leachate in a karst area with a Mediterranean climate (Marbella, southern Spain)

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Abstract Between March 1994 and April 1997, the physical and chemical parameters and chemical composition of the urban solid waste leachate of the Marbella landfill (southern Spain) were determined. The data obtained show an ammonium and sodium chloride and bicarbonate type, a pH>7 and high mineralization, effectively described by the following parameters: Na^+, K^+, NH_4^+, Cl^- and alkalinity. The chemical composition depends on the rainfall: in dry years, the mineralization and component concentrations have values as much as double those found in normal rainfall years. After storm events, a major and rapid dilution (within several hours) is seen in the leachate.

Key words Mediterranean climate · Landfill leachate · Chemical composition

Introduction

As in other places in the world, landfilling is one of the most common waste disposal methods in the southern Spanish towns. The rainwater which percolates through the landfill and dissolves the inorganic and organic substances of the solid waste produces leachates, which can move towards the groundwater and environment (Freeze and Cherry 1979; Baedecker and Back 1979). The amount, quality and movement of such leachates has been studied by many researchers to observe the potential pollution from landfills (Nicholson and others 1983; Radi and others 1987; Arneth and others 1989; Christensen and others 1994, among others).

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The Marbella landfill is located 2 km north of Marbella (Fig. 1). It started operating at the beginning of the 1970s and it is still in use today. The population of Marbella is around 80 000 but in summer rises to 200 000. Considering these data and a waste production of 1 kg/person per day, the total amount of urban solid waste generated is at least 80 tons/day. The Marbella landfill contains typical urban solid waste, composed of organic matter, paper, glass, wood and building waste. Waste disposal involves spreading, compacting and covering the waste with sand and clay.
Geologically, the landfill is situated in the southern part of the Sierra Blanca, on the marbles which form part of the aquifer system of Marbella (Andreo 1997). Depth to the water table is aprox. 130 m. There is no liner between the landfill and the marbles, so a part of the leachate migrates downwards and groundwater degradation occurs. This occurence has been described previously (Carrasco and Andreo 1994; Ortíz 1994).
The study area has a Mediterranean climate, and is of particular interest because the investigation was carried out during a transition between a period of extreme drought (1994 and 1995) and a very wet period (1996 and 1997). For this reason a discussion of the rainfall data is presented, followed by the characterization of the chemical composition of the leachate, and the study of different parameters and their temporal evolution.

Analysis of the rainfall data

Marbella has had a meteorological station since 1945. The annual precipitation varies between 253 mm and 1426 mm, and averages 672 mm. Thus, although the monthly average precipitation is 56 mm/month, Fig. 2a shows that rainfall distribution over time is very irregular, as is typical for the region (Andreo 1997). There are wet years (precipitation 15% above the average rainfall) in which total amount of rainfall is double that of an average year (1955/1956, 1988/1989, 1989/1990, and 1995/1996). In several dry years (precipitation is below 85% of the average rainfall) precipitation is half the average (1949/1950, 1982/1983 and 1994/1995).

