



Partitioning of chlorinated organic compounds from dense non-aqueous phase liquids and contaminated soils from lindane production wastes to the aqueous phase

David Lorenzo, Raul García-Cervilla, Arturo Romero, Aurora Santos*

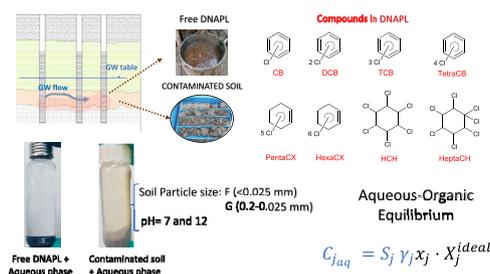
Chemical and Materials Engineering Department. University Complutense of Madrid, Spain



HIGHLIGHTS

- Partitioning behavior in water of 28 COCs in DNAPL has been studied.
- The DNAPL is a liquid waste for lindane production found in Sabinanigo Landfills.
- Concentration of COC in aqueous phase depends linearly on its mole fraction in the DNAPL.
- Similar partitioning in water was found for DNAPL as free phase or trapped into soil.
- Alkaline pH promotes dehydrochlorination to COCs with lower toxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexachlorocyclohexane (HCH) and mainly the γ -HCH isomer, namely lindane, were extensively produced and used as pesticides. Huge amounts of wastes, solids and liquids, were disposed of in the surroundings of the production sites. The liquid residuum was a complex mixture of chlorinated organic compounds, COCs, from chlorobenzene to heptachlorocyclohexane. This Dense Non-Aqueous Phase Liquid, DNAPL, migrated by density through the subsurface to greater depths, being trapped or adsorbed into the soil in this movement posing a significant risk to the groundwater. Knowledge of the partitioning in water of COCs in DNAPL is a key issue to determine its fate in the environment. However, there are no data in literature for the partitioning and/or solubility of many of the COCs in this DNAPL, such as pentachlorocyclohexene, hexachlorocyclohexene and heptachlorocyclohexane despite them constitute about 13–30% of the mole fraction of the DNAPLs. In this work, the partitioning to water of COCs in free and those adsorbed onto soil has been studied. In addition, measured and predicted aqueous concentrations of each COC in the DNAPL mixture have been compared. To do this, the solubility of a compound that is a solid crystal when pure at $P = 298 \text{ K}$ and $P = 1 \text{ atm}$ has been evaluated considering the approach of sub-cooled liquid state of solid organochlorines. Samples were obtained at Sabinanigo landfills and soils used had several grain sizes. Transformation in alkaline media of COCs had a positive environmental impact.

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1. Introduction

Soil and groundwater pollution caused by pesticides are a major

* Corresponding author.

E-mail address: aursan@quim.ucm.es (A. Santos).

problem in many countries all over the world (Ren et al., 2018). Their high persistency in the environment results in a high risk to human and environmental health (Weber et al., 2011; Li and Jennings, 2017). They can be transported to the atmosphere by volatilization, and may enter surface water bodies or can be leached from the superficial soil by run-off and enter to groundwater (Pirsaheb et al., 2017; Kumar and Mukherji, 2018). Among the pesticides, the Organochlorine Pesticides are a relevant group as they were widely used for agricultural pest control and for medical purposes (Cuozzo et al., 2018; Madaj et al., 2018). Many of these substances are listed by the Stockholm convention, which regulates or bans several of them (Karlagnanis et al., 2001; Lallas, 2001).

One of the most extensively used and produced organochlorine pesticides after the Second War World was lindane (Vijgen, 2006; Vijgen et al., 2011), the γ isomer of 1,2,3,4,5,6-hexachlorocyclohexane (HCH). HCHs were considered as persistent organic pollutants (POPs) and they have been banned by the Stockholm Convention since 2009 (Vijgen et al., 2011; Madaj et al., 2018). In Europe, lindane was produced in many countries mainly from the 1950s to the 1970s or 1990s as recently reported by the Directorate General for Internal Policies (EU) (Vega et al., 2016). Lindane was manufactured from photochlorination of benzene with UV light yielding a mixture of five main isomers. The only isomer with insecticide properties was the γ -HCH. Lindane was extracted and purified from the HCH mixture of isomers using fractional crystallization. In this process about 6–10 tons of other waste isomers are also obtained per ton of lindane (Vijgen, 2006; Vega et al., 2016) and the isomers α , β and γ -HCH (lindane) are included in the Stockholm Convention on Persistent Organic Pollutants (POPs) (Dorsey, 2005).

The huge amounts of wastes produced in the lindane manufacturing process have often been dumped without environmental concerns near production sites. As a result, soil and groundwater were highly contaminated (Vijgen, 2006; Fuscoletti et al., 2015; Pinto et al., 2016; Vega et al., 2016; Pawlowicz, 2017; Pirsaheb et al., 2017). Among the wastes from lindane production, a dense non-aqueous phase liquid (DNAPL) composed of HCH isomers, benzene and chlorobenzenes has been found in the subsurface of Sabiñanigo (Spain) landfills (Fernández et al., 2013), and its presence is due to the direct dumping of liquid residues from 1975 to 1992 by the company INQUINOSA. Moreover, polychlorinated dibenzo-p-dioxin/dibenzofuran (PCDD/Fs) were identified in these dense non-aqueous phase liquids (DNAPLs), as well as in landfill leachates, soil and sediments from Sabiñanigo landfills (Gómez-Lavín et al., 2018).

These liquid residues were generated from failed chlorination reactions and distillation tails in lindane production processes. Given that the average density of the DNAPL is about 1.5 g/cm³ (Fernández et al., 2013) this phase was transported by density forces and it was found at different depths at the Sardas and Bailin landfills (Fernández et al., 2013; Casado et al., 2015). Solubilization of the DNAPL in the groundwater has caused significant pollution of the groundwater, with the associated risk for the nearby river and reservoir (Navarro et al., 2000; Fernández et al., 2013).

The detection of this dense organic chlorinated phase at the Sabiñanigo landfills was an important finding, not frequently described in other hot-sites polluted with lindane wastes. However, since a similar lindane manufacturing process was used everywhere, the presence of this DNAPL should be also expected in other sites close to lindane production points and should be more deeply investigated. The transport of this DNAPL to significant depths below ground level, due to its high density, is probably the cause of the lack of information about its occurrence in the subsurface of these hot-sites. Additionally, during the transport of this liquid organic phase through the subsurface, a significant adsorption or

trapping in the soil could occur and therefore the presence of this liquid, adsorbed or trapped in the organic phase of the soil pores, would justify the high levels of HCHs found in the groundwater at these hot-sites (Vijgen, 2006; Fernández et al., 2013; Fuscoletti et al., 2015; Vega et al., 2016).

Due to the low solubility of the Chlorinated Organic Compounds (COCs) that compose this organic phase, its presence supposes a significant risk to groundwater and nearby surface waters. Transport of COCs to the groundwater in contact with this organic phase (found as liquid pools or adsorbed/trapped in the soil) will depend on the solubility and partitioning behaviour of these COCs among the corresponding phases it comes into contact with (Xiao et al., 2004). Therefore, accurate and reliable solubility values and/or partitioning coefficients are a key factor for controlling their environmental distribution and consequences (Chiou et al., 2005; Nizzetto et al., 2011) and, are therefore, required for both the design of an effective remediation strategy and the evaluation of the risk of these COCs for human health and ecosystems.

