of an adequate leachate treatment plant for the Greater Casablanca landfill "Mediouna", taking into consideration the extreme values recorded during the monitoring period, in order to avoid any malfunctioning due to an underestimation of the pollution.

Keywords : Landfill leachate; Physico-chemical characterization; Temporal monitoring; Rainfall; LPI.

INTRODUCTION

In many underdeveloped countries, traditional landfilling is the most practical way to dispose of solid waste by burying it in open areas, selected without regard to environmental, topographical and geological factors (Reddy, 2017). This type of landfill receives thousands of tonnes of various solid wastes daily, which are buried without prior sorting or treatment.

The decomposition of solid waste in a landfill is due to biochemical activity, which generates biogas and leachate (Tatsi & Zouboulis, 2002). In Morocco, the population produces annually more than 7 million tonnes of solid waste, with an estimated daily leachate volume of 9946 m^3/d (B.Mondiale & DEM, 2017), this important leachate volume is due to the typical characteristics of Moroccan waste which are characterized by high moisture (60% to 75%) and high organic matter content (60% to 80%), both of which enhance leachate formation.

Indeed, leachate is considered to be a polluting matrix that affects the quality of the environment, either by deteriorating the quality of groundwater, surface water, soil, and

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vegetation. It is formed from the infiltration of precipitation into the mass of solid waste, water contained in the waste itself and/or water from the river system near the landfill site.

Given the adverse effects of leachate on the deterioration of environmental quality, strategic site selection is the main key to minimising and controlling the nuisance emitted from a landfill, and this is achieved by considering and satisfying a range of multi-criteria factors (Rezaeisabzevar et al., 2020).

Furthermore, the variability of leachate characteristics still depends on several factors such as: climate, solid waste composition, age of the landfill, hydrogeological conditions of the site, evapotranspiration, etc. (Frikha et al., 2017; Rafizul & Alamgir, 2012; Rajoo et al., 2020; Reitzel et al., 1992).

In order to investigate the effect of precipitation on leachate quality, several researches have studied the impact of precipitation on leachate quality in different countries (Filho & Miguel, 2017; Mavakala et al., 2016; H. Mishra et al., 2016; Yang et al., 2019). However, this study is the first one that addressed this impact on leachates from the Greater Casablanca "Mediouna" landfill. With this in mind, the objective of this study is to: (i) Determine the main physico-chemical pollutants, analyse their behaviour over time and compare them to the literature, (ii) Study the effect of rainfall on the quality of leachates, (iii) Determine the possible correlations between the different physico-chemical parameters and (iv) Quantify the pollution generated by the leachates via the calculation of the leachate pollution index (LPI).

MATERIALS AND METHODS

The Greater Casablanca Landfill (Fig.1) is an open-air solid waste landfill site, which has been operational since 1986, is located 10 Km away from the city of Casablanca near the regional road n° 315 connecting Casablanca to Berrechid. It covers an area of 85 hectares and receives a variety of waste from the city of Casablanca and its outskirts. The daily quantity is estimated at more than 96,000 tonnes of household and similar waste, green waste, inert waste, mixed waste and banal industrial waste, also this waste does not undergo any pre-treatment in the landfill (sorting, recycling, etc.).

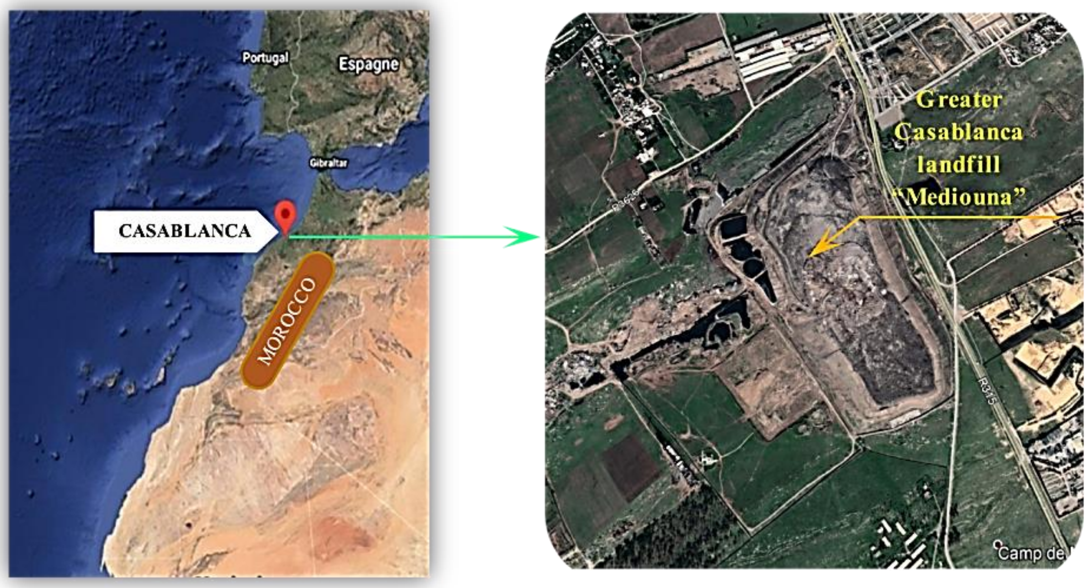


Fig.1. Greater Casablanca landfill "Mediouna"
(Reference: Google earth)

The leachate studied was collected from the main collector of the Greater Casablanca landfill “Mediouna”, this collector drains a mixture of leachate from collection trucks, newly buried waste and layers of old waste (Fig.2). This collector drains the leachate to a large manhole from which it is pumped to 3 recovery basins, with volumes ranging from 10,000 m^3 to 25,000 m^3.

Fig.2. Interior view of the Greater Casablanca "Mediouna" landfill and the leachate sampling site

Specifically, leachate samples (Raw Leachate of Mediouna: RLM) in this study were collected from the main leachate collector in the landfill, which conveys to the leachate accumulation manhole (Fig.2).

Leachate sampling started from the first of June 2016, it was conducted monthly (at the beginning of each month) for 13 months, and it ended on August 1, 2017. A total of 13 samples were subjected to physicochemical analysis of 27 parameters.

Leachate sampling was done manually. Samples were collected in high-density polyethylene bottles pre-rinsed with distilled water and sampled before filling. However, the sampling operation is dependent on several factors such as changes in flow velocity and/or flow rate, temperature changes, precipitation, etc.

Samples of metals were fixed with nitric acid, while samples for analysis of Kjeldahl nitrogen and total phosphorus were fixed with sulphuric acid (ISO Standard 5667-3).

The physico-chemical parameters, such as temperature, pH, conductivity and dissolved oxygen, were measured in situ using a WTW Vario pH meter (pH 2V00-1012), a WTW Vario conductivity meter (Cond 2X00-001A) and a WTW Oximeter (OXi 3310 Set 1) respectively.

The collected samples were stored at a temperature of 4°C, and handled directly in the laboratory after the sampling operation to minimize any changes or deterioration that might occur.

The analysed physico-chemical parameters are as follows: pH, temperature, conductivity, organic matter (BOD_5 and COD), total matter (TS, TVS), nitrogen ($N\text{-}NO_2^-$, $N\text{-}NO_3^-$, $N\text{-}NH_4^+$, TKN), total phosphorus (P total), salts (Cl^-, SO_4^{2-}) and metals (Cd, Co, Cr, Ca, Cu, Fe, K, Mg, Mn, Ni, Pb, Zn). All the methods used are described in the following summary (Table 1).

Table 1. Methods of analysis used

Type of analysis	Standard used	Method description
Biological oxygen demand (5 d)		Manometric method
Chemical oxygen demand	DIN 38409-H41	Potassium dichromate method
Total solids	MA.100-S.T. 1.1	Gravimetric method
Total volatil solids	MA.100-S.T. 1.1	Gravimetric method
Nitric nitrogen	DIN 38405-D9-2	Photometric method
Nitrous nitrogen	NF :T 90-013	Photometric method
Ammonia nitrogen	NF 90-015	Photometric method
Kjeldahl nitrogen	ISO 5663	Volumetric method after mineralization
Total phosphorus	NF :T 90-023	Photometric method after mineralization
Chloride	DIN 38405-D1-1	Volumetric method
Sulphate	DIN 38405-D5-2	Gravimetric method
Metals		Flame atomic absorption spectrometry with flame after digestion

The different physico-chemical parameters of the leachate were treated by multivariate statistical analysis using Pearson correlation, in order to deduce possible relationships between the different variables and to study the effect of precipitation on leachate quality.

Also LPI was used, it is a tool to assess the potential for contamination generated by landfill leachate (Kumar & Alappat, 2005b). As well, LPI is a single, increasing scale environmental index ranging from 5 to 100 to quantify leachate contamination (Kumar & Alappat, 2005a), making it easy to compare landfills with each other, as the LPI is higher, the environmental risk is greater. The LPI calculation includes 18 pollution indicator variables in the leachate (pH, TDS, BOD_5, COD, $N\text{-}NH_4^+$, TKN, Fe, Cu, Ni, Zn, Pb, Cr, Hg, As, phenolic compounds, Cl^-, CN^- and total coliform bacteria) and is calculated using the following equation (Eq.1) (Kumar & Alappat, 2005b):

Eq.1 $$LPI = \sum_{i=1}^{n} w_i p_i \quad \text{with} \quad \sum_{i=1}^{n} w_i = 1$$

Where :

LPI: The weighted additive leachate pollution index,

w_i : the weight for the ith pollutant variable,

p_i : The sub index score of the ith leachate pollutant variable,

n : The number of leachate pollutant variables used in calculating LPI.

When not all 18 variables are available, the LPI is calculated according to the following equation (Kumar & Alappat, 2005b) :

Eq.2 $$LPI = \sum_{i=1}^{m} w_i p_i / \sum_{i=1}^{m} w_i \quad \text{with} \quad m < 18 \ et \ \sum_{i=1}^{m} w_i < 1$$

Where:

m: the number of leachate pollutant parameters for which data is available.

RESULTS AND DISCUSSIONS

All the results obtained are processed by using position and dispersion measurements carried out with the OriginPro software, calculating: mean, median, standard deviation, quartiles (1st, and 3rd). These results are compared with the limits of discharges into the natural environment according to the Moroccan standard. They are listed in (Table 2).