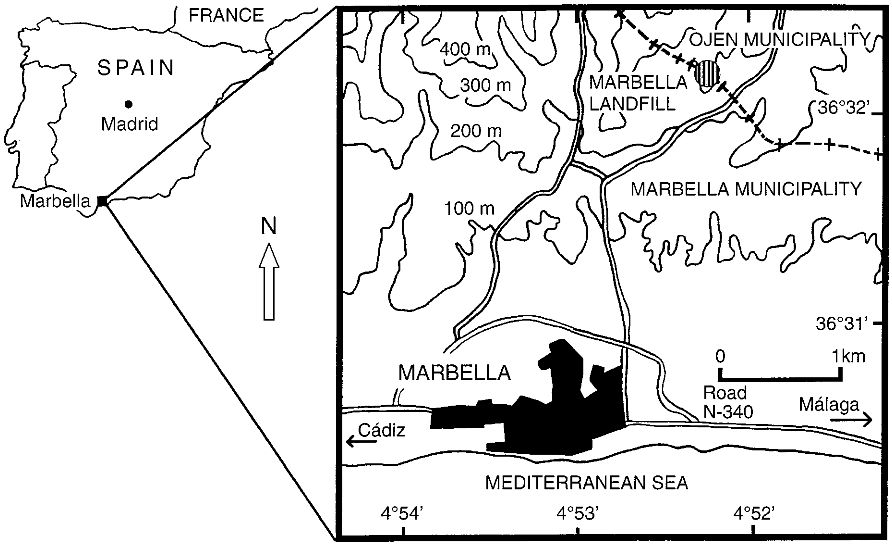


Fig. 1
Geographical location of the Marbella landfill, southern Spain

Figure 2a shows that during a fifty-year period (1945/1946–1995/1996) the annual rainfall varied between 253 mm (1994/1995 water year), and 1420 mm (1995/1996) and the average value was 820 mm. Two main rainfall episodes can be differentiated in the study period (Fig. 2b): December 1995 (400 mm)–January 1996 (393 mm) and December 1996 (494 mm)–January 1997 (289 mm). During two storm events, on the 15 February 1996 and 23–26 November 1997 rainfalls of 30 mm and 54 mm were recorded, respectively. Most of the annual precipitation (almost 90%) is produced between October and April with a dry period between May and September (Fig. 2c).

Material and methods for studying the leachate

In the course of this research, leachate samples were collected between March 1994 and April 1997 from the landfill drainage channel. From October 1995 the sampling frequency was monthly. Sixteen samples were collected and 20 measurements of physical and chemical parameters (EC, T and pH) were recorded.
Leachate flow was normally below 1 l/s rising to 50 l/s during storm events. In normal climatic conditions, between the storm events, the measurement of the leachate flow is very difficult due to the low landfill discharge, of <1 l/s. At such times measurement by a flowmeter is impossible. At the end of 1997 an automatic station to measure electrical conductivity and leachate flow was installed. During the two major storm events of 15 February 1996 and 23–26 November 1997, the chemical variation was recorded; in the first case physical and chemical measurements were taken and 16 samples collected to determinate the total solids dried (TDS) and the chloride content. In the second period, the electrical conductivity and leachate flow were measured hourly.

The major inorganic chemical components (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Cl^{-}, alkalinity, SO_4^{2-} and NO_3^{-}) were analyzed in the Laboratories of Hydrogeology and Analytical Chemistry at the University of Malaga, using internationally recognized methods (Cleresci and others 1989). The total hardness (Ca^{2+} and Mg^{2+}) was determined by titration with 0.02 N EDTA using black eriochrome-T as the indicator. The Ca^{2+} was titrated with 0.02 N EDTA using calcon as the indicator and the Mg^{2+} content was obtained by the difference between the total hardness and the Ca^{2+} content. The Na^{+} and K^{+} concentrations were determined using flame photometry. The Cl^{-} content was obtained by argentometric titration using $AgNO_3$ 0.1 N and K_2CrO_4 as the indicator, SO_4^{2-} by gravimetry using $BaCl_2$, and alkalinity by titration using H_2SO_4 (0.02 N) until a pH of 4.45 is reached. The NO_3^{-} and NH_4^{+} concentrations were measured using a potentiometric method.
A statistical analysis was carried out on the main components, calculating the average, standard deviation, variation and correlation coefficients between different parameters (Table 1). Furthermore, a Schoeller-Berkaloff diagram (Fig. 3) was produced to characterize graphically the hydrochemistry of the leachate, the groundwater in the aquifer and the rainfall of this region. Also a temporal plot was made to show the evolution of different components in the leachate (Fig. 4).

