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# Containment and attenuating layers: An affordable strategy that preserves soil and water from landfill pollution

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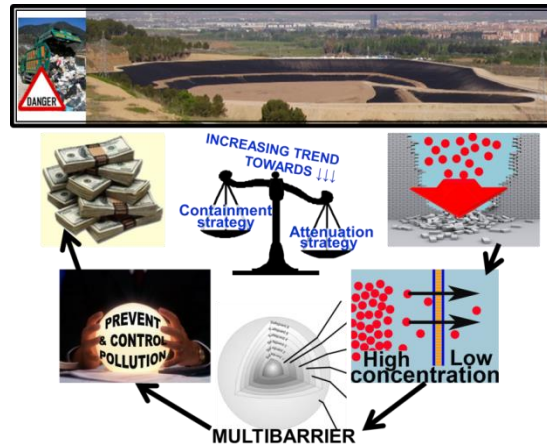
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**ABSTRACT:** The performance of a widely distributed natural clay to attenuate contaminants released from an old landfill was investigated. The objective is to evaluate its potential use as a barrier for waste containment systems. Core samples of the natural clay were collected below the landfill and their parameters distribution with depth was determined. Partition coefficients, retardation factors and percentage values of pollutants concentrations, revealed a rapid decrease of contaminants with depth. The background values of the pollutants were below the maximum limits for drinking and irrigation water and with no need of reactors, collectors, aeration or recirculation systems. Impermeable waste capping is discouraged in order to decrease leachate toxicity, decomposition time and conservative species, and in order to avoid high-reducing conditions that would mobilize redox-sensitive contaminants. A review on leachate-composition evolution and on natural-attenuation processes was undertaken to understand the interactions leachate-substratum, which is essential to properly estimate the leachate transport and implement the attenuation strategy. This strategy complements the traditional containment one regarding (1) the susceptibility of engineering liners to fail, (2) the inevitable diffusion of

contaminants through them, (3) the remaining high number of old landfills before the requirements of liner systems and (4) the low-cost and feasibility for developing countries.

**Graphical abstract:**



**KEYWORDS:** Landfill leachate; Attenuation strategy; Clay; Migration; Sorption.

**ABBREVIATIONS**

BOD, biological oxygen demand; CEC, cationic-exchange capacity; COD, chemical oxygen demand;  $\delta$ , dry density;  $\sigma$ , electrical conductivity; Eh, redox potential; Ex\_Cation, exchangeable cation;  $K_d$ , partition/distribution coefficient; MW, municipal waste; LMMOAs, low-molecular-mass organic acids; pe, the negative logarithmic value of the activity of the free electrons (e);  $R$ , retardation factor; Sol\_ion, soluble ion; S, Supplementary material;  $S^{BET}(N_2)$ , specific-surface area; WSIC, water-soluble inorganic carbon; WSOC, water-soluble organic carbon; XRD, X-ray diffraction.

## 1. Introduction

Human activity inevitably involves a large and increasing amount of refuse, specifically municipal waste (MW). The European Union (EU) annually generates >520 kg of waste per capita (approx. 572 000 olympic pools) which increases around 2% each year (EEA, 2010). The increase of MW generation is linked to the population growth and, to a greater extend, to the Genuine Progress Indicator; the economic growth indicator that incorporates environmental and social factors (Fig. S1, in the supplementary material, S). In the United States, as in the rest of major countries (Canada, Germany, France, Japan, United Kingdom...), waste is mainly handled in landfills (55%) rather than burned (12.5%), recycled or composted (32.5%) (EPA, 2010). This is especially accentuated in developing countries, where the landfilling supposes almost the only way of waste disposal.

Landfills generate and emit leachates; i.e., a toxic liquid that contains pollutants and is produced by percolation of aqueous substances through the deposited wastes. To avoid the leachate affecting surrounding lands, underlying aquifers or nearby rivers and, therefore, protect biodiversity and human health, two approaches exist: the containment strategy and the attenuation strategy. The containment strategy is based on the complete isolation of the waste by means of (1) bottom and top sealing liners, (2) collection systems of the pollutants emissions and (3) an everlasting-aftercare monitoring. The attenuation strategy considers that (i) a proper underlying natural substratum and (ii) the landfill itself, act as a biochemical reactor in which *natural attenuation processes* (dilution, dispersion, biodegradation, redox, precipitation, sorption, exchange reactions) take place, reducing and eliminating the contamination (Allen, 2001; Allen and Taylor, 2006). Although both strategies are meant to be applied jointly (c.f., multibarrier concept in Europe), more effort has traditionally been devoted to the containment one because the attenuation strategy cannot be applied to all areas (e.g., karst limestone) and estimating the substratum behaviour to ensure that it performs properly as, what is called, an *attenuating layer*, is complex. Despite this, the containment strategy should not be the only approach.

First, under containment conditions, the waste itself remains a pollution source and, if something fails, the pollutants will be released: it is the so-called time-bomb effect. Engineering liners are likely to fail in a few years (Buss et al, 1995; Eid, 2011; Lee and Jones-Lee, 2009; Rowe and Sangam, 2002; Surmann et al, 1995), whereas the site remains dangerous for decades after this (EPA, 2007; Ritzkowski et al., 2006). In this event, the underlying natural substratum is the last chance to deal with the pollution. Second, diffusion of contaminants in leachate inevitably takes place through the compacted clay and engineering liners (Potter and Yong, 1993; Rowe, 1994). This transport is negligible relative to advective velocities but can result in significant long term contaminant flux in intact and non-fractured liners (Wiedemeier et al., 1998). From a sustainable perspective, we must act on that issue as we are liable for not leaving the present waste problems for the future generations (Brundtland Report, 1987). Third, the large majority of the existing landfills are old and abandoned dumps from before the imposition of installing composite-liner systems (150 000-500 000 in Europe were estimated by Hogland et al. (2011)). In these cases, landfills are not governed by the containment strategy and predicting the long-term behaviour of the interaction leachate-substratum is the only manner to know where it would be necessary to implement security measures to prevent and control landfill pollution. And finally, the attenuation strategy is independent from engineering or composite liners (expensive and complex structures), involving low installation, operation, maintenance and after-closure economical costs. This is critical for developing countries, due to their financial, technical, institutional and social constraints. The reluctance to believe that the attenuation strategy is safe, rendering water protection against pollution, is still strong. This locates to a second position what would be a more cost-effective plan. The cost to construct the engineered barriers, restore them after failure and remediate leachate-contaminated groundwater is vast. However, this could be mitigated by selecting an appropriate site that presents an attenuating layer, which would also reduce the environmental risk.

For these reasons, it is needed and expected that landfill policies will increasingly take into consideration the attenuation strategy. Despite this, there is a lack of studies that examine if a substratum can be used as an attenuating layer for safe disposal of wastes, as discussed in Cuevas et al. (2012). The current work is an advance over the few prior studies on soil samples

at landfills because, as detailed in Table S1 together with other references reported below, those studies (1) are from samples surrounding the landfill area instead of underlying the layer of waste or (2) analysed a lower number of samples and parameters or/and (3) do not examine the variations with depth (Fracari et al., 2004; Goodall & Quigley, 1977; King et al., 1993; Koutsopoulou et al., 2010; Lake & Rowe, 2005; Marzougui & Ben Mammou, 2006; Munro et al., 1997; Xie et al., 2009; Zhan et al 2014). This makes that the presented work can be applied to a broader range of contexts.

The objective of the present study is to identify if a common natural substratum can act as an attenuating layer and ensure enough protection against landfill pollutants. For that, we have assessed the performance of a widely distributed substratum underlying a no-lined landfill of 14 years old and we have considered that it would ensure enough protection for the environment and human health if the landfill pollutants were within the international authorized limits for drinking- and irrigation-water use. This work also provides information about the behaviour, interaction and effect of the released leachate pollutants on the underlying substratum. Finally, the natural attenuation processes that determine the capacity of a natural substratum as an attenuating layer of leachate pollutants are discussed.

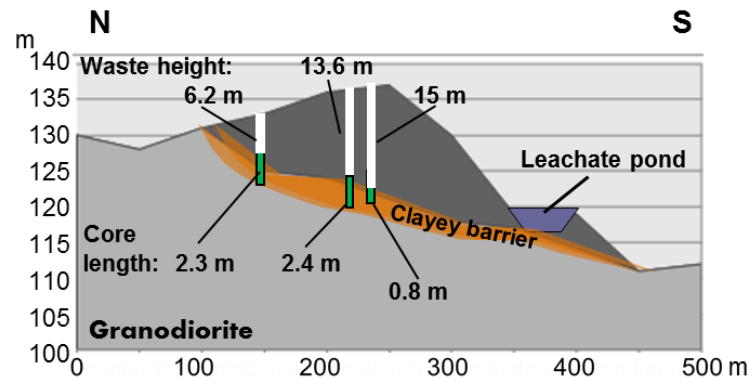
## **2. Materials and methods**

### **2.1. Materials**

Attention was paid to the selection of the landfill substratum that would be analysed. It should be naturally underlying an old-MW landfill without barriers or collection systems. Additionally, the substratum should be a widely distributed and common natural material, with expected desirable characteristics for lessening the pollution of leachate. The selected substratum was chosen by its significant proportion of sodium smectite. Smectite is a 2:1 clay mineral with shrink-swell capacity and with elevated specific surface, ions-exchange capacity and charge (Geological Society of London, 2006). These properties are responsible for the high interaction of smectites with solutes by means of sorption, precipitation or cationic-exchange reactions; all of them natural attenuation processes (Czurda, 2006). Accordingly, monomineral rocks composed of smectite (bentonites) have been in common use as landfill liners (Hoeks et

al., 1987) and have shown to improve the retention of landfill leachate pollutants in arkose sandstone (Ruiz et al., 2012).

The selected landfill was 14 years old and from South of Spain (Andalucía), with a Mediterranean climate. The landfill had an area of 30 ha and received 474 500 t year<sup>-1</sup> of MW. Three boreholes were drilled through 6–15 m of landfill waste to recover between 0.8 and 2.4 m-long of the underlying substratum in continuous vertical cores (Fig. 1). The cores were divided into 22 samples of different thicknesses and at different depths (Table S2), which were homogenized, preserved dark and refrigerated (4 °C) until their analyses. To facilitate the data interpretation, the cores are denoted as B and the samples as S followed by a consecutive number (B1, B2, B3 and S1, S2...). The liner material was composed of clayey sands: poorly graded sand-clay mixtures which typically developed during the erosion and accumulation of coarse detrital materials in fault troughs or low areas adjacent to granite massifs, during the Miocene period in Spanish tertiary basins.



**Fig. 1.** Cross section of the landfill. Location and depth of the boreholes (waste height plus core length).

## 2.2. Methods

The parameters of concern during the material characterization and the study of the leachate infiltration through it, were: percentage-based mineralogy, cationic-exchange capacity (CEC), external specific-surface area ( $S^{BET}(N_2)$ ), dry density ( $\delta$ ), percentage-moisture content ( $H_2O$  (%)), pH, redox potential (Eh), electrical conductivity ( $\sigma$ ), water-soluble species (organic and inorganic carbon, alkalinity, ions) and cations occupying the exchange complex

(exchangeable cations). The microfabric of representative substratum samples was also observed by optical microscopy.

The overall mineralogy was estimated by the random-powder method (Bish and Reynolds, 1997) using the X-ray diffraction (XRD) in pre-dried grinded samples (<5 µm size). From some selected non-altered refrigerated samples, the sheet-silicates mineralogy was also determined by XRD, in which case the samples preparation was according to the oriented-slide method: air dried, 550 °C dried and glycerol solvated (Moore and Reynolds Jr, 1997). Lastly, DRXWIN© software was used for the data treatment (Primo, 2001).

