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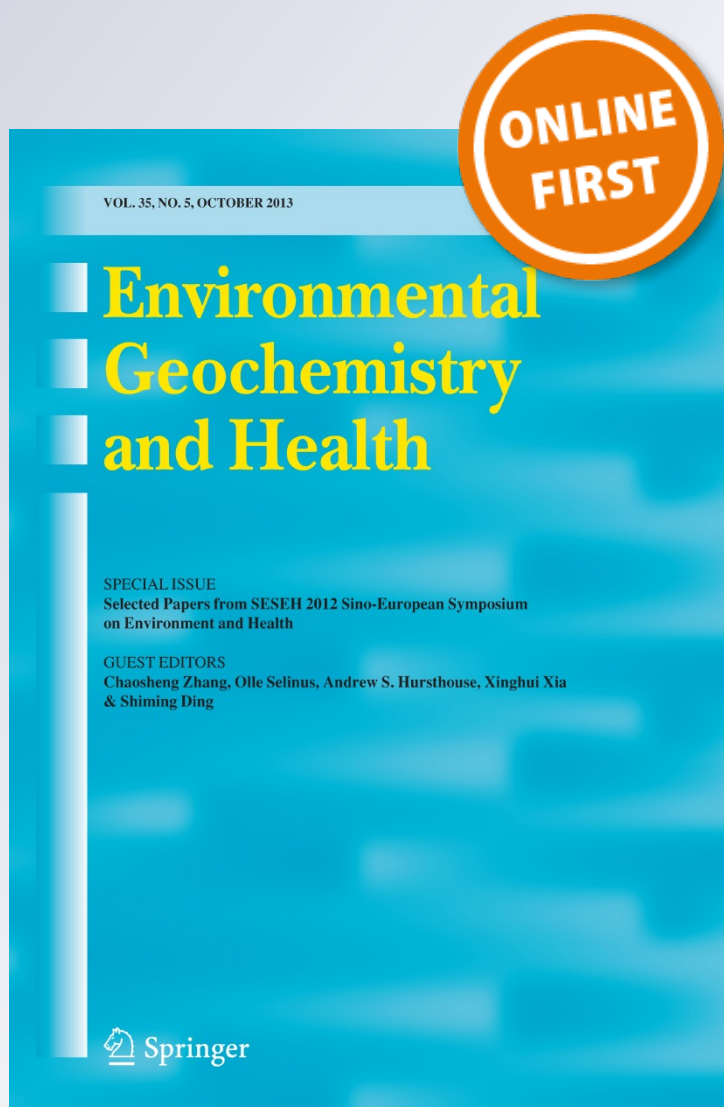
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Identification and assessment of water pollution as a consequence of a leachate plume migration from a municipal landfill site (Tucumán, Argentina)

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Abstract Landfills constitute potential sources of different pollutants that could generate human health and environmental problems. While some landfills currently work under the protection of a bottom liner with leachate collection, it was demonstrated that migration could take place even yet with these cautions. The purpose of this paper is to assess the pollution caused by a leachate plume from a municipal landfill that is affecting both groundwater and surface waters. The research was carried out at Pacará Pintado landfill in northwestern Argentina. Analysis of water samples indicates that leachate is affecting groundwater under the landfill area and an abandoned river channel hydraulically connected. In the center of the landfill area, the plume is anoxic and sulfate, nitrate, iron and manganese reduction zones were identified. Leachate plume presented high concentration of organic matter, Fe, Mn, NH_4^+ , Cl^- and Cr reaching an extension of 900 m. The presence of a leachate

plume in a landfill site with a single liner system implies that the use of this groundwater pollution control method alone is not enough especially if permeable sediments are present below.

Keywords Landfill · Leachate plume · Pollution · Tucumán · Argentina

Introduction

Several cases of groundwater pollution related to the presence of municipal landfills have been reported in different countries (Lyngkilde and Christensen 1992a, b; Kjeldsen 1993; Cozzarelli et al. 2000; Van Breukelen and Griffioen 2004; Fan et al. 2006; Adeolu et al. 2011). Pollution problems in landfill sites were related, at least in part, to the fact that disposal municipal solid waste was largely unregulated prior to the seventies (Christenson and Cozzarelli 2003). Municipal solid waste was disposed in sanitary or open landfills in which there was little regard given in their sitting, construction, operation and closure for the potential impact of leachate generated on groundwater quality.

Landfill leachate is a combination of both water expulsion from waste and rainwater percolating through the ground. During this passage chemical, physico-chemical and microbiological processes occur generating the transference of different pollutants from the waste material to the percolating water (Christensen

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and Kjeldsen 1989). Pollutant characteristics that are present in leachate were described in previous studies (Nicholson et al. 1983; Christensen and Kjeldsen 1989; Christensen et al. 1994; Brun et al. 2002). These investigations indicated that concentrations of dissolved sulfide, methane, major ions, organic nitrogen, ammonia, iron, manganese, organic carbon and zinc commonly are greater in leachate-contaminated water. Biogeochemical processes control the presence of these pollutants during their migration (Cozzarelli et al. 2000). Participation of biogeochemical processes in the transport of landfill pollution plumes has been modeled by Brun and Engesgaard (2002). Dissolved organic matter leaching from landfills usually is degraded in a sequence of redox zones ranging from methanogenic, sulfate, iron/manganese, nitrate to oxygen reducing (Christensen et al. 1994). Landfills often cover large areas. Landfill sizes in the range of 10–20 ha are common (Kjeldsen et al. 1995). The determination of where high-strength leachate is generated should be evaluated from a cost-effective pollution plume delineation method for future remedial actions. Leachate treatment and discharge also possesses risks to the environment through ineffective treatment and/or discharge to particularly sensitive receiving waters (Silva et al. 2004).

Argentina landfill regulations are recent, the first set of laws come from the last decade. Groundwater pollution cases have been little investigated or characterized and were conducted mainly in Buenos Aires (Bocanegra et al. 2001; Martínez et al. 2004; Yunes et al. 2009). The impact of the infiltration of the leachate from a neighboring landfill on loess and thin sand sediments in Mar del Plata city, Buenos Aires Province, was characterized by Martínez and Osterrith (2013). High chloride and nitrate contents result from leachate infiltration. Landfill leachate is a potential pollution source that without an adequate treatment and control may cause harmful effects on the groundwater and surface water near the landfill area. Under pressure from environmental groups, the authorities of the different provinces of Argentina began to conduct monitoring of these landfills in order to identify and characterize potential pollution plumes. In Tucumán province, few pollution problems related to landfills have been studied (Fernández et al. 2010). Legal demands were made by environmental groups against the operators of the main landfill of the province.

The objectives of this study are to assess the pollution caused by a leachate plume from a municipal landfill that is affecting both groundwaters and surface waters and to tentatively delineate the spatial distribution of the plume.

