

Mobility of 4-nonylphenol and di(2-ethylhexyl) phthalate in three agricultural soils irrigated with untreated wastewater

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ABSTRACT

Agricultural irrigation using raw wastewater is a popular practice in developing countries. However, as endocrine disrupting chemicals have been found in this water, the potential pollution of soil and water sources has become a source of concern. Such pollutants may be removed during the passage of wastewater through the soil by degradation and/or sorption. In this study the sorption and mobility of bis-2-ethyl(hexyl)phthalate (DEHP) and 4-nonylphenol (4-NP) in three different soils (Leptosol, Phaeozem and Vertisol) was compared. The distribution coefficients showed that DEHP is rapidly sorbed onto the three tested soils (K_d between 1.8×10^4 and 4.2×10^4 L/kg), while sorption of 4-NP (K_d between 15 and 80 L/kg) was weaker. In batch experiments the soil sorption capacity observed was as follows: Vertisol > Phaeozem > Leptosol for both compounds. However, in column experiments the retardation factor (R_F) for 4-NP was higher than for the DEHP in the three soils. This suggests the possible migration of DEHP through the soil via colloids. The column results were found consistent with those observed in the field. It was concluded that the risk of groundwater contamination is higher for Leptosol soil than for Phaeozem and Vertisol soils and that DEHP can reach the aquifer prior to 4-NP.

Key words | endocrine disrupting chemicals, organic matter, retardation factor, sorption

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INTRODUCTION

In the last two decades, the occurrence of pharmaceutically active substances, personal care products, surfactants, plasticizers and other xenobiotics has been reported in aquatic systems around the world (Santos *et al.* 2010; Fatta-Kassinos *et al.* 2011). These compounds are regularly detected at levels of ng/L to µg/L, and thus they are known as micropollutants. Within this group of pollutants, the plasticizer di(2-ethylhexyl)phthalate (DEHP) and the surfactant metabolite 4-nonylphenol (4-NP) stand out, as they are normally found in raw and treated wastewater as well as soils, at concentrations that easily exceed those of other micropollutants (Vogelsang *et al.* 2006; Cai *et al.* 2008). The presence of both compounds has been observed in water streams and groundwater used for human consumption (Brossa *et al.* 2005; Chávez *et al.* 2011), representing a potential health risk for people who consume this water. It is well known that endocrine disruption is the major effect caused by exposure to

these compounds through the consumption of polluted water (Hausser *et al.* 2007). Although 4-NP and DEHP have a lower potential for endocrine disruption than natural and synthetic hormones (Petrovic *et al.* 2004), their ubiquity and high concentrations in water are the origin of concern with respect to their effects.

To remove the micropollutants from wastewater, membrane and advanced oxidation processes have shown efficiencies above 90% (Liu *et al.* 2009). However, in developing countries where wastewater treatment is almost non-existent, raw wastewater, containing a complex mixture of such micropollutants is frequently disposed of in the soil as irrigation water. In this context, the natural attenuation processes, such as sorption and biodegradation are responsible for the removal of these compounds. Knowing the fate of micropollutants during irrigation with non-treated wastewater is important because there are at least 500 million

hectares irrigated in this way around the world (Jiménez & Asano 2008).

Sorption is an important removal mechanism for compounds that are slowly biodegradable (such as DEHP). In sorption, the physical and chemical properties of the micropollutants, the soil and the liquid phase determine the extent to which the compounds are retained by the soil. There are differences in the physical and chemical properties of DEHP and 4-NP that affect their environmental fate. For instance, DEHP is more hydrophobic than 4-NP (log K_{ow} of 7.5 and 4.48, respectively) and therefore it is more likely for the former to be retained by the soil organic matter (SOM), while 4-NP remains in the liquid phase and thus may potentially pollute groundwater. Furthermore, as the group of emerging pollutants is broad, it is quite possible to find compounds displaying similar physical and chemical properties. Because of this, it would be possible to extrapolate the results obtained in this study to other non-polar compounds, in the case of DEHP, and to other polyethoxylated nonylphenols in the case of 4-NP.

