

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN AGRICULTURAL SOILS APPLYNG QUECHERS, C-ECD AND GC-MS/MS

DETERMINAÇÃO DE PESTICIDAS ORGANOCLORADOS EM SOLOS AGRÍCOLAS UTILIZANDO A METODOLOGIA QUECHERS, GC-ECD E GC-MS/MS

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ABSTRACT

The organochlorine pesticides (OCPs), due the wide use in agriculture until about 30 years (except the most recent bans by the EU for lindane, methoxychlor and endosulfan) and their chemical stability and slow biodegradation became ubiquitous pollutants. Most OCPs are persistent organic pollutants that have long life cycles in the environment and being transported for long distances. The residues of pesticides in soil can be absorbed by plants, entering the food chain, leading to bioaccumulation. The objective of this study was to determine the presence of 14 OCPs (HCH (α , β , ζ), HCB, lindane, aldrin, α -endosulfan, dieldrin, *p*, *p'*-DDE, endrin, endosulfan β -*p-p'*-DDD, *o-p'*-DDT and methoxychlor) in soils of 5 Portuguese regions. The extraction was performed with QuEChERS, analysis by GC-ECD and confirmation by GC-MS/MS. One sample showed a residue above the

LOQ, revealing contamination by dieldrin at a concentration of 45.36 $\mu\text{g} \cdot \text{kg}^{-1}$.

Keywords: Gas chromatography, organochlorine pesticide, QuEChERS, soil.

RESUMO

Os pesticidas organoclorados (OCPs), devido à sua ampla utilização na agricultura até há cerca de 30 anos (exceto as mais recentes proibições, pela UE, de lindano, de metoxicloro e de endossulfão) à sua estabilidade química e à lenta biodegradação tornaram-se poluentes omnipresentes. A maioria dos OCPs são poluentes orgânicos persistentes que se caracterizam por longos ciclos de vida no ambiente e por serem transportados a longas distâncias. Os resíduos dos pesticidas nos solos podem ser adsorvidos pelas plantas, entrando na cadeia alimentar, levando à sua bioacumulação. O objetivo deste estudo foi determinar a presença de 14 OCPs (HCH (α , β , ζ), HCB, lindano, aldrina, α -endossulfão, dieldrina, *p-p'*-DDE, endrina, β -endossulfão *p-p'*-DDD, *o-p'*-DDT e metoxicloro). em solos agrícolas de 5 Regiões Portuguesas. A extração foi realizada com QuEChERS, as análises por GC-ECD e a confirmação por GC-MS/MS. Foi apenas encontrado um resíduo acima do LOQ, evidenciando contaminação por dieldrina na concentração de 45.36 $\mu\text{g} \cdot \text{kg}^{-1}$.

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Palavras-chave: Cromatografia gasosa, pesticida organoclorado, QuEChERS, solo.

INTRODUCTION

Organochlorine pesticides (OCP) are one of the most prevalent contaminants (Negoița, Covaci, Gheorghe *et al.* 2003) and were applied in the second half of the twentieth century worldwide as insecticides and fungicides against pests in fruit growing, horticultural and arable crops (Hilber, Mader, Schulin *et al.* 2008).

Although the human health effects after exposure to OCPs are not adequately understood it has been considered that these contaminants have an endocrine-disrupting activity and that they have also been implicated in the etiology of various diseases and endocrine-related disorders, such as pancreatic cancer, breast cancer, non-Hodgkin's lymphoma, leukemia, uterine cancer, liver cancer, sexual precocity, cryptorchidism, and low sperm concentration (Botella, Crespo, Rivas *et al.* 2004).

In Portugal, according with the legislation (Decreto-Lei nº347/88 and Portaria nº660/88) most of the OCPs were prohibited in 80s (Cruz, Lino and Silveira 2003) but they can be found in the environment even decades after being banned (Negoița, Covaci, Gheorghe *et al.* 2003).

In the last decades the application of pesticides has become an essential matter for discussion (Asensio-Ramos, Hernandez-Borges, Ravelo-Perez *et al.* 2010). Soil is considered to be an important agricultural resource which has an ability to retain agro-chemicals including pesticides (Rashid, Nawaz, Barker *et al.* 2010). It is known that OCPs still persist in soils (Zhang, Luo, Zhao *et al.* 2006) because they are not degraded, nor volatilized, nor even leached due to their lipophilicity (Connell, Miller, Mortimer *et al.* 1999; Shen and Wania 2005) and strong affinity to soil organic matter (SOM) (Ahmad, Nelson and Kookana 2006). Nevertheless

sorption of organic pollutants to SOM and other soil particles (Prosen, Fingler, Zupančić-Kralj *et al.* 2007) could not prevent specific plants of taking them up (Hilber, Mader, Schulin *et al.* 2008)

Consequently it has led to the ingress of OCPs into growing plants and the persistence of their residues (Waliszewski, Carvajal, Gomez-Arroyo *et al.* 2008). Which by its turn affects animals due to the entrance of such pollutants in food chains.