However, there is little information about the solubility of COCs in an aqueous phase in contact with a DNAPL liquid mixture. Most of the studies on the solubility of COCs in the aqueous phase have been obtained from pure compounds (Xiao et al., 2004; Chiou et al., 2005; Nizzetto et al., 2011). However, the aqueous solubility of the COC as a pure species (often as a crystal phase) does not give a proper description of its behavior as a component of a liquid organic phase (Banerjee, 1984; Broholm and Feenstra, 1995; Jain and Yalkowsky, 2001; Yalkowsky and Wu, 2010).

Similarly, the solubility and partitioning of COCs between the soil and the aqueous phase has usually been studied by obtaining the equilibrium isotherms between the soil and this phase after the soil has been spiked with pure compounds (Duan et al., 2008; Macedo et al., 2015; Silvani et al., 2019). This procedure hardly describes the reality where a mix of COCs is historically sorbed or trapped in the soil.

One of the goals of this work is to evaluate the equilibrium of the aqueous phase in contact with seven liquid organic phases extracted from the Sardas and Bailin landfills (Sabiñanigo, Spain). Characterization and composition of six of these seven DNAPL samples was carried out elsewhere, finding that they were composed by 28 COCs (Santos et al., 2018a). Many of these compounds were not commercial and no information about their solubilities—even as pure compounds—was available in the literature. Also, the equilibrium of COCs between the aqueous phase and the soil obtained from a well drilled ad hoc in the Sardas landfill has been investigated here. While a DNAPL liquid phase was near this well, the results obtained in Milli-Q water will be compared with the composition of the groundwater extracted.

Moreover, one of the remediation strategies proposed for COCs abatement in soil and/or groundwater of the Sabiñanigo landfills is In Situ Chemical Oxidation, ISCO, using persulfate activated by alkali as an oxidant. Therefore, the effect of alkali addition on the change in composition of COCs in both soil and aqueous phases is a matter that requires investigation while dehydrochlorination reactions are produced due to the alkaline pH. To our knowledge, the solubility of COCs in an aqueous phase from liquid organic phases and contaminated soil caused by the lindane production waste has not been previously studied.

2. Materials and methods

2.1. Materials

2.1.1. DNAPLs samples

Seven DNAPL liquid samples have been used in this work. All of them have been obtained from the Sabiñanigo Landfills and kindly

provided by the company Emgrisa and the Aragon Government. One DNAPL sample was taken in a well located in the Bailin Landfill (well P55, named O1), and the other six were obtained in wells located at the Sardas landfill (wells S39G, S39I, S39F, PS15, PS23 and PD14D, called O2 to O7, respectively). The location of these wells on the site can be found in [Figures SI-1 and SI-2](#) of the Supplementary Material. Identification of COCs in samples O1 to O6 and their composition was described elsewhere ([Santos et al., 2018a](#)). Sample O7 was extracted from a new borehole drilled in April 2018 and has not been previously reported.

The seven DNAPLs used are summarized in [Tables SI-1](#) of the Supplementary Material. The well's identity, depth of the well and a photo DNAPL PS14D is included (similar to the other DNAPLs appearance). The DNAPL free phase is a black-brown liquid, with a strong smell. DNAPL samples were dissolved in 99% acetone (Sigma-Aldrich) at concentrations ranging from 20 to 25 g kg⁻¹. Then each solution was stored in a 20 mL glass vial closed with a PTFE cap. Vials had no free head space to prevent the evaporation of the most volatile compounds. COCs dissolved in acetone were analyzed by GC/MSD and GC/FID/ECD as indicated below.

2.1.2. Soil samples

The soil samples were obtained from a borehole drilled in April 2018 identified as PS14D in [Figure SI-3](#) (courtesy of the company Emgrisa, that drilled the borehole). As can be seen an anthropic fill was found from 0 to 4.8 m, a homogeneous silt layer from 4.40 to 12.50 m, a gravel-sand layer from 12.50 to 15.50 m and altered marl was identified under this gravel-sand layer. The DNAPL liquid phase obtained at this well PS14D, called O7 here, was located in the contact between the altered marls and the gravel-sand layer (then about 16.5 m below ground level).

The gravel-sand layer was permeable and the groundwater flow was in this layer. Soil samples from drilling core boxes, kindly provided by the company Emgrisa, were taken half-way down the gravel-sand layer (13.5–14.5 m) in order to avoid the presence of the free DNAPL phase. After drying at room temperature for 48 h the soil was sieved and the fraction with a particle diameter higher than 2 mm was rejected. Moreover, while the gravel-sand layer also contained some clay, the fraction with a diameter lower than 2 mm was sieved again to separate the fraction with particles less than 0.25 mm in diameter (called F fraction) from the soil particles that were larger than 0.25 mm (called G fraction).

One month after the borehole was drilled and the DNAPL phase was partially extracted groundwater samples were taken in well PS14D at 14.5 m b.g.l (therefore in the gravel-sand layer).

2.2. Solubility experiments

Solubility of COCS in DNAPL: A weighted mass of about 1 g of each DNAPL sample was in contact with 18.5 g of water in a cap sealed GC 20 mL vial without head space. The vial was sonicated for 15 min and kept at room temperature (23 °C ± 2 °C) for 48 h without agitation during this period to avoid microdroplets of the DNAPL in the aqueous phase. It was experimentally confirmed that equilibrium between organic and aqueous phase was obtained at times lower than 24 h while stable concentration of COCs in the aqueous phase were obtained at both 24 and 48 h. Then, 10 mL of the supernatant aqueous phase was taken with a syringe, filtered with a 0.1 µm nylon filter. It was confirmed that with this procedure the adsorption of COCs in the filter was negligible. Then, the filtered aqueous phase was extracted with hexane and immediately analyzed by GC/MS and GC/FID/ECD. The procedure was carried out in triplicate and differences were lower than 10%. In few cases (about 20% of the determinations) differences higher than 10% were obtained. These values were discarded and the vials were prepared

again.

Besides, it was experimentally confirmed that the equilibrium between the organic and the aqueous phase was obtained at times lower than 24 h after sonication while stable concentration of COCs in the aqueous phase were obtained at both 24 and 48 h.

Solubility of COCs from soil to the Aqueous Phase.

The experiments were carried out in batch mode by using 40 mL PTFE centrifuge tube with PTFE screw caps. In each centrifuge tube, 10 g of each fraction, F and G, of the polluted soil were treated with 30 mL of aqueous solution ($V_L/W_S = 3 \text{ mL g}^{-1}$). Head-Space was minimized by this procedure. The aqueous phase added was Milli-Q water (pH = 6.5) or Milli-Q water with 10 g/L of NaOH (pH > 12). Then, the tubes were stirred at room conditions (23 °C) with a Labolan rotary agitator (ref 51752) for 48 h. After this time, the aqueous and soil phases were separated by centrifugation. COCs in both aqueous and solid phases were extracted and analyzed by GC/MS and GC/FID/ECD. All experiments were performed in triplicate. Experimental error was less than 10%. It was experimentally confirmed that soil-water equilibrium was reached at 24 h of rotary agitation.