The aim of this work is to better understand the retention and mobility processes of 4-NP and DEHP in three different agricultural soils from an area where untreated wastewater is used for irrigation by using batch sorption and column displacement experiments.

METHODOLOGY

In order to understand the retention and mobility of DEHP and 4-NP, batch and column tests were performed and the results compared.

Soil sampling and characterization

Three soil types were selected for the study: Vertisol, Phaeozem and Leptosol. The soils were collected from the same plot in order to ensure that they had been exposed to the same agricultural practices and in this way the experimental behavior observed could be related only to the differences in the soils' physical and chemical characteristics. To collect the soils, the 3 cm organic layer was removed. Samples were taken from the Ap horizon (0–18 cm), using a stainless steel trowel. Samples were then placed in pre-cleaned glass bottles, covered with aluminum foil to avoid photodegradation, and stored at 4 °C. At the laboratory, the soil samples were air-dried and passed through a 2 mm metallic sieve. Prior to the experimental tests, the soils were sterilized using gamma radiation, at a dose of 25 kGy over 5.2 h.

Soil sterilization was confirmed by testing the total concentration of aerobic bacteria, actinomycetes and fungi after gamma irradiation. Each soil was characterized in terms of the parameters shown in Table 1 by using standardized methods (Sparks et al. 1996).

Batch sorption experiments

The sorption tests were conducted for DEHP and 4-NP separately, according to the OECD guideline No. 106 (OECD 2000). Ten grams of soil were accurately weighed in glass Erlenmeyer flasks, then 50 mL of 10 mmol/L CaCl₂ solution were applied (soil/solution ratio: 1:5). The flasks were then shaken at 150 rpm for 24 h at 25 °C. Next, the DEHP or the 4-NP was added to achieve the six tested concentrations (200, 500, 1,000, 1,500, 2,000 and 3,000 µg/L). The soil/water mixture was again agitated under the above mentioned conditions. After 24 h of agitation, 10 mL of solution were withdrawn and centrifuged at 1,800 rpm for 5 min. The supernatants were stored at 4 °C prior to chromatographic analysis. All the tests were carried out in triplicate. Blanks without the compounds' addition and with no soil were run in parallel to determine the possible release of the micropollutants from the soil as well as their possible sorption onto the glass walls of the flasks.

The distribution coefficient K_d (L/kg) and the distribution coefficient normalized to the soil organic carbon content, K_{oc} (L/kg) were determined using Equations (1) and (2):

$$q_{eq} = K_d C_{eq} \quad (1)$$

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2)$$

where C_{eq} : compound concentration (mg/L) in the liquid phase once equilibrium is reached, q_{eq} : compound

Table 1 | Physical and chemical characteristics of soils

Parameter	Vertisol	Leptosol	Phaeozem
Specific surface area (m ² /g)	71	47	47
Sand (%)	17	28	34
Loam (%)	31	48	40
Clay (%)	52	24	26
Electric conductivity (mS/cm)	402	485	399
Total organic carbon (mg/g)	25	19	22
pH	7.3	6.9	6.8

concentration (mg/kg) in the solid phase when equilibrium is reached, f_{oc} : organic carbon fraction for each soil.

Transport experiments

The tests were performed using borosilicate SR 25 AB *Pharmacia Fine Chemicals* columns with 7.07 cm² of transversal area and 15 cm in length. The compounds were studied separately. DEHP was analyzed in the three soils, while for the 4-NP only Leptosol and Vertisol soils were studied, this is because they represented the two extreme soil types in terms of clay and organic matter content (clay-loamy versus silt-loamy). All of the experiments were conducted in triplicate and a blank column test, without the addition of the compounds was carried out for each soil. Columns were packed using the procedure outlined by [Smith & Hegazy \(2006\)](#). This is based on packing the soil per centimetre in order to have the same bulk density in the whole packed column. The displacement experiments were performed in three stages. In the first stage the soil was moistened using 300 mL of 10 mmol/L CaCl₂ solution. In the second stage, the micropollutants were added as a 100 mL pulse using a 1,000 µg/L solution of each compound. In the third stage, in order to displace the compounds through the soil column, 300 mL of CaCl₂ solution were added. The displacement experiments lasted 32 days, which is equivalent to 20 pore volumes. The irrigation solution was introduced to the columns using a peristaltic pump at a flow rate of 0.013 mL/s. The leachates were collected by gravity at the bottom of the columns in pre-cleaned glass flasks and stored at 4 °C prior to chromatographic analysis. At the end of the transport experiments, the soil columns were divided into three parts of the same length; the soil was analyzed to determine the remaining concentration of the compounds and to perform the mass balance.