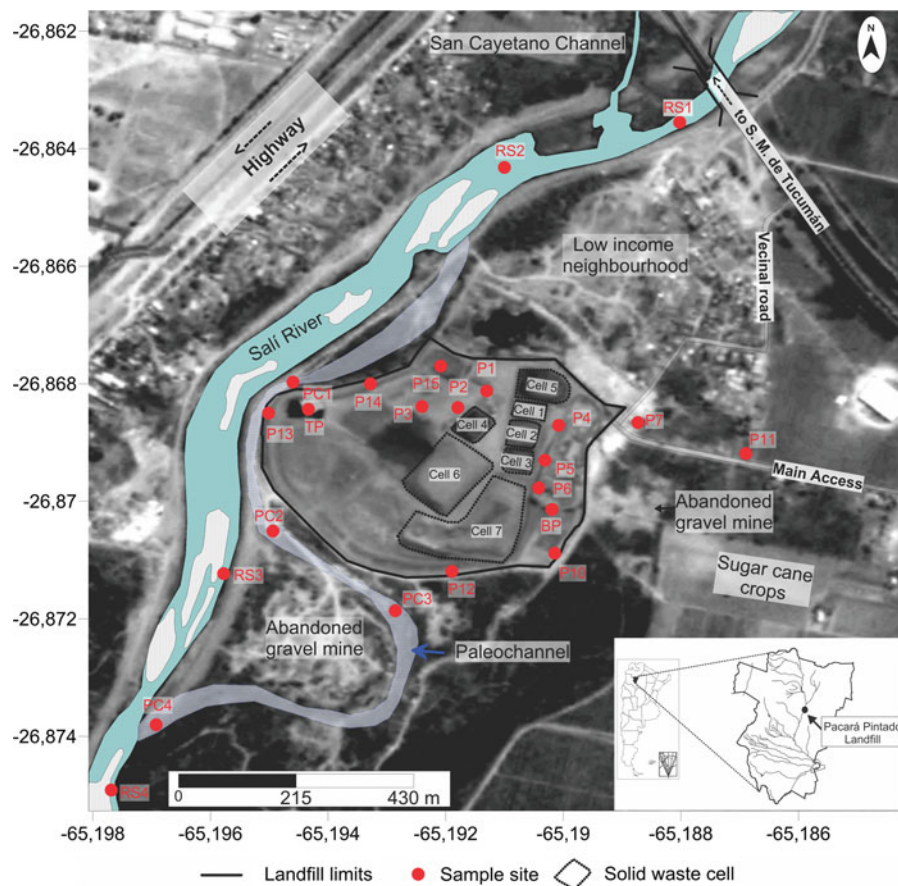
Materials and methods

Site characteristics

The investigation was performed at Pacará Pintado landfill which is located in a suburban area of Tucumán province at northwestern Argentina (Fig. 1). The site involves a portion (18.5 ha) of a fluvial bar belonging to Salí-River and receives 800 tons of residues per day coming from five cities located near the area since 1995. Around of landfill, which is the floodplain of a river, a low-income neighborhood, abandoned gravel mining pits and crop fields are allocated (Fig. 1). The landfill is composed by seven cells where during the sampling times five were covered by membrane and two remain uncovered. Groundwater protection measures include a composite liner of compacted soil and polyurethane membrane and leachate collection in a treatment pond (TP). In this pond, leachate collected receives the addition of lime. Lime can cause changes in the values of pH, conductivity and alkalinity, but essentially the rest of the compounds do not suffer significant changes. Part of the leachate is used for cells irrigation to avoid high temperatures. The pond shows an inadequate isolation with porous and friable sediments observed over walls. Landfill plant counts also with a biofilter pond (BP) where truck's wash water is conducted. The final removal step was not operable yet during the sampling times.

As was mentioned above, the landfill was constructed over an active channel bar of Salí River on the left margin of the fluvial stream. These materials constitute the fluvial channel belt of the river formed by lateral migration and can be re-occupied by erosion or avulsion processes during floods. On this channel bar, there are bare soils with poor development and the sediment characteristics are inappropriate for a landfill site. Principal soil properties of the landfill are as follows: coarse grain size, low organic matter content, low cation exchange capacity (CIC) and moderate to high infiltration rates (hydraulic conductivity (k): 10^{-5} – 10^{-1} cm/sec).

Fig. 1 Map of the Pacará Pintado landfill area, showing the location of sample sites, the distribution of solid waste cells inside the plant and surrounding land uses. Cbers satellite image (date: 04-17-2009) was used as base map



The shallow alluvial aquifer consists of unconsolidated sands and gravels with some silt beds, these last represent final channel fill or thin strata among floods. Shallow groundwater level is directly connected with Salí River and the paleochannel being highest during the summer and lowest during winter, due to a normal decrease in precipitation and increased evapotranspiration in the winter. Water table levels range between 5.33 m below ground level (mbgl), outside the landfill and 1.34 (mbgl) inside the site. Mean depth of water table level in the landfill was 2.56 (mbgl).

Methods

Twenty-five sample sites were emplaced in landfill area in order to evaluate the possible influence of leachate on groundwater and surface water. Sample sites location can be observed in Fig. 1.

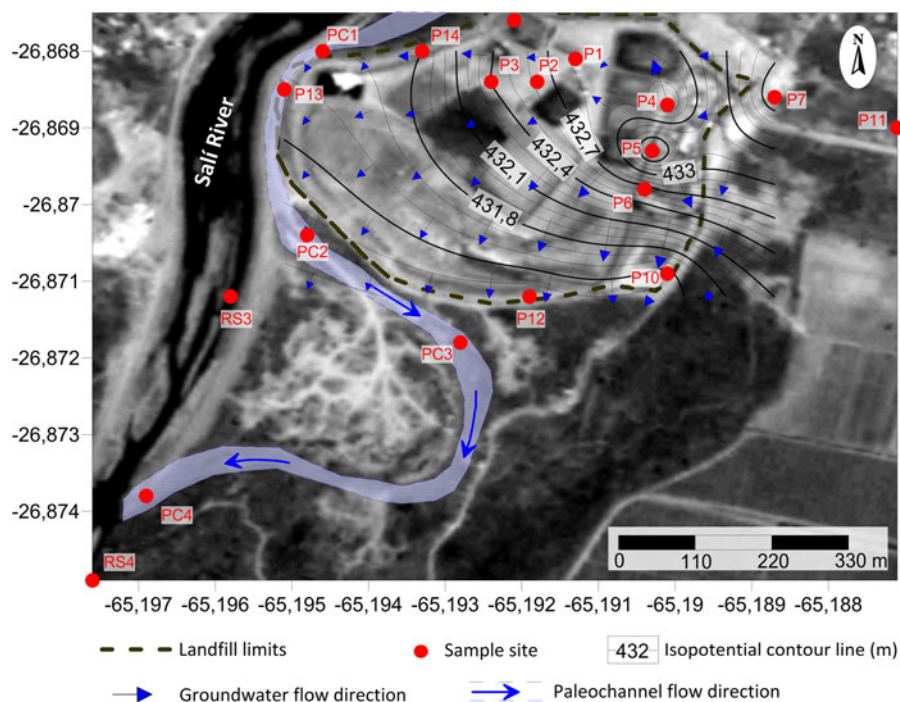
Data were collected from groundwater and surface water. In the case of groundwater, 12 piezometers, installed before by local environmental agency, were

used. P11 and P7 (Fig. 1) are located upward and outside of the landfill, and the rest of sample points are spread inside the landfill area. Topographic features were considered in order to place these piezometers for an adequate characterization of groundwater flow. Phreatic water outcrops inside the landfill forming a pond. Samples from this pond were collected. This sample site is denominated P15 (Fig. 1). Water sampling methods were according to Kent and Payne (1988).