2.3. Analytical methods

2.3.1. Extraction of COCS from soil samples

In the case of soil samples, the 10 g of each soil fraction G (diameter from 2 to 0.25 mm) or F (diameter <0.25 mm) was mixed with anhydrous sodium sulfate and milled in a ceramic mortar. Subsequently, 25 ml of hexane/acetone mixture was added and the mixture was introduced in a microwave extraction device (Milestone Ethos One) following EPA method 3546. The temperature extraction program begins with an initial ramp of 15 min from room temperature to 110 °C, followed by a sustained temperature of 110 °C for 15 min, under a maximum power of 1000 W. Once the extraction program ends, approximately 15 ml of organic extraction phase were recovered from the supernatant, filtered with a 0.45 µm filter. The supernatant was analyzed by GC/MS and GC/FID/ECD. The extraction and analyses were carried out in triplicate.

2.3.2. Extraction of COCs from aqueous samples

A volume of 8 mL of aqueous phase was added to 2 mL of hexane in a GC 10 mL vial and sonicated for 10 min. The supernatant organic phase was taken and analyzed by GC/MS and GC/FID/ECD.

2.3.3. COCS analysis

The GC method used for COC identification and quantification in DNAPL organic phases has been described elsewhere ([Santos et al., 2018a](#)) and are summarized below:

GC/MSD analysis: COCs were identified by gas chromatography (Agilent 6890 N) coupled to a Mass Selective Detector (Agilent MSD 5975B), which operates under a vacuum. A HP-5MS column (30 m × 0.25 mm ID × 0.25 µm) was used for the COC analysis. A flow rate of 1.7 mL min⁻¹ of helium was used as carrier gas and 1 µL of liquid samples was injected. The GC injection port temperature was set to 250 °C and a programed temperature gradient was used for the GC oven, starting at 80 °C, increasing the temperature at a rate of 18 °C min⁻¹ up to 180 °C, and then keeping it constant for 15 min.

GC/ECD-FID analysis: The quantification of COCs was carried out using an Agilent 6890 gas chromatograph with both flame ionization detector (FID) and electron capture detector (ECD). An HP-5MS column (30 m × 0.25 mm ID × 0.25 µm) was also used and the Carrier gas was Helium (flow rate of 1.7 mL min⁻¹). The same temperature of the injector and GC oven as that indicated for GC/MS was used in this case. The output flow of the capillary column was split (1:1) using FID and ECD simultaneously. More details of

the procedure can be found elsewhere (Santos et al., 2018a).

3. Results

3.1. Solubility of DNAPL liquid samples in the aqueous phase

As described elsewhere (Santos et al., 2018a) the COCs identified in DNAPL liquid samples could explain about 95% of the mass of each DNAPL sample analyzed. The difference up to 100% could be attributed to the water content, to the presence of minor peaks from e.g. PCDD/Fs (Gómez-Lavín et al., 2018) or traces of tetrachlorocyclohexene isomers or to an error in the chromatographic response assigned to Pentaclorocyclohexenes (PentaCX) and Heptachlorocyclohexanes (HeptaCH) due to the same GC/FID response factor obtained for HCHs being assigned to these non-commercial compounds. Samples O1 to O7 were analyzed and mass percentages for COCs were determined. COC distribution (in weight) obtained in the analysis of samples O1 to O6 were very similar to that found elsewhere, with differences lower than 5%. Weight percentages for O1 to O7 samples are summarized in Tables SI–2 of the Supplementary Material. Values shown for O1 to O6 correspond to those obtained elsewhere (Santos et al., 2018a). Sample O7 (well PS14D), which has not been previously analyzed, has high trichlorobenzenes (TCBs) and tetrachlorobenzenes (TetraCBs) percentages, similar to those found in PS15 and PS23. This can be explained as PS14D, PS15 and PS23 were obtained in the same alluvial aquifer (Figure SI-1) and some alkaline dehydrochlorination of HCHs and HeptaCHs could take place producing TCBs and TetraCBs, respectively (Santos et al., 2018a, 2018b). From the weight percentages of each COC (%COC_{iw}) shown in Tables SI–2, the mole fraction of compound *j* in each DNAPL sample has been calculated as:

$$x_j = \frac{\frac{\%COC_{iw}}{M_j}}{\sum \frac{\%COC_{iw}}{M_j}} \quad (1)$$

Being *M_j* the molecular weight of the *j* compound. The values of *x_j* obtained are summarized in Table 1 for the seven DNAPL samples studied.

The liquid waste dumped in Sabiñanigo has been characterized elsewhere (Santos et al., 2018a) containing all the compounds summarized in Fig. 1, from chlorobenzene to heptachlorocyclohexane (HeptaCH), in agreement with reported in the literature for other wastes of the lindane production process (Wise et al., 1948; Bala et al., 2012; Fernández et al., 2013).

After the aqueous phase was equilibrated with each DNAPL sample, the concentration of each COC in this phase was determined. The results are shown in Tables SI–3 of the Supplementary Material. Due to the low mole fraction of 1,3,5 TCB; θ-PentaCX, β-PentaCX, HexaCX-b, HexaCX-c, HexaCX-d, β-HCH in all DNAPL liquid samples, the concentration of these compounds in the aqueous phase was very low and was reported as n. d. in this Tables SI–3. Moreover, the COCs measured in the groundwater extracted at well PS14D (14.5 m b.g.l) have also been included in Tables SI–3. The groundwater (GW) sample has a conductivity of 6039 μS/cm, a chloride content of 1382 mg L⁻¹ and bicarbonates of about 820 mg L⁻¹. In spite of the high conductivity of the GW, its COC composition is quite similar to that found in the Milli-Q water equilibrated with the O7 DNAPL sample, as can be seen in Tables SI–3, confirming the saturation of this groundwater with the closer DNAPL in well PS14D (O7).

The study of the equilibrium liquid-liquid (LLE) between the liquid organic phase (DNAPL) and the aqueous phase at room conditions has been accomplished using the approach of Banerjee

(1984) and Broholm et al. (Broholm and Feenstra, 1995). However, as these authors indicate, when a component in a mixture is solid (pure) and the mixture is a liquid, the difference in phase should be corrected to predict its solubility in the aqueous phase. To do this, the approach of sub-cooled liquid state of solid compounds has been applied (Jain and Yalkowsky, 2001; Yalkowsky and Wu, 2010; Schwarzenbach and Gschwend, 2016). In this way, when the equilibrium is reached, the aqueous concentration of each compound *j* present in the liquid organic phase can be predicted by the following expression:

$$C_j^{aq} = S_j \gamma_j^{DNAPL} x_j \frac{f_j^{liq}}{f_j^c} \quad (2)$$

being *C_j^{aq}* and *x_j* the concentration of the compound *j* in the aqueous phase in mg L⁻¹ (provided in Tables SI–3) and the molar fraction of the compound *j* in the DNAPL when equilibrium is reached, respectively. *S_j* is the pure-phase aqueous solubility in mg L⁻¹ of the *j* compound and *γ_j^{DNAPL}* the activity coefficient of the *j* compound in the organic phase. This *γ_j^{DNAPL}* can be assumed to be close to unity (Broholm and Feenstra, 1995). Moreover, for *x_j* in Eq. (2) the values shown in Table 1 can be used due to the ratio for mass of DNAPL to water volume used (as explained in the experimental section) is high enough to assume that the solubilized COCs in the aqueous phase yield a minor change in DNAPL composition.