Results and discussion

Chemical composition of the leachate

Table 1 shows the physico-chemical parameters and the chemical composition of the samples. The pH varies between 7.8 and 8.6, with an average value of 8.2. The temperature of the leachate fluctuates between 12.3 °C and 36.4 °C, though it is influenced by the air temperature. The electrical conductivity varies between 4 and 41 mS/

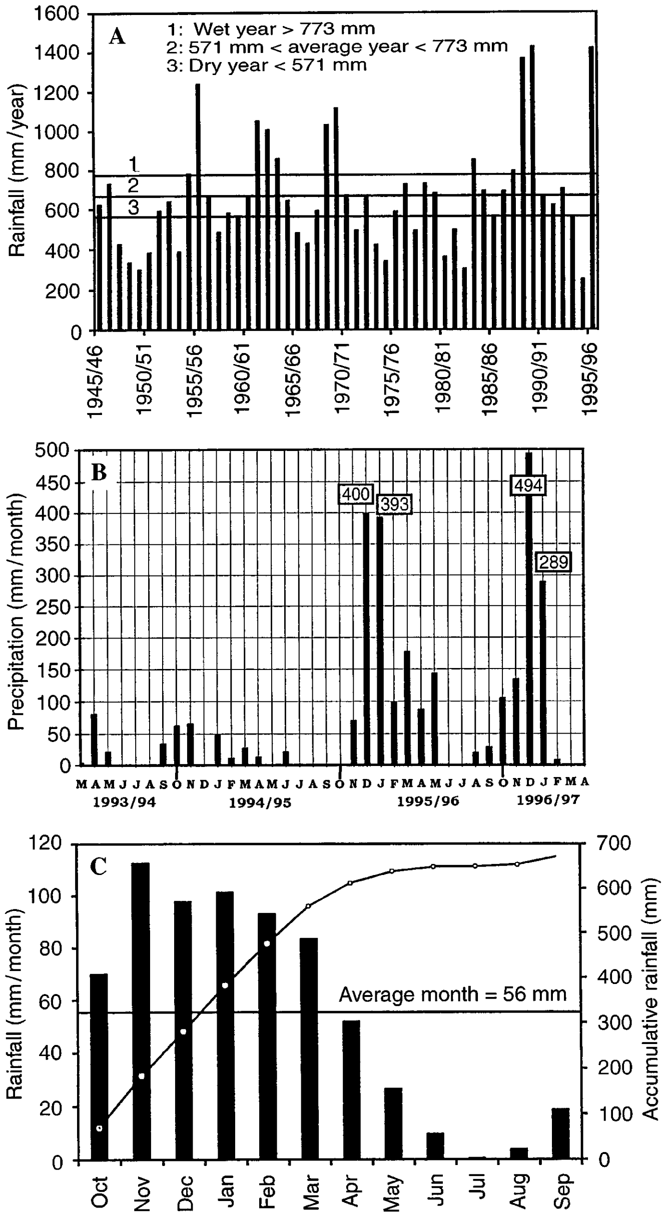


Fig. 2A–C
Rainfall graphs: **A** Annual precipitation since 1945/1946; **B** monthly precipitation during the study period; **C** Average monthly rainfall

cm, with an average value of 24.2 mS/cm, due to the high mineralization of the leachate; a consequence of high concentrations of all the chemical components (Table 1). It is worth noting the high contents of Cl^- (4.7 g/l, on average), Na^+ (2.8 g/l), K^+ (1.5 g/l), and NH_4^+ (3.2 g/l), this contrasts with the NO_3^- (0.6 g/l) and SO_4^{2-} (0.4 g/l) values, resulting from the reducing conditions in the leachate (Christensen and others 1994). Also high values of alkalinity were detected (8.8 g/l). The maximum values of electrical conductivity and the concentrations of some of the chemical components are higher than those found in landfill leachates described by Johansen and Carlson (1976), Ehrig (1983), Reitzel and others (1992) and Gómez-Martín (1997).