The experimental breakthrough curves were analyzed based on the method of temporal moments developed by [Pang *et al.* \(2003\)](#). According to this method, the retardation factor (R_F), representing the time that the transport of the compounds is delayed within the soil columns compared to the water transport, can be calculated with:

$$R_F = 1 + \frac{\rho k_d}{\theta} \quad (3)$$

where ρ : soil bulk density in g/cm³, k_d : linear sorption coefficient in cm³/g, θ : volumetric water content cm³/cm³.

The dispersion coefficient D (cm²/min), representing the extent of the dispersion and the diffusion of the

compound in the soil, was estimated with:

$$D = v\lambda \quad (4)$$

where v : pore water velocity (cm/min), λ : dispersivity factor (cm).

Analytical methods

The concentration of DEHP and 4-NP in the supernatants and leachates was determined using the method validated by [Gibson *et al.* \(2007\)](#). Briefly, samples were passed through Waters OASIS cartridges, 3 cm³ and 200 mg (Milford, MA, USA), previously preconditioned twice with 5 mL of acetone and twice with 5 mL of 5% acetic acid solution. Subsequently, the compounds were eluted with 5 mL of acetone. The resulting liquid phase was evaporated to dryness under a gentle flow of ultra high purity nitrogen. The silyl ester derivatives were obtained by using the derivatizing agent *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). For the extraction and preparation of the soil samples for the chromatographic analysis, the method validated by [Durán-Álvarez *et al.* \(2009\)](#) was used. Chromatographic analysis was carried out using an Agilent 6890N gas chromatograph coupled to a HP-5MS fused silica column (30 m × 0.25 mm × 0.25 µm film thickness). The temperature program used was 100 °C for 1 min, then a ramp of 20 °C/min up to 280 and 280 °C for 10 min quantification was carried out using a selective mass detector 5973N and the internal standards [²H₄] DEHP and [²H₁₆] bisphenol-A. Further information referring to the analytical method can be found in [Gibson *et al.* \(2007\)](#).

RESULTS AND DISCUSSION

The physicochemical properties of the three studied soils are shown in [Table 1](#).

Batch experiment

[Table 2](#) shows the sorption parameters for DEHP and 4-NP. Data were analyzed by using the linear model because they fitted it better than other models, as evidenced by the linear correlation coefficient ([Table 2](#)). The sorption coefficients (K_d) obtained for DEHP and 4-NP are in the same range as those obtained by [Staples *et al.* \(1997\)](#) and [Düring *et al.* \(2002\)](#) using soils with similar chemical properties and treated with biosolids. The similarity of our results, which were

Table 2 | Sorption parameters of the two micropollutants in the three studied soils

Parameter	4-NP			DEHP		
	Vertisol	Leptosol	Phaeozem	Vertisol	Leptosol	Phaeozem
^a K_d (L/kg)	80	15	50	4.2×10^4	1.8×10^4	2.4×10^4
^b R^2	0.979	0.823	0.981	0.934	0.791	0.892
^c $\log K_{oc}$	3.6	2.9	3.3	6.3	5.9	6.1

^aDistribution coefficient.^bLinear correlation coefficient.^cLogarithm of the distribution coefficient normalized to the soil organic carbon content.