Four surface water samples are located in the Salí River (RS1 to RS4, Fig. 1) and other four samples in the paleochannel (PC1 to PC4, Fig. 1). Sampling sites on the river were located upstream of the plant, in front of the plant and after receiving the input from paleochannel. Treatment and biofilter ponds were also sampled (TP and BP, Fig. 1).

Based on the existing literature on the characteristics of landfill leachate plumes and on the types of waste received by the plant expressed by the authorities, a set of parameters were selected. Specific

Fig. 2 Groundwater flow direction *vectors* over potentiometric surface map contours



conductance (CE), pH, water temperature and redox potential (Eh) were measured in the field using specific electrodes. Alkalinity was determined by titration in the field. Biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), nitrates (NO₃⁻), nitrites (NO₂⁻), ammonium (NH₄⁺), chloride (Cl⁻), dissolved iron (Fe), dissolved manganese (Mn), dissolved chromium (Cr), dissolved cadmium (Cd), dissolved lead (Pb) and dissolved Zinc (Zn) were analyzed in laboratory and stored at 4° C to avoid any major chemical alteration (APHA 1998). For heavy metals, 100 ml samples was filtered using 0.45 µm filter paper and preserved on site with ultra pure nitric acid and determinations were made by an atomic absorption spectrometry (Cd and Cr graphite furnace QPT 35–77; Fe flame QPT 35–88; Zn flame QPT 35–80; Mn flame QPT 35–82; Pb graphite furnace QPT 35–95). For anions, samples were collected in 500-ml clean bottles and capped airtight and were analyzed following standard methods (Cl⁻: APHA QPT 35–26; SO₄²⁻: APHA 4500E, NO₂⁻: APHA QPT 35–44; NO₃⁻: spectrophotometry QPT 35–37). Dissolved oxygen (DO) was fixed in the field and analyzed in laboratory (APHA, QPT 35–29). BOD₅ and COD were analyzed in laboratory using APHA QPT 35–40 and 35–28 methods, respectively. The data quality was

checked by careful standardization, procedural blank measurements and duplicate samples.

Based on isopotential lines for the groundwater table as measured in piezometers, the flow shows a direction from northeast to southwest toward the paleochannel of Salí River (Fig. 2). The original course of the river was changed in order to prevent futures flood events over the plant. Fig. 2 shows local flow directions among the piezometers that are indicated as flow vectors plotted over a satellite image of landfill area. Groundwater flow in the alluvial aquifer has a main direction west–east outside and upward of the landfill and turns to northeast–southwest in the landfill area discharging into an adjacent abandoned river channel referred as paleochannel. The paleochannel is recharged by groundwater flow and discharge far downward into the Salí River.

Results and discussion

Leachate composition

The analysis of treatment pond (Fig. 1) shows absence of dissolved oxygen, an extremely reduced state (–118 mV) and high concentrations of BOD₅

(631 mg/l), COD (3.855 mg/l), chloride (586 mg/l), chromium (84, 2 µg/l) and zinc (50 µg/l). Sulfate concentration was moderate (120 mg/l), and nitrate value was low (1 mg/l). The BOD₅/COD ratio was 0.16. These values are according to leachate compositions shown by Christensen et al. (2001) from landfills of less than 25 years of age. Usually for landfills older than 10–15 years, the BOD₅/COD ratio is lower than 0.1 (Fatta et al. 1999). COD and BOD₅ values that were found in Pacará Pintado are similar to active landfill leachates described by Fan et al. (2006) for more than 300 landfills of Taiwan, but BOD₅/COD ratio is lower on average, suggesting that leachate from Pacará Pintado is less biodegradable. High organic parameter concentrations were described by González Herrera et al. (2007) in a landfill of Merida city, Mexico, where COD values are much higher than DBO₅ values. However, leachate from TP sample has not suffered groundwater dilution and soil filtration, but differences with leachate found in groundwater are evident.

The other reservoir of pollutants generated in the landfill is the biofilter pond (BP, Fig. 1). Biofilter pond receives waste water with high concentrations of ammonium (NH₄⁺: 18 mg/l), chromium (Cr: 126 µg/l) and zinc (Zn: 100 µg/l) from truck wash facilities. Heavy metal concentrations exceeded those observed in the treatment pond.

Groundwater

Table 1 summarizes the groundwater analysis results. Indicators of environmental conditions such as dissolved oxygen and redox potential vary greatly. In the case of DO, while the site P11 shows aerobic conditions of the phreatic water (3.7 mg/l), the site P7 located near the landfill and still upstream shows that oxygen concentration descends to 1.7 mg/l. Inside the landfill DO values range between 1 and 1.6 mg/l in sample sites P4, P10, P13 and P14, descending to anoxic values (0–0.6 mg/l) in sample sites P1, P2, P3, P5, P6 and P12 (Fig. 2). Redox potential values were high in piezometers located outside of the plant (P11 = 387 mV and P7 = 247 mV), but inside the plant Eh values are much lower ranging between 100 and 158 mV (Fig. 3). This indicates a considerable change in natural redox conditions of groundwater in the landfill area. The pH of all groundwater samples was slightly acid to neutral, the range being 6.6 to 7. Electrical conductivity is increased in groundwater

flow direction from 1,496 µS cm⁻¹ in P11 to 4,035 µS cm⁻¹ in P1. Total alkalinity also increases along the groundwater flow line from 373 mg/l (P11) to 1,296 mg/l (P1). This increase would indicate degradation of the organic compounds to inorganic carbon. Distribution of EC and alkalinity values are shown in Fig. 3.

The dissolved organic matter indicators showed increases in their concentrations in sample sites located within the plant limits. The COD is used as a parameter indicative of the presence of total organic matter, biodegradable or not, liable to oxidation which is present in the water. COD values greater than 150 mg/l were observed in sample sites P1, P2, P3 and P12 (Fig. 3). In contrast, natural groundwater of the area (P11) presented 17 mg O₂/l. In the case of BOD₅, indicative of the presence of biodegradable organic matter, values are low although in most cases are higher than in sample site P11 (< 5 mg/l). This fact would be related to the stage found in the leachate plume.

The BOD₅/COD ratio is a reliable indicator of the organic matter state. When the ratio is below 0.2, it indicates that the organic matter is considered as not biodegradable and composed mainly by recalcitrant acids (Christensen et al. 1994). According to Kjeldsen et al. (2002), the BOD/COD ratio generally will fall below 0.1 when carboxylic acids are consumed as rapidly as they are produced. BOD/COD ratios are less than 0.1 in most of the sample sites located inside the landfill. These values indicate that the remaining dissolved organic matter is stable and recalcitrant for microbial degradation at present redox conditions (Thomsen et al. 2012). The ratio could not be established for sample sites P4, P5, P7, P11, P13 and P15 due to BOD concentrations were below the technique detection level (5 mg/l).