The characteristics of the leachate (RLM) were compared according to the age of the landfill (Table 3). As a result, the age fluctuates between intermediate and stable. However, this classification is still approximate as there are no clearly defined ranges (Reshadi et al., 2020).

Also, a comparison of the results of this study with the leachate results from landfills in other countries is shown in (Table 4).

Table 2. Results of the physico-chemical characterisation of the temporal monitoring of leachates from the Greater Casablanca landfill "Mediouna"

Parameters	Unit	Min	Max	Mean	Median	S.D	Q_1	Q_3	Number of observations	General limit values for discharges into the natural environment (DEM, 2014)
Temperature	°C	15.7	31.3	23.56	24	5.0991	20	28.4	13	30
pH		7.27	8.38	7.88	7.76	0.3921	7.63	8.3	13	5.5-9.5
Conductivity	ms/cm	20.2	38.54	32.39	32.25	4.8901	30.44	36.6	13	2.7
BOD_5	mg O_2/l	1000	21250	10192	10500	5327.947	7000	12500	13	100
COD	mg O_2/l	3925	46800	21817	18100	13263.68	14300	25850	13	500
BOD /COD		0.207	0.771	0.50	0.524	0.1744	0.387	0.617	13	-
TS	mg/l	18005	41035	28393	25300	8591.192	21565	34600	13	-
TVS	mg/l	4790	21260	12302	10570	5957.422	7425	17530	13	-
TVS/TS	%	23.65	64.64	41.43	41.78	10.7802	36.39	46.37	13	-
N-NO_2^-	mg N/l	0.1	1.5	0.86	0.8	0.4875	0.575	1.207	8 and NA'S=5	-
N-NO_3^-	mg N/l	4	30	16.69	15	8.4595	10	25	13	-
N-NH_4^+	mg N/l	2175	4926	3317	3350	709.3406	2757	3718	13	-
TKN	mg N/l	2368	5234	3574	3745	721.0534	3015	3952	13	40
N-NH_4^+/TKN	%	87.65	97.47	92.65	93.08	3.4608	89.93	95.33	13	-
TP	mg P/l	21.09	72	45.32	43.23	14.86	35.09	55.45	13	15
Cl^-	mg/l	4609	6382	5713	5743	528.2438	5389	6098	13	--
SO_4^{2-}	mg/l	62	486	235	165	153.3155	115.3	312.8	13	600
Ca	Mg/l	0.1	1414.38	611.12	596.33	470.85	117.37	1050.32	13	-
Cd	mg/l	0.005	0.047	0.0251	0.025	0.0164	0.0109	0.0371	8 and NA'S=5	0.25
Co	mg/l	a	a	a	a	a	a	a	NA'S=13	0.5
Cr	mg/l	1.192	16.118	7.976	5.419	5.1474	3.9	12.377	13	2
Cu	mg/l	0.039	0.665	0.49	0.495	0.1622	0.452	0.58	13	2
Fe	mg/l	43.16	86.4	59.53	54.26	13.949	50.99	64.51	13	5
K	mg/l	a	a	a	a	a	a	a	NA'S=13	-
Mg	mg/l	5.594	8.436	7.708	7.774	0.737	7.52	8.132	13	-
Mn	mg/l	1.513	8.523	3.586	2.682	2.0485	2.344	4.271	13	2
Ni	mg/l	0.275	1.133	0.7725	0.739	0.2616	0.629	1.022	13	5
Pb	mg/l	a	a	a	a	a	a	a	NA'S=13	1
Zn	mg/l	0.024	0.897	0.2346	0.1525	0.2698	0.1045	0.331	9 and NA'S=4	5

a, means values below the detection limit of the method used; Min, minimum value; Max, maximum value; S.D, standard deviation; Q_1, first quartile; Q_3, third quartile; NA'S, means number of missing observations.

Table 3. Comparison of the quality of leachates from the Greater Casablanca "Mediouna" landfill in relation to the age of the landfills

Parameters	Unit	pollution range of this study (Raw Leachate of Mediouna)	Young leachate (<5 years)	Intermediate leachate (5-10 years)	Stabilised leachate (10-20 years)	Old Leachate (>20 years)
			(Reshadi et al., 2020)			
Temperature	°C	15.7- 31.3	-	-	-	-
pH		7.27- 8.38	3-7	6-8	>7.5	**>7.5**
Conductivity	ms/cm	20.2-38.54	2-50	1-15	-	-
BOD_5	mg O_2/l	1000- 21250	2000-50000	500-15000	50-1000	**<300**
COD	mg O_2/l	3925-46800	4000-90000	1000-30000	1000-5000	**<3000**
BOD_5 /COD		0.207-0.771	0,5-1	0,1-0,5	<0,1	**<0,1**
$N\text{-}NH_4^+$	mg N/l	2175-4926	500-4500	-	-	**<1500**
TKN	mg N/l	2368-5234	500-4500	400-2000	50-2000	**<2000**
P-total	mg P/l	21.09-72	50-500	5-200	-	**<20**
Cl^-	mg/l	4609-6382	500-6000	200-4000	50-500	**<200**
SO_4^{2-}	mg/l	62-486	300-4000	100-2000	20-200	**<100**
Zn	mg/l	a-0.897	50-400	100-2000	20-200	**<100**
Ca	mg/l	0.1-1414.38	1000-7000	200-4000	100-500	**<400**
Mg	mg/l	5.594-8.436	300-3000	200-2000	50-500	**<200**

a, means values below the detection limit

Table 4. Comparison of the physico-chemical characteristics of leachate from the Greater Casablanca Landfill "Mediouna" compared to other countries

Parameters	Unit	This study: Raw Leachate of Mediouna	Tunisia Sousse landfill (Frikha et al., 2017)	Greece Thessaloniki landfill (Tatsi & Zouboulis, 2002)	Malaysia Simpang Renggam Landfil (Detho et al., 2020)	Sweden Swedish landfill (Oman & Hynning, 1993)	USA Dyer Boulevard Landfil (Statom et al., 2004)	China Zhejiang Landfill (Zhang et al., 2013)
Temperature	°C	23.56	-	-	-	2-25	-	-
pH		7.88	8.3	7.3-8.8	7.96	6.4-8.5	6.56-8.01	8.01
Conductivity	ms/cm	32.39	54.6	6.2-34.0	-	2.3-27.3	3.6-15	-
BOD_5	mg O_2/l	10192	-	50-4200	138,66	4-110*	<1-184	1000.7
COD	mg O_2/l	21817	5100	685-15000	1712	250-1300	222-2000	1491
BOD_5 /COD		0.50	-		0,07	0-0.14**	-	0.67
TS	mg/l	28393	-	3100-18000	-	-	-	-
TVS	mg/l	12302	-	130-11000	-	-	-	-
$N\text{-}NO_2^-$	mg N/l	41.43	11.5	0-7.5	-	-	-	-
$N\text{-}NO_3^-$	mg N/l	0.86	1540	2.5-300	-	-	<0.01-53.2	9.4
$N\text{-}NH_4^+$	mg N/l	16.69	892	39-1750	405.37	4.2-870	5.6-1350	467.5
TKN	mg N/l	3317	-	370-1800	-	42-860	79-1100	
P-total	mg P/l	3574	8	1.27-19.9	-	0.13-4	<0.05-8.7	15.43
Cl^-	mg/l	92.65	19900	1162-9209	-	360-4900	63-1580	1429.6
SO_4^{2-}	mg/l	45.32	5570	55-500	-	22-650	<1-118.2	54.95
Ca	Mg/l	5713	313	3.8-138	-	20.8–440	132-220	
Cd	mg/l	235	<0.0018	-	-	a-0.003	a	0.01
Co	mg/l	611.12	-	-	-	0.0017-0.021	<0.005-0.025	0.02
Cr	mg/l	0.0251	1.7	0.2	-	0.0014-0.045	<0.005-0.06	0.17
Cu	mg/l	a	0.1	0.10-0.53	-	0.0058-0.08	<0.002-0.08	0.18
Fe	mg/l	7.976	3.5	0.11-25	-	0.16-42.7	1.6-9.72	1.94
K	mg/l	0.49	9010		-	44.4-3500	-	-
Mg	mg/l	59.53	570	0.02-193	-	13.8-135	41.1-63	-
Mn	mg/l	a	-	0.05-0.42	-	0.165-5.2	0.075-0.28	0.54
Ni	mg/l	7.708	0.5	0.08-5.1	-	0.0098-0.091	<0.01-0.228	0.06
Pb	mg/l	3.586	<0.036		-	a-0.0154	<0.004-0.1	0.23
Zn	mg/l	0.7725	0.9	0.07-0.2	-	0.013-0.342	<0.006-0.488	17.21

a, means values below the detection limit
*BOD_7
**BOD_7/COD

With regard to rainfall, monthly rainfall data were obtained from the National Directorate of Meteorology (Fig.3). They range from 0 mm to 109.9 mm. Maximum rainfall has been observed from November 2016 to March 2017.