obtained using wastewater irrigated soils, to those of these authors, using biosolids amended soils suggests that soil treatment has no significant impact on its capacity for sorbing the two micropollutants. In the three soils, the K_d values obtained for DEHP were higher than those for 4-NP, which is consistent with the higher hydrophobicity of DEHP. Sorption of the DEHP in the three soils may be taking place by the simple partition of the compound into the SOM through unspecific hydrophobic interactions (Karickhoff *et al.* 1979). This is particularly notable for the Vertisol soil, displaying the higher SOM content, in which the $\log K_{oc}$ value for DEHP (Table 2) tends to the $\log K_{ow}$ value (7.73), indicating that hydrophobic interactions are occurring. For 4-NP, sorption may be occurring not only by partition into the SOM, but other soil properties, such as the specific surface area as well as the clay content and type may also be playing an important role in its retention by the soil (Düring *et al.* 2002). 4-NP is more polar and hence less hydrophobic than DEHP. At the pH value of the soils (Table 1), a fraction of 4-NP (estimated at around 8% of the total molecules) is in its dissociated state and is repelled by the negatively charged particles of the soil (i.e. organic matter and clays). This phenomenon may contribute to the decrease in the 4-NP sorption. On the other hand, the remaining 92% of the molecules are in the neutral state and thus sorption into the soil may be occurring through hydrogen bridge bonds between the phenol group in the 4-NP molecule and the hydroxyl radicals within the SOM (Aquino *et al.* 2011).

According to Friedel *et al.* (2000), the clay mineralogy of the three studied soils is dominated by smectite (80–90%). This type of clays has been shown to efficiently sorb organic micropollutants (Zhang *et al.* 2010); therefore, the higher sorption of 4-NP, in the Vertisol soil may be related not only to the SOM and clays content, but also to the clay type.

For the two micropollutants, sorption onto the soil is clearly related to the SOM content, as the higher the SOM content the greater the K_d value (Tables 1 and 2). In fact,

the K_d value for DEHP in the Vertisol soil with a SOM content of 25 mg/g is 2.3 fold higher than for the Leptosol soil, while for 4-NP this ratio is 5.2. Such ratios indicate that a small increase in the organic carbon content (of 6 mg/g between Leptosol and Vertisol soils) is sufficient to increase the sorption of both compounds. For 4-NP, the larger increase in the K_d value compared with that achieved for the DEHP confirms that the sorption of 4-NP depends not only on the SOM but also on the increase in the clay content (116% higher in the Vertisol soil than in the Leptosol soil).

The absence of the micropollutants in the blanks' supernatants indicates no release of the compounds' mass previously retained in the soil; and reveals the strong sorption of the micropollutants into the three soils.

Compound mobility

The micropollutants' dispersivity factor (Table 3) was calculated with a Darcy flow of 0.14 mm/min. As the experiments were performed on packed columns of the same size using the same pore velocity, the differences in the dispersivity values can be then attributed only to the differences in the soil textures. The high dispersivity factor value observed in the Vertisol soil suggests that the compounds diffuse into the soil particles, retarding their transport through the soil.

Retardation factors for 4-NP were higher than the ones found for DEHP (Table 3), indicating that 4-NP is retained in the soil to a greater extent than DEHP. The higher mobility of DEHP may be due to its binding to the dissolved organic matter released by the soil during the column irrigation, increasing the DEHP solubility and mobility through the soil (De Jonge *et al.* 2002). This idea is supported by the observation of a yellowish color in the column leachates.

K_d values for the soil columns were calculated using Equation (3). Sorption coefficients obtained in the column experiments are considerably lower than those obtained in batch tests. This is because of the differences between

Table 3 | Mobility parameters of the compounds in the soil columns

Compound/Soil	^a ρ (g/cm ³)	^b Porosity (%)	Calculated pore velocity (mm/min)	Calculated dispersivity λ (mm)	^c R _F	K _d (L/kg)
DEHP Vertisol	0.97	62	0.18	13.5	7.15	3.93
DEHP Leptosol	1.14	57	0.21	2.23	4.09	1.55
DEHP Phaeozem	0.98	63	0.23	6.80	6.04	3.19
4-NP Vertisol	0.97	62	0.28	12.45	11.6	6.56
4-NP Leptosol	1.13	57	0.27	2.24	11	4.42

