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Enantiomeric fraction and isomeric composition to assess sources of DDT residues in soils

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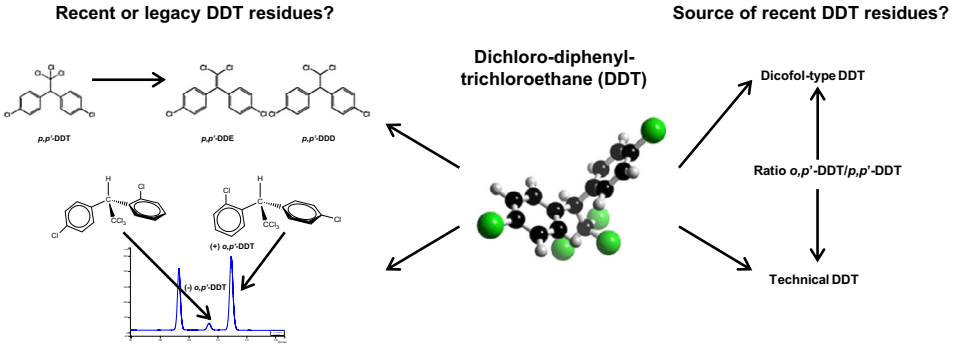
HIGHLIGHTS

- Accurate analysis of DDT isomers and their derivatives in soils has been performed.
- DDT/(DDE + DDD) and the EF of chiral *o,p′*-DDT were compared for source apportionment.
- DDT/(DDE + DDD) is less efficient than EF for discriminating recent from legacy DDT.
- We find recent DDT inputs in the Ebro River basin despite its ban in Spain since 90s.
- Technical DDT and dicofol-related DDT were identified as pollution sources of DDT.

GRAPHICAL ABSTRACT



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ABSTRACT

Chiral pesticides such as *o,p′*-DDT can undergo enantioselective microbial degradation in soil. Hence, the enantiomeric fraction (EF) of *o,p′*-DDT was used as an approach to assess potential recent inputs of DDT in the lower part of the Ebro River basin (NE Spain), a region heavily impacted by agricultural and industrial activities, including a dicofol production and a chloro-alkali plants. The EFs of five out of nineteen soils were not different from the racemic value (0.505 ± 0.010), confirming that the Ebro River and some of its tributaries, Segre and Cinca rivers, transported fresh DDT residues despite its ban in Spain during the 90s. *o,p′*-DDT/*p,p′*-DDT ratios in soils suggest that recent use of technical DDT and/or DDT-contaminated dicofol may be responsible for the fresh DDT inputs in the Segre River, while in the Ebro River, they indicate a dominant contribution of technical DDT, likely related to the residues accumulated by the chloro-alkali plant discharges.

1. Introduction

Dichlorodiphenyltrichloroethane (DDT) was widely used as an agricultural and domestic pesticide during the last century. Its persistence and ecotoxicological effects led to its ban in almost all industrialized countries during the 1970s (EEC, 1979). In addition, DDT production and use are restricted by the Stockholm Convention on Persistent Organic Pollutants (POPs). However, the Stockholm Convention and the World Health Organization (WHO) have recently endorsed an exemption for the use of technical DDT for indoor application in malaria-endemic countries (WHO, 2011). DDT is also an intermediate on the production of the current-use acaricide dicofol (2,2,2-trichloro-1,1-bis(4-chloro phenyl)ethanol), which may contain up to 0.1% of DDT residues

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(van de Plassche et al., 2002). This use of DDT in closed systems constitutes also an exemption under the Stockholm Convention. In addition to these primary DDT sources, emissions to the atmosphere of legacy DDT accumulated in contaminated environmental reservoirs such as water bodies, soils and glaciers (secondary sources) nowadays represent a significant DDT input to the environment, favored by the global warming (Noyes et al., 2009).

In the environment, DDT is transformed primarily to the more stable metabolites dichlorodiphenyldichloroethane (DDD) and dic hlorodiphenyldichloroethylene (DDE) under anaerobic and aerobic conditions, respectively, by either biotic (microbial conversion) or abiotic processes (i.e. chemical breakdown, photodegradation). Experiments have shown that approximately 66% of DDT applied to agricultural fields is transformed into DDE within one year (Cliath and Spencer, 1972). The transformation rates depend on several factors. The main parameters in the case of soils are soil type, temperature, moisture and organic carbon content. Usually, ratios of *p,p′*-DDT to *p,p′*-DDD or/and *p,p′*-DDE concentrations have been used to discriminate past *versus* fresh DDT inputs, as well as to characterize the dominant environmental degradation pathways (Rapaport et al., 1985).

Several organochlorine (OC) pesticides and their derivatives, such as *o,p′*-DDD and *o,p′*-DDT, are chiral and manufactured as racemic mixtures of enantiomers (1:1). These enantiomers have identical physical–chemical properties and abiotic degradation rates, but often show different toxicological properties and rates of metabolism (Müller and Kohler, 2004). Several studies have shown that this enantioselective degradation by microorganisms can result in nonracemic signatures of these chiral pesticides (Bidleman and Falconer, 1999; Leone et al., 2001), which can be used for discriminating recent inputs of technical DDT from residues of past applications (Kurt-Karakus et al., 2005; Li et al., 2006). In this sense, it has been observed that residues of *o,p′*-DDT have a nonracemic signature after 209 days of starting a field experiment with spiked soil (Kurt-Karakus et al., 2007), although transformation rates are extremely soil specific and can be highly variable.