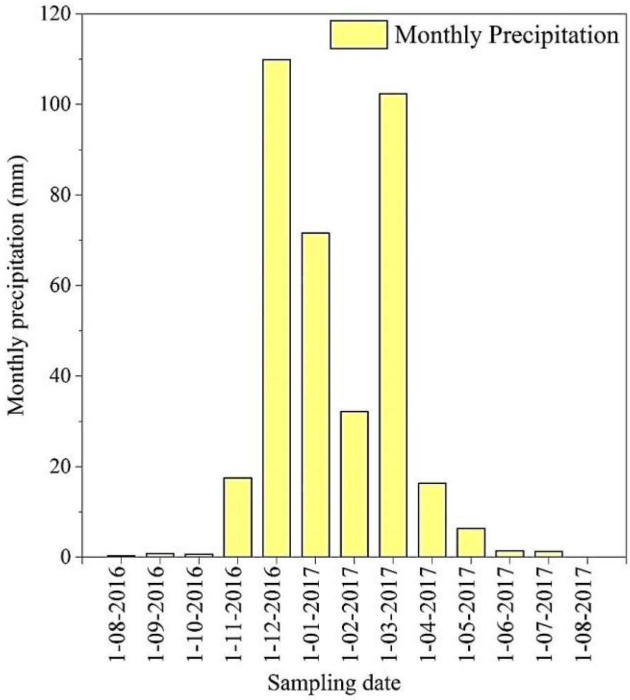


Fig.3. Evolution of monthly rainfall

In order to study the effect of precipitation on the leachate quality of the Greater Casablanca landfill “Mediouna”, several hypotheses were reformulated in order to determine the adequate period for sampling after precipitation. In this study, the monthly rainfall was recorded prior to the 30-day sampling date. Indeed, (Statom et al., 2004) simulated a likely delay in the infiltration of precipitation through the landfill and found that the best time for sampling was 30 days after precipitation. In the same framework, (Al-Yaqout & Hamoda, 2003) examined the effect of heavy rains on leachate quality in an arid climate, for which sampling was carried out after the 15-day rainfall. For example, (Chu et al., 1994) studied the interval of several days of cumulative rainfall ranging from 3 days to 28 days prior to sampling. (Khattabi et al., 2002) pointed out that a time lag between rainfall and leachate evolution may occur, as the landfill's behaviour towards precipitation does not react immediately due to several flow paths at the landfill site.

As for the physico-chemical parameters, their variation over time is explained by:

The leachate temperature records values ranging from 15.7°C to 31.3°C with a median value of 24°C (Fig.4). The maximum value of 31.3°C is observed between late spring and the summer period, while the minimum value of 15.7°C is recorded in the winter period. This parameter is crucial for the presence of anoxic and/or anaerobic bacteriological activity in the leachate. Indeed, microbial growth can take place in the leachate via biochemical reactions, if favourable conditions exist other than temperature, e.g. pH, dissolved oxygen, nutrients, etc.

The pH fluctuates from the minimum value of 7.27 observed in July 2017 to the maximum value of 8.38 recorded at the end of the summer period in 2016 (Fig.4). All measured values are completely basic. As a result, the curve evolves unsteadily and remains above 7. The pH is a key parameter for investigating the presence of aerobic and/or anaerobic conditions in the landfill, and an indicator of leachate aggressiveness (El-Fadel et al., 2002). In addition, pH is an important factor in determining the solubility of metals and the metabolic activity of microorganisms. Seasonal variation shows that in periods of precipitation, the pH becomes slightly basic, either because of the production of volatile fatty acids (Rafizul & Alamgir, 2012) by improving the biodegradation of solid wastes in the presence of moisture, or because of dilution due to precipitation water. (Åkesson & Nilsson, 1997) explain that variations in leachate characteristics are due to alternating acidogenic and methanogenic conditions in the landfill. However, during the summer period, the pH is basic, which is due to several factors: i) predominance of high molecular weight humic and fulvic acids (Calace et al., 2001) in favour of decreasing concentrations of short-chain volatile fatty acids (Chu et al., 1994); ii) arrival at the leachate stabilization stage (Johansen & Carlson, 1976); iii) presence of the methanogenic phase in this period (Baziene et al., 2013; Fatta et al., 1998).

In this respect, the Greater Casablanca landfill “Mediouna” receives solid waste daily and continuously, while the pH remains alkaline. It appears that the waste degradation process and the formation of volatile fatty acids do not contribute to the decrease in pH, as the ratio between old stabilized waste and new landfilled waste is high (Demirbilek et al., 2013). Indeed, the Greater Casablanca landfill “Mediouna” contains several layers of waste of different ages. The new layers are buried with the old layers, causing fresh leachate to flow over the old waste, so the characteristics of the leachate can fluctuate continuously (Vahabian et al., 2019).

However, an acidic pH (which was not observed in this study) characterizes leachates dominated by the production of volatile fatty acids during the anaerobic decomposition of waste in the landfill (Johansen & Carlson, 1976). This production of organic acids results in a decrease in pH, which promotes solubility of inorganic elements (Hans-Jurgen Ehrig, 1989).

The observed variations are similar to the results of (Farhana Zakaria & Abdul Aziz, 2018; Hussein et al., 2019; Vadillo et al., 1999; Vahabian et al., 2019).

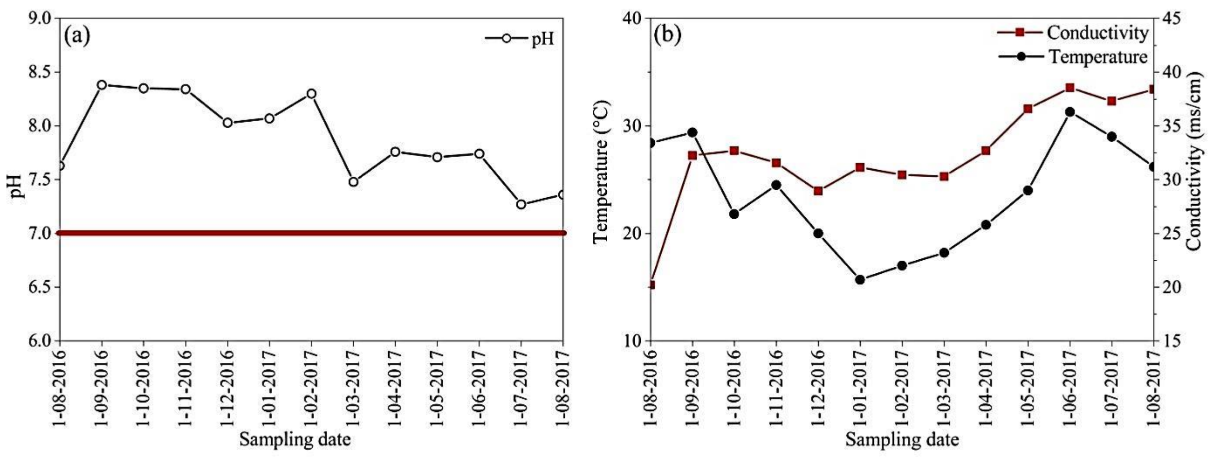


Fig.4. (a) Evolution of pH, (b) Evolution of temperature and conductivity

The electrical conductivity recorded significant values ranging from 20.2 ms/cm to 38.54 ms/cm with a median value of 32.25 ms/cm (Fig.4). These values provide information on leachate mineralisation by the presence of high concentrations of dissolved mineral salts (ammonium, chloride, sulphate, etc.). Indeed, the highest values were recorded between the spring and summer of 2017.

The conductivity recorded throughout the monitoring is significant, indicating strong mineralization by the presence of dissolved inorganic matter. The main cationic elements that contribute to increased conductivity are Na^+, K^+, Ca^{2+} and Mg^{2+}, while the anionic elements are HCO_3^-, Cl^- and SO_4^{2-} (Park et al., 1999). According to (Fig.3), it can be seen that temperature and conductivity fluctuate appropriately and simultaneously; i.e. when the temperature rises, the conductivity also rises, and vice versa. The minimum values are observed in the wet season. It appears that precipitation causes dilution to the leachate. However, this explanation is still insufficient, as other factors are involved in the landfill: the quantity and quality of the landfilled waste, the technical operations in the landfill, etc. (Chen, 1996) observed a decrease in electrical conductivity during the precipitation period (continuous or discontinuous precipitation flow during the day). On the other hand, the dry period is characterized by the recording of maximum values. Evaporation of leachate appears to be the main cause. According to (Rafizul & Alamgir, 2012; Vadillo et al., 1999) the decrease in electrical conductivity occurs in the wet period in contrast to the dry period. The electrical conductivity of this discharge is high in comparison with studies conducted by (Fatta et al., 1998; Frascari et al., 2004).

With regard to biodegradable organic matter. The BOD_5 varies from 1000 mg O_2/l to 21250 mg O_2/l with a median value of 10500 mg O_2/l (Fig.5). The maximum value is observed in July 2017, while the minimum value was noted in September 2016. For its part, the curve shows an increasing trend.

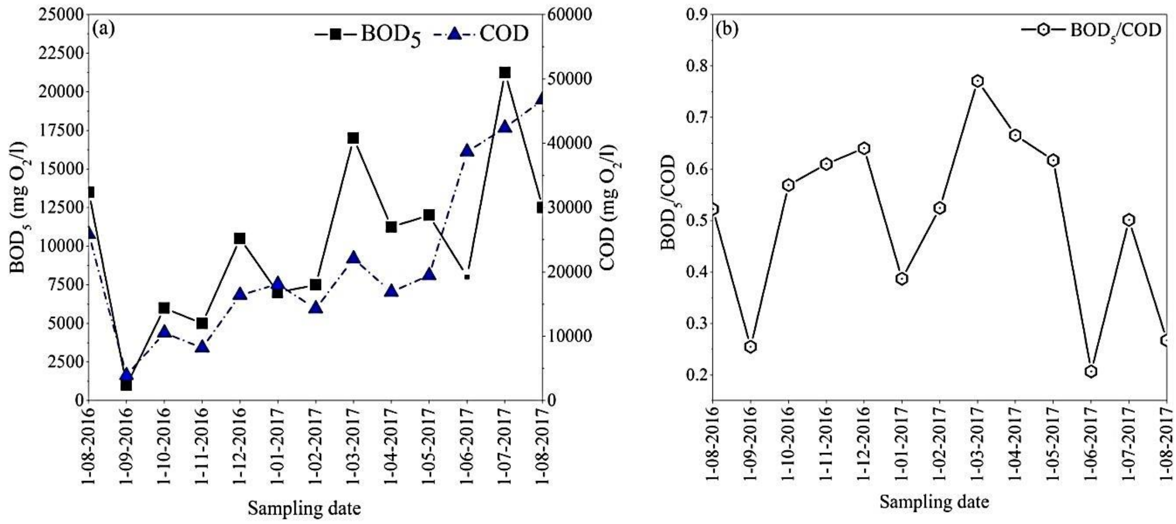


Fig.5. (a) Evolution of COD, BOD_5, (b) Evolution of BOD_5/COD ratio

BOD_5 decreases faster than COD due to the biodegradation of readily degradable compounds (Naveen et al., 2016). Indeed, the increase in BOD_5 in the wet season is due to the microbial degradation of the organic matter of solid waste, this action is favoured by precipitation. (Tränkler et al., 2005) indicates that the biodegradation of organic matter takes place during rainy periods and decreases during dry periods due to the decrease in humidity. Therefore, recirculation of leachate during dry periods is crucial to enhance the biodegradation and leaching of organic matter in wastes. On the other hand, significant concentrations can occur in the dry period, which means that factors other than moisture promote the degradation of organic matter (quantity of waste, leachate recirculation rate, landfill operation processes, level of compaction, etc.). In addition, the Casablanca Grand landfill is characterized by the presence of the methaongene phase. On the other hand, the acidogenic phase is limited and occurs rapidly in the areas that contain the new daily input of solid waste (Demirbilek et al., 2013), in these areas of the landfill, the waste is not yet stabilised (Hussein et al., 2019). BOD_5 values are significant and exceed those reported in the literature (Fatta et al., 1998; Kjeldsen et al., 1998; S. Mishra et al., 2018; Tatsi & Zouboulis, 2002).