Table 1 also shows the values of the maximum allowable concentrations (MAC) set in Spanish public water legislation (Decreto 849/1986), which give an indication of the toxicity of the leachate. The Cl^- and NH_4^+ levels exceed the MAC values.

In Fig. 3 the mean composition of the leachate is shown, its hydrochemical type is ammonium and sodium chloride and bicarbonate. Large variations, sometimes of an order of magnitude, are observed in the contents of the chemical components. This agree with the variation coefficients, more than 40% in all the parameters except pH and temperature (Table 1).

Temporal evolution of the chemical composition of the leachate

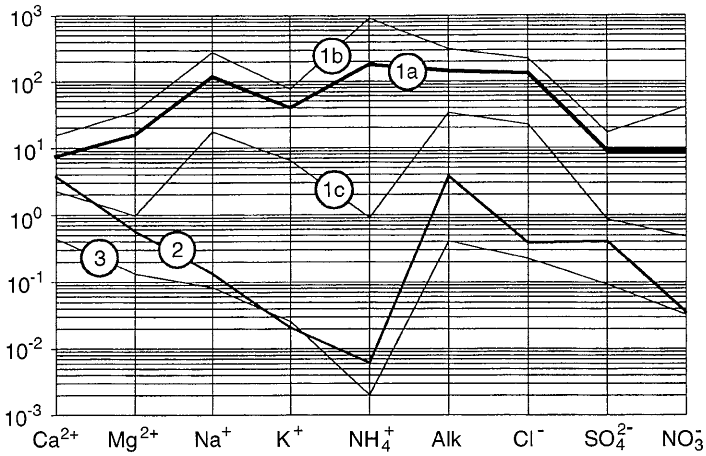
No clear trend in the evolution of the leachate composition can be detected. The temporal evolution of the parameters shows no correlation with the landfill age, such as an increase in NH_4^+ content, as indicated by some authors (Farquhar 1987; Ehrig 1983). This may be due to sampling gaps and the short study period (approx. 3 years) which is not long enough to reach such conclusions, as have been described for other landfills (Reitzel and others 1992).

The electrical conductivity of the leachate shows maximum values in excess of 41 mS/cm, during the last period of drought (October–November 1995). A high dilution was produced by the December 1995 and January 1996 rainfall, decreasing the electrical conductivity to 4 mS/cm (Fig. 4). Then a rising trend starts, broken only by the spring rains which produced a dilution. This increase in electrical conductivity continued until the end of summer (July–September) when values of 23 mS/cm occurred. The autumn rains (October–November 1996) lowered the mineralization of the leachate and the winter rainfall (December 1996–January 1997) resulted in minimum conductivity (14 mS/cm). This was followed in turn by rising values. A similar evolution in the concentration of the other parameters that affect mineralization (alkalinity, Cl^-, Na^+, K^+ and NH_4^+) can be seen, and rainfall is responsible for dilution of the leachate.

During a storm on the 15 February 1996, between 8 00 hours and 13 00 hours, there was a large increase of flow from 1 to 50 l/s, and a rapid decrease in conductivity (4 mS/cm), TSD and Cl^- (Fig. 5a). This situation was rapidly reversed when the rain stopped, as the increase in the analyzed parameters shows. The data demonstrate the quick response of the landfill to a rainfall episode. During the storm event at the end of November 1997, a very quick leachate dilution was produced by the rainwater (Fig. 5b). The electrical conductivity decreased from 25 mS/cm at the start of the storm event to 5 mS/cm at the end.