In Spain, DDT has been banned since 1994; however recent studies show the presence of significant concentrations of DDT and its metabolites in top predators and abiotic samples (Gómara et al., 2008; Lacorte et al., 2006). Additionally, high DDT concentrations and high *p,p′*-DDT/(*p,p′*-DDE + *p,p′*-DDD) ratios have been reported in soils from several locations pointing to recent inputs of this pesticide, which raises the need for investigating their origin.

One of these DDT-impacted areas is the lower part of the Ebro River basin, situated in the northeastern Spain, including its tributaries, Cinca and Segre Rivers. This area is characterized by both agricultural and industrial activities. Two possible pollution sources of DDT in this region are the chloro-alkali plant located in Flix (Tarragona Province, Catalonia, Spain) and the chemical facility in Monzón (Huesca Province, Aragón, Spain). During several decades, DDT was manufactured in Flix till its production was banned. As a consequence, DDT and other OC pollutants were accumulated in the wastes dumped in a water reservoir of the Ebro River located besides the chloro-alkali plant, which have been mobilized downstream mostly in suspension with high river flows (Bosch et al., 2009) and to the atmosphere (Garí et al., 2014). DDT releases in Monzón are mainly related to the production of dicofol (de la Cal et al., 2008). In the past, dicofol was manufactured in the chemical plant of Monzón, involving the in-house production of DDT, until the facility ceased its production in 2009 (UN-ECE, 2010). Taking into account these considerations, current concentrations of DDT in the lower Ebro river basin may be caused by: (a) recent applications of technical DDT; (b) DDT inputs related to its presence in technical dicofol; (c) residues from historic applications; or (d) deposition of long-range transported DDT from regions where this pesticide is currently applied.

In the present study, DDT content and the enantiomeric fraction (EF) of *o,p′*-DDT was determined in soils collected along the Ebro River basin with the aim of determining levels and composition of DDT residues in soils and investigate the different available approaches used to establish their origin: EF of *o,p′*-DDT and DDT to its degradation product ratios.

2. Experimental

2.1. Study area and sample collection

Thirty soil samples from the lower part of the Ebro River basin were collected in winter 2006 and spring 2007 (Fig. 1 and Table S1). Four samples were located in the surroundings of a dicofol production plant (Monzón, Huesca Province, Spain) (M1–M4) and two more close to Cinca river, upstream (UPM) and downstream (DWM) the chemical plant. Seven soils were collected along the main tributaries of the Ebro River, Cinca (C1–C4) and Segre Rivers (SE), at their confluence (A) and in the Mequinensa water reservoir (ME). The rest of the samples were from agricultural fields irrigated with water abstracted upstream (UPF1, UPF2) and downstream (DWF1–DWF6) of the chloro-alkali in Flix and in the Ebro River delta (D1–D3). Moreover, two urban soils were collected in Flix (F1 and F2). Sástago, close to Ebro River (R1–R3), was used as a reference site, since it is located upstream of both chemical factories of Monzón and Flix. Finally, two additional soil samples from a remote area such as the Pyrenees, where DDT occurrence is the consequence of a long-range atmospheric transport, were also analyzed for comparison (P1 and P2).

Surface litter was removed before sample collection. Surface soil (upper 10 cm) was collected with a 7 cm (diameter) × 20 cm (long) stainless steel cylinder. This cylinder was cleaned with deionized water and acetone between samples to avoid cross-contamination. Samples were stored in glass jars, transported to the laboratory at −4 °C, where they were stored at −20 °C until further analysis. Four different commercial dicofol products used in the area were also analyzed in order to determine their DDT content.

2.2. Materials

A mix of DDT isomers and derivatives (pesticide Mix-164) was from Dr. Ehrenstorfer, GmbH (Augsburg, Germany). Deuterium labeled *p,p′*-DDE-d_8 and *p,p′*-DDD-d_8 and isotopically labeled *p,p′*-DDT-$^{13}C_{12}$ used as surrogate standards were also purchased from Dr. Ehrenstorfer except *p,p′*-DDD-d_8 which was from Cambridge Isotope Laboratories (Andover, MA USA). Additional information on solvents and other materials used and their pretreatment is included in the supplementary material.

2.3. Extraction and clean-up

DDT isomers and derivatives (DDX) determination was based on the optimized method reported by Kurt-Karakus et al. (2006). Soil was mixed with sodium sulfate and spiked with *p,p′*-DDE-d_8, *p,p′*-DDD-d_8 and *p,p′*-DDT-$^{13}C_{12}$. Then, they were Soxhlet-extracted with DCM for 16 h. Concentrated extracts were cleaned up by column adsorption chromatography and treated with activated copper for the removal of sulfur-containing compounds. Further details on sample extraction and clean-up are included in the supplementary materials. Additionally, total organic carbon (TOC) content in soils was determined as described in supplementary materials.