The chemical oxygen demand (COD) ranges from 3925 mg O_2/l to 46800 mg O_2/l, with a median value of 18100 mg O_2/l (Fig.5). The minimum value is observed in September 2016, while the maximum value of 46800 mg O_2/l is recorded in August 2017. The temporal variation is similar to that observed for BOD_5. The COD is an indicator of the presence of organic matter in the leachate, consisting mainly of fatty acids, humic and fulvic acids, proteins and carbohydrates, as the landfill ages and methanogenic bacteria become more prevalent and stable, and thus COD decreases (James, 1977; Reitzel et al., 1992)

In addition, the seasonal evolution shows that rainfall favours the degradation of waste by increasing its humidity. (Chen, 1996) states that the high COD values in wet periods can be explained by the leaching of solid wastes containing significant organic matter, while the low values recorded in the same period can be explained either by less leaching of organic matter and/or dilution, due to the fact that precipitation may be in continuous or discontinuous streams during the day. However, this study did not consider the type of precipitation flow; it focused only on cumulative monthly precipitation. Several authors (Åkesson & Nilsson, 1997; Al-Yaqout & Hamoda, 2003) have also noted an increase in COD during the rainy period. According to (Åkesson & Nilsson, 1997), there is a relationship between the increase in COD values and the period of high leachate production. Conversely, the dry period is characterized by a decrease in COD, which may result in a decrease in the moisture content of the waste and a decrease in the rate of leachate recirculation in the waste.

The COD values observed during monitoring are significant compared to other studies (Durmusoglu & Yilmaz, 2006; Farhana Zakaria & Abdul Aziz, 2018; Fatta et al., 1998; Khattabi et al., 2002; Vahabian et al., 2019; Zhang et al., 2013).

The ratio BOD_5/COD varies between 0.207 and 0.771, with a median value of 0.524 (Fig. 5). The maximum value of 0.771 is detected in March 2017, while the minimum value of 0.2 is observed in June 2017. In general, the trend curve shows an irregular variation. This parameter indicates the proportion of the biodegradable organic fraction in the leachate. (Chen, 1996), established a relationship between landfill age and leachate biodegradability, as the landfill ages, the leachate contains refractory compounds. In wet periods, the leachate biodegradability is high, which is consistent with the BOD_5 results observed in the same period. (Vahabian et al., 2019) confirm that high biodegradability is a sign of the presence of waste degradation activity. However, the dry period is characterised by low biodegradability. (Hans-Jurgen Ehrig, 1989), reports that a ratio greater than 0.4 is a factor in good biodegradability, while a ratio less than 0.1 is an indicator of low leachate biodegradability accompanied by an increase in pH. In this sense, authors such as (Chen, 1996; Frascari et al., 2004; Naveen et al., 2016) confirm that old wastes and limited microbiological degradation in wastes are the causes of this decrease.

Total solids (TS) range from 18005 mg/l to 41035 mg/l with a median value of 10570 mg/l (Fig. 6). The maximum value is observed in spring 2017, for the minimum value is recorded in the winter period of 2016. Total solids show significant values and fluctuations in the leachate from Grand Casablanca. Peaks are observed in both wet and dry periods. In wet periods, variations in TS are due to the alternation of intense rains and a few dry periods during the rainy season (Rafizul & Alamgir, 2012). On the other hand, (Chu et al., 1994) explain that rains penetrate through the waste, resulting in leaching of organic and mineral matter and high volumes of leachate. With regard to the dry period, leachates are highly concentrated due to a decrease in the percolation of water into the waste, and increased evaporation favoured in high temperatures (Chu et al., 1994). However, other factors can affect the total solids content: sampling techniques (sampling was done manually by direct filling of the bottles under the leachate stream); waste management techniques in the landfill; leachate flow rate; quantity and quality of solid waste, etc. The results in total solids content are significant and exceed those mentioned in (Chu et al., 1994; Fan et al., 2006; Gounaris et al., 1993).

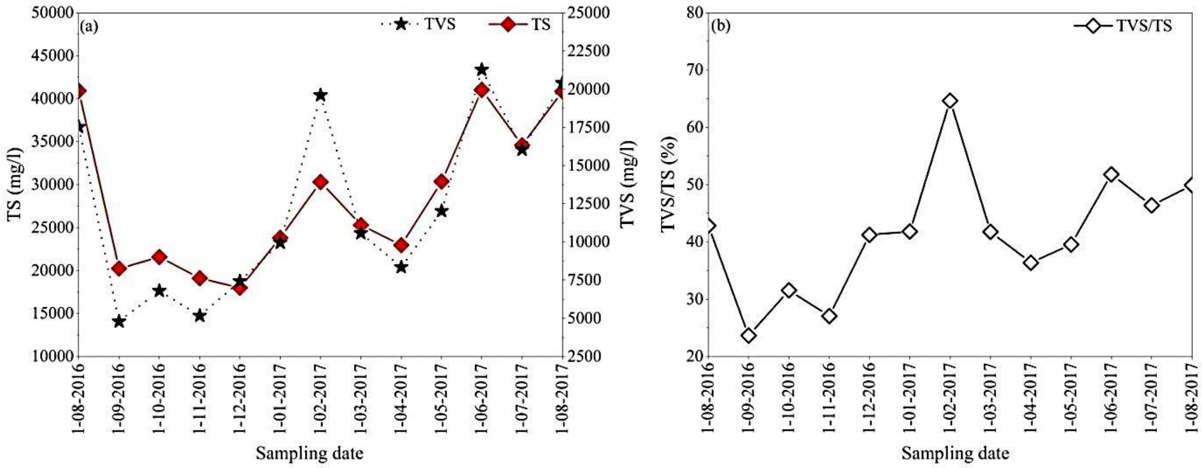


Fig.6. (a) Evolution of TS and TVS, (b) Evolution of TVS/TS ratio

For the organic fraction of total solids, the TVS content fluctuates between 4790 mg/l and 21260 mg/l with a median value of 10570 mg/l (Fig. 6). The maximum concentration was observed in June 2017, and the minimum value was observed in September 2016. The trend curve shows a similar variation in relation to the total solids. In the wet period, there are significant values, this is reflected in a TVS/TS ratio of 65%. On the other hand, the dry period is characterized by less important values, since the minimum TVS/TS ratio is 24%.

Considering the nitrogenous compounds, nitrates range from 4 mg N/l to 30 mg N/l with a median value of 15 mg N/l (Fig.7). The maximum value is observed in the summer period of 2016, while the minimum value is noticed in the winter period of 2016. It seems that the curve has an unstable trend.

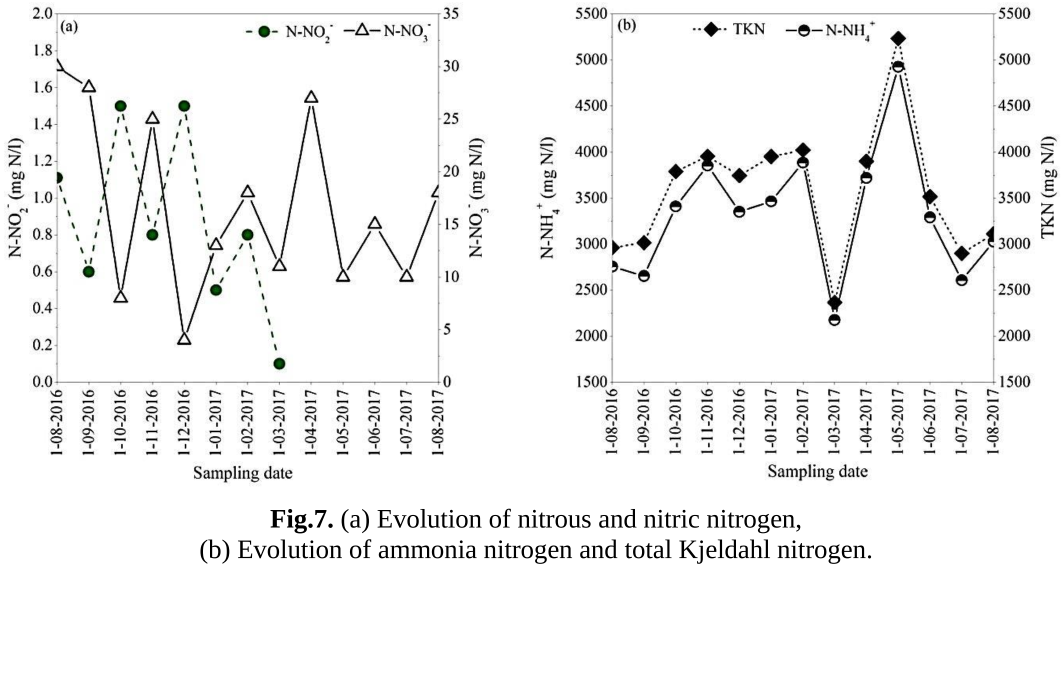


Fig.7. (a) Evolution of nitrous and nitric nitrogen,
(b) Evolution of ammonia nitrogen and total Kjeldahl nitrogen.