The CEC was determined as defined in Rhoades (1982), measuring the final Na<sup>+</sup> concentration, equivalent to the CEC, in a Buck Scientific® PFP-7 flame photometer. The external S<sup>BET</sup>(N<sub>2</sub>) was measured by the BET method (Brunauer et al., 1938), using an analysis-protocol software (Micromeritics® GEMINI V) which obtains a five-point N<sub>2</sub> gas adsorption isotherms at 77 K. The dry density (δ) was calculated after estimating the water-saturated density (δ<sub>b</sub>) by the hydrostatic-balance method (McIntyre and Loveday, 1974) and applying Eq. (1).

$$\delta = \delta_b / (1 + h_r) \quad (1)$$

where  $h_r$  is the ratio-moisture content.

The percentage-moisture content was calculated by Eq. (2).

$$\text{H}_2\text{O} (\%) = (m_m - m_d) / m_d \cdot 100 \quad (2)$$

where  $m_m$  is the mass of a portion of non-altered sample and  $m_d$  is the mass of the same fraction after 48 hours at 105 °C.

The measurements of pH, redox potential (Eh), electrical conductivity (σ) and soluble species were done in aqueous extracts: the soil samples were mixed and stirred with distilled water in a ratio of 1:2.5 (pH, Eh, σ), 1:5 (carbon analyses) and 1:10 (alkalinity and ions). The pH, Eh and σ (1:2.5) were analysed with a glass combined electrode, a combined platinum electrode and a multi-range cell, respectively, following official methods (MAPA, 1994).



Water-soluble organic and inorganic carbon (WSOC, WSIC) were quantified from aqueous extracts too (1:5), in a carbon analyser Shimadzu® TOC-5000. The soluble ions (Sol\_Na<sup>+</sup>, Sol\_K<sup>+</sup>, Sol\_Ca<sup>2+</sup>, Sol\_Mg<sup>2+</sup>, Sol\_NH<sub>4</sub><sup>+</sup>, alkalinity and anions) were also analysed in aqueous extracts (1:10), while the exchangeable cations (Ex\_Na<sup>+</sup>, Ex\_K<sup>+</sup>, Ex\_Ca<sup>2+</sup>, Ex\_Mg<sup>2+</sup>, Ex\_NH<sub>4</sub><sup>+</sup>) were extracted as described by Thomas (1982). The Na<sup>+</sup> and K<sup>+</sup> were determined using a Buck Scientific® PFP-7 flame photometer. The Ca<sup>2+</sup> and Mg<sup>2+</sup> were analysed by Flame Atomic Absorption Spectroscopy (Unicam™ Solaar M series atomic absorption spectrometer). The NH<sub>4</sub><sup>+</sup> was determined using an ammonia-gas sensing electrode (ion-selective potentiometer ORION® 9512). The main anions were analysed by ion chromatography (METROHM™ 761 Compact IC), except for the alkalinity that was determined with an ORION® 960 potentiometer by titration using a normalized H<sub>2</sub>SO<sub>4</sub> solution as the titrant and a pH-meter to obtain the titration curve.

The microfabric was analysed in thin sections observed under the polarized-petrographic optical microscope *Ortho Plan Pol Leitz Carl Zeiss*. Five thin sections of 30-μm thickness were prepared from vertical cuts of shallow substratum samples between 0.03–0.17 m-depth. The vertical cuts were dried and frozen under N<sub>2</sub> gas, embedded in a LR-White resin Standard until the desired hardening, glued to a glass slide, grinded to the correct thickness, polished by hand on a glass plate with fine powder of 600 and 800 grade and then, added a cover slip (Cobena et al., 1999). Additionally, the hydraulic conductivity was measured in one sample per core between 0.2 and 0.4 m-depth that was paraffined and reserved for permeability tests under triaxial cells (Rogel et al., 2010).

The state of the starting samples (non-altered wet sample, air dried, 105 °C dried...), the ratios *soil/distilled water* in the aqueous extracts and the replicates when done, are schematized for most of the methods described above in Fig. S2. All aqueous extracts were done with refrigerated-wet sample to avoid any alteration of the original conditions; for instance, a previous heating treatment that could modify alkalinity or NH<sub>4</sub><sup>+</sup>. The aqueous-extracts data will be expressed in units of dry-solid mass (mmol kg<sup>-1</sup>), except when compared to the leachate, to the international legislation limits, and when calculated the partition coefficient, in which cases they will be expressed in units of pore-water volume (mg L<sup>-1</sup>).

Finally, the chemical oxygen demand (COD) and the biological oxygen demand (BOD) of the leachate were determined following the recommendations of APHA (2012). The COD was measured as the oxidation of water soluble organic carbon in an acid medium of  $\text{K}_2\text{Cr}_2\text{O}_7$  0.25 N and the BOD as the consumption of oxygen by wastewater microorganisms measured in a biometer WTW- Oxitop.

### 3. Results

To get a preview of the potential pollutants, a one-liter sample of the landfill leachate was pumped and collected with a silicone tube in overflowed and opaque bottles, from a landfill well. The main components of the leachate resulted to be organic matter,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  (Sect. S1, Table S3). They are released in amounts higher than the ones naturally present, causing toxicity to living organisms, eutrophication and acidification (Christensen et al., 2001; Ganigue et al., 2007; Knobeloch et al., 2000).

The following results are referred to substratum samples. Mineralogy, external  $\text{S}^{\text{BET}}(\text{N}_2)$  and CEC were determined to characterize the substratum properties (Table S4). The mineralogy results of mean and standard error show a  $38 \pm 3$  wt% of sheet silicates of which  $18 \pm 3$  wt% is smectite,  $15 \pm 2$  wt% is illite and  $7 \pm 3$  wt% is chlorite. Within the non-sheet silicates minerals, other than the ever-present quartz ( $37 \pm 5$  wt%) and feldspars ( $8 \pm 1$  and  $1 \pm 0$  wt% for Na- and K-rich feldspars, respectively); carbonate minerals stand out with  $15 \pm 4$  wt% of calcite ( $\text{CaCO}_3$ ) and  $<1$  wt% of dolomite ( $\text{CaMg}(\text{CO}_3)_{2(\text{s})}$ ). Lastly, the iron sulphide pyrite ( $\text{FeS}_{2(\text{s})}$ ) is detected in  $<1$  wt%. The external  $\text{S}^{\text{BET}}(\text{N}_2)$  ( $14 \pm 2 \text{ m}^2 \text{ g}^{-1}$ , from 4 to  $33 \text{ m}^2 \text{ g}^{-1}$ ) varies along the cores depths parallel with the sheet-silicates relative abundance and with the CEC (Table S4). The CEC has the highest variability ( $7\text{--}42 \text{ cmol}^+ \text{ kg}^{-1}$ ), with an average of  $16 \pm 2 \text{ cmol}^+ \text{ kg}^{-1}$ . Both external  $\text{S}^{\text{BET}}(\text{N}_2)$  and smectite content in the first 0.05–0.17 m are lower than the samples underneath.

The dry density ( $\delta$ ) of the substratum samples is high ( $1.67 \cdot 10^3 \pm 0.25 \cdot 10^3 \text{ kg m}^{-3}$ ) with a noteworthy variation ( $1.35 \cdot 10^3\text{--}2.11 \cdot 10^3 \text{ kg m}^{-3}$ ) and not positively related to the waste height (Fig. S3). The behaviour is similar within the cores: the  $\delta$  fluctuates a lot in the first centimetres, then it follows an increasing trend up to a depth where it is stabilized (Fig. S3). The study of the

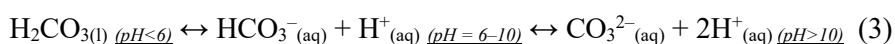
microfabric by polarized-petrographic optical microscopy (Sect. S2) exhibits carbonate gravels at shallow samples and the natural-carbonate character of the clayey substratum at deep samples. The mineralogical, density and microfabric results indicate that the landfill base was presumably filled with debris material from the surroundings, poorly compacted and with high water (leachate) content (Sect. S3).

The percentage-moisture content of the substratum samples ( $20 \pm 7\%$ ) decreases with depth from 31 to 9%, with relative low values of  $\approx 15\%$  near the surface related to quartz sand-like materials. The substratum below the landfill has a basic pH with maxima values of 8.5–9 in the first 0.25 m, remaining virtually constant with depth to values of  $8.3 \pm 0.4$ , except where the minimum moisture was detected, with a pH of 6.8. The Eh is positive,  $(128 \pm 28) \cdot 10^{-3}$  V on average, denoting a relative oxidizing capacity of the substratum, and increases with depth as pH decreases, from  $\approx 110 \cdot 10^{-3}$  V up to  $(180-215) \cdot 10^{-3}$  V. The detailed evolutions with depth of moisture, pH and Eh are shown in Fig. S5.

Finally, to know the total-quantity of dissolved salts and follow the dissolved organic and inorganic species; the  $\sigma$ , the WSOC, the WSIC, the alkalinity and the ions were measured in the aqueous extracts filtered out of the resulting solution of distilled water mixed and stirred with the substratum samples. A detailed description of the results is included in the Sect. S4. In general, the shallowest samples show the greatest levels of  $\sigma$ , WSOC, alkalinity and ions (Fig. 2, Fig. S6); all of them related to leachate pollutants. These high values which are referred to as *initial levels*, decrease with increase of depth until *background levels* are reached; i.e., constant values with depth and which presumable correspond to those naturally present. This corresponds to what was considered as *attenuation* in Regadío et al (2012). The only exception is the deepest-acidic sample S6 of the core B1 at 1.75 m-depth, where the decreasing trend of the  $\sigma$  and WSOC is broken.

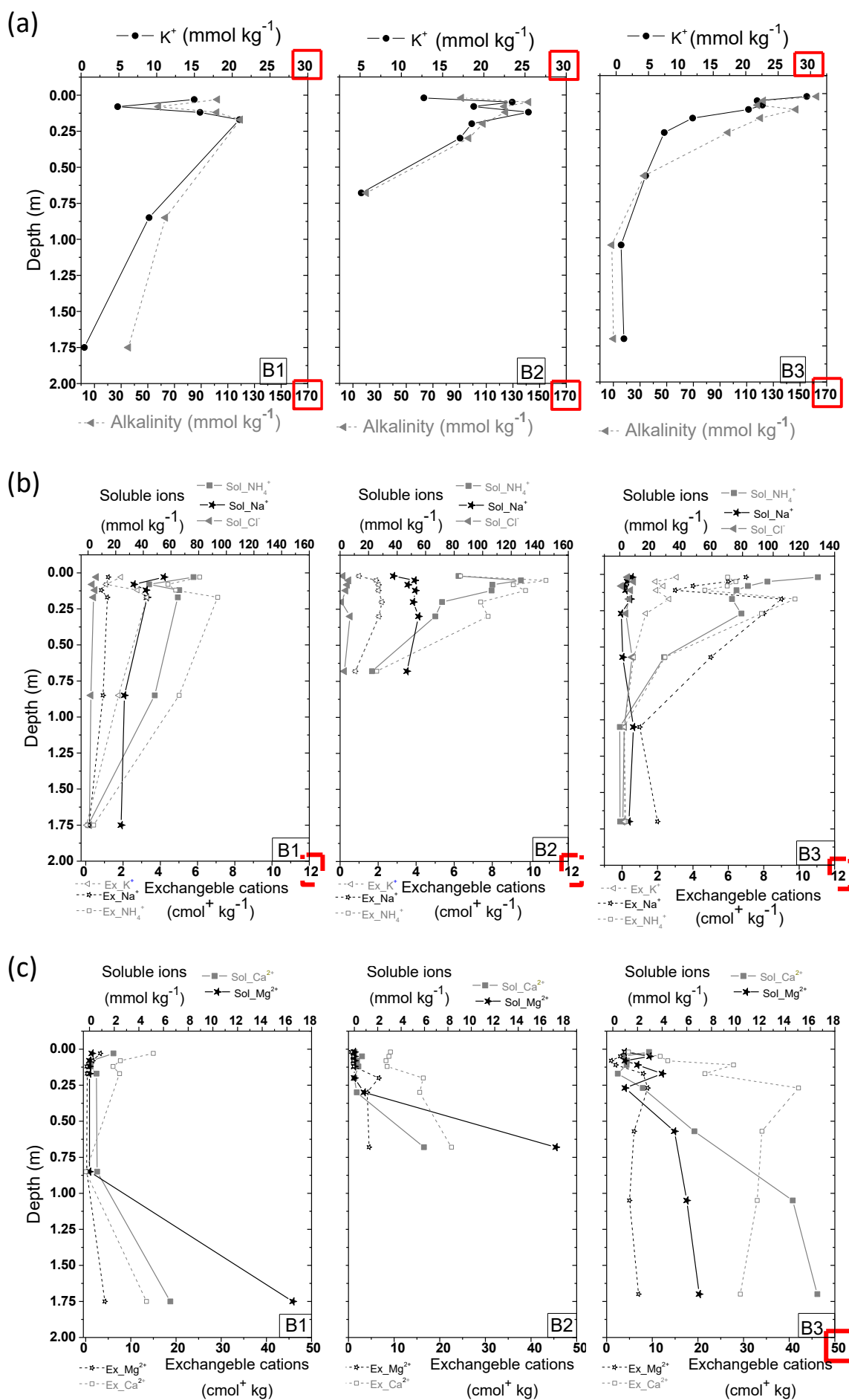
The  $\sigma$  (on average  $(2.3 \pm 0.5) \cdot 10^2$  mS m<sup>-1</sup>) and WSOC (on average  $814 \pm 551$   $\mu$ g g<sup>-1</sup>) decrease 64% and 94%, respectively in 1.05 m in the core B3. Regarding the WSIC ( $313 \pm 129$   $\mu$ g g<sup>-1</sup>), the minima levels correspond to deeper samples than the maxima values. Yet, the WSIC does not show such an easily recognisable-remarkable reduction trend (Fig. S6), because it is