In this study, the concentrations of some macroinorganic components such as chloride, sulfate, manganese and iron are used as indicators of leachate plume. Chloride concentrations in sample sites outside the landfill remain below 125 mg/l. A significant increase in chloride values takes place in the sampling sites P1, P2, P3 and P12 which have values greater than 220 mg/l. Sample site P1 showed a value of 576 mg/l, four times higher than groundwater background value for the area. Sulfate concentrations show a clear distribution pattern where the sample sites outside the landfill present values over 135 mg/l

Table 1 Chemical characteristics of groundwater analysis

Parameters	Groundwater sample sites												
	P1	P2	P3	P4	P5	P6	P7	P10	P11	P12	P13	P14	P15
pH	7.0	6.8	6.7	6.9	6.9	6.7	6.7	6.8	6.8	6.9	6.9	6.8	7.3
DO (mg/l)	0	0	0.5	1.2	0.6	0	1.7	1.2	3.7	0.4	1.6	1	4
EC ($\mu\text{S}/\text{cm}$)	4,035	2,819	1,830	1,496	1,725	1,518	1,692	1,844	1,663	2,101	1,683	1,496	1,746
Eh (mV)	108	100	112	124	139	117	247	115	387	124	120	119	320
WT ($^{\circ}\text{C}$)	24	25	25	24	25	27	26	27	25	25	25	25	25
BOD ₅ (mg/l)	10	8	7	<5	<5	10	<5	7	<5	9	<5	5	<5
COD (mg/l)	477	372	159	68	96	135	72	137	17	189	62	50	105
BOD/COD	0.02	0.02	0.04	–	–	0.07	–	0.05	–	0.05	–	0.1	–
Alkalinity (mg/l)	1,296	865	665	510	670	579	418	733	373	806	446	569	428
Cl [–] (mg/l)	576	384	230	109	95	105	124	106	123	220	151	158	175
SO ₄ ^{2–} (mg/l)	<5	<5	<5	59	46	<5	158	<5	135	<5	119	<5	<5
NO ₃ [–] (mg/l)	6	11	11	17	12	10	38	17	80	15	10	16	2
NO ₂ [–] (mg/l)	<0.007	<0.007	0.027	0.035	0.047	0.026	0.088	0.028	0.024	0.057	<0.007	<0.007	0.184
NH ₄ ⁺ (mg/l)	0.219	0.187	0.117	3.370	0.491	0.367	0.494	0.731	0.069	89	0.062	0.055	<0.013
Fe (mg/l)	3.49	17.12	9.75	1.19	1.89	9.52	2.24	5.64	0.15	10.03	2.13	2.51	0.12
Mn (mg/l)	18.64	14.96	10.08	6.19	4.99	5.82	1.20	7.80	0.13	4.12	3.84	4.09	0.09
Cr ($\mu\text{g}/\text{l}$)	18.8	8.4	6.1	1.6	7.6	6.9	1.4	7.2	1	9.4	7	<0.5	6.2
Zn ($\mu\text{g}/\text{l}$)	80	80	40	40	60	90	110	40	<30	70	120	50	70
Pb ($\mu\text{g}/\text{l}$)	19	<5	10	6	<5	20	23	12	19	35	60	75	<5
Cd ($\mu\text{g}/\text{l}$)	0.11	0.61	<0.1	<0.1	<0.1	0.18	0.31	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

(P7 and P11, Fig. 3). These values are reduced in downward direction to reach the area with sulfates concentration below 5 mg/l observed in sample sites P1, P2, P3, P10, P12 and P14 (Fig. 3). The decrease in sulfates content could be due to a strong oxidation in the dissolved organic matter catalyzed by bacteriological activity present in groundwater in landfill area.

Iron and manganese concentrations show similar distribution between them but inverse to the sulfates (Fig. 3). Concentrations of Fe and Mn have a remarkable increase in downstream direction up to two magnitude orders. Background concentrations of Fe and Mn were 0.15 and 0.13 mg/l, respectively. Maximum Fe concentration was found in sample site P2 (17.1 mg/l), while maximum Mn concentration was found in sample site P1 (18.6 mg/l). Fe increments were associated generally to the presence of Fe(II) on mineral surfaces and in silicates (Heron and Christensen 1995). Mn oxides can be reduced into dissolved Mn(II) increasing their concentration in groundwater.

The nitrogen present in the natural waters is in the form of anion (NO_3^- and NO_2^-), in cationic form as

ammonium (NH_4^+) and intermediate oxidation stages as part of the organic solutes. In anaerobic environments such as those observed in landfill groundwater nitrates can be reduced by anaerobic bacteria and form nitrogen oxides and nitrogen gas in a process denominated denitrification (Christensen et al. 2001). Denitrification evidences were found in sample sites of the landfill where NO_3^- values are below 17 mg/l. Sample site P11 shows a concentration of 80 mg/l, a too high value for natural groundwater. A possible source of nitrate in P11 site is the runoff water from agricultural fields around this point. Nitrites have a spatial variation similar to nitrates, with high values in sample sites located upward of the landfill, intermediate values in sample sites P4, P5, P6 and P10 and low values in the rest of sample sites located inside the landfill.

Ammonium is a major reducing agent in landfill leachates and probably a critical long-term pollutant (Christensen et al. 2001). The ammonium spatial distribution in the study area was quite irregular due to a combination of processes. Background concentration (P11) was very low (69 $\mu\text{g}/\text{l}$) and was largely