Nitric nitrogen concentrations in leachate are low and fluctuate irregularly between wet and dry periods. This result is consistent with several studies (Johansen & Carlson, 1976; Zhang et al., 2013) which state that nitrate levels are modest because they are only produced in the upper layer of the waste that is in direct contact with air, or in limited aerobic areas within the landfill, or from recirculation of nitrified or pre-treated leachate (Burton & Watson-Craik, 1998). In the same context, (Tatsi & Zouboulis, 2002) explain that mature leachates are characterized by low nitrate concentrations. This is due to the stabilization process in the landfill and not to a dilution effect of precipitation in the wet season. According to (Burton & Watson-Craik, 1998) who state that during the wet season, rainfall seeps through the waste, it likely contains nitrate from the oxidation of ammonia gas in the landfill, which may also be oxidized by oxygen from the cover vegetation.

In these circumstances, several hypotheses can explain this flucuation: (a) Rare nitritation (Eq.3) and nitration (Eq.4) reactions that oxidize ammonium to nitrate under aerobic conditions (Benoit, 2014); (b) Oxygen-poor environment (e.g. landfills) that inhibits the nitrification reaction (Huang et al., 2008).

Eq.3 $$2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_2^- + 4H^+ + 2\ H_2O + ATP$$

Eq.4 $$2\ NO_2^- + O_2 \rightarrow 2\ NO_3^- + ATP$$

(c) During the denitrification reaction in an anoxic and/or anaerobic environment, this reaction will promote the transformation of nitrates in the presence of assimilable carbon into a gaseous compound in the form of nitrogen oxide: NO, N_2O and/or N_2 by the intervention of heterotrophic bacteria (Benoit, 2014; Price et al., 2003), according to (Eq.5).

Eq.5 $$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$$

(d) And dissimulating reduction of nitrates to ammonium, according to the following equation (Eq.6) (Price et al., 2003):

Eq.6 $$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

For nitrite (NO_2^-), the maximum value is 1.5 mg N/l, observed in the winter period, while the values become below the detection limit of the method from April 2017 until the end of the monitoring (Fig.7), the median of available observations is 0.8 mg N/L. Nitrites are very little contained in the leachates of the Greater Casablanca “Mediouna”. This result is in agreement with (Johansen & Carlson, 1976) who assert their presence in very low concentrations, and sometimes below the detection limit of the method. It seems that the nitrite content does not depend on seasonal variation, it is directly related to the anoxic or aerobic conditions that may arise in the leachate, because nitrites are transition ions during the nitrification phenomenon, this ammonium oxidation reaction requires oxygen (Burton & Watson-Craik, 1998).

Ammonium (NH_4^+) shows significant concentrations ranging from 2175 mg N/l to 4926 mg N/l with a median value of 3350 mg N/l (Fig.7). In principle, ammonium is characterized by a slight variation, except for a sudden increase and decrease recorded in May 2017 (spring period) and March 2017 (winter period) respectively.

Ammonia nitrogen is generated from the decomposition of nitrogenous organic matter in solid wastes (Huang et al., 2008; Kjeldsen et al., 2002). Indeed, by comparing the ammonia nitrogen content with other nitrogen compounds, it can be deduced that this form represents the dominant part of the nitrogen forms in the leachates from the Greater Casablanca landfill “Mediouna”, with a maximum NH_4^+/NTK ratio of 97%, this is similar to other results (Burton & Watson-Craik, 1998; Chu et al., 1994; Hans-Jurgen Ehrig, 1989; Johansen & Carlson, 1976; Öman & Junestedt, 2008; Park et al., 1999; Statom et al., 2004; Zhang et al., 2013).

Seasonal variation is slight, such that ammonium values are close to each other between dry and wet periods, except for exceptional peaks. Thus its concentration does not decrease over time, which could be one of the main long-term pollutants in landfill leachate (Kjeldsen et al., 2002). According to (H.-J. Ehrig, 1989), who states that there is no significant change in ammonia concentrations from the acid phase to the methanogenic phase. In the same context, the peaks observed in the wet period can be explained by a high deamination of amino acids during the decomposition of solid wastes (Chu et al., 1994), and ammonium can accumulate in the leachate due to the lack of favourable conditions for its transformation to N_2. Also (Kuruparan et al., 2003) observed that the greatest amount of leachate, carbon and nitrogen production was released during the rainy seasons. Consequently, the ammonium levels recorded during this study exceed those reported in the literature (Aziz et al., 2010; Chu et al., 1994; Fatta et al., 1998; Jensen & Christensen, 1999; Müller et al., 2015; Rafizul & Alamgir, 2012).

The Kjeldahl nitrogen (TKN) ranges from 2368 mg N/l to 5234 mg N/l with a median value of 3745 mg N/l (Fig.7). The maximum value is observed in May 2017, while the minimum value is recorded in March 2017. Kjeldahl nitrogen represents the sum of ammonia nitrogen and organic nitrogen, the latter being contained in proteins, nucleic acids, chitins, phospholipids and adenosine triphosphate (ATP) (Burton & Watson-Craik, 1998). The seasonal evolution of this parameter is similar to that of NH_4^+. The high values of NTK are noticed in the wet period, it turns out that precipitation favours the degradation of solid wastes, and thus the release of organic nitrogen. Indeed, organic nitrogen is transformed into ammonia nitrogen by the reaction of ammonification in an aerobic environment, this reaction takes place in the first phase of microbial degradation of solid waste when the oxygen is not yet exhausted, this explains the high concentrations of ammonia nitrogen compared to organic nitrogen.

Total phosphorus (Tp) concentrations range from 21.09 mg P/l to 72 mg P/l, with a median value of 43.23 mg P/l (Fig.8). The maximum value is recorded in December 2016, while the minimum value is noted in July 2017.

Phosphorus comes from the decomposition of organic phosphorus matter (mainly phospholipids and phosphoproteins) contained in wastes (Fatta et al., 1998). Total phosphorus is characterized by low to medium concentrations, a finding that is consistent with studies conducted by (Chu et al., 1994; Durmusoglu & Yilmaz, 2006; Reitzel et al., 1992). Indeed, this observation is explained by the fact that the waste already contains a small amount of the phosphorus material or at leachate maturity (Tatsi & Zouboulis, 2002). In wet periods, total phosphorus reaches its maximum value of 72 mg P/l, which coincides with the results of (Åkesson & Nilsson, 1997) which confirmed the relationship between high phosphorus values and the increase in the leachate production stream in this period. Also, (Mavakala et al., 2016) noted that in the rainy season the values are higher than those observed in the dry season. Furthermore, it appears that phosphorus also comes from soil leaching since the leachate is in direct contact with the soil in the Greater Casablanca landfill. Conversely, the dry period is characterized by low values. In this context, other factors can affect the phosphorus content in the leachate: the change in the decomposition and synthesis phases between organically bound and oxidized inorganic forms, the assimilation of phosphorus by microorganisms, the adsorption and precipitation phenomena that take place in the leachate (Reitzel et al., 1992).

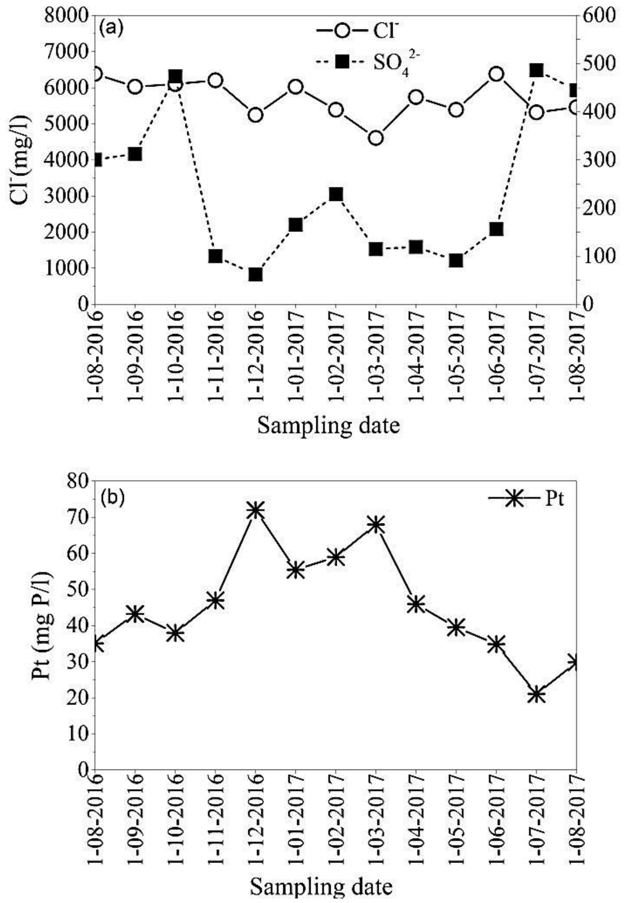


Fig.8. (a) Evolution of chlorides and sulphates, (b) Evolution of total phosphorus

Chloride (Cl^-) contents range from 4609 mg/l to 6382 mg/l, with a median value of 5743 mg/l (Fig.8). The high concentration is noticed both in August 2016 and June 2017, while the minimum value is recorded in March 2017.

Throughout the monitoring period, chlorides are significant and vary moderately between dry and wet periods, which can be demonstrated by the fact that chlorides are not affected by redox reactions or biological activity in the landfill (Reitzel et al., 1992). According to (Statom et al., 2004), chlorides are highly soluble and result from the decomposition of fresh solid waste in active landfills, with concentrations increasing during the precipitation period. However, in the case of closed sites, the dilution factor comes into play because the concentration of chlorides becomes constant over time. In this regard, chlorides are considered to be complexing agents for some metals (Gould et al., 1990). According to (Erses et al., 2008; Rafizul & Alamgir, 2012), they are very conservative and are only attenuated by dilution, so they are considered inert and non-biodegradable compounds. They can be used as an indicator of the extent of environmental contamination by leachate (Tatsi & Zouboulis, 2002).

Indeed, in the case of the Greater Casablanca landfill, there are two processes at the same time: a leaching of chlorides from the new waste and a dilution of the leachate in the stabilized areas of the landfill. The results obtained for chlorides exceed the levels reported in the literature (Kjeldsen et al., 1998; Rafizul & Alamgir, 2012; Yildiz et al., 2004).