not oxidisable or reducible and, at those pHs, WSIC is mainly  $\text{HCO}_3^-$ , the component of the pH-buffer system shown below (3), with high capacity for adjusting pH by distributing the proton ( $\text{H}^+$ ) within the carbon species. This fact contributes to the observed variable concentration of the WSIC.



The concentrations of Zn, Cd, Pb, Cr and Cu in the substratum samples (minor elements in the leachate, Table S2) were  $19.6 \pm 5.9$ ,  $1.6 \pm 1.3$ ,  $24.7 \pm 5.5$ ,  $122.1 \pm 5.8$  and  $17.7 \pm 3.1 \mu\text{g g}^{-1}$ , respectively. This is far below the limits established by the corresponding regional geology and legislation (Proyecto de Decreto, 2012).

The nature of the compounds dissolved in the substratum water determines the major ions. The leachates can increase the concentrations of these ions, turning them into pollutants which can travel in the aqueous solution through the substratum pores. These soluble ions are responsible for the high  $\sigma$  detected in the shallowest samples. The main anions are the alkalinity components; i.e., the soluble ions that can neutralize acidity:  $\text{HCO}_3^-$  and organic acid anions (Fig. 2.a). Alkalinity decreases with depth up to 94% in 1.05 m, B3. Another anion present is the  $\text{Cl}^-$  (Fig. 2.b) that keeps background levels between 2 and 5  $\text{mmol kg}^{-1}$  throughout the cores. Lastly, no more anions, not even the  $\text{SO}_4^{2-}$ , were detected. Among the soluble cations, ammonium is the dominant, followed by sodium and then potassium ( $\text{Sol\_NH}_4^+$ ,  $\text{Sol\_Na}^+$ ,  $\text{Sol\_K}^+$ ), which decrease 93–100% in 1.05 m, B3. In all cases, the attenuation is again reflected by a marked decrease with depth of the initial levels, that is, the concentrations at the shallowest samples; until reach constant natural-background levels, generally at 1 m-depth (Fig. 2).

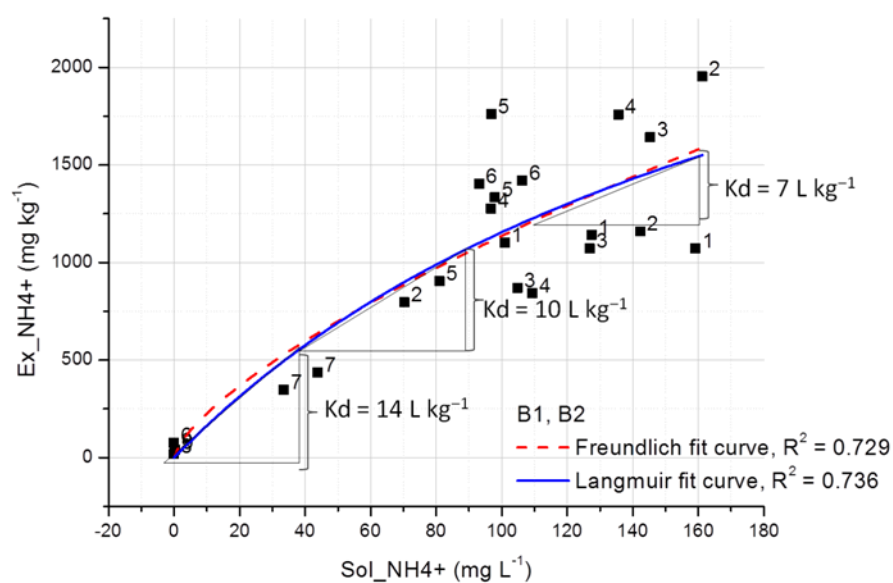
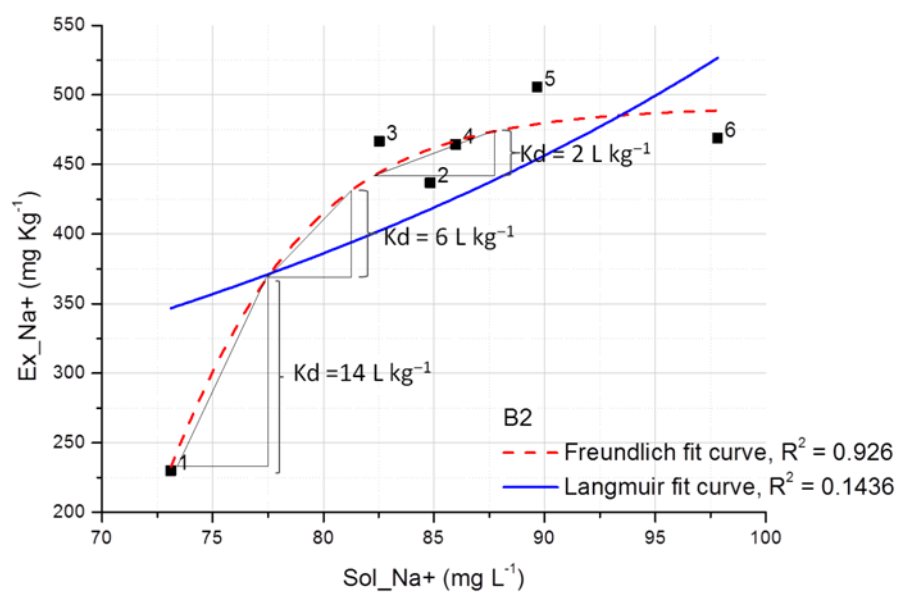
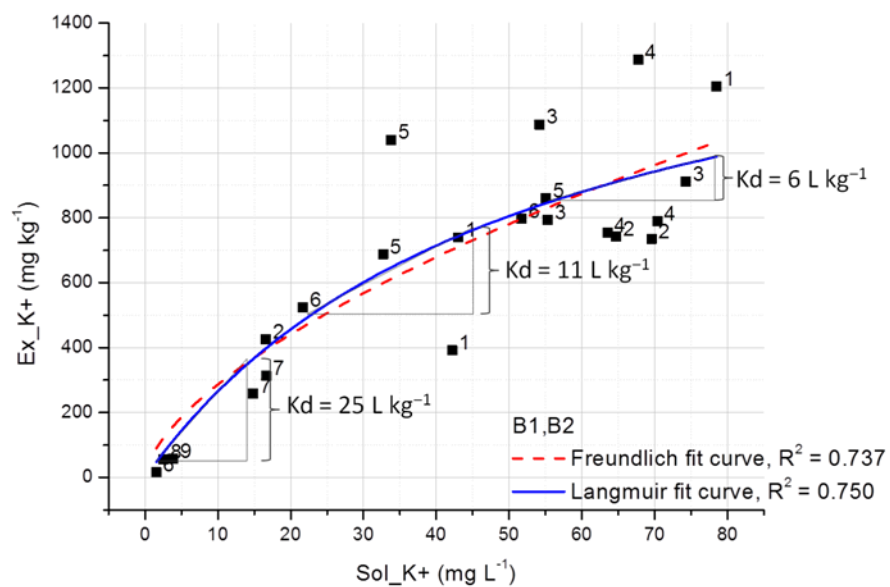


**Fig. 2.** Alkalinity, soluble ions and exchangeable cations profiles with depth classified by cores

(B1, B2, B3).

Despite the presence of carbonate minerals (Table S4), soluble calcium (Sol\_Ca<sup>2+</sup>) is present at low levels (0–3 mmol kg<sup>-1</sup>) and soluble magnesium (Sol\_Mg<sup>2+</sup>) is negligible (Fig. 2.c). Both cations increase in the deepest samples because the Ex\_Ca<sup>2+</sup> and the Ex\_Mg<sup>2+</sup> in the shallow clayey material are exchanged with the cations that come from the leachate, thus being released and transported in the pore water (Sect. 4).

The soluble ions give an idea of the composition of the substratum-pore water interface, which is highly related to the exchangeable cations in the soil by thermodynamic equilibrium. Knowing both is fundamental to describe the main processes that retard and attenuate contaminants (solutes) in soil and groundwater: cation exchange, adsorption, absorption and chemisorption. Because these processes cannot be separated in a natural system, they are usually grouped together as *sorption* and measured jointly by sorption isotherms. The isotherms are graphical models that represent the equilibrium distribution of solute mass between different phases: the so-called *partitioning*. This can be quantified by the constant partition/distribution coefficient ( $K_d$ ), which is the ratio of the concentrations of the solute in each phase at equilibrium, in this case, the quantity of the cation adsorbed per unit mass of solid to the quantity of the cation remaining dissolved per unit volume of solution. Following Freeze and Cherry (1979), the  $K_d$  of the representative cations of the leachate impact was graphically calculated by the slope of the fitted isotherm to the data of the concentrations in the solid phase (the minerals) vs. the concentrations in the liquid phase (the pore water) (Fig. 3). According to it, sorption of cations exists, increasing the concentration of the sorbed compound when the concentration of the dissolved one increases, which takes place in the shallow samples; i.e., those that are closest to the landfill leachate. Saturation of the sorption sites is not reached as only in the case of the Na<sup>+</sup> fitted with a Freundlich isotherm, a threshold can be foreseen for the range of samples studied in Fig. 3. Thus, as shown in this figure, the concentrations of these metals emitted by the leachate did not exceed the maximum load capacity of the material, which preferably sorbs K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>.



**Fig. 3.** Isotherms and partition/distribution coefficients ( $K_d$ ) for  $K^+$ ,  $Na^+$  and  $NH_4^+$  in the substratum samples labelled with the sample designation appointed in Table S2.

Assuming sections of linear partitioning, the  $K_d$  of the  $K^+$  during the initial stage of the sorption ( $25 \text{ L kg}^{-1}$ ) is larger than those of the  $NH_4^+$  and the  $Na^+$  ( $14 \text{ L kg}^{-1}$ ). As the number of sorbed cations increases, the  $K_d$  of the  $K^+$  and the  $NH_4^+$  become similar to each other and higher than that of the  $Na^+$  (Fig. 3). These high sorption affinities explain the high percentage decreases for the  $Sol\_NH_4^+$ ,  $Sol\_Na^+$  and  $Sol\_K^+$  mentioned above in a shallow substratum layer of 1.05–1.75 m.