Table 1
Field and laboratory values of leachate composition from the Marbella landfill. The reference values correspond to the maximum allowed concentration in wastewaters in the current Spanish regulations

Sample	Date	pH	T[a] (°C)	E.C. (μS/cm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	NH_4^{+} (mg/l)	Alkalinity (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	NO_3^{-} (mg/l)
Reference values		5.5–9.5	–	–	–	–	–	–	15.0	–	2000.0	2000.0	–
1	16/03/94	8.56	16.9	36300	68.0	145.8	6375.0	2812.5	11092.5	17946.2	7703.5	699.6	2524.3
2	28/04/94	8.51	15.3	38400	80.0	99.6	5275.0	2812.5	16358.9	17873.0	7668.0	555.5	2021.0
3	23/05/94	8.28	26.1	37200									
4	11/10/95	8.13	24.0	40900	100.0	43.7	5850.0	2975.0	10771.1	18727.0	7810.0	329.2	731.4
5	9/11/95	8.61	13.7	39200									
6	29/11/95	8.43	13.3	40900									
7	10/01/96	7.81	16.5	18210	44.8	11.7	2110.0	1230.0	485.8	8320.4	3798.5	246.9	188.5
8	15/02/96	8.08	12.3	4050	164.0	128.8	400.0	250.0	16.1	2025.2	781.0	576.1	426.6
9	9/03/96	7.97	36.4	20600	136.0	255.2	2550.0	1387.5	1498.4	6954.0	4863.5	267.5	28.9
10	21/03/96	7.98	21.8	17480	212.0	422.8	2250.0	1200.0	1979.4	7588.4	4011.5	41.2	127.4
11	17/04/96	7.97	32.3	19080	116.0	274.6	2690.0	1200.0	1963.9	5673.0	5183.0	432.1	758.1
12	9/05/96	7.86	27.3	12470	308.0	216.3	1680.0	840.0	281.3	4050.4	2946.5	658.4	77.9
13	17/07/96	8.27	20.1	21500	132.0	245.4	2820.0	1687.5	491.2	7515.2	5112.0	802.4	173.7
14	3/09/96	8.56	20.2	23400	172.0	158.0	3040.0	1800.0	555.3	8930.4	5573.5	267.5	169.5
15	19/09/96		15.4	23900									
16	18/11/96		19.6	18810	216.0	269.7	2250.0	1477.5	444.3	7100.4	4189.0	679.0	138.7
17	22/01/97	8.16	28.3	14040	84.0	247.9	1225.0	1000.0	1041.7	5368.0	2769.0	144.0	422.6
18	17/02/97	8.16	26.8	18310	260.0	145.8	1800.0	1325.0	1425.9	6990.0	3869.5	267.5	383.8
19	17/03/97	8.14	29.9	19360	152.0	182.3	1925.0	1400.0	1681.5	7454.2	3976.0	185.2	367.1
20	11/04/97	8.33	28.5	19790	132.0	179.8	2050.0	1450.0	1891.5	8113.0	4189.0	555.5	351.1
	N° Samples	18	20	20	16	16	16	16	16	16	16	16	16
	Average	8.21	22.2	24195	148.6	189.2	2768.1	1553.0	3248.7	8789.3	4652.7	419.2	555.7
	Stand. Dev.	0.25	7.0	10715	71.9	99.8	1657.9	742.0	4888.2	4964.9	1894.6	229.8	708.5
	Variation (%)	3.03	31.4	44	48.4	52.7	59.9	47.8	150.5	56.5	40.7	54.8	127.5



		Ca^{2+} (meq/l)	Mg^{2+} (meq/l)	Na^{+} (meq/l)	K^{+} (meq/l)	NH_4^{+} (meq/l)	ALK. (meq/l)	Cl^{-} (meq/l)	SO_4^{2-} (meq/l)	NO_3 (meq/l)
LEACHATE	Maximum value	15.37	34.79	277.29	76.09	908.83	307.00	220.31	16.71	40.71
	Average value	7.41	15.57	120.41	39.72	180.48	144.09	131.25	8.73	8.96
	Minimum value	2.24	0.96	17.40	6.39	0.89	33.20	22.03	0.86	0.47
	Groundwater	3.72	0.56	0.13	0.02	0.01	3.72	0.38	0.40	0.04
	Rainfall	0.43	0.13	0.08	0.03	0.00	0.40	0.22	0.09	0.03