Sulphates (SO_4^{3-}) ranges from 62 mg/l to 486 mg/l with a median value of 165 mg/l (Fig.

8). Indeed, the maximum value is observed in July 2017, and the minimum value is noted in December 2016. Sulphates do not have a regular trend, they are characterized by large fluctuations.

In the dry period, there are high sulphate values compared to the wet period. They come from the leaching of demolition waste, ashes, sediments and gypsum (Thomas H. Christensen et al., 2001; Naveen et al., 2017). According to (T. H. Christensen & Kjeldsen, 1989), The initial high content of sulphate may slowly be reduced as the redox potential drops.

On the other hand, in the wet season, sulphates appear to be attenuated by the effect of dilution due to precipitation (Thomas H. Christensen et al., 2001), or by anaerobic reduction to sulphides in the landfill (Bozkurt et al., 2000; Frikha et al., 2017; Gould et al., 1990; Tatsi & Zouboulis, 2002). In this regard, (Fairweather & Barlaz, 1998) point out that sulphur is used as an oxidant in redox reactions by sulphate-reducing bacteria that convert it to sulphide or by complexation with metals (Thomas H. Christensen et al., 2001).

In another section, metals come mainly from batteries, electronic products, used motor oil, plastics, inks, etc. Indeed, the concentration of metals is always high at acidic pH because of the solubility of the metals in this state, characterizing the early stages of anaerobic degradation (Bozkurt et al., 2000; Naveen et al., 2016), whereas at basic pH the concentrations decrease due to adsorption and precipitation reactions (Tatsi & Zouboulis, 2002).

In reference to (Bozkurt et al., 2000), who adds that the mobility of metals is conditioned by several factors: pH, oxidation-reduction reactions, the presence of complexing agents (sulphates, carbonates, chlorides and organic acids). In this sense, the studies provided by (Baun & Christensen, 2004) indicate that metals are found in leachates mainly in the form of colloids and complexes. Colloids associated with metals are of organic origin, but inorganic colloids have also been identified in the form of sulphide precipitation. Furthermore, (Baun & Christensen, 2004) indicates that the concentration of metals in the leachate is also dependent on the sampling procedure and sample handling.

Throughout the temporal monitoring, the concentrations of heavy metals fluctuate considerably:

- Cobalt (Co) and lead (Pb) concentrations remained below the detection limit of the method. These elements are affected by the basic nature of the leachate, the pH remained basic throughout the monitoring period. While these elements should not be overlooked, they can pose health and environmental risks at low concentrations (James, 1977; Öman & Junestedt, 2008).
- Copper (Cu) fluctuates between 0.038 mg/l to 0.665 mg/l, with a median value of 0.495 mg/l. The maximum value is recorded in both March 2017 and August 2017 (Fig.9), while the minimum value is observed in August 2016. The seasonal evolution shows an increase in concentrations in wet and dry periods, which can be explained by the important leaching of solid waste in the Greater Casablanca landfill “Mediouna” during the rainy period. Admittedly, the copper content remains below the limit for discharge into the natural environment according to the Moroccan standard (DRPE, 2014). The result obtained is consistent with that observed by (James, 1977). In the same context, (Xiaoli, Shimaoka, Xianyan, Qiang, & Youcai, 2007) found that copper remained below the detection limit. On the other hand, (Kim, Jang, & Townsend, 2011) indicate that this element is easily precipitated under anaerobic conditions in the form of copper sulphide complexes.
- Nickel (Ni) concentrations are unstable during the monitoring period (Fig.9). The maximum value of 1.13 mg/l is observed in March 2017, while the minimum value of

0.275 mg/l is observed in April 2017 with a median value of 0.739 mg/l. In the wet season, the nickel contents decrease compared to the values obtained in the dry season, this can be explained by the dilution factor (Thomas H. Christensen et al., 2001). In fact, the result obtained coincides with the result found by (Xiaoli et al., 2007), so it remains lower than the Moroccan discharge standards (DEM, 2014). According to (Kjeldsen et al., 2002), nickel forms a complex with organic ligands in the leachate, and precipitates with sulphides and carbonates.

- Zinc (Zn) levels are sporadic (Fig.9). Indeed, the minimum concentration is below the detection limit, this observation is noticed from October 2016 to January 2017. However, the maximum value of 0.9 mg/l is recorded in August 2016, with a median value of the available observations of 0.15 mg/l. It appears that Zinc is affected by dilution since values below the detection limit were observed in the wet period, unlike the dry period. This result is consistent with the study by (Xiaoli et al., 2007). However (Kim et al., 2011) demonstrated that zinc is a dominant metal in the anaerobic phase in the landfill. According to (Gould et al., 1990; Kjeldsen et al., 2002), who reported the precipitation of Zinc by sulphides (produced from sulphate reduction) and carbonates.
- Cadmium (Cd) concentrations fluctuate between the minimum value below the detection limit observed from August 2016 to January 2017 and the maximum value of 0.047 mg/l recorded in August 2017 (Fig.10), with a median value of the available observations of 0.025 mg/l. In the wet season, cadmium is affected by the dilution factor, whose values fluctuate from values below the detection limit to values below the limit of discharges into the natural environment according to the Moroccan standard (DEM, 2014). On the other hand, the dry period is characterized by an increase in cadmium contents. (Reitzel et al., 1992) explains that the presence of cadmium is limited in cadmium salts (chlorides, nitrates and sulphates) and organic and inorganic complexes. It can be adsorbed by sediments. Its mobility is subject to several phenomena, such as adsorption, ion exchange, chemical precipitation and complexation with organic ligands (Thomas H. Christensen et al., 2001). In the same context, (Reitzel et al., 1992) explain that during the aerobic and anoxic phases in the degradation of solid wastes by microbial activity, the pH of the leachate is acidic; therefore, metals are more mobile and cadmium levels are high. With the beginning of methanogenesis, a decrease in the levels results.
- Chromium (Cr) contents are considerable and intermittent (Fig.10), and fluctuate between 1.192 mg/l and 16.117 mg/l with a median value of 5.41 mg/l. The minimum value is recorded in August 2016, while the maximum concentration is recorded in September 2016.

Chromium concentrations exceed the limits for discharges into the natural environment according to the Moroccan standard (DEM, 2014). Seasonal evolution reveals that chromium does not have a stable trend during the same period (wet or dry). (Thomas H. Christensen et al., 2001) mentions that chromium can be attenuated by the dilution factor. Admittedly the fluctuation observed in the same period can be caused by several factors such as: the quantity and quality of the waste put in landfill, ageing of the waste layers, thickness of the waste compartments, and burial operations in the site, etc. According to (Thomas H. Christensen et al., 2001; Jensen & Christensen, 1999; Kjeldsen et al., 2002) indicating that chromium does not form precipitates with sulphides and carbonates, chromium does, however, tend to form insoluble precipitates with hydroxides.

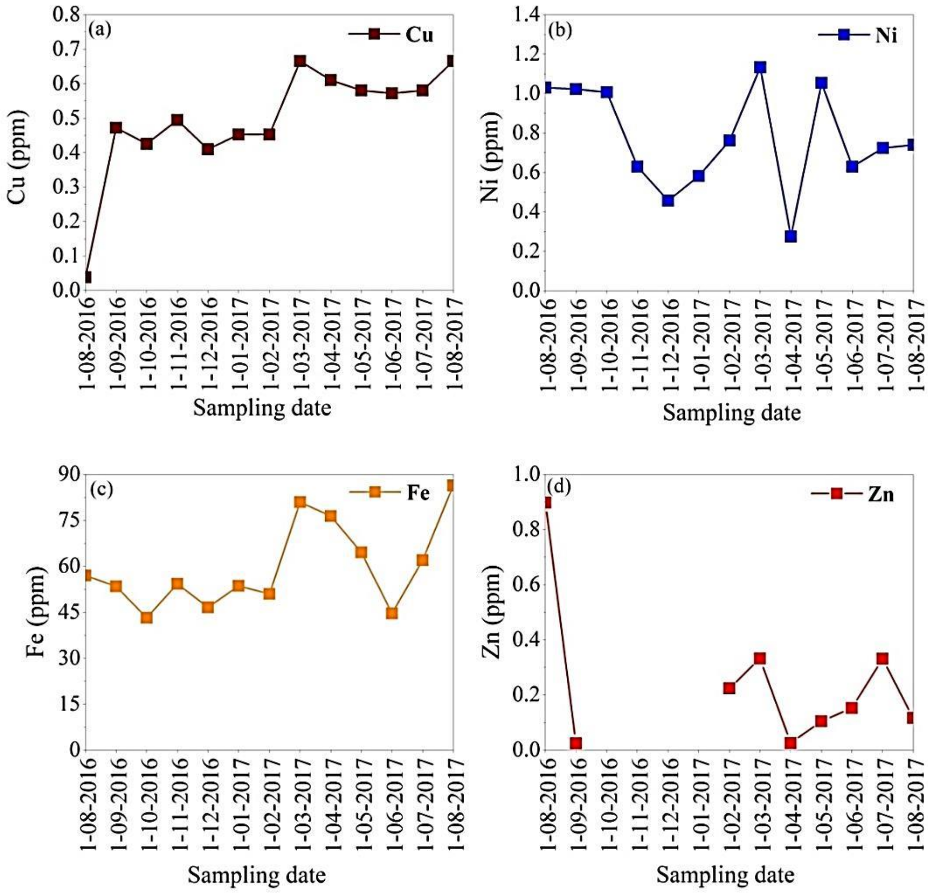


Fig.9. (a) Evolution of Cu, (b) Evolution of Ni, (c) Evolution of Fe and (d) Evolution of Zn