The fugacity ratio of the pure compound at the right-side of Eq. (2) has been called *X_j^{ideal}*, shown in Eq. (3). It was defined in literature as the crystal/liquid solubility or fugacity ratio of a pure compound which is solid at T = 298 K and P = 1 atm (Jain and Yalkowsky, 2001; Yalkowsky and Wu, 2010):

$$X_j^{ideal} = \frac{f_j^c}{f_j^{liq}} \quad (3)$$

X_j^{ideal} is the unity when the compound *j* is liquid at 298 K and 1 atm (Smith et al., 2005). The value of the fugacity ratio can be estimated using the entropy of fusion at the melting point and the melting temperature at P = 1 atm (Yalkowsky and Wu, 2010).

$$\log_{10}(X_j^{ideal}) = \left(-\frac{\Delta S_m}{2.303 \cdot R} \cdot \frac{T_m - T}{T} \right) \quad (4)$$

Values of *ΔS_m* and *T_m* have been obtained from literature (Jain and Yalkowsky, 2001; Frenkel et al., 2005; Yalkowsky et al., 2016) being shown in Table 2. As can be seen in Table 2 this information is lacking for compounds as PentaCX, HexaCX, HeptaCH isomers. The value of *X_j^{ideal}* has been predicted by Eq. (4), and it is shown in Table 2.

Using the experimental values of *x_j* in Table 1 and *C_j^{aq}* in Tables SI–3, the product *S_jγ_j(X_j^{ideal})⁻¹* has been calculated for samples O1 to O6 by using Eq. (2). Results are shown in Table 2. Values of *S_jγ_j(X_j^{ideal})⁻¹* have also been calculated using the concentration of COCs in the GW extracted in PS14D and considering this GW in equilibrium with the organic sample O7. As can be seen in Table 2, similar values of *S_jγ_j(X_j^{ideal})⁻¹* for GW to those obtained with O7 in equilibrium with distilled water are acquired.

Besides, as can be seen in Table 2, close values of *S_jγ_j(X_j^{ideal})⁻¹* for each *j* compound have been obtained for samples O1 to O7 and for GW. Therefore, an average value of *S_jγ_j(X_j^{ideal})⁻¹* has been calculated for each specie *j*, as shown in Table 2.

If the activity coefficient is assumed to be the unity (*γ_j* = 1) the solubility *S_j* can be predicted by Eq. (5) and values obtained are shown in Table 2.

Table 1
COC Mole fraction (x_j) in each DNAPL liquid samples analyzed. Sum of COCs explain 95–97% of the DNAPL mass.

Sample			O1	O2	O3	O4	O5	O6	O7	
j Acronym	Name	CAS	M _j	BAILIN	SAR S39G	SAR S39I	SAR S39F	SAR PS15	SAR PS23	SAR PS14D
CB	chlorobenzene	108-90-7	112	0.215	0.253	0.231	0.249	0.198	0.223	0.187
1,3 DCB	1,3-dichlorobenzene	541-73-1	146	0.003	0.006	0.007	0.005	0.007	0.007	0.009
1,4 DCB	1,4-dichlorobenzene	106-46-7	146	0.033	0.055	0.077	0.056	0.083	0.071	0.080
1,2 DCB	1,2-dichlorobenzene	95-50-1	146	0.027	0.047	0.068	0.048	0.062	0.061	0.063
1,3,5 TCB	1,3,5-trichlorobenzene	108-70-3	180	0.000	0.000	0.001	0.000	0.002	0.003	0.002
1,2,4 TCB	1,2,4-trichlorobenzene	120-82-1	180	0.071	0.067	0.097	0.068	0.175	0.189	0.155
1,2,3 TCB	1,2,3-trichlorobenzene	87-61-6	180	0.006	0.009	0.013	0.009	0.031	0.026	0.024
TetraCB (1,2,4,5 + 1,2,3,5)	1,2,4,5–1,2,3,5 tetrachlorobenzene	95-94-3/634-90-2	214	0.015	0.012	0.013	0.013	0.059	0.055	0.053
TetraCB (1,2,3,4)	1,2,3,4 tetrachlorobenzene	634-66-2	214	0.026	0.004	0.014	0.004	0.077	0.083	0.074
γ-PentaCX	γ-pentachlorocyclohexene	342631-17-8	252	0.036	0.018	0.021	0.019	0.010	0.014	0.017
PentaCB	1,2,3,4,5 pentachlorobenzene	608-93-5	248	0.002	0.010	0.004	0.005	0.009	0.004	0.005
δ-PentaCX	δ-Pentachlorocyclohexene	643-15-2	252	0.031	0.015	0.015	0.015	0.012	0.020	0.016
θ-PentaCX	θ-Pentachlorocyclohexene	319-94-8	252	0.009	0.006	0.004	0.006	0.002	0.002	0.001
HexaCX-a	Hexachlorocyclohexene	1890-41-1	289	0.010	0.012	0.006	0.011	0.006	0.006	0.005
β-PentaCX	β-Pentachlorocyclohexene	319-94-8	252	0.007	0.005	0.004	0.005	0.002	0.002	0.002
η-Penta CX	η-Pentachlorocyclohexene	54083-24-8	252	0.039	0.020	0.009	0.018	0.006	0.004	0.001
HexaCX-b	Hexachlorocyclohexene	1890-41-1	286	0.011	0.004	0.002	0.003	0.001	0.002	0.002
HexaCX-c	Hexachlorocyclohexene	1890-41-1	286	0.006	0.007	0.005	0.006	0.004	0.003	0.005
α-HCH	α-hexachlorocyclohexane	319-84-6	291	0.035	0.038	0.031	0.036	0.026	0.024	0.029
HexaCX-d	Hexachlorocyclohexene	1890-41-1	286	0.016	0.002	0.001	0.003	0.001	0.000	0.000
β-HCH	β-hexachlorocyclohexane	319-85-7	291	0.000	0.000	0.000	0.000	0.000	0.001	0.000
γ-HCH	γ-hexachlorocyclohexane	58-89-9	291	0.112	0.114	0.104	0.113	0.078	0.080	0.095
HeptaCH-1	Heptachlorocyclohexane	707-55-1	322	0.108	0.102	0.097	0.110	0.052	0.039	0.072
δ-HCH	δ-hexachlorocyclohexane	319-86-8	291	0.085	0.100	0.090	0.098	0.042	0.041	0.051
ε-HCH	ε-hexachlorocyclohexane	6108-10-7	291	0.012	0.014	0.013	0.014	0.008	0.008	0.012
HeptaCH-2	Heptachlorocyclohexane	707-55-1	322	0.064	0.061	0.051	0.067	0.033	0.024	0.028
HeptaCH-3	Heptachlorocyclohexane	707-55-1	322	0.020	0.021	0.019	0.022	0.010	0.009	0.014