The retardation factor ( $R$ ) describes the potential delay of the solute (the pollutant) with respect to the water velocity. Accordingly,  $R$  is defined as the ratio of the average velocity of the groundwater ( $V_w$ ) to the average velocity of the adsorbing contaminant ( $V_p$ ), through a control volume (Domenico and Schwartz, 1998:299 and EPA, 1999:2.17) (Eq. (4)).

$$R = \frac{V_w}{V_p} \quad (4)$$

Retention processes can play a major role in the fate and transport of cations in the subsurface. In such cases, the one-dimensional transport equation of advection-diffusion is expanded by adding a term representing the retention of solute by sorption reactions. The differential equation with respect to time developed to describe the linear partitioning is presented in Eq. (5) (Domenico and Schwartz, 1998:299).

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \left( 1 + \frac{1-n}{n} \rho_b K_d \right) \quad (5)$$

where  $D_x \frac{\partial^2 C}{\partial x^2}$  is the term that describes mass transport by diffusion,  $-V_x \frac{\partial C}{\partial x}$  is term that describes mass transport by advection,  $\frac{\partial C}{\partial t}$  denotes the manner in which solute mass is moved from one point to another by advection as modified by diffusion and retention in the one-dimensional transport equation, and  $\left( 1 + \frac{1-n}{n} \rho_b K_d \right)$  is the constant retardation factor  $R$  (dimensionless) for saturated flow (Freeze and Cherry, 1979). Particularly,  $D_x$  is the diffusion coefficient ( $\text{m}^2 \text{ s}^{-1}$ ),  $C$  is the concentration of the solute dissolved in the solution ( $\text{mg L}^{-1}$ ),  $x$  is the distance travelled by the solute from the inflow towards the flow direction (m),  $V_x$  is the pore



water linear velocity ( $\text{m s}^{-1}$ ),  $t$  is the time passed since the transport started (s),  $\frac{n}{1-n}$  is the volumetric soil water content or effective porosity ( $\theta$ , fraction, dimensionless),  $\rho_b$  is the bulk density of soil ( $\text{kg L}^{-1}$ ) and  $K_d$  is the partition/distribution coefficient discussed earlier ( $\text{L kg}^{-1}$ ).

Thus, the retardation factor decreases the values of the transport parameters  $D_x$  and  $V_x$  (Eq. (5)).

Combining and rearranging Eqs. (4) and (5) gives the formula (6) which is valid for linear sorption isotherms and is known as the retardation equation (Domenico and Schwartz, 1998:375).

$$R = \left(1 + \frac{1-n}{n} \rho_b K_d\right) = 1 + \frac{\rho_b}{\theta} K_d = \frac{V_w}{V_p} \quad (6)$$

When there is no sorption,  $K_d$  is zero and the velocities of the solute (contaminant) and the pore-water flow are the same (Eq. (6)). The mean coefficient of permeability at 0.4 m–depth measured in the triaxial permeability tests is  $3.9 \cdot 10^{-10} \text{ m s}^{-1}$ , being within the range of  $1 \cdot 10^{-11}$  –  $4.7 \cdot 10^{-9} \text{ m s}^{-1}$ , average values for clay materials (Domenico and Schwartz, 1998). Taking into account this and the average of  $\rho_d$  and  $\theta$  for these kind of clayey materials ( $1.67 \text{ kg L}^{-1}$  and  $0.358$ ), the retardation  $R$  in the intermediate stage of the sorption of  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$  in Fig. 3 is 52, 29 and 48, with an estimated speed of only the 2–3% of the water velocity; i.e.,  $(7.5, 0.13$  and  $8.2) \cdot 10^{-12} \text{ m s}^{-1}$ , respectively (Table 1).

**Table 1.** Retardation parameters and velocities of  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ .

	Retardation factor			% decrease of the $V_p$ as compared to the $V_w$ due to sorption retention			Velocity of the pollutant		
	$R = 1 + \rho_d / \theta \cdot K_d$			$100 - (1/R \cdot 100)$			$V_p = V_w / R$		
	E	I	L	E	I	L	E	I	L
$\text{K}^+$	118	52	29	99.1	98.1	96.6	$3.3\text{e}^{-12}$	$7.5\text{e}^{-12}$	$0.13\text{e}^{-12}$
$\text{Na}^+$	66	29	10	98.5	96.6	90.3	$5.9\text{e}^{-12}$	$0.13\text{e}^{-12}$	$0.38\text{e}^{-12}$
$\text{NH}_4^+$	66	48	34	98.5	97.9	97.0	$5.9\text{e}^{-12}$	$8.2\text{e}^{-12}$	$0.12\text{e}^{-12}$

$\rho_d$ , bulk density;  $\theta$ , effective porosity;  $K_d$ , partition/distribution coefficient; E, Early sorption stage in Fig. 3; I, Intermediate sorption stage in Fig. 3; L, Latter sorption stage in Fig.

3;  $V_p$ , velocity of the pollutant ( $\text{m s}^{-1}$ );  $V_w$ , average measured velocity of the pore-water flow ( $3.9 \cdot 10^{-10} \text{ m s}^{-1}$ );  $R$ , retardation factor.

Retention delays the appearance of pollutants in groundwater, in this case 90–99% compared to the pore water velocity (Table 1) and increases their migration time, thereby allowing more time for the chemicals to undergo degradation. This shows the relative importance of sorption processes to lessen the movement of solutes.

The main cations sorbed in the exchange sites vary depending on the depth. The  $\text{Ex\_Ca}^{2+}$  and  $\text{Ex\_Mg}^{2+}$  are naturally present in the substratum and diminish with the proximity to the landfill base, as they are exchanged by the  $\text{Ex\_NH}_4^+$ ,  $\text{Ex\_Na}^+$  and  $\text{Ex\_K}^+$ , which come from the leachate. This explains the duality in the profiles trends of the sorbed cations: the  $\text{Ex\_Ca}^{2+}$  and  $\text{Ex\_Mg}^{2+}$  increase with depth, while the  $\text{Ex\_NH}_4^+$ ,  $\text{Ex\_Na}^+$  and  $\text{Ex\_K}^+$  diminish (Fig. 2). The latter group decrease  $\approx 100\%$  in 1.05 m (B3), which is the same depth where the respective soluble cations are attenuated (Fig. 2), denoting again the strong relationship and equilibrium between the soluble ions concentrations in the pore water and the exchangeable cations on the mineral surface.

In order to be able to compare the aqueous-extracts data from the samples where the background levels of the leachate pollutants were reached, to the water quality for drinking use, the units of the first were referred to pore water and they were changed to suit the limits units given in  $\text{mg L}^{-1}$ . Accordingly, no background values of pH,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$  or  $\text{Cl}^-$  exceed the enforceable guidelines in the cores B1 and B3, whereas in the B2, 0.68–m-depth are not enough for attenuating the  $\text{NH}_4^+$  and the  $\text{Cl}^-$  (Table 2). As for the high background levels of the measured  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , it is an analytical artifact explained in the Sect. S5, not being reliable their comparison to the water limits. In addition, the intake of  $\text{Na}^+$  at those concentrations through drinking water is insignificant compared to the addition of salt (NaCl) to the food and harmless compare to other more hazardous species such as  $\text{NH}_4^+$ , that would notably suppose more severe consequences (Sect. S6).

**Table 2.** Guidelines for drinking water (WHO, EPA and Spain) and the measured values at the attenuation depth (mg L<sup>-1</sup>).

Parameters (mg L <sup>-1</sup> )	WHO (1971, 1983)		EPA	Spain	Measured background levels for pore water		
	MDL <sup>a</sup>	MAL <sup>b</sup>	816–F– 09–004	RD 140– 2003	1.75 m S6 B1	0.68 m S7 B2	1.05 m S8 B3
pH	7–8.5	9.2	6.5–8.5 <sup>c</sup>	6.5–9	8.4– 6.8	8.4	7.7
Na <sup>+</sup>	—	200	—	200	1 379	2 506	460
Ca <sup>2+</sup>	75	200	—	—	681	561	1 403
Mg <sup>2+</sup>	50	150	—	—	1	1	0.2
NH <sub>4</sub> <sup>+</sup>	—	—	—	0.5	n.d.	939	n.d.
Cl <sup>-</sup>	200	600	250 <sup>c</sup>	250	142	284	177
NO <sub>3</sub> <sup>-</sup>	45	—	10 <sup>d</sup>	50 <sup>e</sup>	n.d.	n.d.	n.d.
SO <sub>4</sub> <sup>2-</sup>	200	400	250 <sup>c</sup>	250	n.d.	n.d.	n.d.
F <sup>-</sup>	—	1.5	2.0 <sup>c</sup>	1.5	n.d.	n.d.	n.d.

TDS: total dissolved solids, —: not established, n.d.: not detected.

<sup>a</sup> Most-desirable limit. <sup>b</sup> Maximum-allowable limit.

<sup>c</sup> Non-enforceable guidelines: EPA recommends but does not require to comply them. Even so, some states may choose to adopt them as enforceable standards.

<sup>d</sup> Nitrite: 1 mg L<sup>-1</sup>, measured as nitrogen. <sup>e</sup> Nitrite: 0.5 mg L<sup>-1</sup>, measured as nitrogen.

Finally, the sodium adsorption ratio and the sodium percentage (%Na) calculated according to Karanth (1987) were used to assess the suitability of groundwater for irrigation. The whole set of samples show a *permissible* %Na for irrigation and the background levels fell under *good to excellent* sodium adsorption ratio (Table S5).

#### 4. Discussion

This section is structured as follows: First, the variability and characteristics of the leachate according to the climate, the landfill age, the pH or the mineralogy; along with the major effects of the leachate and the attenuation processes of the percolating species are explained in detail. Following, the migration of leachate components is compared to other studies about landfills located over different substrata and subjected to different technologies. In addition, the time-effect on the pollution front and the efficiency of the observed attenuation processes are discussed. In the end, relevant and reasonable criteria to protect the environment from MW landfill pollution are established.

The factors that most influence leachate chemical composition are climate (Kulikowska and Klimiuk, 2008; Mangimbulude et al., 2009) and landfill age (Kulikowska and Klimiuk, 2008; Nanny and Ratasuk, 2002; Owen and Manning, 1997; Renou et al., 2008; Salem et al., 2008; Shouliang et al., 2008; Statom et al., 2004). The studied area receives low rainfall, mostly in a short period of time during the winter (which has mild to cool temperatures); whereas in summer (warm to hot temperatures) no significant precipitation occurs for 4–6 months, except occasional thunderstorms. Dry periods and high temperatures, which are typical in Mediterranean climates as is the case here, produce such a high concentrated leachate that the leachate dilution by a storm is rapidly reversed a few hours after the rain stops (Lee et al., 2006; Tatsi and Zouboulis, 2002; Vadillo et al., 1999). Thus, the examined leachate is expected to have an elevated electrical conductivity, with high concentrations of major inorganic ions typical of leachates, such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  (Regadio et al., 2012). This is in concordance with the high  $\sigma$  in the substratum samples closest to the waste contact:  $(29.4 \pm 7.7) \cdot 10^2 \text{ mS m}^{-1}$  in terms of pore water while the normal values in natural freshwaters are between  $(0.1\text{--}2) \cdot 10^2 \text{ mS m}^{-1}$ . Regarding the landfill age, leachate pH and Eh increase with age, whereas COD, BOD and subsequently low-molecular-mass organic acids (LMMOAs) decrease quickly to low values in only five years (Fig. S7: Eq. (S1), Eq. (S2)). Ammonium decreases rapidly in the first 3–8 years up to still high concentrations that remain the same for decades (Belevi and Baccini, 1992). Dissolved inorganic salts ( $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) also decline with landfill age, but they are more influenced by the climate conditions (Kulikowska and Klimiuk, 2008; Mangimbulude et

al., 2009). Therefore, their decrease occurs over longer periods of time than do changes in COD, BOD or LMMA, as a result of the fluctuation of dry and wet seasons.