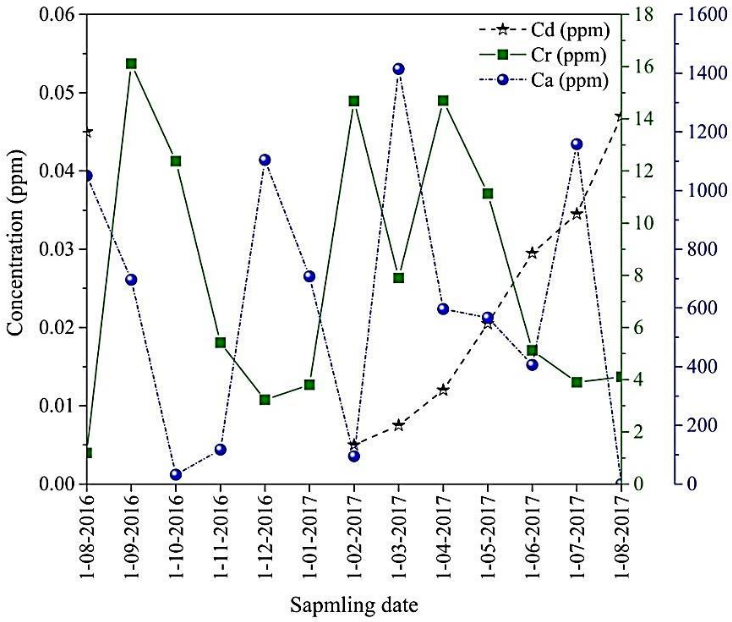


Fig.10. Evolution of Cd, Cr and Ca

Concerning the metal cations or inorganic macrocomponents, the temporal monitoring shows that:

- Potassium (K) remained below the detection limit of the method.
- Iron (Fe) contents are significant and vary between 43.16 mg/l and 86.4 mg/l (Fig.9) with a median value of 54.26 mg/l. The maximum value is observed in August 2017, while the minimum value is observed in October 2016. Iron is derived from the degradation process of the iron complex caused by biological activity and chemical reactions in the landfill, also by the leaching of steel components in the waste (Reitzel et al., 1992). Thus, the levels of iron in the Greater Casablanca landfill are significant and higher than those found by (Khattabi et al., 2002; Vahabian et al., 2019), so they exceed the Moroccan discharge limit values (DEM, 2014). In addition, (James, 1977; Kim et al., 2011) observed that iron is the most abundant element in the leachate in the heavy metal category, it is present as ferrous ions due to the reducing conditions in the landfill (Park et al., 1999). Seasonal trends show that high values are recorded in both wet and dry periods, which is consistent with (Thomas H. Christensen et al., 2001), who reported that iron is not affected by dilution. (Bozkurt et al., 2000; Thomas H. Christensen et al., 2001), reported that it is attenuated by sorption, especially since oxidized iron is characterized by its adsorptive properties.
- Calcium (Ca) concentrations range from 0.1 mg/l to 1414.37 mg/l with a median value of 596.33 mg/l (Fig.10). The maximum value is recorded in March 2017, while the minimum value is detected in August 2017. Calcium appears to be unaffected by the dilution factor, as high levels were noted in both wet and dry periods. According to (Demirbilek et al., 2013) high calcium concentrations can be explained by the formation of organic complexes with calcium, so it can be attenuated by ion exchange phenomena and precipitation (Thomas H. Christensen et al., 2001).
- Magnesium (Mg) concentrations range from 5.6 mg/l to 8.43 mg/l with a median value of 7.77 mg/l (Fig.11). Indeed, the maximum value is observed in both August 2016 and June 2017, while the minimum value is found in January 2017. The seasonal evolution shows that the Mg content varies slightly, it seems that it is not affected by dilution except for a sudden decrease which can be explained by the operating conditions in the landfill.
- Manganese (Mn) contents range from 1.51 mg/l to 8.52 mg/l with a median value of 2.68 (Fig.11). The maximum value is noticed in August 2018, and the minimum value is recorded in February 2017. In addition, Mn does not have a stable trend, with high values being recorded in both the wet and dry periods. It appears that manganese is also not affected by the dilution factor. Consequently, (Kjeldsen et al., 2002) explains that the low concentrations are mainly due to sorption and precipitation and not to the absence of metals in the waste. According to (Jensen & Christensen, 1999), magnesium and manganese can precipitate in leachates as $MgCO_3$, $CaMg(CO_3)_2$, $CaMg_3(CO_3)_4$, $MnHPO_4$ and $MnCO_3$.

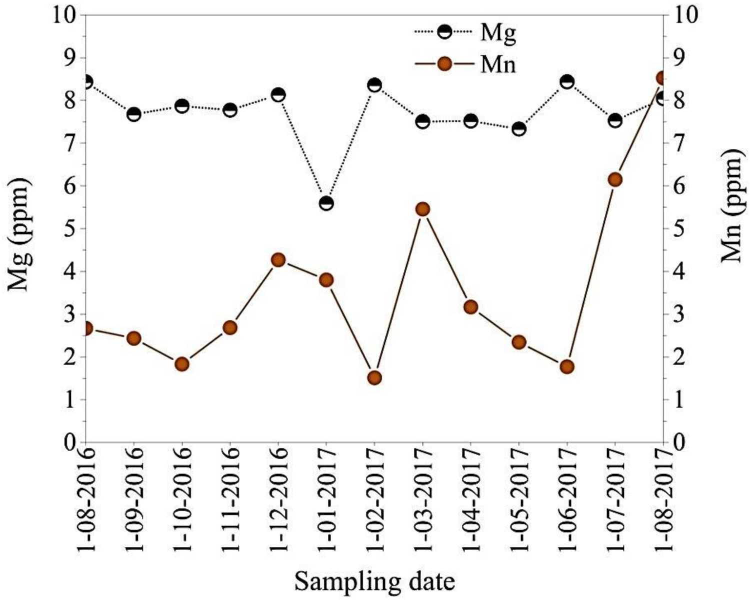


Fig.11. Evolution of Mg and Mn

Statistical correlation

First, the observations of the different variables were evaluated to prove whether the data follow a normal distribution, for which a normality test was carried out. In a second step, the multivariate correlation matrix was developed using the OriginPro software. The results obtained are presented in (Table 5). The correlation is significant at a significance level of 0.05 (values in bold and red), and is considered significant or strong when the correlation coefficient is greater than 0.5 (M.Trochim et al., 2015).

Table 5. Statistical analysis of Pearson correlation type applied to the different physico-chemical parameters of the leachate from the Greater Casablanca landfill site

	Temp	**pH**	**Cond**	**BOD_5**	**COD**	**TS**	**TVS**	**$N\text{-}NO_2^-$**	**$N\text{-}NO_3^-$**	**$N\text{-}NH_4^+$**	**TKN**	**Tp**	**Cl^-**	**SO_4^{2-}**	**Ca**	**Cr**	**Cd**	**Cu**	**Fe**	**Mg**	**Mn**	**Ni**	**Zn**	**Rf**
Temp	1.0000																							
pH	-0.2851	1.0000																						
Cond	0.2542	-0.2488	1.0000																					
BOD_5	0.0525	**-0.8882**	0.0655	1.0000																				
COD	0.4186	**-0.8524**	0.4395	**0.6681**	1.0000																			
TS	0.5209	**-0.6627**	0.1749	0.4476	**0.8282**	1.0000																		
TVS	0.2838	**-0.5555**	0.2013	0.4115	**0.7858**	**0.9275**	1.0000																	
$N\text{-}NO_2^-$	0.2039	0.3219	-0.1998	-0.1603	-0.0962	-0.0472	-0.0615	1.0000																
$N\text{-}NO_3^-$	0.3328	0.1463	-0.3546	-0.3134	-0.1938	0.1261	-0.0087	-0.2491	1.0000															
$N\text{-}NH_4^+$	-0.2387	0.3274	0.2161	-0.3046	-0.2841	-0.1499	-0.0774	0.4174	-0.1004	1.0000														
TKN	-0.2675	0.3703	0.2014	-0.3337	-0.3312	-0.2182	-0.1516	0.4657	-0.1782	**0.9850**	1.0000													
Tp	**-0.7599**	0.3807	-0.4103	-0.1996	-0.5389	**-0.6100**	-0.3890	-0.2502	-0.2415	0.0360	0.0654	1.0000												
Cl^-	0.4401	0.4112	-0.1620	**-0.5803**	-0.1540	0.1261	-0.0254	0.3624	0.5122	0.1443	0.1591	-0.4229	1.0000											
SO_4^{2-}	0.3884	-0.1865	0.1886	0.1658	0.3787	0.3681	0.2749	0.3472	0.0116	-0.4112	-0.4048	**-0.6836**	0.1286	1.0000										
Ca	-0.0159	-0.4470	-0.3647	**0.5767**	0.0967	-0.0520	-0.1216	-0.3087	-0.1693	-0.5199	-0.4562	0.2691	-0.4185	-0.2167	1.0000									
Cr	-0.1934	0.4769	0.1602	-0.4378	**-0.5689**	-0.4065	-0.3263	-0.1415	0.1958	0.2837	0.2788	0.1216	-0.0880	-0.0193	-0.3218	1.0000								
Cd	**0.8242**	-0.5955	0.0206	0.2345	**0.7746**	**0.8585**	0.5223	0.6976	0.2194	-0.2831	-0.2797	**-0.8285**	0.5046	0.6971	-0.0648	**-0.8550**	1.0000							
Cu	-0.0991	-0.2842	**0.8323**	0.1758	0.2665	-0.0839	-0.0006	-0.5285	-0.3259	0.0784	0.0429	-0.0041	-0.5212	-0.0846	-0.1394	0.2697	-0.3489	1.0000						
Fe	-0.0773	**-0.6707**	0.1990	0.5343	0.4017	0.2347	0.1634	**-0.7965**	0.1645	-0.2009	-0.2833	-0.0892	-0.5440	0.0415	0.1606	-0.0070	0.0261	0.5087	1.0000					
Mg	0.4644	-0.0459	-0.1045	0.0378	0.1732	0.3607	0.3815	0.4686	0.1844	-0.1115	-0.2070	-0.1575	0.0658	0.1577	-0.1766	0.0314	0.3320	-0.2118	-0.1194	1.0000				
Mn	0.0321	**-0.6928**	0.2890	**0.5993**	**0.6469**	0.2591	0.2256	-0.4241	-0.2114	-0.4586	-0.4860	-0.1502	-0.5259	0.3343	0.2346	-0.4572	0.4386	0.4189	**0.7099**	-0.1341	1.0000			
Ni	0.1842	-0.0392	-0.1745	0.0591	-0.0964	0.1737	0.0346	-0.2912	-0.0302	-0.2334	-0.2231	-0.1332	-0.1271	0.3028	0.1405	0.1342	0.0744	-0.1910	0.0434	0.1199	-0.0838	1.0000		
Zn	0.1324	-0.2904	**-0.7690**	0.4161	0.1681	0.4801	0.3275	0.5431	0.2173	-0.3672	-0.3767	-0.0956	0.2059	0.1995	0.4902	-0.6580	0.4109	**-0.8046**	-0.1454	0.4309	-0.0221	0.3880	1.0000	
Rf	**-0.6994**	0.0417	-0.3045	0.1386	-0.2166	-0.4702	-0.2886	-0.2356	-0.4746	-0.1748	-0.1216	**0.8897**	**-0.5669**	**-0.5580**	0.5193	-0.2134	-0.6620	0.0834	0.0380	-0.3036	0.1862	-0.1625	0.0520	**1.0000**

* Correlation is significant at the 0.05 level (values in bold and red).