^aMeasured bulk density.^bCalculated by Equation (1)-(ρ/ρ_s).^cCalculated retardation factor.

batch and column experimental conditions. Higher contact area and time between the compounds and the soil, as well the activation of micropores in the batch sorption tests, resulted in greater sorption of the compounds in the latter; although the conditions achieved in the batch experiments seem to be far from emulating those in the field. In batch experiments, the sorption of the compounds depends on the SOM and clay content solely. However, in the columns experiment the mobility of the compounds is also the result of the soils' physical characteristics such as water content and soil bulk density. For instance, in soils with equal SOM and clay contents, the compounds' migration velocity would be higher in the soil with higher water content, as water is the vehicle of all the compounds, while for the soil bulk density, the retention behavior would be the opposite: the higher the soil bulk density the lower the migration velocity. This is because of the occurrence of a greater number of sorption reactive sites. The important fact is that while results from batch tests are in line with what has been reported in the literature, the column test results are similar to those observed in the study zone, where DEHP has been detected in groundwater at a larger number of sites and in higher concentrations than 4-NP (Gibson *et al.* 2007). The duration of the experiment, 32 days, is 7 days longer than the duration of an irrigation cycle in the field, in which the wastewater passes through the first 15 cm of soil in approximately 6 h, and subsequently a period of 25 days passes before the next irrigation. Therefore, the results of this study actually reproduce some of the conditions observed in the field.

Mass balance showed that DEHP and 4-NP were not completely displaced through the soil columns. Remaining concentrations of the mass applied at the beginning of the experiments (70–80% for 4-NP and 90–95% for DEHP) were found in the soil after the transport experiments. The strong retention of the micropollutants by the soil implies a lower risk of groundwater contamination and explains

why the compounds' concentration in the wastewater is 1,000 fold higher than in the groundwater (Gibson *et al.* 2007). However, the micropollutants retained in the soil could be available to the crops. Herklotz *et al.* (2010) observed the uptake of small amounts of pharmaceuticals by edible plants, although studies on the uptake of 4-NP and DEHP by plants were not found reported in the literature. Losses of 4-NP were higher than those found for DEHP, being higher in the Leptosol soil (27 and 2% of the added amount, respectively) than in the Vertisol soil (15 and 1% of the added amount, respectively). These losses may be attributable to the microbial degradation. Even though the soils were sterilized before the experiments, laboratory conditions did not allow aseptic conditions to be maintained. 4-NP has been reported as readily biodegradable in aerobic soils (Hesselsøe *et al.* 2001), and as the experiments were performed using aerobic conditions (the applied Darcy flow was smaller than the saturated hydraulic conductivity in columns for all tested soils), biodegradation of 4-NP was possible. Another explanation for the losses could be the irreversible sorption of the compounds into the soil by strong binding with the SOM and clays. This phenomenon would be greater for DEHP than for 4-NP due to the higher hydrophobicity of the former.

CONCLUSIONS

Batch and column sorption experiments were carried out in order to better understand the transport of two micropollutants in three agricultural soils. The results obtained in the two types of tests contrasted. In the batch tests, high retention of the two compounds by the three soils was found. The sorption capacity of the soils was as follows: Vertisol > Phaeozem > Leptosol, with the sorption of DEHP higher than that of 4-NP. In contrast, in the column tests, DEHP was more mobile than 4-NP. The

results obtained in the column study are in agreement with the observations made in the field, where DEHP incidence and concentration is higher than for 4-NP in the ground-water of the irrigated zone. One explanation for the higher mobility of DEHP in the column experiments could be the formation of complexes of this compound with the dissolved organic matter released from the soil during the irrigation event. The present study was useful to describe the sorption behavior of these two micropollutants in the soil surface layer (15 cm depth) and its relation to the soils' chemical properties. Further studies should aim to understand the impact of the soils' physical properties on the sorption of micropollutants; this may be achieved through undisturbed soil column experiments. One aspect still to be investigated is the possible uptake of these compounds by plants.

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