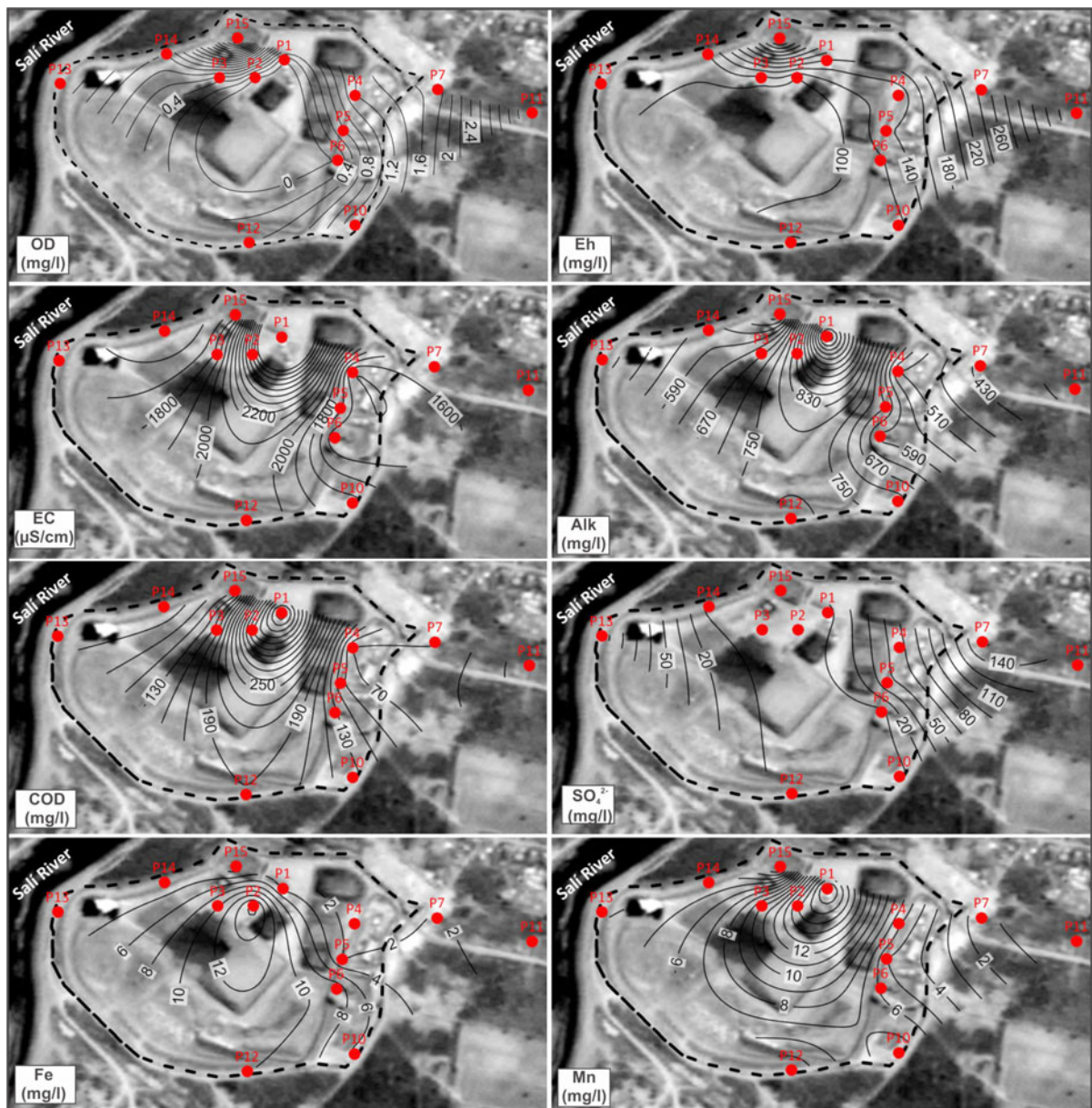


Fig. 3 Spatial distribution of OD, Eh, EC, Alk, COD, SO_4^{2-} , Fe and Mn in groundwater of landfill area (see text for details and explanations)

exceeded in the rest of the sample sites except in P13 and P14 where similar concentrations were recorded. This indicates that the organic matter present in landfill groundwater is degrading by fermentation process. However, spatial distribution of the ammonium inside the landfill has showed that those sample sites present the lowest concentrations, which correspond with the areas where strong reducing conditions have been observed. Ammonium could be attenuated

in sample sites P1, P2 and P3 as a consequence of anaerobic oxidation. This attenuation process has been reported in others landfills (Cozzarelli et al. 2000 and Christensen et al. 2001). Sample site P12 has showed a very high ammonium concentration (89 mg/l), suggesting a new source of organic matter in this area. Their origin could be related to leachate from waste cell number 7 or a fissure in leachate pumping chamber located in front of P12.

Four elements (Cd, Cr, Pb and Zn) were analyzed for the assessment of landfill heavy metals pollution. Heavy metal concentrations were determined as total dissolved metal on acidified samples after removal of solids by a 0.45- μm filter. Usually, total dissolved heavy metals do not constitute a frequent pollution problem according to the studies of Arneeth et al. (1989) and Andersen et al. (1991). In Pacará Pintado landfill, leachate plume has shown relatively high concentrations of Cr, Zn and Pb. Cadmium values were very low ($< 0.6 \mu\text{g/l}$) and in most sample sites were below the detection limit of the technique ($< 0.1 \mu\text{g/l}$). Chromium showed low concentrations in sample sites located upward of the landfill (P11: $1 \mu\text{g/l}$, P7: $1.4 \mu\text{g/l}$). Inside the landfill highest concentrations were observed in the reducing zone (P1: $18.8 \mu\text{g/l}$, P2: $8.4 \mu\text{g/l}$ and P12: $9.4 \mu\text{g/l}$), but none of them have exceeded the drinking water standards (Cr: $50 \mu\text{g/l}$). Concentrations obtained are consistent with results of Richard and Bourg (1991) who argued that chromium is usually present in the reduced zone of the landfill leachate plume as Cr^{+3} in a relative insoluble hydroxide forms, resulting in low water dissolved concentrations of around $10 \mu\text{g/l}$ at neutral pH.

Lead concentrations were high in sample sites P13 (Pb: $60 \mu\text{g/l}$) and P14 (Pb: $75 \mu\text{g/l}$) located in the outskirts of the landfill. In both cases, lead concentrations exceeded the drinking water standards (Pb: $50 \mu\text{g/l}$). In the center of the landfill, lead concentrations are lower with maximum values of $35 \mu\text{g/l}$ recorded in sample sites P2 and P12. Natural groundwater concentration of the region was $19 \mu\text{g/l}$.

Zinc concentrations showed similar behavior than lead with high concentrations in sample sites located on the outskirts of the landfill (P7: $110 \mu\text{g/l}$ and P13: $120 \mu\text{g/l}$). However, all the sample sites of the landfill presented zinc concentrations higher than in the sample site P11 ($< 30 \mu\text{g/l}$). This shows that waters affected by leachate plumes cause an increase in the concentrations of heavy metals.

Heavy metal concentration in Pacará Pintado could be influenced by precipitation mechanisms in a reducing environment. In the center of the landfill, sulfates are reduced to sulfides generating Cd, Pb and Zn precipitation. In the case of Cr, precipitation would not happen because it does not form insoluble sulfides, but it could migrate forming complexes with organic matter. In North Bay Landfill in Canada (Barker et al. 1986) and Vejen Landfill in Denmark (Andersen et al.

1991), SO_4^{2-} reducing environments have been identified supposedly providing significant attenuation of heavy metals by sulfide precipitation.

Surface water

Surface water sampling was carried out over a paleochannel that surround the landfill and in the Salí River. Phreatic water from the landfill area discharge into the paleochannel and flows downward to the Salí River. Surface water results are shown in Table 2.

The concentrations of chemical compounds increase in the paleochannel immediately before (PC2) or at the beginning of discharge area (PC3) located in front of groundwater sample site P14 (Fig. 2). This is particularly clear for EC, chloride, ammonium, alkalinity, manganese and chromium (Fig. 4). In sample site PC4, located before the discharge into Salí River, chemical compounds showed attenuation and only ammonium and manganese remain high. Several researchers have identified ammonium as the most significant component of leachate for the long term (Kruempelbeck and Ehrig 1999; Christenson et al. 1999 and Kjeldsen et al. 2002) because there is no mechanism for its degradation under methanogenic conditions (Burton and Watson-Craik 1998).

Salí River was sampled in four points, two before the landfill (SR1 and SR2) and two after the landfill (SR3 and SR4) in water flow direction (Fig. 1). Water quality of the sample sites located upstream of the landfill is low. OD concentration in SR1 was 2.4 mg/l and descends to 1.3 mg/l in sample site SR2 after receiving the contribution from San Cayetano Channel, which is an open sewage channel. In sample site SR3, OD concentration was 1.7 mg/l and drops sharply after receiving paleochannel discharge to 0.4 mg/l in sample site SR4 (Fig. 4). Electrical conductivity shows significant variations in Salí River, and it increases from $969 \mu\text{S/cm}$ to $1,378 \mu\text{S/cm}$ between sample sites SR1 and SR2 due to the discharge of polluted waters from San Cayetano Channel. Downstream EC continued increasing to $1,640 \mu\text{S/cm}$ (SR3) and $1,589 \mu\text{S/cm}$ (SR4) which means an important impact on Salí River salinity as a consequence of the leachate plume (Fig. 4).