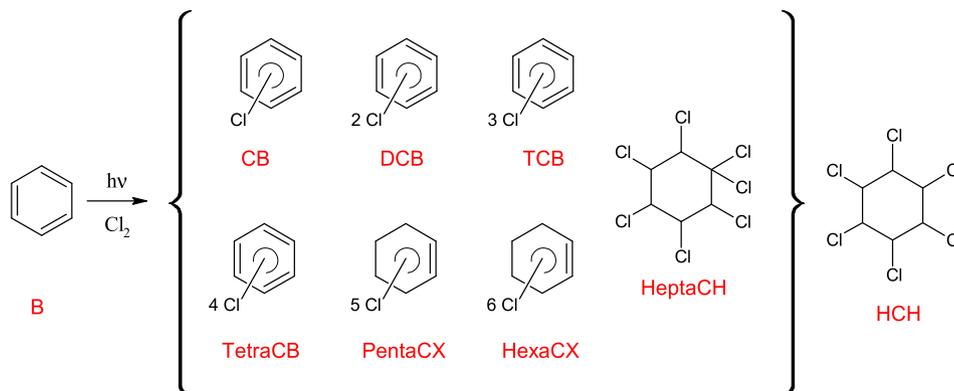


Fig. 1. Identified Chlorinated Organic Compounds in the chlorination of benzene to HCH.

$$S_j \text{ pred} = \frac{S_j \gamma_j (X_j^{\text{ideal}})^{-1}}{(X_j^{\text{ideal}})^{-1}} \quad (5)$$

The S_j values predicted with Eq. (5) have been compared with S_j values found literature (also shown in Table 2). As can be seen, a reasonable agreement has been obtained for most of the compounds which literature data is available. On the other hand, as can be seen in Table 2, there is no bibliographic data for solubility of compounds such as PentaCx, HexaCX, HeptaCH isomers. The Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2019 ACD/Labs) coupled with SciFinder (educational license) was used to estimate the solubility of the latter compounds whose experimental values are not available in literature. As can be seen in Table 2, the software provides the same value for all the stereoisomers of PentaCX, HexaCX and HeptaCH. To check the reliability of the values estimated by the software, the estimated values of

solubility and the experimental values of those compounds that are found in literature are compared in Table 2. The software provides different solubility values for positional isomers of DCB, TCB and TetraCB, and the same value for the stereoisomers of HCH. In addition, the estimated values and the experimental determinations are often different. In spite of this disparity, the solubility values estimated by the software gives an adequate order of magnitude of the solubility values of the chlorinated compounds.

3.2. Solubility of COC in aqueous phase from contaminated soil

The soil obtained from 13.5 to 14.5 m b.g.l. at PS14D (Figure SI-3) was dried and sieved as explained in the experimental section. The fraction lower than 0.25 mm (F) was 31.2% of the soil with size lower than 2 mm. Therefore, the G fraction, with particle sizes between 2 and 0.25 mm, was 68.8% of the soil lower than 2 mm. During the drying and sieving procedure, the most volatile chlorinated compounds were lost. The composition in COCs of each

Table 2
Product $S_j \gamma_j (X_j^{ideal})^{-1}$ for each j compound, T_m , ΔS_{mv} , X_j^{ideal} and literature and predicted solubilities of pure compounds at $T = 298\text{ K}$ and $P = 1\text{ atm}$.

	$S_j \gamma_j (X_j^{ideal})^{-1}$ (mg L^{-1})									Appearance	T_m (+) °C	ΔS_{mv} (+) J/mol/K	$\frac{1}{X_j^{ideal}}$ Eq	S_{jpred} Eq(5) mg L^{-1}	S_j Literature ^a estimated mg L^{-1}	Literature S_j
	O1	O2	O3	O4	O5	O6	O7	GW	Average							
CB	390.1	424.6	426.3	446.4	436.0	486.5	404	404.0	428.4	L			1	428.4	472–502/86	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
1,3 DCB	120.0	155.0	114.1	193.3	159.8	142.6	95.0	79.8	140.0	L			1	140	125–143/160	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
1,4 DCB	98.9	120.0	113.2	117.9	141.3	114.4	108.5	86.7	116.3	S	52.99	55.78	1.88	61.94	65–81.3/180	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
1,2 DCB	88.9	132.3	116.6	129.7	144.1	123.7	111.6	82.3	121.0	L			1	121	137–156/180	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
1,3,5 TCB	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	S	63.5	55.82	2.38	8.97	6/3.4	(Banerjee, 1984; Yakata et al., 2006; Tsai and Chen, 2007)
1,2,4 TCB	39.5	35.7	29.4	35.2	40.1	29.3	27.8	27.7	33.9	L			1	33.9	31–49/3.6	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
1,2,3 TCB	34.2	42.4	32.4	40.7	45.9	31.9	29.4	21.8	36.7	S	52.5	56.78	1.88	19.54	16.3–18/3.8	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
TetraCB (1,2,4,5 + 1,2,3,5)	16.5	13.9	9.0	11.3	11.9	9.1	8.7	12.0	11.5	S	50.67	57.37	1.81	6.34	0.3–0.56 and 3.4/0.82 and 0.80	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
TetraCB (1,2,3,4)	15.4	14.0	13.6	13.0	12.5	7.8	7.5	7.3	12.0	S	46.65	53.06	1.59	7.53	3.4–5.92/0.84	(Banerjee, 1984; Chiou et al., 2005; Tsai and Chen, 2007)
γ -PentaCX	78.0	121.6	126.8	130.2	64.1	101.3	54.2	37.0	96.6	S					- ^a 7.6	
PentaCB	8.0	10.0	6.0	9.0	4.4	9.0	7.6	12.1	7.7	S	84.12	56.79	3.88	1.99	0.32–0.4/0.20	(Chiou et al., 2005; Yakata et al., 2006)
δ -PentaCX	92.7	98.2	90.2	94.1	62.4	75.3	79.6	33.7	84.7	S					-7.6	
θ -PentaCX	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	21.6	n.q.	S					-7.6	
HexaCX-a	12.5	15.7	9.4	12.8	5.4	10.9	12.0	27.8	11.2	S					-2.4	
β -PentaCX	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	S					-7.6	
η -PentaCX	38.8	42.1	36.3	47.9	38.3	40.5	60.9		43.6	S					-7.6	
HexaCX-b	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	24.0	n.q.	S					-2.4	
HexaCX-c	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	S					-2.4	
α -HCH	34.2	35.3	34.5	38.4	40.1	35.3	36.9	35.3	36.4	S	157.42	62.45	28.14	1.29	1.2–2/7.9	(Shiu et al., 1990; Health and Services, 1993; Xiao et al., 2004; Ke et al., 2007)
HexaCX-d	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	S					-2.4	
β -HCH	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	S	309.0			n.q.	0.15–0.7/7.9	(Shiu et al., 1990; Xiao et al., 2004; Ke et al., 2007)
γ -HCH	43.0	45.1	45.9	48.1	52.4	54.3	45.4	39.3	47.7	S	114.85	43.18	4.79	9.98	2.1–15.3/7.9	(Shiu et al., 1990; Health and Services, 1993; Xiao et al., 2004)
HeptaCH-1	19.4	21.2	14.6	17.8	8.1	16.9	8.9	14.7	15.3	S					-2.8	
δ -HCH	96.2	70.9	84.2	72.7	90.0	97.4	85.6	82.7	85.3	S	136.97	51.81	10.39	8.21	8.6–31/7.9	(Weil et al., 1974; Shiu et al., 1990; Health and Services, 1993; Ke et al., 2007)
ϵ -HCH	77.0	52.9	71.3	68.7	69.4	68.2	69.8	40.3	68.2	S	218.5				-7.9	
HeptaCH-2	10.9	14.2	9.1	11.1	7.9	11.3	10.9	9.3	10.8	S					-2.8	
HeptaCH-3	24.8	29.2	27.0	26.4	18.6	25.1	19.0	25.8	24.3	S					-2.8	

(·) Appearance at 25 °C of pure COC: L = liquid S = Solid crystal.