Fig. 3
Modified Schoeller-Berkaloff diagram and table of hydrochemical values for the Marbella landfill leachate (*1a* average; *1b* maximum and *1c* minimum), groundwater (*2*), and rainfall (*3*)

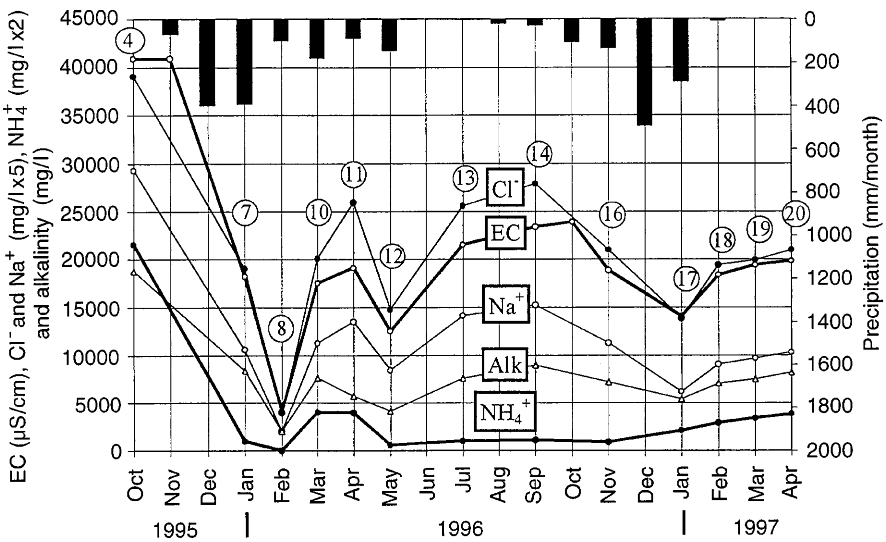


Fig. 4
Temporal evolution of some parameters of the controlled leachate from October 1995 to April 1997. The numbers indicate the samples from Table 1

Hydrochemical parameters conditioning the leachate chemistry

The correlation matrix obtained from all the available data (Table 2), shows that the conductivity is strongly and positively correlated with alkalinity, Cl^-, Na^+, K^+ and NH_4^+, which has been confirmed in numerous scientific papers (Johansen and Carlson 1976; Ehrig 1983; Christensen and others 1994). The highest correlation values are graphically represented in Fig. 6. In all the graphs, three groups of samples can be distinguished:

1. Samples taken during the drought periods of 1994 and 1995 (group I) which show the highest mineralization, with high alkalinity and high values of Cl^-, Na^+, K^+, and NH_4^+.
2. Samples taken during high rainfall periods (group II, February and May 1996 and January 1997) which show the lowest alkalinity, Cl^-, Na^+, K^+, NH_4^+, and conductivity values.
3. Samples with intermediate composition (group III) between the two previous groups. These samples were collected during average rainfall conditions.

