



Extraction and quantification of chlorophenolate molecules in soils spiked with 2,4-dichlorophenol and 2,4,5-trichlorophenol



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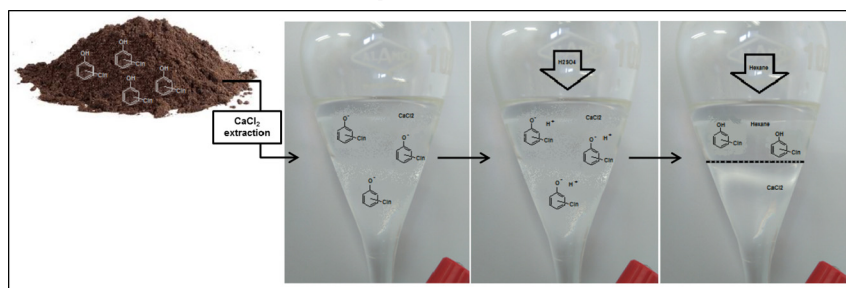
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HIGHLIGHTS

- A simple and effective method of determining chlorophenolates in soil was developed.
- Identification and quantification of chlorophenolates by gas chromatography are possible.
- The method enables the analysis of neutral and anionic forms of chlorophenols in soils.
- The bioavailability and transformation of chlorophenols in soils should be investigated further.

GRAPHICAL ABSTRACT

Illustration of ionized molecules extraction procedure.



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ABSTRACT

The compounds 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) are classified as priority pollutants, with potentially hazardous impacts on the environment. In soil, dissociation of the phenol group occurs, resulting in the simultaneous presence of neutral phenol and anionic phenolate. Although the toxicity of 2,4-DCP and 2,4,5-TCP to soil microbiota has been suggested to be mainly due to the phenolate anion, this hypothesis cannot be tested due to the lack of appropriate methods of extracting and quantifying the anionic form of these compounds (unlike the neutral form, which can be easily quantified). In this study, we developed a method that enables extraction and quantification of phenolate ions. The method could therefore be used to elucidate the processes that regulate the behaviour of chlorophenolic molecules in soil and to clarify the distribution and toxicity of these compounds in the edaphic environment. The proposed method uses saline solutions (CaCl_2 , KCl and K_2SO_4) of low ionic strength to extract the chlorophenolate anion from soil, followed by sequential transformation of the anion from the aqueous solution to an organic solvent that enables subsequent identification and quantification of the molecule by gas chromatography. Two soils of contrasting pH were used to test whether the proposed method was practicable. The method enabled analysis of the distribution of the neutral and anionic forms of the chlorophenols in both types of soil considered and revealed the influence of soil pH in this distribution.

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1. Introduction

The organochlorine compounds 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP), classified as priority pollutants by

both the US Environmental Protection Agency (USEPA) and the European Union (EU), are widespread throughout the environment, including soils (Gao et al., 2008; Persson et al., 2008; Chasib, 2013). Both 2,4-DCP and 2,4,5-TCP are generally found in soils because of their use in silviculture (as antifungal agents to slow down the rotting of timber) and agriculture (as precursors of various herbicides) or because of accidental spillage of wastewater from the paper bleaching process

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(Kookana and Rogers, 1995; Cea et al., 2007; Olaniran and Igbinoso, 2011). The widespread distribution of these compounds in the environment has led to research on their behaviour in the environment, particularly in relation to their effects on living organisms and soil functioning (Boucard et al., 2005; Moscoso et al., 2007; Martí et al., 2011; Arora and Bae, 2014; Liu et al., 2015). These studies have shown that the transformation undergone by both chlorophenols in soil is influenced by the concentration and chemical characteristics (e.g. the degree of chlorination) of the compounds, and also by soil characteristics such as pH, organic matter content and inorganic colloid content (Czaplicka, 2004; Martí et al., 2007; Bello et al., 2013). In soil, dissociation of the phenol group occurs, thus releasing a proton from the hydroxyl group and producing an equilibrium in which the neutral phenol and the anionic phenolate coexist. The speed of the dissociation reaction will be regulated by the pK_a of the compound and by the pH of the soil solution. The pK_a values of 2,4-DCP and 2,4,5-TCP are 7.5–8.1 and 7.0–7.7, respectively. The presence of the neutral forms will thus be favoured in acidic soils, while the equilibrium will shift towards generation of the anionic forms in calcareous soils (with pH closer to the pK_a of both chlorophenols) (Fig. 1). However, it has also been shown that, apart from dissociation, the main process regulating the distribution and toxicity of chlorophenols in the edaphic environment is adsorption onto solid particles, mainly organic matter and clays (He et al., 2006; Frankki et al., 2007; Scelza et al., 2008; Stipicević et al., 2009; Cea et al., 2010; Bosso et al., 2015a; Liping et al., 2015; Hechmi et al., 2016). Adsorption of chlorophenols will mainly occur as a result of physical, hydrophobic and π - π interactions with the neutral form of chlorophenols (Chiou et al., 1983; McBride, 1994; Fukushima et al., 2014; Bosso et al., 2015b; Chien et al., 2017; Rao et al., 2017). However, adsorption of the anionic form will be greatly limited by the strong electrostatic repulsion between the ionized compound and the organic matter and soil colloids due to the hydrophilic nature and negative charge of the compound. Indeed, diverse studies have indicated that adsorption of the phenolate anion is almost non-existent (Lagas, 1988; Boyd et al., 1989; Jafvert, 1990; Stapleton et al., 1994). The anionic molecule derived from the dissociation of chlorophenol should therefore remain in the soil solution. On the other hand, because of its negative charge, solubility in water and relatively small size, the phenolate anion can pass through the cell membranes and, once inside the cytoplasm, cause the death of the soil microorganisms. The toxicity of 2,4-DCP and 2,4,5-TCP to the soil microbiota has thus been suggested to be mainly due to the presence of the phenolate anion (Packham et al., 1982; Bello et al., 2008, 2013). However, this hypothesis cannot be proven because there is no method available for determining the anionic form in soil samples. Thus, while the