The BOD/COD ratio of a leachate is an indicator of the waste stabilization and thus of the landfill age, decreasing with time (Qasim and Chiang, 1994). High BOD/CODs mean high biodegradability of the present organic matter and low maturity of the leachate and the landfill. This corresponds to new landfills where the waste is in the initial degree of decomposition and the stabilization level is low: that is the aerobic-thermophile acetogenic stage. Conversely, small BOD/CODs represent a high oxidized state of the carbon from the organic matter which is less readily available as an energy source. This corresponds to leachates from landfills in an advanced stage of anaerobic methanogenesis; i.e., a high grade of decomposition and stabilization. BOD/COD ratios less than or equal to 0.1 are commonly considered to be from stabilized waste leachate (Sinan-Bilgili et al., 2012), although there is no widely accepted agreement on the BOD/COD values that separate each class of landfill age (Table 3). Here, the BOD/COD is 0.10, denoting a relatively stabilized leachate difficult to be further biologically degraded, which is consistent with the landfill age. The significant WSOC percentage decrease commented earlier, the BOD/COD = 0.1 and the higher WSOC in the shallow samples (2 000 mg L<sup>-1</sup>) compared to the leachate (703 mg L<sup>-1</sup>) prove that the attenuation of the organic matter by biodegradation, followed by the sorption in clays and iron-oxides complexes, are the driven natural attenuation processes, also confirmed by microscopy (Fig. S4).

440 **Table 3.** Dependency of BOD/COD ratios on leachate stabilization and thus on landfill age.

Reference	BOD/COD in <5 year-old landfills	BOD/COD in 5–10 year-old landfills	BOD/COD in >10 year-old landfills
Banar et al. (2006)	0.5	$0.2 < X < 0.5$	0.2
Chofqi et al. (2004)	0.85	$0.05 < X < 0.85$	0.05
Ehrig (1988)	>0.4	—	—
Kjeldsen et al. (2002)	—	—	<0.1
Renou et al. (2008)	>0.3	$0.1 < X < 0.3$	<0.1
Robinson (1995)	>0.7	—	—
SWANA (1997)	>0.5	$0.1 < X < 0.5$	<0.1
Taylor and Allen (2006)	>0.7	—	<<0.7

441

442 As for the leachate pH, it is presumably >7 due to the landfill age and the low presence of

443 LMMOAs because of the advanced organic-waste decomposition and the methanogenic stage

444 mentioned above. The alkaline pH is in concordance with the low metals contents in the

445 leachate (Table S3). Basic pH promotes metals/cations immobilization by mineral-formation

446 and sorption because it favours: (1) redox states of metals that precipitate as oxy-hydroxides,

447 carbonates or sulphides minerals and (2)  $H^+$  depletion with a consequent decrease in the cations

448 competition for being sorbed in negatively charged surfaces such as those of clays (Regadío et

449 al., 2013). Though MW are not toxic by themselves, their organic matter releases  $H^+$  during the

450 biodegradation in the acetogenic stage, making the leachate acidic. An acid leachate is highly

451 aggressive because it solubilizes many compounds, such as  $NH_3/NH_4^+$ , heavy metals, Fe,  $Cl^-$ ,

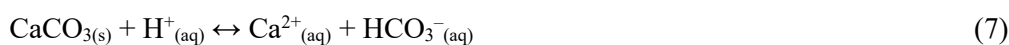
452  $SO_4^{2-}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  (some of which may form complexes with free volatile acids (Harmsen,

453 1983)) and it favours the mobility of dangerous substances such as metals and solvents (Taylor

454 and Allen, 2006). Only one substratum sample (S6, in B1) showed an acid pH, consistent with

its high values of inorganic and organic pollutants despite its great depth (1.75 m) (Fig. S6).

When  $H^+$  are present, calcite is dissolved, releasing  $Ca^{2+}$  and  $HCO_3^-$  (Eq. (7)):



The absence of calcite and the elevated  $Sol\_Ca^{2+}$  in the sample S6 (Table S4, Fig. 2.c) denotes the complete dissolution of calcite, an important source of  $HCO_3^-$  in methanogenic landfills, depleting the pH-buffer capacity of the carbonate system (Eq. (3)). This confirms the importance of calcite and its pH-buffering to keep a less-aggressive leachate and background-pollutants concentrations (Brun et al., 2002; Regadío et al., 2013) and to offer appropriate conditions for heavy metals to suffer natural attenuation processes such as redox, coprecipitation, sorption reactions and incorporation in the crystal structure (Hua et al., 2007; Mostbauer, 2003; Sanchez-Pastor et al., 2011; Tang et al., 2007; Yanful et al., 1988).

Regarding the major ions, although  $SO_4^{2-}$  was in the leachate above the drinking-water limits (Table S3, Table 2), it was not detected in the substratum samples. This anion is the sulphur species that normally appears dissolved in natural waters, though at much lesser quantities than in this leachate. In reducing environments rich in organic matter; anaerobic bacteria use electron acceptors to oxidize organic compounds, obtain energy and grow. These microorganisms use the electron acceptors according to the pH and in an orderly sequence from the most oxidized species to the least oxidized agent available (Christensen et al., 2000). The available oxygen is rapidly use up, creating an anoxic environment in leachates, which will progressively have lower and lower Eh ( $O_2 > NO_3^- > MnO_4^{2-} > Fe(OH)_3 > SO_4^{2-} > CO_2 > CH_4$ ). This matches with the observed Eh decrease as samples approached the leachate-pollution source (Fig. S5, Fig. S8). The leachate provided such reducing and organic-rich conditions, where the  $SO_4^{2-}$  (the leading electron acceptor after complete reduction of oxidized iron, manganese and nitrogen) would be consumed during the biological reduction half-reaction to  $HS^-$ , at the same time that the organic matter acting as electron donor would be degraded during the oxidation half-reaction, in bacteria redox reactions for obtaining energy. This agrees with the significant WSOC biodegradation observed before and the presence of pyrite (Table S4), and it would explain the  $SO_4^{2-}$  absence in the samples. Some discrepancies found in the

constructed pe-pH diagrams are discussed in the Sect. S7. The different redox zones in a transition in accordance with the thermodynamic principles were previously identified as essential attenuation processes in groundwater samples downgradient of a landfill by Bjerg et al. (1995).

As regards the  $\text{Cl}^-$ , its low amount below the water limits in all samples (Fig. 2) is contrary to its high content in the leachate (Table S3). This might be due to the relative high mobility of  $\text{Cl}^-$  through the top surface of the clayey soil supported by the effects of anion exclusion. Alkalinity anions dominate the shallow samples (Fig. 2) because they are the main byproducts of labile organics alteration. Thus, the alkalinity negative charges can be continuously renewed, counteracting the cationic species. In addition, the dominant clay mineral is the swelling smectite type and the dry density of the material increases from  $1.4 \cdot 10^3$  to  $1.7 \cdot 10^3 \text{ kg m}^{-3}$  in the first 0.05–0.10 m downwards. All this could contribute to the anion exclusion of  $\text{Cl}^-$  (Appelo and Wersin, 2007; Muttrinen et al., 2007; Wersin et al., 2004). In that event, the closely packed electrical double layers of smectite clay platelets in the dense material would repel the  $\text{Cl}^-$  in the leachate and act as a barrier that the  $\text{Cl}^-$  is not able to pass through, migrating laterally through the low density top clay surface layer. This is consistent with that the  $\text{Cl}^-$  in the leachate ( $\approx 7\,000 \text{ mg L}^{-1}$ ) was much higher than that in the samples S1; i.e., those immediately in contact with the landfill base ( $\approx 300 \text{ mg L}^{-1}$ ).

The recalculated leachate composition established  $\text{Na}^+$  and  $\text{K}^+$  as the dominant cations (Table S3). Conversely, the major cation in the shallow samples was the  $\text{NH}_4^+$ . This might be due to the analytical artifact explained in the Sect. S5: the new  $\text{Ca}^{2+}$  released from calcite dissolution during the preparation of aqueous extracts would have displaced the exchangeable cations with the lowest sorption affinities ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ), explaining their abundance in the pore water. Nevertheless, the  $\text{NH}_4^+$  content, both soluble and exchangeable, was remarkably high in this zone (Fig. 2.b), suggesting the importance of  $\text{NH}_4^+$  formation processes, such as further biodegradation of proteins and amino acids (Hutchings et al., 1998). This finding, together with other studies (Allen and Taylor, 2006; Belevi and Baccini, 1992; Buss et al., 2004; Chu et al., 1994; Hutchings et al., 1998; Nanny and Ratasuk, 2002; Pivato and Raga, 2006; Renou et al., 2008; Rowe et al., 1995; Shouliang et al., 2008; Tatsi and Zouboulis, 2002), corroborates that

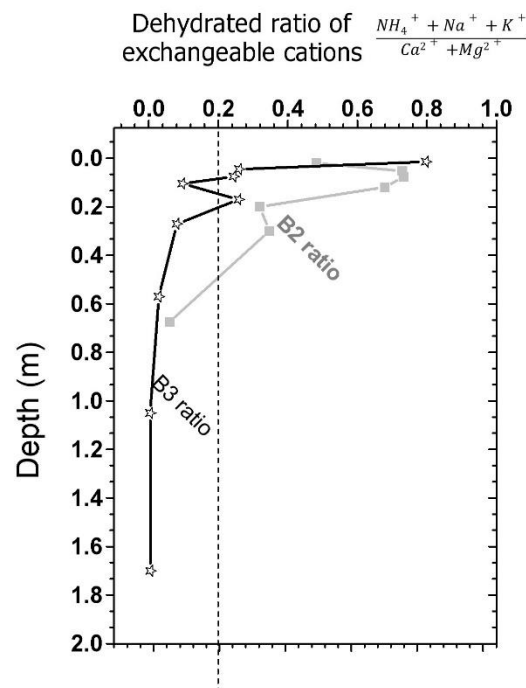


NH<sub>4</sub><sup>+</sup> formed under reducing conditions persists in constant, high concentrations for prolonged periods, contrary to the rest of non-conservative ions whose concentrations decrease quickly to low values with time (Kjeldsen et al., 2002; Kjeldsen and Christophersen, 2001). Despite this broad identification of NH<sub>4</sub><sup>+</sup> as the main leachate pollutant, no mechanism, other than aerobic landfilling, was found to degrade NH<sub>4</sub><sup>+</sup> in prior literature (Sinan-Bilgili et al., 2012). However, the present study showed that NH<sub>4</sub><sup>+</sup> was retained in 1.05–1.75 m by sorption without exceeding the maximum load capacity of the material and with calculated K<sub>d</sub> between 7 and 14 L kg<sup>-1</sup>, which implies a high specificity of the mineral surface for the solute and prevents it from traveling further (Fig. 2.b). The K<sub>d</sub> of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> are similar, which is consistent with the positive correlation between NH<sub>4</sub><sup>+</sup>, K<sup>+</sup> and salinity linked to K<sup>+</sup>–NH<sub>4</sub><sup>+</sup> exchange in smectitic/illitic materials under landfill sites, discovered by Manning and Hutcheon (2004).

Knowing that natural clay deposits can have heterogeneities, the calculated K<sub>d</sub> and R for the representative cations of the leachate pollution (Fig. 3 and Table 1) showed that diffusion and sorption are the dominant processes even in a fractured clay media, as also noted by Sharma and Dixit (2014). The present study supports the hypothesis that soils containing mainly smectite, followed by illite and calcite, are appropriate to remove large amounts of cationic pollutants and fix them by cations exchange, under similar physico and geochemical conditions. The deepest samples presented the exchangeable cations Ca<sup>2+</sup> and Mg<sup>2+</sup> that are released from the solution equilibrium of carbonates minerals and, therefore, naturally occupy the exchangeable sites. In contrast, the shallow samples contained the leachate major cations Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, which displaced the naturally-present exchangeable cations in the shallowest region, which is the most affected by the high-concentrated solution of leachate (Fig. 2). This explains the lower external S<sup>BET</sup>(N<sub>2</sub>) and smectite content in the shallowest samples compared to the underlying ones (Table S4), since smectite would partially collapse to an illite-like structure after the accommodation of monovalent cations in the exchangeable sites (Cuadros, 1997; Mooney et al., 1952).