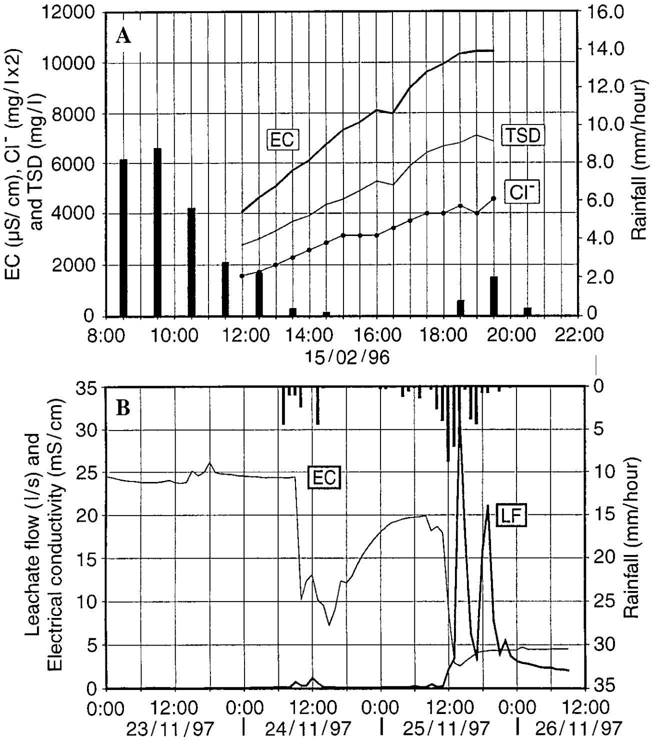


Fig. 5
A Evolution of electrical conductivity (*EC*), chloride content (*Cl⁻*) and total solids dried (*TSD*) in the Marbella landfill leachate generated during a stormy day (15 February 1996). **B** Temporal evolution of electrical conductivity (*EC*) and leachate flow (*LF*) generated during a stormy period (23–26 November 1997)

Conclusions

The leachate originating in the urban solid waste landfill of Marbella, has a pH above 7 and a very high electrical conductivity due to the high concentrations of the major inorganic components. Some of these components (NH_4^+ and Cl^-) exceed the limits of the Spanish water quality regulations. The alkalinity, Cl^-, Na^+, K^+ and NH_4^+ control the mineralization. The mean hydrochemical type is ammonium and sodium chloride and bicarbonate, but with high variations in most of the parameters (sometimes an order of magnitude).

The amount of rainfall has a major influence on the leachate chemistry. The rainwater infiltration produces a decrease in conductivity and in all the chemical components, due to mixing within the landfill. Low-conductivity rainfall with a high infiltration velocity (several hours) is mixed with leachate held in storage within the landfill. From a hydrogeological point of view, it is a low inertial system.

Taking into account the chemical composition and the rainfall distribution, three types of leachates have been distinguished: leachates produced during severe droughts, leachates of high rainfall periods and leachates of normal rainfall periods. The first type, show the highest mineralization. The second type, are samples with low mineralization and low concentration of chemical components, these are the most diluted samples. The third type belongs to the mean composition of the leachate and occurs in normal rainfall conditions.

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Table 2
Correlation matrix composed of the parameters measured in the landfill leachate

	pH	T	E.C.	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	ALK.	Cl^-	SO_4^{2-}	NO_3^+
pH	1.000											
T	−0.269	1.000										
E.C.	0.546	−0.292	1.000									
Ca^{2+}	−0.361	0.190	−0.465	1.000								
Mg^{2+}	−0.282	0.378	−0.371	0.418	1.000							
Na^+	0.438	−0.221	0.966	−0.453	−0.332	1.000						
K^+	0.449	−0.190	0.993	−0.445	−0.367	0.964	1.000					
NH_4^+	0.471	−0.297	0.874	−0.455	−0.390	0.874	0.858	1.000				
ALK.	0.454	−0.282	0.976	−0.499	−0.442	0.961	0.974	0.916	1.000			
Cl^-	0.430	−0.068	0.974	−0.434	−0.254	0.960	0.966	0.804	0.918	1.000		
SO_4^{2-}	−0.004	−0.357	0.115	0.056	−0.125	0.227	0.170	0.177	0.115	0.150	1.000	
NO_3^-	0.528	−0.374	0.679	−0.487	−0.319	0.767	0.686	0.857	0.749	0.653	0.331	1.000