COD concentrations in Salí River were around 170 mg/l , and BOD_5 showed values higher than in

Table 2 Summary of surface water chemical analysis

Parameters	Surface water sample sites									
	PC1	PC2	PC3	PC4	SR1	SR2	SR3	SR4	TP	BP
pH	7.6	7.3	7.2	7.3	7.5	7.4	7.5	7.5	8.7*	8.9
DO (mg/l)	3.2	3.4	3.1	2.0	2.4	1.3	1.7	0.4	0	7.2
EC ($\mu\text{S}/\text{cm}$)	1,325	1,337	1,630	1,508	969	1,378	1,640	1,589	7,370*	1,787
Eh (mV)	244	12	246	296	231	197	240	161	−122	243
WT ($^{\circ}\text{C}$)	19	22	23	22	19	19	21	22	26	18
BOD ₅ (mg/l)	11	9	<5	<5	64	69	65	69	631	96
COD (mg/l)	111	71	78	57	171	177	163	179	3,855	376
BOD/COD	0.10	0.13	–	–	0.37	0.39	0.40	0.38	0.16	0.25
Alkalinity (mg/l)	349	411	578	468	267	295	291	303	2,611*	275
Cl [−] (mg/l)	161	132	198	173	166	167	160	153	586	203
SO ₄ ^{2−} (mg/l)	69	104	33	48	278	277	241	235	120	127
NO ₃ [−] (mg/l)	5	13	15	13	3	3	3	3	1	2
NO ₂ [−] (mg/l)	0.035	0.026	0.011	<0.007	3.540	0.770	0.229	0.128	0.184	0.099
NH ₄ ⁺ (mg/l)	3.000	4.000	16.000	6.000	0.870	0.780	1.050	2.050	–	18.000
Fe (mg/l)	<0.08	0.33	0.35	0.16	0.13	0.13	0.11	0.13	1.04	0.52
Mn (mg/l)	<0.005	5.39	5.75	0.95	0.30	0.30	0.29	0.29	<0.05	0.24
Cr ($\mu\text{g}/\text{l}$)	0.8	4.5	5.4	1.8	1.4	1.2	0.9	2.5	84.2	126.0
Zn ($\mu\text{g}/\text{l}$)	<30	<30	<30	<30	60	70	100	130	50	100
Pb ($\mu\text{g}/\text{l}$)	<5	<5	<5	<5	<5	<5	<5	<5	5	6
Cd ($\mu\text{g}/\text{l}$)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.10	0.11

* Value affected by lime treatment

landfill groundwater samples (64–69 mg/l). BOD/COD ratio was around 0.35 in the four sample sites.

Ammonium concentrations showed a significant increase in sample sites located downstream of the landfill. In SR1 and SR2, ammonium concentrations were 0.870 and 0.780 mg/l, respectively, while in SR3 was 1.050 mg/l increasing to 2.050 mg/l in SR4 after receive the paleochannel discharge (Fig. 4).

Chloride values were increased after San Cayetano Channel discharge but in downstream direction show a dilution effect, and landfill leachate influence was not noted perhaps as a consequence of a dilution effect. Heavy metal concentrations were low in all sample sites. Nevertheless, chromium concentrations increased from 1.4 to 2.5 $\mu\text{g}/\text{l}$ after the paleochannel discharge showing leachate influence (Fig. 4).

Redox processes

Leachate infiltration with high organic matter contents in shallow and oxidized aquifers usually leads to the

development of a redox zonation (Barcelona and Holm 1991; Lyngkilde and Christensen 1992b). In Pacará Pintado area, high dissolved organic matter concentrations are present in groundwater that largely exceeded background values that were observed upstream.

According to Christensen et al. (2001), the processes related to organic matter oxidation follow a series where O₂ will be used first, followed by NO₃[−], Mn, Fe, and SO₄^{2−}. Final stage is dominated by methanogenesis reactions when the most favorable electron acceptors are depleted. Important redox processes have been observed along the landfill leachate plume in downward direction. Degradation parameters' behavior linked with redox zonation in groundwaters is shown in Fig. 5.

OD concentration shows a decrease in piezometers located inside the landfill plant with respect to those located outside. This decrease is due to the entry of large amounts of dissolved organic matter into landfill groundwater that is reveal by a conspicuous peak of

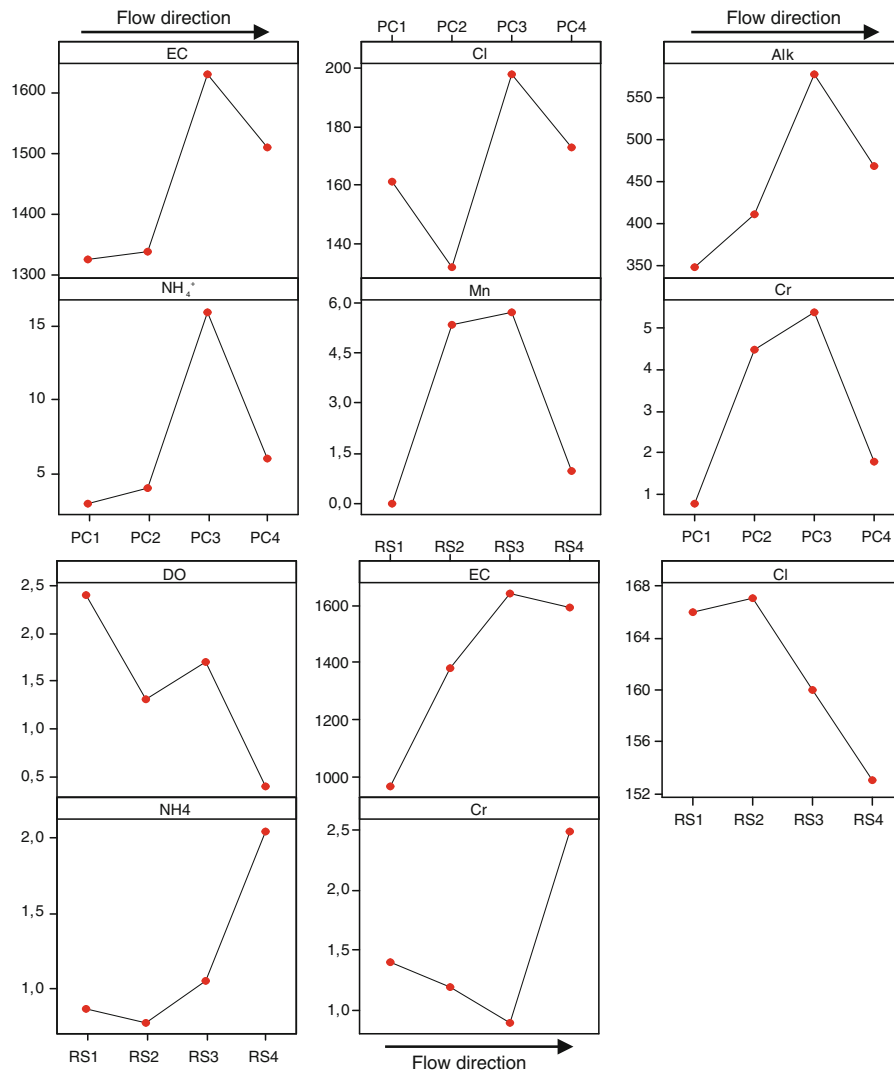


Fig. 4 Chemical data variations on selected parameters along paleochannel and Salí River. Electrical conductivity is expressed in $\mu\text{S}/\text{cm}$ and concentration in mg/l except for chromium which is in $\mu\text{g}/\text{l}$