neutral molecule is hydrophobic, and can therefore be readily extracted from the soil matrix with organic solvents and quantified by gas-chromatography (GC) (Llompert et al., 1997; Jakubowska et al., 2009), the negatively charged phenolate anion is soluble in aqueous solutions and therefore cannot be extracted with organic solvents and directly quantified by GC.

The first difficulty in determining the anionic molecule involves the extraction stage. Due to its polar and hydrophilic nature, chlorophenolate must be extracted with polar solvents. Saline solutions of low ionic strength, such as those commonly used to extract labile soil compounds (Kowalenko, 1993; Zeng et al., 2014), could therefore be used to extract the anionic molecule. Nonetheless, even if these saline solvents could be used to extract chlorophenolate from soil, direct determination by GC would not be possible, for two main reasons. First, in GC, the analytes must be injected into a highly volatile organic solution to facilitate their volatilization and transport along the column. Second, interactions between the negative charge of the anionic molecule and the stationary phase of the chromatographic column impede transport of the chlorophenolate to the detector. To resolve this problem, transformation of the anionic form contained in the saline solution is required. The transformation process should consist of two steps: 1) annulment of the repulsions generated by the negative charge on the anionic molecule, and 2) transfer of the molecule to an organic solvent. An acidic solution could be used to neutralize the negative charge of the chlorophenol, so that the acid would donate one of its protons to the phenolate and the phenolic ring would recover its hydroxyl group. Thereafter, all of the chlorophenolate extracted from the soil and contained in the saline solution would be present in the neutral form, which will be more hydrophobic and therefore unstable in the saline solution. To make them more stable, the molecules must be transferred from the aqueous phase to an organic phase, for which they will show greater affinity. We propose a final step that would enable this transfer, producing extracts of the chlorophenolate, transformed to the chlorophenol form, in a solvent that can be injected in the chromatographic column for quantification.

The aims of the present study were to develop a method of extracting the anionic forms of 2,4-DCP and 2,4,5-TCP from soil and also produce molecules that can be quantified by chromatography. The behaviour of these chlorophenols in the environment could then be analysed and their bioavailability and the transformation processes that they undergo in soil determined, thus helping to clarify the mechanisms of action in soils (Peuravuori et al., 2002).

The study is based on the following hypotheses: i) the anionic forms of 2,4-DCP and 2,4,5-TCP can be extracted from the soil matrix with saline solutions of low ionic strength and concentration; ii) the negative charge on chlorophenol can be neutralized with an acidic solution, so all of the chlorophenolate extracted from the soil will be present in the neutral form, and iii) once transformed to the neutral form, the 2,4-DCP and 2,4,5-TCP molecules can be transferred by liquid-liquid extraction to an organic phase (for which they would display greater affinity) and can then be injected in the chromatographic column for quantification by gas chromatography.

2. Material and methods

2.1. Soils

As pH is one of the main parameters that determines the concentration of chlorophenolate in soil, we selected two agricultural soils of contrasting pH ($pH_{\text{acidic soil}} = 5.09$, $pH_{\text{calcareous soil}} = 7.65$) for study. Soil samples were obtained from the upper 10 cm of the soil (Ah horizon), sieved to <4 mm and thoroughly mixed. One portion of each sample was then stored at 4 °C before being spiked with the chlorophenols for development of the extraction method. The other portion of each sample was air-dried at ambient temperature for subsequent analysis to determine general properties. Air-dried and finely ground subsamples

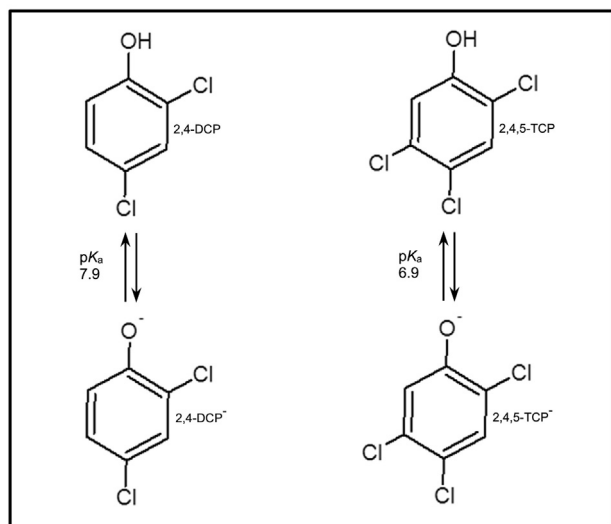


Fig. 1. Dissociation reaction for 2,4-DCP and 2,4,5-TCP.

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