Determination of OCPs is therefore of relevant importance and it is fundamental that the methodology for determining residues guarantees true and precise results at appropriately low limits of detection (Wiilkowska and Biziuk 2011).

Recent studies have applied ultrasonic solvent extraction (Tor, Aydin and Ozcan 2006), pressurized liquid extraction (Vega Moreno, Sosa Ferrera, Santana Rodriguez *et al.* 2008), shake-flask extraction (Dabrowska, Dabrowski, Biziuk *et al.* 2003), microwave assisted micellar extraction (Vega Moreno, Sosa Ferrera and Santana Rodriguez 2006) followed in some cases by a clean-up step with solid-phase extraction (SPE) (Dabrowska, Dabrowski, Biziuk *et al.* 2003) or solid-phase microextraction (SPME) (Vega Moreno, Sosa Ferrera and Santana Rodriguez 2006).

The QuEChERS methodology has also been recently applied for the determination of pesticides in soils (Asensio-Ramos, Hernandez-Borges, Ravelo-Perez *et al.* 2010; Rashid, Nawaz, Barker *et al.* 2010). Anastasiades *et al.* introduced this methodology in 2003 as an original analytical method which combined the extraction/isolation of pesticides from food matrices and extract clean-up (Wiilkowska and Biziuk 2011). Although it started to be applied to food matrices nowadays the application of the method to other matrices and also to other analytes has occurred (Wiilkowska and Biziuk 2011).

In the determination of OCPs gas chromatography coupled to an electron-capture detector has been considered highly sensitive for the quantification of these compounds (Fenik J. 2011; Fernandes, Domingues, Ma-

Table 1 – Pesticides ecotoxicology and impact in Human health.

| Pesticide | Ecotoxicology | Human health and protection |
|---------------------|---|--------------------------------------|
| HCH | POP B5 <i>Colinus virginianus</i> B5 <i>Oncorhynchus mykiss</i> P3 Unknown species fish B4 <i>Daphnia magna</i> F4 <i>Americamysis bahia</i> F4 <i>Chironomus riparius</i> F4 <i>Lemna gibba</i> F4 <i>Scenedesmus abundans</i> Q2 Algae unknown species B4 Contact Honeybees L3 <i>Eisenia foetida</i> HarmlessAA2 <i>Chrysoperla carnea</i> | Neurotoxicant |
| HCB | POP, PBT G4 <i>Colinus virginianus</i> F4 <i>Oncorhynchus mykiss</i> F2 <i>Daphnia magna</i> F4 <i>Scenedesmus abundans</i> F4 <i>Eisenia foetida</i> | Carcinogen |
| DDT | POP G4 <i>Anas platyrhynchos</i> L3 <i>Oncorhynchus mykiss</i> J4 <i>Daphnia magna</i> F3 <i>Chironomus riparius</i> , 1 day L3 Oral Honeybees Moderately harmful AB1 <i>Typhlodromus pyri</i> | Mutagen Endocrine disrupter |
| aldrin | POP, PBT Q2 <i>Colinus virginianus</i> J3 <i>Lepomis macrochirus</i> J4 <i>Daphnia magna</i> F2 Oral Honeybees F2 Earthworms | Neurotoxicant Carcinogen |
| dieldrin | POP, PBT F3 <i>Anas platyrhynchos</i> F4 <i>Oncorhynchus mykiss</i> F4 <i>Daphnia magna</i> F4 <i>Chlorella pyrenoidosa</i> , F3 Honeybees | Mutagen; Neurotoxicant |
| endrin | POP, PBT R3 <i>Anas platyrhynchos</i> F4 <i>Oncorhynchus mykiss</i> F4 <i>Daphnia magna</i> F4 Contact Honeybees F4 <i>Lumbricus terrestris</i> | Neurotoxicant |
| endosulfan | POP L3 <i>Anas platyrhynchos</i> F4 <i>Oncorhynchus mykiss</i> Q1 <i>Oncorhynchus mykiss</i> , 28 day F4 <i>Daphnia magna</i> F4 <i>Americamysis bahia</i> F3 <i>Chironomus riparius</i> , 2 day F4 <i>Anabaena doliolum</i> C4 Contact Honeybees C4 <i>Eisenia foetida</i> HarmlessAA2 <i>Chrysoperla carnea</i> | Mutagen; Neurotoxicant |
| methoxychlor | POP L3 <i>Anas platyrhynchos</i> | Endocrine disrupter Neurotoxicant |

POP – persistent organic pollutant; PBT – persistent, bioaccumulative and toxic.

teus *et al.* 2011).