In this context, there is a strong and significant linear correlation between precipitation and total phosphorus, also there is a significant negative relationship at medium intensity between precipitation and the following three parameters: temperature, chlorides and sulphates.

However, it is assumed that the absence of significant correlations between precipitation and other variables such as BOD_5 , DOC, $N\text{-}NH_4^+$, etc., does not necessarily mean that there is no effect, as other parameters may interact with them, such as waste quantity and quality, leachate flow, etc.

In addition, other significant correlations of positive direction were noted between: temperature and cadmium; conductivity and copper; BOD_5 and (COD, Ca, Mn); COD and (TS, TVS, Cd, Mn); TS and (TVS, Cd); $N\text{-}NH_4^+$ and TKN; Fe and Mn.

Parallel to the above, significant correlations of negative direction were found between: temperature and total phosphorus; pH and (COD, BOD_5, TS, TVS, Fe and Mn); conductivity and Zn; BOD_5 and Cl^-; COD and Cr; TS and Tp; $N\text{-}NO_2^-$ and Fe; Tp and (SO_4^{2-}, Cd); Cr and Cd; Cu and Zn.

Leachate pollution Index (LPI)

Table 6 represents the calculation of the LPI of the Greater Casablanca "Mediouna" landfill, based on (Eq.2), which is applied in the case where not all 18 variables are available. For this, the variables used in the calculation are: pH, BOD_5, COD, TKN, $N\text{-}NH_4^+$, Fe, Cu, Ni, Zn, Cr, Cl^-, where Pb has not been included because its concentration is below the detection limit of the method.

Table 6. Leachate pollution index for Greater Casablanca landfill "Mediouna"

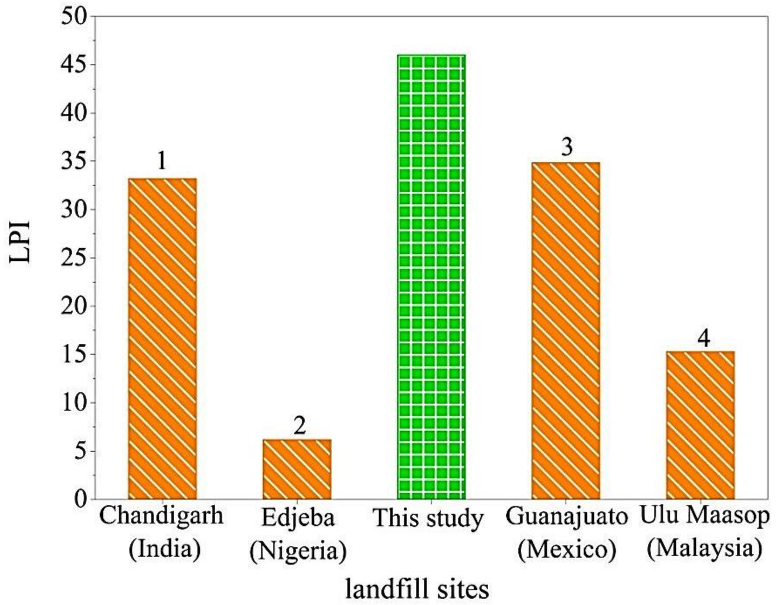
Pollutant	Unit	Pollutant concentrations	Significance	Pollutant weight *wi*	Sub-index value *pi*	Overall pollution rating *pi wi*
pH		7.88	3.509	0.055	5	0.275
BOD_5	mg O_2/l	10192	3.902	0.061	67	4.087
COD	mg O_2/l	21817	3.963	0.062	84	5.208
TKN	mg N/l	3574	3.367	0.053	100	5.3
Ammonia Nitrogen	mg N/l	3317	3.25	0.051	100	5.1
Iron	mg/l	59.53	2.83	0.045	5	0.225
Copper	mg/l	0.49	3.17	0.05	6	0.3
Nickel	mg/l	0.77	3.321	0.052	6	0.312
Zinc	mg/l	0.15	3.585	0.056	5	0.28
Lead	mg/l	BDL	-	-	-	-
Chromium	mg/l	7.98	4.057	0.064	59	3.776
Chlorides	mg/l	5713	3.078	0.048	54	2.592
Total				**0.597**		**27.455**
LPI value using Eq.2						**45.99**

The Greater Casablanca "Mediouna" landfill is characterized by a high LPI (45.99), this is explained by the high COD, BOD_5 , nitrogen, chromium and chloride values recorded during monitoring, these values caused an increase in the sub-index scores, leading to an increase in the aggregation value.

According to (Kumar & Alappat, 2005b), a high LPI is an indicator that the landfill has not stabilized, in which case it is considered a transfer site of contamination. Therefore, the leachate should be treated immediately and appropriately, and monitored on an ongoing basis.

From the research provided by (Luo et al., 2020), they found that leachate toxicity is mainly dependent on high concentrations of ammonium and organic matter (COD). In this context, these concentrations themselves lead to an increase in the LPI value. Therefore, the higher the LPI, the more certain the leachate toxicity.

In this respect, the comparison of the LPI of the Greater Casablanca landfill “Mediouna” with other landfills in other countries shows that the LPI is significant (Fig.12), this parameter indicates that the leachate from this study is characterized by a relatively higher contamination potential and that the landfill requires urgent attention in terms of introducing remediation measures. In addition, the variation in LPI from one landfill to another is mainly due to the variability in the physico-chemical composition of the leachate, which depends on several factors: age of the landfill, quantity and quality of the waste disposed of, landfilling techniques used, humidity and climate, etc.



1. (Mor et al., 2018)
2. (Agbozu et al., 2015)
3. (Guerrero-Rodríguez et al., 2014)
4. (Hussein et al., 2019)

Fig.12. Comparison of LPI of the Greater Casablanca “Mediouna” landfill resulting from this study with other landfills in other countries.

Conclusion

This research made it possible to highlight the characteristics of the leachate from the “Mediouna” landfill in Greater Casablanca located in a Mediterranean climate, by monitoring the evolution of the physico-chemical parameters over a 13-month period, in order to study the impact of rainfall on the quality of the leachate.

At the end of this study, it can be concluded that leachates are highly concentrated in all forms of pollution. Nevertheless, their fluctuations over time do not affect their aggressiveness. Indeed, the quality of the leachate studied is influenced by several changes between dry and wet periods. It can be stated that:

1- The organic matter contained in the solid waste is favoured for leaching during precipitation;
2- Ammonia nitrogen is the dominant form of nitrogenous forms in the leachate from the Greater Casablanca landfill “Mediouna”;

3- The seasonal variation in the physico-chemical parameters of the leachate is certainly due to the precipitation factor which enhances the degradation of the waste, and consequently the leaching of organic and mineral compounds contained in the landfilled waste, resulting in significant values for COD, BOD_5, ammonium and some metals.
4- As the landfill is still in operation and more than 30 years old, there are significant fluctuations in the characteristics of the leachate, as the acidogenic and methanogenic phases are present simultaneously in dispersed areas within the landfill;
5- Phosphorus remains less important in the leachate, which can be a problem during biological treatment;
6- Chlorides are attenuated by the dilution factor caused by precipitation, while sulphates are also mitigated by dilution and reduction to sulphide;
7- Metals are characterized by highly variable concentrations, particularly iron and calcium, which are the major elements in the leachate from the Greater Casablanca landfill. Certainly, it is difficult to present complete and detailed interpretations of the behaviour of metals in the leachate based on temporal monitoring. Indeed, the use of a speciation of each metal will allow a better understanding of its mobility in the leachate surveyed;
8- The Pearson correlation shows that not all physico-chemical leachate parameters are significantly associated with precipitation;
9- The LPI of 45.99 indicates that the leachate is highly polluted and requires immediate treatment;
10- This study will be useful for the design of a typical leachate treatment plant for the “Mediouna” landfill in Greater Casablanca, based on the maximum values recorded in the different periods of the year, so it can contribute to the understanding of leachate behaviour in a Mediterranean region.
11- To this end, the leachates studied must undergo biological treatment with free or fixed growth in order to eliminate the high concentrations of organic matter and ammonium by biological means. In a second stage, a finishing treatment of physico-chemical type will allow the elimination of the coloration and the rest of the pollutants.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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Nomenclature and Abbreviation:

BOD_5	Biochemical oxygen demand in 5 days	$N\text{-}NO_2^-$	Nitrous nitrogen
Ca	Calcium	$N\text{-}NO_3^-$	Nitric nitrogen
Cd	Cadmium	$N\text{-}NH_4^+$	Ammonia nitrogen
Cl^-	Chloride	Pb	Lead
Co	Cobalt	ppm	Parts per million
COD	Chemical oxygen demand	Pt	Total phosphorus
Cr	Chromium	Rf	Rainfall
Cu	Copper	RLM	Raw leachate of Mediouna
Fe	Iron	SO_4^{2-}	Sulphate
K	Potassium	TKN	Total Kjeldahl Nitrogen
LPI	Leachate pollution index	TS	Total Solids
Mg	Magnesium	TVS	Total Volatile Solids
Mn	Manganese	Zn	Zinc
Ni	Nickel		

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