(+) (Jain and Yalkowsky, 2001; Frenkel et al., 2005; Yalkowsky et al., 2016).

n.q.: non-quantifiable.

^a Estimated solubility values using the Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994–2019 ACD/Labs).

fraction F and G after drying and sieving is summarized in Table 3. As can be seen in Table 3 the most volatile COCs in the soil such as CB, DCBs are found in low concentration, due to their loss by vaporization during drying and sieving. Besides, at neutral pH, the content in TCBs is also low. In spite of the loss of the volatile compounds, the COCs content in the F soil fraction is quite high (34.57 mmol/kg that correspond to 9946 mg/kg of total COCs) and higher than the concentration found in the G fraction (11.53 mmol/kg that correspond to 3193 mg/kg of total COCs). The differences in the COC content of both soil fractions can be explained by the lower particle size of the F fraction. It is widely documented in literature that soil is comprised of various particle size fractions and most often, the contaminants are concentrated in the fraction corresponding to finer silts and clays. The higher adsorption of contaminants in the fine fraction is explained by the increased surface area, cationic exchange potential, and the innate shape of these particles. (Anderson et al., 1999).

Due to the high content of both carbonates in soil (>40% in weight in dry soil) and bicarbonates in the groundwater (820 mg L⁻¹) of the landfills (Fernández et al., 2013) and the nature of the pollutants, the persulfate activated by alkali seems to be the most reliable treatment for the groundwater of the site (Santos et al., 2018b). This can be achieved by injecting an alkali (NaOH aqueous solution) into the subsurface to reach a pH value about 10–12. Then, alkali and oxidant will be simultaneously injected. When the alkali is injected, a dehydrochlorination reaction can take place. It has been previously described that HCHs and PentaCXs are transformed into TCBs and HexaCXs and HeptaCHs are transformed to TetraCBs (Santos et al., 2018a, 2018b) as shown in Fig. 2.

However, the occurrence and distribution of TCBs and TetraCBs during these transformations in the soil phase has not been reported previously. After the alkaline treatment of F and G soil fractions –as described in the experimental section- COCs concentration in soil was analyzed and values obtained are shown in Table 3. For the scope of an easier analysis of the effect of alkali addition on the transformation of COCs in soil the concentration of

COCs is shown as mmol kg soil⁻¹. As can be seen in Table 3, 48 h after the soil has been kept at alkaline conditions (pH > 12) the PentaCX, HexaCX, HCHs and HeptaCHs have almost disappeared. On the contrary, the concentrations of TCBs and TetraCBs in the soil have significantly increased after the alkaline treatment, as predicted by reactions in Fig. 2.

An example of the GC chromatograms of the COCs extracted from the F soil before and after the addition of alkali is shown in Figure SI-4 a and SI-5 (ECD and FID detectors, respectively). This change can be explained by the dehydrochlorination reaction proposed elsewhere (Santos et al., 2018a) and summarized in Fig. 2. As these reactions do not involve a change of moles, the sum of mmol of COC per kg of soil is expected to remain constant before and after the alkaline treatment. This complies with the experimental values of total COCs as mmol kg_{soil}⁻¹ obtained and summarized in Table 3, for both F and G fractions.

For each soil fraction, the mole fraction of a compound of the j compound in the sum of COCs before and after addition of the alkali has been calculated by Eq (1) and the values obtained are shown in Figure SI-6 (pH 7) and SI-7 (pH 12).

The moles of HCHs and PentaCX that have disappeared from the soil after alkali addition are called Δ HCHs + PentaCX (mmol kg soil⁻¹). The moles of TCBs generated when pH changes from neutral to alkaline conditions is called Δ TCBs (mmol kg soil⁻¹).

The moles of HeptaCHs and HexaCXs that have disappeared from the soil after alkali addition are called Δ HexaCX + HeptaCHs (mmol kg soil⁻¹). The moles of TetraCBs generated when pH changes from neutral to alkaline conditions is called Δ TetraCBs (mmol kg soil⁻¹). From data in Table 3, the redistribution of COCs in soil due to the pH change is summarized in Fig. 3 and Tables SI–4. As can be seen, the balance of moles between the disappearing Δ HCHs + PentaCX and appearing Δ TCBs and between the disappearing Δ HexaCX + HeptaCHs and generated Δ TetraCBs matches quite well. The ΔTCBs produced are distributed among isomers 1,3,5; 1,2,4 and 1,2,3 and the ΔTetraCBs generated are distributed between TetraCBs a (1,2,4,5 + 1,2,3,5) and TetraCBs b

Table 3
Composition of COCs in soil (mmol j kg_{soil}⁻¹), fractions F (size < 0.25 mm) and G (size between 2 and 0.25 mm), at neutral and alkaline conditions.

Compound (mmol/kg soil)	M _j	F soil fraction pH 7	F soil fraction pH > 12	G soil fraction pH 7	G soil fraction pH > 12
CB	112	0.001	0.00	0.004	0.00
1,3 DCB	146	0.007	0.02	0.002	0.02
1,4 DCB	146	0.024	0.05	0.013	0.01
1,2 DCB	146	0.030	0.12	0.032	0.05
1,3,5 TCB	180	0.016	0.50	0.008	0.16
1,2,4 TCB	180	0.414	19.72	0.156	5.87
1,2,3 TCB	180	0.112	3.22	0.051	0.89
TetraCB (1,2,4,5 + 1,2,3,5)	214	0.673	3.40	0.383	1.46
TetraCB (1,2,3,4)	214	1.335	6.16	0.682	2.70
γ-PentaCX	252	0.777		0.463	
PentaCB	248	0.127	0.18	0.068	0.08
δ-PentaCX	252	0.822		0.447	
θ-PentaCX	252	0.065		0.028	
HexaCX-a	289	0.228		0.116	
β-PentaCX	252	0.126		0.065	
η-Penta CX	252	0.059		0.027	
HexaCX-b	286	0.100		0.036	
HexaCX-c	286	0.339		0.151	
α-HCH	291	2.672		0.851	
HexaCX-d	286	0.000		0.002	
β-HCH	291	0.057		0.013	
γ-HCH	291	14.930		3.288	
HeptaCH-1	322	3.747		1.291	
δ-HCH	291	4.328		1.303	
ε-HCH	291	1.168		0.444	
HeptaCH-2	322	1.640		0.583	
HeptaCH-3	322	0.771		0.291	
Total mmol/kg		33.568	33.38	11.158	11.25