The relationship between the total concentration of Ex\_NH<sub>4</sub><sup>+</sup> + Ex\_K<sup>+</sup> + Ex\_Na<sup>+</sup> and the concentration of Ca<sup>2+</sup> + Mg<sup>2+</sup>, sorbed in the substratum at different depths is represented in Fig. 4. to illustrate the aforementioned cation replacement. The subsequent displacement of Ca<sup>2+</sup> and

Mg<sup>2+</sup> to the solution during the cations exchange would be undertaken by the calcite-solubility equilibrium (Eq. (7)) and the abundant HCO<sub>3</sub><sup>-</sup> that comes from biodegradation (Fig. S7). This would produce precipitation of carbonate minerals (Eq. (7) displaced to the left) and the consequent decline in the porosity and hydraulic conductivity, in agreement with the positive relationship between calcite, sheet silicates and attenuation depths (Sect. 3).

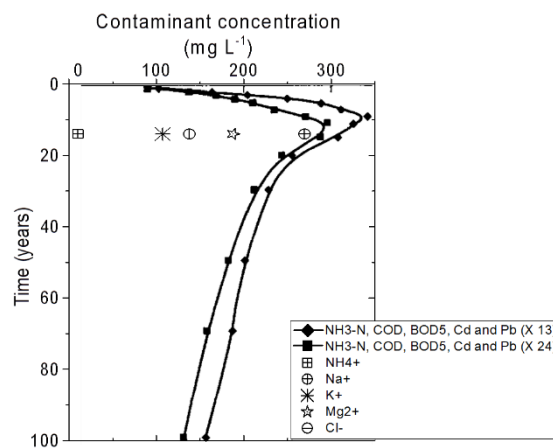


**Fig. 4.** Evolution of the ratio  $(\text{NH}_4^+ + \text{Na}^+ + \text{K}^+)/(\text{Ca}^{2+} + \text{Mg}^{2+})$  with depth.

The migration of leachate contaminants here is substantially shallower than the hundred metres in sandstone and sandy overburden materials determined by Butler et al. (2003), Christensen et al. (1994) or Williams (1999), which demonstrates the importance of mineralogy in making a natural substratum a proper attenuating layer for leachate pollutants. This is in concordance with the statistical results of seven boreholes from three landfills in Regadío et al. (2012) that shown that sheet silicates, external  $\text{S}^{\text{BET}}(\text{N}_2)$ , CEC and calcite are positively correlated with low attenuation depths. The present results of percentage decreases of leachate contaminants are comparable and, in some cases, better than those estimated for a clay:solidified-grouting-curtain (83–95% in Chen et al., 2005). Likewise, the substratum studied here had higher removal percentages than those from a landfill subjected to aeration with added

active sludge and with leachate-recirculation reactors (74–88% in Jun et al., 2007). Similarly, the WSOC decrease shown in the core B3 (94%) is higher than in the case of using leachate bioreactors described in Swati et al.(2007) (88%). This indicates that natural substrata can be as good for attenuating contaminants as some engineering barriers, and aerobic and reactors installations.

Particularly the retention of leachate pollutants in clayey substrata is time-sensitive as its soluble components decrease with time (Chen et al., 2005; Kjeldsen and Christophersen, 2001; Rowe et al., 2004). Thus, the pollutants concentrations through clays decrease mostly in the early stages (acetogenic and beginning of methanogenic stages) rather than in later stages, reaching a maximum value sometime after landfilling started ( $\approx 10$  years) and then weaken and drop gradually with time (Fig. 5, modified from Chen et al., 2005). In Fig. 5, the background concentrations of soluble-species from the sample S8 in the core B3 (which were below the water limits) in terms of pore water are depicted. This figure illustrates that the elimination of leachate-pollution risk in this substratum is time-lasting, as it is predicted to become less concentrated. The study presented here is all the more important given the lower depth of the sample S8 (1.05 m) and the higher leachate pollutants concentration (4150, 2150, 6920 mg L<sup>-1</sup>) compared to those used for the simulation of contaminant migration by Chen et al. in Fig. 5 (2 m and 2000 mg L<sup>-1</sup>).



**Fig. 5.** Evolution curves of leachate pollutants with time through a clay-solidified grouting curtain with cement:clay ratio of 1:3 and 2:4 (X13 and X24, respectively), modelled by Chen et al. (2005:170) and dots of the pore water values of soluble NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> measured

in the present study (S8 B3). (The figure was adjusted from Chen et al. (2005:170), Copyright 2005, co-published by Central South University of Technology and Springer).

Two more reasons confirm the efficiency of the attenuation. First, two  $\text{Na}^+$ ,  $\text{NH}_4^+$  or  $\text{K}^+$  ions remove one  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , thus, the number of sorbed sites is twice as high for the monovalent ions (pollutants) than for the divalent ones (naturally occurring), being  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  released half the ratio of the sorbed pollutants. This is supported by the earlier observation that the maximum sorption capacity of the solid material was not exceeded (Fig. 3). In addition, the cation exchange was proved to exhibit hysteresis; i.e. to be irreversible, when cations with different charge, as in this case, are exchanged. This is because the  $\text{NH}_4^+$  along with the  $\text{K}^+$  and, to a lesser extent the  $\text{Na}^+$ , cause the loss of interlayer water in smectites, decreasing the d-spacing of these minerals, which are partially collapsed to an illite-like structure (Thornton et al., 2001; Verburg and Baveye, 1994). Monovalent cations such as  $\text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ , dominate MW leachates (Regadio et al., 2012; Singh and Prasad, 2007) and divalent cations, specifically  $\text{Ca}^{2+}$ , are distributed worldwide and broadly presented in all kinds of substrata because of their greater charge, which makes their sorption affinities higher. For these reasons, the long-term retention of the cationic pollutants by exchange reactions is ensured. These findings are important since the  $\text{NH}_4^+$  constitutes a major threat, as seen in Sect. S6.

The relatively fast attenuation is also attributed to not covering the waste. Conventionally, capping and sealing the waste has been a widespread measure to avoid rainwater entry and thus, avoid additional infiltration that would generate more leachate drainage. The problem with this, especially with a fully impermeable water cover, is that the waste-degradation rate to inert states is strongly slowed down, the organic contaminants will persist for much longer and the period susceptible to leachate-pollution risk is extended. In addition, the peak value of pollutant concentrations in the evolution curves of Fig. 5 would possibly exceed the water limits and migrate gradually with time down along the *Y*-axis of Fig. 5, causing pollution even when pollution **sources** begin to decay or had decomposed completely, which would happen much later due to the inhibited biodegradation. Moreover, capping further enhances anaerobic-reducing conditions, which would mobilize the redox-sensitive metals and explain the increases of reduced

ammonia, manganese and iron with time (Statom et al., 2004). Sensing this, landfilling, at least for relatively dry climates, has led to waste moistening via leachate-recirculation and basal-irrigation systems, or/and aeration techniques to improve waste degradation and keep metal immobilized (Barber and Maris, 1984; Jun et al., 2007). The results presented here have showed that the same processes can be realized naturally, always operating under good practices in order not to produce mechanical dispersion of debris or undesired seepage of leachate towards unpolluted fresh surface waters (Oakley and Jimenez, 2012).

## 5. Conclusions

This study presents new relevant knowledge for adequately implementing the attenuation strategy jointly with the containment one. The results are useful for predicting the behaviour of leachate emissions in similar sites and therefore designing more efficient emergency plans. Good practices were also identified for a sustainable landfill waste management to prevent pollution of soil and water, in regions where containment barriers are beyond the reach of their incomes.

The (i) sharp decrease of the WSOC, the electrical conductivity and the ions from the leachate, comparable to engineering installations and reaching background levels below the maximum-permissible limits, the (ii) stabilization of wastes ( $BOD/COD = 0.10$ ) and the (iii) permanence-efficiency of the attenuation, suggest that natural attenuation processes in smectite, illite and calcite substrata can be suitable to ensure MW landfill safety in a short time and space. This supports the multi-barrier concept and the safeguard “site selection” of sanitary landfills. Adding to the technical barriers, choosing a site with an appropriate geological and hydrogeological situation ensures safety in the long term against possible emissions. The reason is that the two types of barriers operate independently, so both safeguards act as additional systems to prevent pollution. Some work related to the implementation of the system and its monitoring for many years, remains to be done. Similarly, further research with rainy climates is needed to find the value of water entrance which corresponds to the optimum equilibrium between (i) a rapid waste stabilization and a redox-metals immobilization, and (ii) a low leachate production, as the present study illustrates a low-rainfall Mediterranean climate.

**Supplementary material (S)**

Additional figures, tables and explanations related to this article are available online free of charge at <https://ars.els-cdn.com/content/image/1-s2.0-S0956053X15300829-mmc1.pdf>.

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## 649 REFERENCES

- 650 Allen, A., 2001. Containment landfills: the myth of sustainability. *Engineering Geology* 60, 3-19.
- 651 Allen, A., Taylor, R., 2006. Waste disposal and landfill: Control and protection, in: Schmoll, O., Howard, G.,  
652 Chilton, J., Chorus, I. (Eds.), *Protecting Groundwater for Health: Managing the Quality of Drinking-*  
653 *water Sources*, London, pp. 631-651.
- 654 APHA (American Public Health Association), 2012. *Standard Methods for the Examination of Water and*  
655 *Wastewater*. 22th Edition. 1.496 pp
- 656 Appelo, C.A.J., Wersin, P., 2007. Multicomponent diffusion modeling in clay systems with application to  
657 the diffusion of tritium, iodide, and sodium in opalinus clay. *Environmental Science & Technology*  
658 41, 5002-5007. DOI: 10.1021/es0629256
- 659 Banar, M., Ozkan, A., Kurkcuoglu, M., 2006. Characterization of the leachate in an urban landfill by  
660 physicochemical analysis and Solid Phase Microextraction-GC/MS. *Environmental Monitoring and*  
661 *Assessment* 121, 439-459.
- 662 Barber, C., Maris, P.J., 1984. Recirculation of leachate as a landfill management option - Benefits and  
663 operational problems. *Quarterly Journal of Engineering Geology* 17, 19-29. DOI:  
664 10.1144/gsl.qjeg.1984.017.01.05
- 665 Belevi, H., Baccini, P., 1992. Long-term leachate emissions from municipal solid waste landfills, in:  
666 Christensen, T.H., Cossu, R., Setegman, R. (Eds.), *Landfilling of waste: Leachate*. Elsevier,  
667 London, pp. 431-440.
- 668 Bish, D.L., Reynolds, R.C.J., 1997. Sample preparation for X-Ray Diffraction, in: Bish, D.L., Post, J.E.  
669 (Eds.), *Modern Powder Diffraction*. Mineralogical Society of America. *Reviews in Mineralogy*, pp.  
670 73-98.
- 671 Bjerg, P.L., Rugge, K., Pedersen, J.K., Christensen, T.H., 1995. Distribution of redox-sensitive  
672 groundwater quality parameters downgradient of a landfill (Grindsted, Denmark). *Environmental*  
673 *Science & Technology* 29, 1387-1394.
- 674 Brun, A., Engesgaard, P., Christensen, T.H., Rosbjerg, D., 2002. Modelling of transport and  
675 biogeochemical processes in pollution plumes: Vejen landfill, Denmark. *Journal of Hydrology* 256,  
676 228-247.
- 677 Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. *Journal of the*  
678 *American Chemical Society* 60, 309-319.
- 679 Brundtland Commission (1987). "Report of the World Commission on Environment and Development".  
680 United Nations.
- 681 Buss, S.E., Butler, A.P., Johnston, P.M., Sollars, C.J., Perry, R., 1995. Mechanisms of leakage through  
682 synthetic landfill liner materials. *Journal of the Chartered Institution of Water and Environmental*  
683 *Management* 9, 353-359.