COD in sample site P1. Sulfates presented values greater than 100 mg/l outside of the landfill but inside show a drastic reduction in its central part where is almost absent (sample sites P1, P2, P3 and P12). Fe concentration showed an increase in the values along the streamline until reaching a peak of 17 mg/l in sample site P2 and then descends to values of around 10 mg/l . Alkalinity has shown a similar behavior to COD with a maximum value in sample site P1 descending in flow direction. NO_3^- concentrations had a similar distribution than sulfates. Similar redox

conditions were observed in an alluvial aquifer affected by landfill leachate (Milosevic et al. 2012) where the concentration of dissolved iron was elevated, whereas sulfate, nitrate and oxygen were depleted in the center of the plume. The lack of enhanced attenuation among piezometers in central part of the landfill can be attributed to the fact that the anoxic plume, comprised largely of recalcitrant dissolved organic matter and reduced inorganic constituents, interacted with anoxic bottom sediments, rather than encountering a change in redox conditions

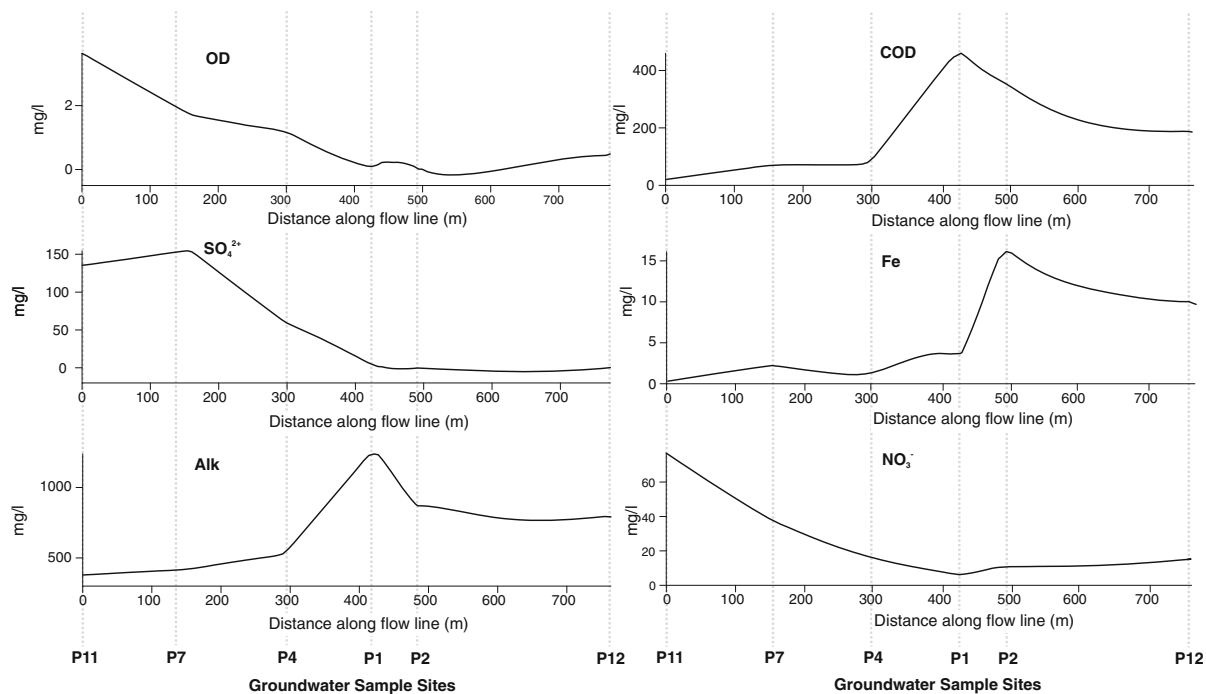
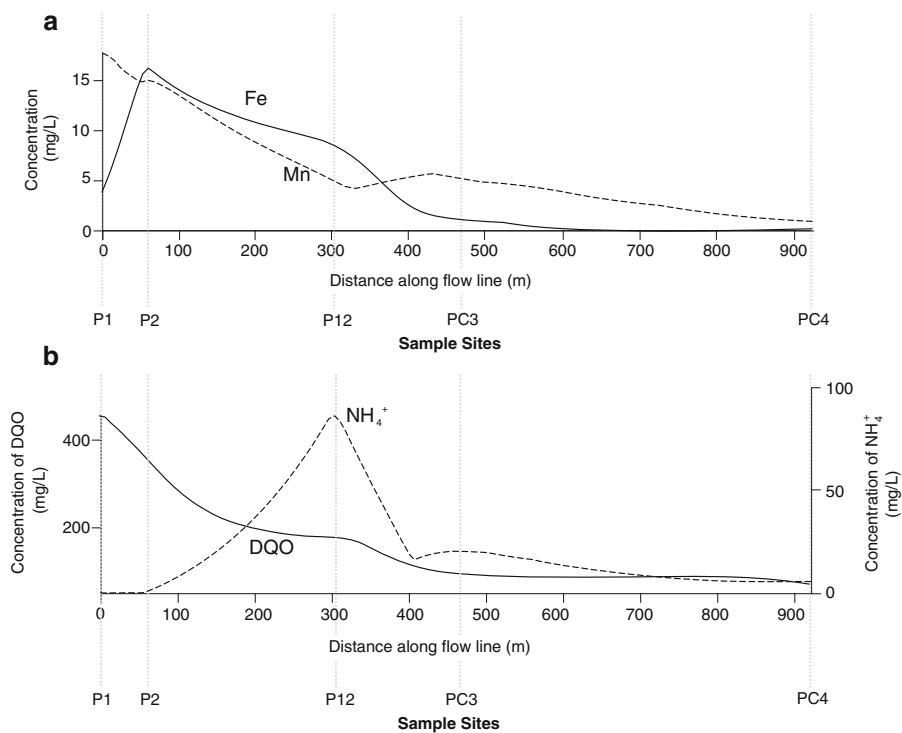


Fig. 5 Longitudinal profiles of common degradation parameters found in groundwater redox zones generated by landfills leachate

Fig. 6 Distribution along the leachate plume of **a** Fe and Mn and **b** NH_4^+ and COD at Pacará Pintado landfill



that could cause transformation reactions. This type of geochemical interaction between groundwater and bottom sediments porewater was proposed by Lorah et al. (2009) for a wetland sediment–alluvial aquifer interface in a landfill leachate plume.

According to trends analysis along the streamline, a sulfate reducing zone is present in the center of the landfill area. This zone is overlapped by a nitrate and manganese reducing zone and remains completely anoxic. Iron reduction takes place further down gradient, in sample site P2, where conditions became less reducing (Fig. 6a). Dissolved manganese is released earlier than iron because Mn^{2+} is stable over a wide range of redox potential conditions in contact with hematite, while inversely Fe^{2+} is unstable in contact with MnO_2 (Appelo and Postma 1999). However, in order to make a more precise description of the redox zonation, more piezometers should be installed and vertical samples should be taken.

When only reduced zone is analyzed, a new entrance of dissolved organic matter is revealed in sample site P12 evidenced by a great ammonium concentration peak (NH_4^+ : 89 mg/l) and moderate peaks in COD and alkalinity values. Fig. 6b shows NH_4^+ and COD behavior in the plume from sample site P1 to sample site PC4. Ammoniacal nitrogen (ammonia and/or ammonium) is recorded at high levels in most landfill leachate studies with Robinson (1995) and Kjeldsen et al. (2002) both describing it as the dominant pollutant.