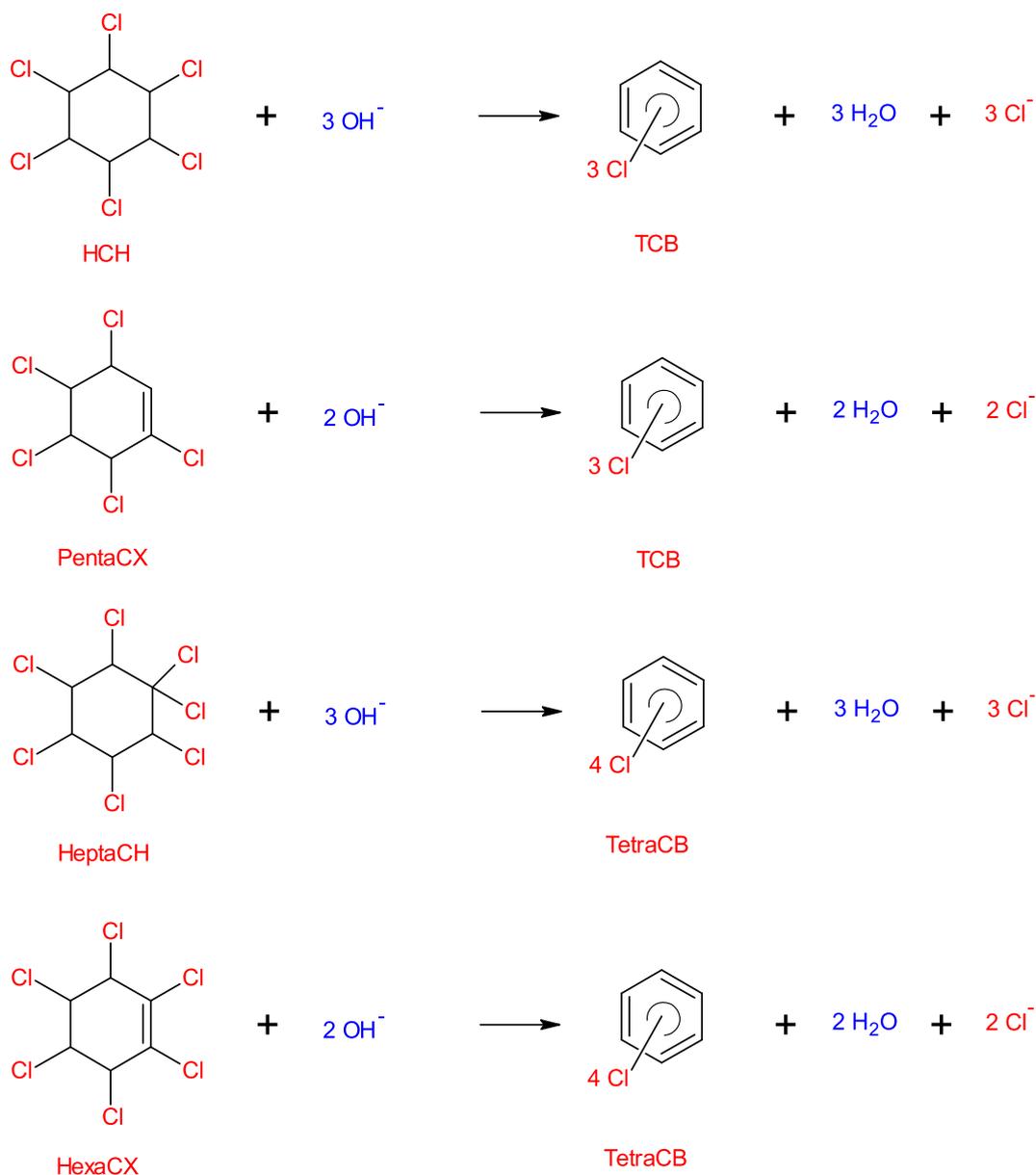


Fig. 2. Dehydrochlorination reactions at alkaline pH.

(1,2,3,4). The percentage of the Δ TCBs and Δ TetraCBs going to each isomer is also summarized in Fig. 3. As can be seen, the most favored isomer is 1,2,4 TCB (about 85% in both F and G fractions), followed by 1,2,3 TCB (13%) and finally 1,3,5 TCB (2%). The transformation to TetraCBs is favored towards 1,2,3,4 TCB (about 65%) while the sum of isomers 1,2,3,5 and 1,2,4,5 explains the 35% of the TetraCBs generated by dehydrochlorination reactions in alkaline conditions.

It should be noted that dehydrochlorination reactions take place in the soil in up to 48 h after the pH is changed from neutral to alkaline conditions (pH about 12) and that the COCs generated are much less toxic than the parent compounds (Willett et al., 1998; Tsai and Chen, 2007; Tsaboula et al., 2016). As an example, the available data on persistence of 1,2,4-trichlorobenzene, obtained from dehydrochlorination of HCHs, indicates a half-life in water of a few days and a significant biodegradation potential (van Wijk et al., 2006). Therefore, despite other treatments could be applied for soil and groundwater remediation (ISCO, S-ISCO, ISCR, etc.) the change

from neutral to alkaline pH alone could be considered a positive accomplishment from an environmental point of view.

The concentration of COCs in the aqueous phase in equilibrium with F and G fractions at neutral or alkaline pH is shown in Tables SI-4.

With data in Table 3 and Tables SI-4, the linear partition coefficient in soil-water has been calculated, defined by Eq (6), and used in some works in the literature (Djohan et al., 2005)

$$K_D = \frac{C_{js} \left(\frac{\text{mg}}{\text{kg soil}} \right)}{C_{jaq} \left(\frac{\text{mg}}{\text{L}} \right)} \quad (6)$$

Being C_{js} and C_{jaq} the concentration of j compound in soil and aqueous phase, respectively. Calculated values of K_D are also summarized in Tables SI-4. The differences in K_D between F and G soil fractions indicates that a constant linear partition coefficient soil-water cannot be used for both soil fractions.