684 Buss, S.R., Herbert, A.W., Morgan, P., Thornton, S.F., Smith, J.W.N., 2004. A review of ammonium  
685 attenuation in soil and groundwater. *Quarterly Journal of Engineering Geology and Hydrogeology*  
686 37, 347-359. DOI: 10.1144/1470-9236/04-005

687 Butler, A.P., Brook, C., Godley, A., Lewin, K., Young, C.P., 2003. Attenuation of landfill leachate in  
688 unsaturated sandstone, in: Christensen, T.H., Cossu, R., Stegmann, R. (Eds.), 9<sup>th</sup> International  
689 Landfill Symposium. Environmental Sanitary Engineering Centre (CISA) Cagliari (Sardinia).

690 Cobeña, J.C., Cuevas, J., Martín, M., Ramírez, S., Vigil, R., Leguey, S., 1999. Estudio de la mineralogía y  
691 microestructura de una bentonita compactada. Efectos de calentamiento e hidratación. *Boletín de*  
692 *la Sociedad Española de Mineralogía* 22, 235–247.

693 Cuadros, J., 1997. Interlayer cation effects on the hydration state of smectite. *American Journal of Science*  
694 297, 829-841.

695 Cuevas, J., Ruiz, A.I., de Soto, I.S., Sevilla, M.T., Procopio, J.R., da Silva, P., Gismera, M.J., Regadío, M.,  
696 Jiménez, N.S., Rastroero, M.R., Leguey, S., 2012. The performance of natural clay as a barrier to  
697 the diffusion of municipal solid waste landfill leachates. *Journal of Environmental Management* 95,  
698 S175-S181. DOI: 10.1016/j.jenvman.2011.02.014

699 Czurda, K., 2006. Clay liners and waste disposal, in: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.),  
700 *Handbook of Clay Science*. Elsevier Ltd., pp. 693-716.

701 Chen, Y.G., Zhang, K.N., Huang, C.B., 2005. Analysis on contaminants transport process through clay-  
702 solidified grouting curtain in MSW landfills. *Journal of Central South University of Technology* 12,  
703 168-172. DOI: 10.1007/s11771-005-0393-2

704 Chofqi, A., Younsi, A., Lhadi, E.K., Mania, J., Mudry, J., Veron, A., 2004. Environmental impact of an  
705 urban landfill on a coastal aquifer (El Jadida, Morocco). *Journal of African Earth Sciences* 39, 509-  
706 516.

707 Christensen, T.H., Bjerg, P.L., Banwart, S.A., Jakobsen, R., Heron, G., Albrechtsen, H.-J., 2000.  
708 Characterization of redox conditions in groundwater contaminant plumes. *Journal of Contaminant*  
709 *Hydrology* 45, Issues 3–4, 165–241. DOI:10.1016/S0169-7722(00)00109-1).

710 Christensen, T.H., Kjeldsen, P., Albrechtsen, H.J., Heron, G., Nielsen, P.H., Bjerg, P.L., Holm, P.E., 1994.  
711 Attenuation of landfill leachate pollutants in aquifers. *Critical Reviews in Environmental Science and*  
712 *Technology* 24, 119--202.

713 Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.J.,  
714 Heron, C., 2001. Biogeochemistry of landfill leachate plumes. *Applied Geochemistry* 16, 659-718.

715 Chu, L.M., Cheung, K.C., Wong, M.H., 1994. Variations in the chemical-properties of landfill leachate.  
716 *Environmental Management* 18, 105-117.

717 Domenico, P. A., Schwartz, F. W., 1998. *Physical and Chemical Hydrogeology*, (2nd edition): John Wiley  
718 and Sons, New York, 506. EEA (European Environment Agency), 2010. *The European environment state*



719 and outlook 2010 - Material resources and waste. Publications Office of the European Union, 2010,  
720 Copenhagen.

721 EPA, Environmental Protection Agency of United States, 2007. EPA Guidelines-Environmental  
722 management of landfill facilities (mucipal solid waste and commercial and industrial general waste).  
723 Environment Protection Authority.

724 EPA, Environmental protection agency, 1999. Understanding variation in partition coefficient, Kd, values.  
725 Volume I: The Kd Model, Methods of Measurement, and Application of Chemical Reaction Codes.  
726 EPA 402-R-99-004A. 212.

727 EPA, Environmental Protection Agency of United States, 2010. Municipal Solid Waste (MSW) in the United  
728 States: Facts and Figures. EPA530-R-13-001.

729 Ehrig, H.J., 1988. Water and element balances of Landfills, in: Baccini, P. (Ed.), The landfill. Ed., Springer,  
730 Verlag, Berlin, Germany, p. 83.

731 Eid, H.T., 2011. Shear strength of geosynthetic composite systems for design of landfill liner and cover  
732 slopes. *Geotextiles and Geomembranes* 29, 335-344. DOI: 10.1016/j.geotexmem.2010.11.005

733 Frascari, D., Bronzini, F., Giordano, G., Tedioli, G., Nocentini, A., 2004. Long-term characterization, lagoon  
734 treatment and migration potential of landfill leachate: a case study in an active Italian landfill.  
735 *Chemosphere* 54, 335-343. DOI: 10.1016/j.chemosphere.2003.08.013

736 Freeze, A.R., Cherry, J.A., 1979. Groundwater. Prentice Hall, Englewood Cliffs, NJ. 604 pp.

737 Ganigue, R., Lopez, H., Balaguer, M.D., Colprim, J., 2007. Partial ammonium oxidation to nitrite of high  
738 ammonium content urban landfill leachates. *Water Research* 41, 3317-3326.

739 Geological Society of London, 2006. The composition of clays, *Engineering Geology Special Publications*,  
740 pp. 13-27. DOI: 10.1144/GSL.ENG.2006.021.01.02

741 Goodall, D.C., Quigley, R.M., 1977. Pollutant migration from two sanitary landfill sites near Sarnia, Ontario.  
742 223-236.

743 Harmsen, J., 1983. Identification of organic compounds in leachate from a waste tip. *Water research*.

744 Hoeks, J., Glas, H., Hofkamp, J., Ryhiner, A.H., 1987. Bentonite liners for isolation of waste-disposal sites.  
745 *Waste Management & Research* 5, 93-105. DOI: 10.1177/0734242x8700500113

746 Hogland, W., Hogland, M., Marques, M., 2011. Enhanced landfill mining: material recovery, energy  
747 utilization and economics in the EU (Directive) perspective, *International Academic Symposium on*  
748 *Enhanced Landfill Mining*, Houthalen-Helchteren, Belgium, pp. 233-247.

749 Hua, B., Deng, B.L., Thornton, E.C., Yang, J., Amonette, J.E., 2007. Incorporation of chromate into  
750 calcium carbonate structure during coprecipitation. *Water Air and Soil Pollution* 179, 381-390. DOI:  
751 10.1007/s11270-006-9242-7

752 Hutchings, J.J., Hammel, J.E., Osiensky, J.L., 1998. Nitrogen leaching from unlined cull-onion landfills.  
753 *Journal of Environmental Quality* 27, 1254-1260.

754 Jun, D., Zhao, Y.S., Henry, R.K., Mei, H., 2007. Impacts of aeration and active sludge addition on leachate  
755 recirculation bioreactor. *J. Hazard. Mater.* 147, 240-248. DOI: 10.1016/j.jhazmat.2007.01.001

756 Karanth, K.R., 1987. *Groundwater Assessment, Development and Management*. Tata McGraw Hill, New  
757 Delhi.

758 King, K.S., Quigley, R.M., Fernandez, F., Reades, D.W., Bacopoulos, A., 1993. Hydraulic conductivity and  
759 diffusion monitoring of the Keele Valley landfill liner, Maple, Ontario. *Canadian Geotechnical*  
760 *Journal* 30, 124-134.

761 Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., Christensen, T.H., 2002. Present and long-  
762 term composition of MSW landfill leachate: A review. *Critical Reviews in Environmental Science*  
763 *and Technology* 32, 297-336. DOI: 10.1080/10643380290813462

764 Kjeldsen, P., Christophersen, M., 2001. Composition of leachate from old landfills in Denmark. *Waste*  
765 *Management & Research* 19, 249-256.

766 Knobeloch, L., Salna, B., Hogan, A., Postle, J., Anderson, H., 2000. Blue babies and nitrate-contaminated  
767 well water. *Environ. Health Perspect.* 108, 675-678. DOI: 10.2307/3434890

768 Koutsopoulou, E., Papoulis, D., Tsois-Katagas, P., Kornaros, M., 2010. Clay minerals used in sanitary  
769 landfills for the retention of organic and inorganic pollutants. *Applied Clay Science* 49, 372-382.  
770 DOI: 10.1016/j.clay.2010.05.004

771 Kulikowska, D., Klimiuk, E., 2008. The effect of landfill age on municipal leachate composition.  
772 *Bioresource Technology* 99, 5981-5985.

773 Lake, C.B., Rowe, R.K., 2005. The 14-year performance of a Compacted Clay Liner used as part of a  
774 composite liner system for a leachate lagoon. *Geotechnical and Geological Engineering* 23, 657-  
775 678.

776 Lee, J.Y., Cheon, J.Y., Kwon, H.P., Yoon, H.S., Lee, S.S., Kim, J.H., Park, J.K., Kim, C.G., 2006.  
777 Attenuation of landfill leachate at two uncontrolled landfills. *Environmental Geology* 51, 581-593.

778 Lee, G.F., Jones-Lee, A., 2009. Comments on 'Assessment of the Performance of Engineered Waste  
779 Containment Barriers'. 1-10.

780 MAPA (Ministerio de Agricultura, Pesca y Alimentación, 1994. *Métodos Oficiales de Análisis*, Madrid.

781 Mangimbulude, J.C., van Breukelen, B.M., Krave, A.S., van Straalen, N.M., Roling, W.F.M., 2009.  
782 Seasonal dynamics in leachate hydrochemistry and natural attenuation in surface run-off water  
783 from a tropical landfill. *Waste Management* 29, 829-838. DOI: 10.1016/j.wasman.2008.06.020

784 Manning, D.A.C., Hutcheon, I.E., 2004. Distribution and mineralogical controls on ammonium in deep  
785 groundwaters. *Applied Geochemistry* 19, 1495-1503. DOI: 10.1016/j.apgeochem.2004.01.019

786 Marzougui, A., Ben Mammou, A., 2006. Impacts of the dumping site on the environment: Case of the  
787 Henchir El Yahoudia Site, Tunis, Tunisia. *Comptes Rendus Geoscience* 338, 1176-1183. DOI:  
788 10.1016/j.crte.2006.09.020

789 McIntyre, D., Loveday, J., 1974. Bulk density, Methods for analysis of irrigated soils. Commonw. Bur. Soils  
790 Tech. Commun, pp. 38-42.

791 Mooney, R.W., Keenan, A.G., Wood, L.A., 1952. Adsorption of water vapor by montmorillonite. 1. Heat of  
792 desorption and application of BET theory. Journal of the American Chemical Society 74, 1367-  
793 1371. DOI: 10.1021/ja01126a001

794 Moore, D.M., Reynolds Jr, R.C., 1997. X - Ray Diffraction and the identification and analysis of clay  
795 minerals. Oxford University Press.

796 Mostbauer, P., 2003. Criteria selection for landfills: do we need a limitation on inorganic total content?  
797 Waste Management 23, 547-554. DOI: 10.1016/s0956-053x(03)00028-x

798 Munro, I.R.P., MacQuarrie, K.T.B., Valsangkar, A.J., Kan, K.T., 1997. Migration of landfill leachate into a  
799 shallow clayey till in southern New Brunswick: A field and modelling investigation. Canadian  
800 Geotechnical Journal 34, 204-219.