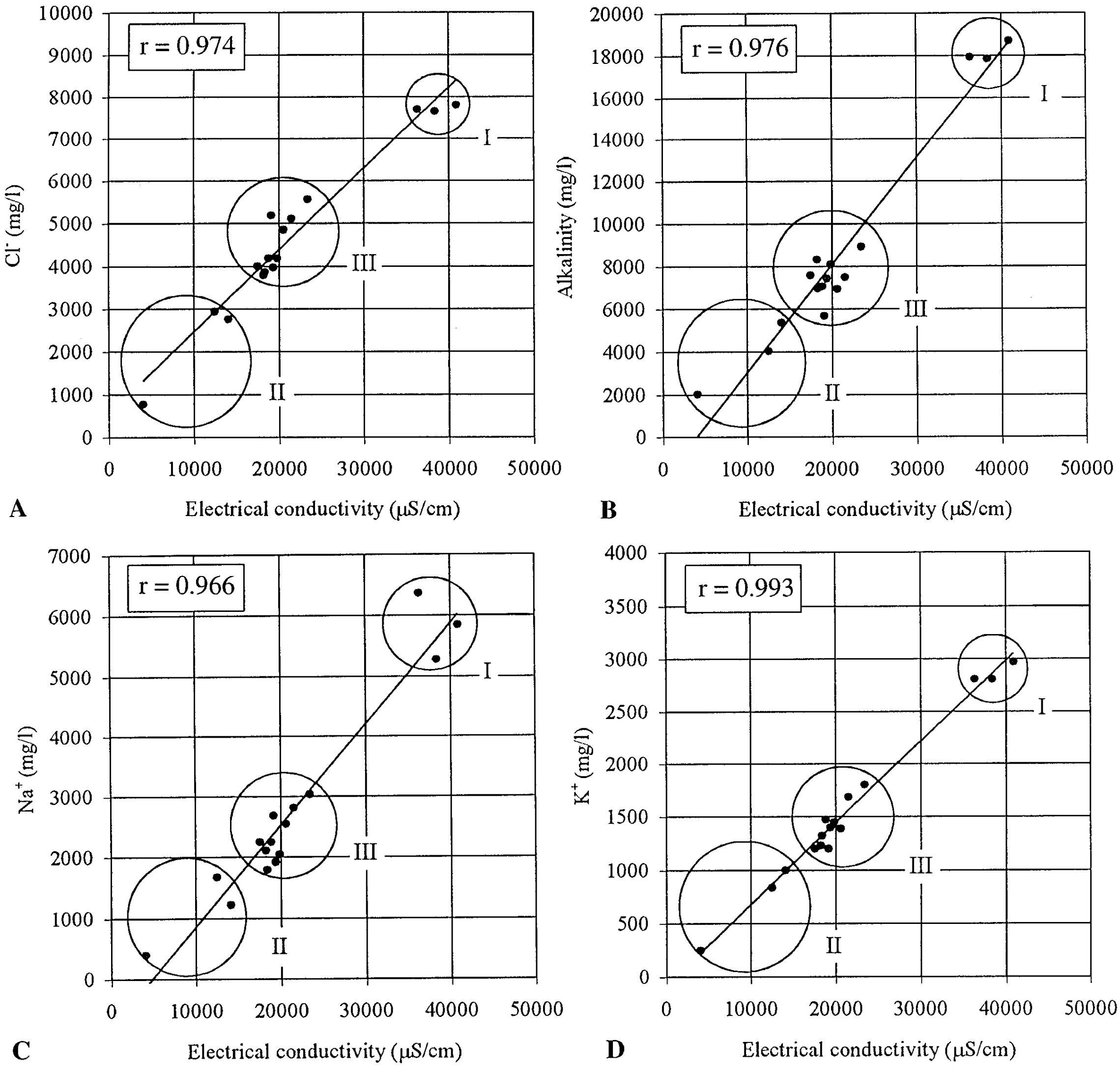

Fig. 6A–D
Regression lines and differentiation of several groups of leachates (*I* samples from drought periods; *II* samples from high water periods, *III* samples from intermediate periods)

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