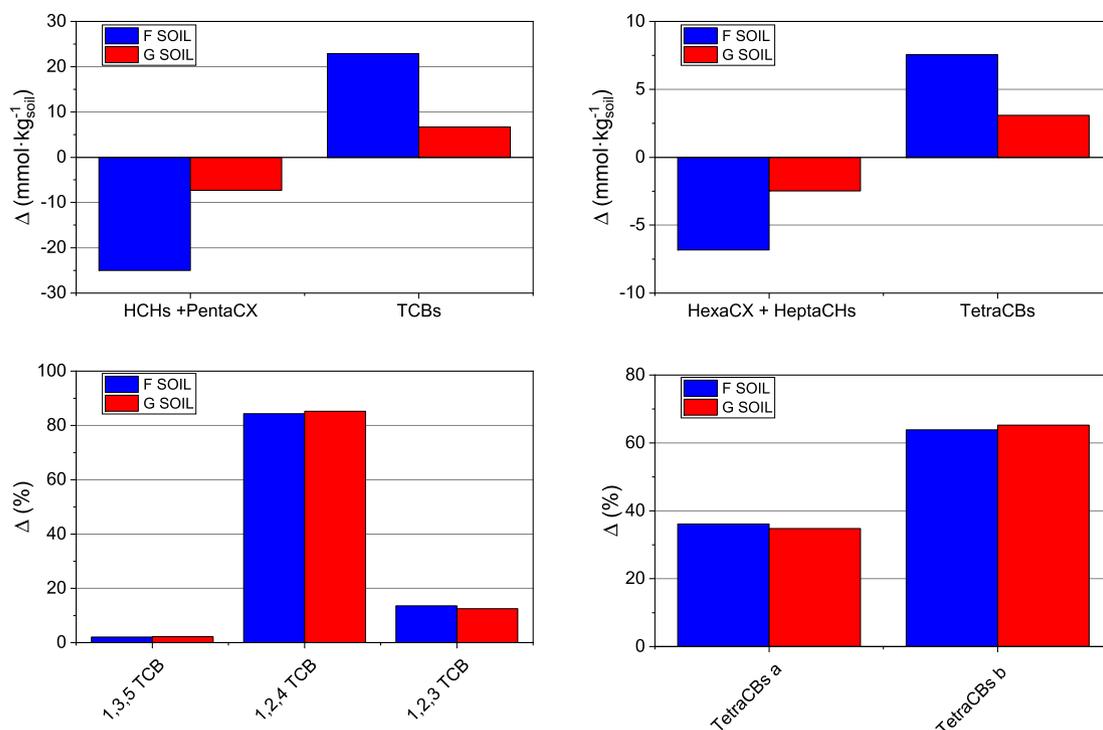


Fig. 3. Transformation of COCs in soil (fraction F and G) by dehydrochlorination reactions from neutral to alkaline pH (TetraCBs a: 1,2,4,5 + 1,2,3,5 isomers, TetraCBs b: 1,2,3,4 isomer).

To predict the solubility of each COC in the mixture of COCs in the soil, this mix has been considered as a DNAPL phase and Eq (2) has been used to calculate the $S_j \gamma_j (X_j^{ideal})^{-1}$ product of each compound for each soil fraction and pH, using the corresponding mole fraction of j , x_j , shown in Table 3 (pH = 7 and pH > 12) and the corresponding concentration of j in the aqueous phase given in

Tables SI–4.

Results are shown in Table 4. For the scope of comparison, the values of average $S_j \gamma_j (X_j^{ideal})^{-1}$ in Table 2, calculated for each compound when the aqueous phase was in equilibrium with the organic liquid phase, are also summarized in Table 4. As can be seen the values obtained for $S_j \gamma_j (X_j^{ideal})^{-1}$ after the equilibrium between

Table 4
Product $S_j \gamma_j (X_j^{ideal})^{-1}$ (mg L⁻¹) for the compounds present in soil, fractions F and G, at neutral and alkaline pH.

Compound	F soil fraction pH 7	G soil fraction pH 7	F soil fraction pH > 12	G soil fraction pH > 12	Average exptal from DNAPL liquid, Table 2
CB	nd	nd	nd	nd	428.4
1,3 DCB	nd	nd	nd	nd	140.0
1,4 DCB	nd	nd	nd	nd	116.3
1,2 DCB	nd	nd	nd	nd	121.0
1,3,5 TCB	nd	nd	9.42	7.04	n.q.
1,2,4 TCB	33.78	29.05	11.82	11.59	33.9
1,2,3 TCB	41.66	28.69	13.21	13.78	36.7
TetraCB (1,2,4,5 + 1,2,3,5)	14.38	8.15	2.75	2.70	11.5
TetraCB (1,2,3,4)	15.28	10.88	2.66	2.54	12.0
γ -PentaCX	58.98	29.54			96.6
PentaCB	8.14	4.93	1.51	1.34	7.7
δ -PentaCX	152.87	86.55			84.7
θ -PentaCX	155.98	95.22			n.q.
HexaCX-a	31.08	21.72			11.2
β -PentaCX	137.16	67.95			n.q.
η -Penta CX	120.50	68.53			43.6
HexaCX-b	39.94	32.52			
HexaCX-c	62.28	41.99			
α -HCH	39.65	38.21			36.4
HexaCX-d	nd	nd			
β -HCH	0.00	0.00			
γ -HCH	15.94	20.83			47.7
HeptaCH-1	25.60	21.57			15.3
δ -HCH	124.35	112.58			85.3
ϵ -HCH	77.12	60.83			68.2
HeptaCH-2	28.87	22.98			10.8
HeptaCH-3	59.17	49.07			24.3

the soil and the aqueous phase is reached at neutral pH are quite similar to those obtained at the equilibrium of a DNAPL liquid organic phase with an aqueous phase at neutral pH (Table 2). This could be explained if the COC mixture in the soil behaves as a DNAPL phase. Therefore, the solubility in the soil-water equilibrium could be predicted by Eq (5) using the same $S_j \gamma_j (X_j^{ideal})^{-1}$ values shown in Table 2.

Furthermore, in strong enough alkaline conditions (pH about 12), the $S_j \gamma_j (X_j^{ideal})^{-1}$ of the COCs is lower than the value obtained at neutral pH (Table 4). This means that lower concentration of the COC is expected in the aqueous phase, for the same mole fractions of COCs in soil. In fact, as it can be deduced from Table 3, the sum of COCs in the aqueous phase in alkaline conditions is about 1/3 of the sum of COCs at neutral pH, in addition to the lower toxicity of the compounds present in alkaline conditions.

4. Conclusions

The fate of Dense Non-Aqueous Phase Liquids, DNAPLs, in the environment strongly depends on their solubility in water. The partitioning behavior in water of pollutants in DNAPL phases present at Sabiñanigo landfills, Spain, has been studied here for the first time. This DNAPL was a liquid waste obtained in the lindane production in a factory nearby. About 28 Chlorinated Organic Compounds, COCs, from chlorobenzene to heptachlorocyclohexane were identified. Among these 20 are solid crystals as pure-phases.

The approach of Banerjee (1984) and Broholm et al. (Broholm and Feenstra, 1995) considering the sub-cooled liquid state of solid compounds (Jain and Yalkowsky, 2001; Yalkowsky and Wu, 2010) has been successfully applied to predict the solubility of the organochlorines in aqueous phase. However, for compounds as pentachlorocyclohexene, hexachlorocyclohexene and heptachlorocyclohexane isomers, which constitute 20–45% in weight of the DNAPL organic phase, neither the solubility nor other data as the entropy of fusion at the melting point and the melting temperature at $P = 1 \text{ atm}$ are available in literature. Therefore, their solubility as pure compounds has not been calculated but the product $S_j \gamma_j (X_j^{ideal})^{-1}$ has been obtained. This value would allow to predict the concentration in the aqueous phase from the composition of the organic phase, when both phases are in equilibrium.

The solubility values obtained at neutral pH were similar for both DNAPL as free liquid phase or for DNAPL trapped into the soil. Moreover, it was found in this work that alkaline condition promotes dehydrochlorination of PentaCX, HexaCX, HCHs and Hep-taCHs in soil to pollutants with lower toxicity in less than 48 h. Moreover, a decrease of the solubility of the dehydrochlorination products in alkaline conditions was found.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124798>.

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