801 Muttrinen, A., Karnland, O., Lehtikainen, J., 2007. Effect of homogenization on the microstructure and  
802 exclusion of chloride in compacted bentonite. Physics and Chemistry of the Earth 32, 485-490. DOI:  
803 10.1016/j.pce.2006.02.058

804 Nanny, M.A., Ratasuk, N., 2002. Characterization and comparison of hydrophobic neutral and hydrophobic  
805 acid dissolved organic carbon isolated from three municipal landfill leachates. Water Research 36,  
806 1572-1584.

807 Oakley, S.M., Jimenez, R., 2012. Sustainable sanitary landfills for neglected small cities in developing  
808 countries: the semi-mechanized trench method from Villanueva, Honduras. Waste Management 32,  
809 2535-51. DOI: 10.1016/j.wasman.2012.07.030.

810 Owen, J.A., Manning, D.A.C., 1997. Silica in landfill leachates: Implications for clay mineral stabilities.  
811 Applied Geochemistry 12, 267-280. DOI: 10.1016/s0883-2927(96)00069-8

812 Pivato, A., Raga, R., 2006. Tests for the evaluation of ammonium attenuation in MSW landfill leachate by  
813 adsorption into bentonite in a landfill liner. Waste Management 26, 123-132.

814 Potter, H.A.B., Yong, R.N., 1993. Waste disposal by landfill in Britain: problems, solutions and the way  
815 forward, in: Sarsby, R.W. (Ed.), Waste Disposal by Landfill. Balkema, Rotterdam, pp. 167-173.

816 Primo, V., 2001, DRXWIN® vs 2.2.56, A Graphical and analytical tool for powder XRD Patterns.

817 Proyecto de Decreto, 2012, por el que se aprueba el Reglamento de Suelos Contaminados, Comunidad  
818 de Andalucía. Andalucía regional legislation.

819 Qasim, S.R., Chiang, W., 1994. Sanitary Landfill Leachate: Generation, Control and Treatment.  
820 Technomic Publishing Company, Lancaster, Pennsylvania.

821 Regadio, M., de Soto, I.S., Rodriguez-Rastrero, M., Ruiz, A.I., Gismera, M.J., Cuevas, J., 2013. Processes  
822 and impacts of acid discharges on a natural substratum under a landfill. Science of the Total  
823 Environment 463-464, 1049–1059. DOI: 10.1016/j.scitotenv.2013.06.047

824 Regadío, M., Ruiz, A.I., de Soto, I.S., Rodríguez Rastrero, M., Sánchez, N., Gismera, M.J., Sevilla, M.T.,  
825 da Silva, P., Rodríguez Procopio, J., Cuevas, J., 2012. Pollution profiles and physicochemical  
826 parameters in old uncontrolled landfills. *Waste Management* 32, 482-497. DOI:  
827 10.1016/j.wasman.2011.11.008

828 Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., Moulin, P., 2008. Landfill leachate treatment:  
829 Review and opportunity. *J. Hazard. Mater.* 150, 468-493.

830 Rhoades, J.D., 1982. Cation exchange capacity, in: Miller, R.H., Keeney, D.R. (Eds.), *Methods of soil*  
831 *analysis*. American Society of Agronomy, Madison, pp. 149-157.

832 Ritzkowski, M., Heyer, K.U., Stegmann, R., 2006. Fundamental processes and implications during in situ  
833 aeration of old landfills. *Waste Management* 26, 356-372. DOI: 10.1016/j.wasman.2005.11.009

834 Robinson, H.D., 1995. The technical aspects of controlled waste management. A review of the  
835 composition of leachates from domestic wastes in landfill sites. *Waste Science and Research*,  
836 Aspinwall & Company, Ltd., London, UK.

837 Rogel, J.M., Cuevas, J., Martínez, J.M., Carrera, J. (2010). Study of pollutants diffusion in urban landfills  
838 barriers and its evolution over time. I+D+i Final Project Report - A 113/2007/03-02.6. Ministry of the  
839 Environment. 417 pp. In Spanish

840 Rowe, R.K., 1994. Design options for hydraulic control of leachate  
841 diffusion, in: Christensen, T.H., Cossu, R., Stegmann, R. (Eds.), *Landfilling of Waste: Barriers*. E.  
842 and F.N. Spon, London, pp. 101-113.

842 Rowe, R.K., Quigley, R.M., Brachman, R.W.I., Booker, J.R., 2004. *Barrier Systems for Waste Disposal*  
843 *Facilities*. Taylor & Francis, London.

844 Rowe, R.K., Quigley, R.M., R., B.J., 1995. *Clayey barrier systems for waste disposal facilities*. Spon Press,  
845 Abingdon, Oxon.

846 Rowe, R.K., Sangam, H.P., 2002. Durability of HDPE geomembranes. *Geotextiles and Geomembranes*  
847 20, 77-95. DOI: 10.1016/s0266-1144(02)00005-5

848 Ruiz, A.I., Fernández, R., Jiménez, N.S., Rastrero, M.R., Regadío, M., de Soto, I.S., Cuevas, J., 2012.  
849 Improvement of attenuation functions of a clayey sandstone for landfill leachate containment by  
850 bentonite addition. *Science of the Total Environment* 419, 81–89.

851 Salem, Z., Hamouri, K., Djemaa, R., Allia, K., 2008. Evaluation of landfill leachate pollution and treatment.  
852 *Desalination* 220, 108-114.

853 Sanchez-Pastor, N., Gigler, A.M., Cruz, J.A., Park, S.H., Jordan, G., Fernandez-Diaz, L., 2011. Growth of  
854 calcium carbonate in the presence of Cr(VI). *Crystal Growth & Design* 11, 3081-3089. DOI:  
855 10.1021/cg200357c

856 Sharma, P.K., Dixit, U., 2014. Contaminant transport through fractured-porous media: An experimental  
857 study. *Journal of Hydro-Environment Research* 8, 223-233. DOI: 10.1016/j.jher.2013.08.003

858 Shouliang, H., Beidou, X., Haichan, Y., Liansheng, H., Shilei, F., Hongliang, L., 2008. Characteristics of  
859 dissolved organic matter (DOM) in leachate with different landfill ages. *Journal of Environmental*  
860 *Sciences-China* 20, 492-498.

861 Sinan-Bilgili, M., Top, S., Sekman, E., Varank, G., Demir, A., 2012. Aerobic Landfill Application in  
862 Developing Countries: A Case Study.

863 Singh, S., Prasad, A., 2007. Effects of chemicals on Compacted Clay Liner. *EJGE* 12, 1-15.

864 Statom, R.A., Thyne, G.D., McCray, J.E., 2004. Temporal changes in leachate chemistry of a municipal  
865 solid waste landfill cell in Florida, USA. *Environmental Geology* 45, 982-991.

866 Surmann, R., Pierson, P., Cottour, F., 1995. Geomembrane liner performance and long term durability, in:  
867 Christensen, T.H., Cossu, R., Stegmann, R. (Eds.), 5th International Landfill Symposium.  
868 Environmental Sanitary Engineering Centre (CISA), Cagliari (Sardinia), pp. 405-414.

869 SWANA, 1997. Leachate generation, collection and treatment at municipal solid waste disposal facilities.  
870 Publication No. GR-D 0535, Solid waste association of North America, Silver Spring, Maryland.

871 Swati, M., Karthikeyan, O.P., Joseph, K., Nagendran, R., 2007. Landfill bioreactor: A biotechnological  
872 solution for waste management. *Journal of Scientific & Industrial Research* 66, 670-674.

873 Tang, Y.Z., Elzinga, E.J., Lee, Y.J., Reeder, R.J., 2007. Coprecipitation of chromate with calcite: Batch  
874 experiments and X-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta* 71, 1480-  
875 1493. DOI: 10.1016/j.gca.2006.12.010

876 Tatsi, A.A., Zouboulis, A.I., 2002. A field investigation of the quantity and quality of leachate from a  
877 municipal solid waste landfill in a Mediterranean climate (Thessaloniki, Greece). *Advances in*  
878 *Environmental Research* 6, 207-219.

879 Taylor, R., Allen, A., 2006. Waste disposal and landfill: information needs, in: Schmoll, O., Howard, G.,  
880 Chilton, J., Chorus, I. (Eds.), *Protecting Groundwater for Health: Managing the Quality of Drinking-*  
881 *water Sources*. World Health Organization, IWA Publishing London, pp. 339-362.

882 Thomas, G.W., 1982. Exchangeable cations, in: Miller, R.H., Keeney, D.R. (Eds.), *Methods of Soil*  
883 *Analysis*, 2nd ed. American Society of Agronomy, Madison.

884 Thornton, S.F., Lerner, D.N., Tellam, J.H., 2001. Attenuation of landfill leachate by clay liner materials in  
885 laboratory columns: 2. Behaviour of inorganic contaminants. *Waste Management & Research* 19,  
886 70-88.

887 Vadillo, I., Carrasco, F., Andreo, B., García de Torres, A., Bosch, C., 1999. Chemical composition of  
888 landfill leachate in a karst area with a Mediterranean climate (Marbella, southern Spain).  
889 *Environmental Geology* 37, 326-332.

890 Verburg, K., Baveye, P., 1994. Hysteresis in the binary exchange of cations on 2/1 clay-minerals - A  
891 critical-review. *Clays and Clay Minerals* 42, 207-220. DOI: 10.1346/ccmn.1994.0420211

- Wersin, P., Curti, E., Appelo, C.A.J., 2004. Modelling bentonite-water interactions at high solid/liquid ratios: swelling and diffuse double layer effects. *Applied Clay Science* 26, 249-257. DOI: 10.1016/j.clay.2003.12.010
- Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Gordon, E.K., Wilson, J.T., Wilson, B.H., Kampbell, D.H., EPA/600/R-98/128, 1998. Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water. US Environmental Protection Agency.
- Williams, G.M., 1999. Natural Attenuation of contaminants in a lacustrine sand aquifer at Villa Farm, UK, in: Christensen, T.H., Cossu, R., Stegmann, R. (Eds.), 7<sup>th</sup> International Landfill Symposium. Environmental Sanitary Engineering Centre (CISA), Cagliari (Sardinia), pp. 229-236.
- Xie, H.J., Chen, Y.M., Zhan, L.T., Chen, R.P., Tang, X.W., Chen, R.H., Ke, H., 2009. Investigation of migration of pollutant at the base of Suzhou Qizishan landfill without a liner system. *Journal of Zhejiang University-Science A* 10, 439-449. DOI: 10.1631/jzus.A0820299
- Yanful, E.K., Quigley, R.M., Nesbitt, H.W., 1988. Heavy metal migration at a landfill site, Sarnia, Ontario, Canada—2: metal partitioning and geotechnical implications. *Applied Geochemistry* 3, 623-629.
- Zhan, T.L.T., Guan, C., Xie, H.J., Chen, Y.M., 2014. Vertical migration of leachate pollutants in clayey soils beneath an uncontrolled landfill at Huainan, China: a field and theoretical investigation. *Science of the Total Environment*. DOI: 10.1016/j.scitotenv.2013.09.081

#### Inserted figures and tables from Supporting Information:

- Fig. S1. MW generation rates
- Fig. S2. Flow chart of the analytical procedures
- Fig. S3. dry density
- Fig. S4. Thin-section photos
- Fig. S5. pH, redox potential (Eh) and moisture
- Fig. S6. WSOC, WSIC, EC
- Fig. S7. alkalinity vs. WSIC
- Fig. S8. Eh vs. pH
- Fig. S9. pe–pH diagrams
- Table S1
- Table S2. Waste thicknesses
- Table S3. Chemical analysis of the landfill leachate
- Table S4. Semi-quantitative mineralogical
- Table S5. SAR