The aim of this work was the determination of 14 organochlorine pesticides residues in agricultural soils from 5 Portuguese Agricultural Regions, applying the QuEChERS methodology and the GC-ECD.

MATERIAL AND METHODS

Reagents and materials

For this study 14 OCPs (Table 1) were used: α -, β -, γ - and ζ - hexachlorocyclohexanes (HCH), hexachlorobenzene (HCB), *o,p'*-DDT ([1,1,1 trichloro-2,2-bis-(*p*-chlorophenyl) ethane]), *p,p'*-DDE ([2,2-bis(*p*-chlorophenyl)-1,1-dichloroethylene]), *p,p'*-DDD (dichlorodiphenyldichloro-ethane), aldrin, dieldrin, endrin, α -, β - endosulfan, and methoxychlor. Pesticide standards (purity > 97.0%) were obtained from Chemservice (West Chester, PA, USA), Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Sigma-Aldrich Co. A mixed stock solution of 350 $\mu\text{g L}^{-1}$, containing all of the OCPs, was prepared in *n*-hexane.

The internal standard (IS) of 4,4' - dichlorobenzophenone was purchased from Sigma-Aldrich and was 7400 $\mu\text{g.L}^{-1}$. All solutions were prepared in *n*-hexane. The *n*-hexane and the acetonitrile used were of HPLC

grade from Merck.

The selected QuEChERS (EUMIV50CT-VP) and cleanup (CUMPS15C18CT) were obtained from UCT (Bristol, PA).

Sampling

The samples were collected between December 2010 and July 2011 from 5 Portuguese Agricultural Regions, according to the Atlas from the Portuguese Geographic Institute (IGEO) (IGEO). All the soils were from conventional or organic farms (more than 5 years of organic practices), collected from 10-20 cm deep in the ground and placed directly in a suitable plastic bag (1 kg). Before use, soil samples were air-dried at room temperature and then sifted. Soils were divided in two groups. (Table 2)

Soil organic carbon (SOC)

For determining SOC in soils it was used a dry oxidative combustion method, Shimadzu-make TOC analyser (model VCSN, Shimadzu®, Japan) with a solid sample module (SSM-5000A).

Extraction procedure and method validation

The soil samples were extracted according to a previously described method

Table 2 – Soil sampling description.

| Soils n° | Group | Portuguese Agricultural Regions | Place | Type of farming | Date |
|----------|-------|---------------------------------|-------------------|-----------------|------------|
| 1 | A | Entre Douro e Minho | St Tirso-Trofa | Conventional | 23-12-2010 |
| 2 | B | Oeste | Nazaré | Conventional | 30-03-2011 |
| 3 | A | Algarve | Lagos | Organic | 26-04-2011 |
| 4 | A | Entre Douro e Minho | Gondomar | Conventional | 30-04-2011 |
| 5 | B | Alentejo | Odeceixe | Conventional | 05-05-2011 |
| 6 | B | Entre Douro e Minho | Póvoa Varzim | Conventional | 22-05-2011 |
| 7 | B | Entre Douro e Minho | Marco Canaveses | Organic | 04-06-2011 |
| 8 | B | Beira Litoral | Vagos | Organic | 18-06-2011 |
| 9 | A | Oeste | Rio Maior | Organic | 24-06-2011 |
| 10 | A | Entre Douro e Minho | Grijó | Organic | 27-06-2011 |
| 11 | A | Entre Douro e Minho | Oliveira do Douro | Conventional | 08-07-2011 |

Group A (high amount of organic carbon) and B (Low amount of organic carbon) of soils.