Leachate characteristics in landfill groundwater indicate that the plume is in a stable methanogenic stage comparable with the phase 4 of Kjeldsen et al. (2002). The BOD/COD ratio is < 0.1 with very low concentration of BOD_5 (< 10 mg/l), moderate concentration of COD (< 500 mg/l) and the absence of sulfate. The values are in accordance with the ranges proposed by Ehrig (1988) for parameters in methanogenic phase.

Leachate plume delineation

In order to delineate the leachate plume distribution chloride spatial variation along streamline was used. Fig. 7 shows a horizontal dimension sketch of contour lines for chlorine along the groundwater flow lines. Chloride was selected as an indicator of the leachate plume because is a nonreactive parameter where the only attenuation mechanism is dilution. The delineation of the plume was made based on a minimum value of

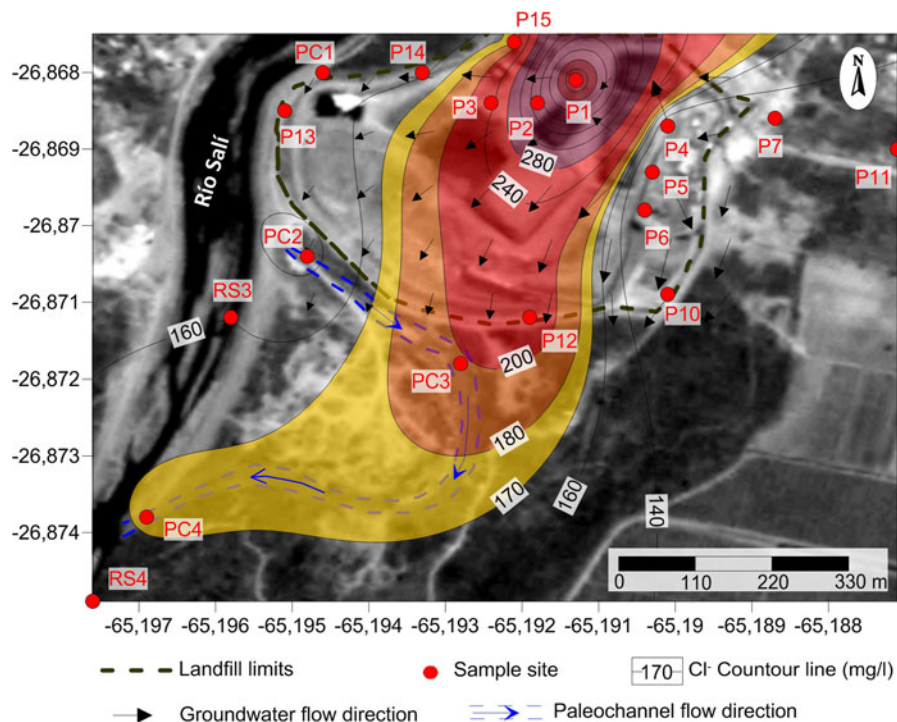
170 mg/l of chlorides. This value is higher than those values recorded in groundwater and surface water without the influence of the landfill, so its origin can only be assigned to the plant leaching. Leachate plume movement direction was constructed using potentiometric head measurements.

Leachate plume in Pacará Pintado reaches a length of 930 m and includes both groundwater and surface water media. Leachates present in groundwater are discharged into the paleochannel and transported almost to the Salí River. The plume length estimated in Pacará Pintado is only valid for the sampling period and could be influenced by suffer seasonal variations. The length of the plume is governed mainly by downward hydraulic gradient groundwater and their density (MacFarlane et al. 1983). Other factor in the control of the plume length is the natural attenuation capacity of the system to control the contaminants (NJDEP 2012). Natural attenuation depends on the geological characteristics of the aquifers. Most plumes have lengths less than 1000 m, and very few exceed 2,000 m, probably due to dilution of the contaminants (Christensen et al. 2001). Evidences from leachate plumes that occur in fast-flowing aquifers, such as alluvial deposits (sand and gravel), show extensions over 300 m (MacFarlane et al. 1983; Reinhard et al. 1984; Becker 2002). According to Yaqout and Hamoda (2005), vertical Darcy velocity has a significant impact on migration behavior of contaminants. The concentration was increased by 24.5 % by increasing the vertical Darcy velocity from 0.005 to 0.009 m/year. In aquifers with low hydraulic conductivity, leachate plumes have less extension. Bocanegra et al. (2001) reported the presence of a plume of contamination reaching 100 m from landfill in loesslike (silt and silty-sand) aquifer from Mar del Plata city in Buenos Aires Province.

The most significant intrusion of leachate into the groundwater was around the sample sites P1 and P2 with chloride concentrations higher than 380 mg/l. Then plume shows a gradually attenuation in downward direction from 240 mg/l, in sample sites P3 (230 mg/l) and P12 (220 mg/l), to lower than 200 mg/l in all paleochannel sample sites. The attenuation effect of pollutants by dilution across the leachate plume can be inferred from chloride and COD distribution curves of Figs. 3, 4 and 7.

A new entrance of pollutants at sample site P12 is indicated by COD peak. This fact has great influence in the plume extension generating a large dispersion of

Fig. 7 Horizontal distribution of leachate plume mapped using chloride concentration contour lines at Pacará Pintado landfill



NH_4^+ , Mn and Cr over the paleochannel environment ($\text{O}_2 > 2 \text{ mg/l}$). Distribution of ammonium showed that high concentrations reach sample site PC4 exceeding limits for aquatic life (NH_4^+ : 1.37 mg/l). Ammonium concentration measured in sample site RS4 (2 mg/l), located after paleochannel discharge, duplicates ammonium values observed in Salí River before the landfill.

Conclusions

Evidences of water pollution by landfill leachate were found in both groundwater and surface water of the study area. Leachate plume presented high concentration of organic matter, Fe, Mn, NH_4^+ , Cl^- and Cr, reaching an extension of 900 m with an orientation NE–SW. Seasonal monitoring should be performed in order to evaluate temporal variations of the plume length.

Redox zones were identified in the leachate pollution plume through characterization of inorganic groundwater samples. Groundwaters present an overall redox gradient with SO_4^{2-} , Fe, Mn and NO_3^- reducing conditions from sample site P1 to sample site P12 along streamline. A new source of leachate would be located close to sample site P12 since high values of NH_4^+ ,

COD and HCO_3^- have been recorded. Low BOD_5/COD ratio observed (< 0.1) indicates that the leachate is on a stable methanogenic phase. Heavy metals content in the leachate plume is generally low as a result of metal precipitation. However, high Pb and Zn concentrations were found in sample sites located near the treatment pond suggesting percolation problems.

Paleochannel waters have showed high concentrations of NH_4^+ , Mn and Cr that exceed national regulations limits for aquatic life. Salí River waters showed increased concentrations of ammonium and chromium after receiving paleochannel discharge. However, the other elements do not showed an increase that could mean a consequence of a dilution effect due to its higher flow rate.

The presence of a leachate plume in a landfill site with a single liner system implies that the use of this groundwater pollution control method alone is not enough especially if permeable sediments are present below.

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