(Correia-Sá L., Fernandes V. C., Carvalho M. *et al.* 2012 in press). The method was validated according to the SOC (Correia-Sá L., Fernandes V. C., Carvalho M. *et al.* 2012 in press). Five grams of soil were hydrated by adding 3 mL of water and after 7 mL of acetonitrile. The tubes were capped tightly and shaken in vortex. Then it was added 6 g magnesium sulphate (MgSO₄), 1.5 g sodium chloride (NaCl), 0.750 g disodium citrate sesquihydrate (Na₂H₂Cit 1.5H₂O), 1.5 g sodium citrate dihydrate (Na₃Cit 2H₂O), from UCT® and it were shaken by a vortex. After the mixture was sonicated for 1 min. Samples were then centrifuged at 5,000 rpm for 10 min. A 1.5 mL of the supernatant was removed and transferred to the clean-up tube containing 50 mg of primary secondary amine (PSA), 150 mg of MgSO₄ and 50 mg of C18, CUMPS15C18CT from UCT® (Bristol, PA). The tubes were capped tightly and shaken by vortex for 1 min followed by centrifugation at 4,500 rpm for 5 min. An aliquot of the supernatant (1 mL) was transferred to a vial, and the extract was concentrated just to dryness using a gentle stream of nitrogen. Residue was reconstituted in 1.0 mL of n-hexane. Finally, the sample was capped, vortexed and placed into an autosampler vial for GC analysis (Correia-Sá L., Fernandes V. C., Carvalho M. *et al.* 2012 in press).

Gas Chromatography – Electron Capture Detector

OCP were analysed using a Shimadzu GC-2010 with an ECD apparatus, equipped with a capillary column of 30 m, ZB-XLB (0.25 mm i.d., 0.25 µm film thickness, Zebron- Phenomenex). The oven temperature was programmed starting at 65°C and held for 2 min, followed by increases of 8°C/min to 160°C, then 2°C/min to 235°C, and then 15°C/min to 250°C. The injection port was at 250°C splitless mode, and the detection was carried out at 300°C. Helium (Linde Sogás) was used as carrier gas at constant flow rate of 1.3 mL/min, whereas nitrogen (Linde Sogás, purity ≥99.999%) was employed as

makeup gas at flow of 30 mL/min. The system was operated by GC Solution Shimadzu software.

Gas Chromatography - Mass Spectrometry (GC-MS/MS).

In addition, the real samples with positive results by GC-ECD were analyzed using a Thermo Trace-Ultra gas chromatograph coupled to an ion trap mass detector Thermo Polaris, operated in the electron impact ionization (EI) at 70 eV. The ion source temperature was 250 C and the MS transfer temperature, 250 C. The system was operated by Xcalibur v 1.3 software. Confirmation of residues was carried out by GC-MS/SIM and MS/MS using a Supelco column fitted with an SLB-5MS (30 m 0.25 mm, 0.25 µm film thickness) column operating in the splitless mode; helium was used as carrier gas at a constant flow rate of 1.3 mL/min. The injector was maintained at 240 C. The oven temperature was programmed starting at 40 C and held for 2 min, followed by increases of 30 C/min to 220 C, held for 5 min, then 10 C/min to 270 C, and held for 1 min. For the identification of pesticides, the retention time, and three ions, the NIST and Wiley pesticide libraries were used. The MS/MS conditions were fixed for each compound, trying to select as precursor ion the one with the highest m/z ratio and abundance.

RESULTS AND DISCUSSION

The method yield good recoveries for both groups of soils and acceptable limits of quantification (Table 3) (Correia-Sá L., Fernandes V. C., Carvalho M. *et al.* 2012 in press).

Positive findings were found in soils for **HCH** isomers and **dieldrin**. The residues were found in samples produced by organic farming as well as in conventional farming. Only in one sample, from Entre Douro e Minho Region, was detected a residue above the LOQ, with a concentration of 45.36 µg.kg⁻¹

Table 3 – Recoveries, limits of detection and quantification.

| Pesticides | | Recovery | | | | Recovery | | |
|---------------|--------------------------------------|--|-------|-------|-------------------------------------|--|-------|-------|
| | | ±RSD (added $\mu\text{g kg}^{-1}$) | LOD | LOQ | | ±RSD (added $\mu\text{g kg}^{-1}$) | LOD | LOQ |
| α -HCH | Group A SOC from 2.36 to 4.73% | 84 ± 12 (80) | 13.96 | 46.53 | Group B SOC from 0.3 to 2.24% | 93 ± 5 (100) | 9.65 | 32.17 |
| HCB | | 70 ± 12 (80) | 23.77 | 79.23 | | 70 ± 4 (100) | 14.78 | 49.27 |
| β -HCH | | 101 ± 8 (80) | 11.33 | 37.77 | | 93 ± 5 (100) | 10.38 | 34.60 |
| lindane | | 70 ± 17 (80) | 10.68 | 35.59 | | 131 ± 6 (100) | 9.59 | 31.97 |
| δ -HCH | | 72 ± 15 (80) | 10.49 | 34.97 | | 120 ± 11 (100) | 8.67 | 28.90 |
| aldrin | | 77 ± 9 (80) | 9.94 | 33.12 | | 83 ± 3 (100) | 9.55 | 31.83 |
| End I | | 100 ± 8 (80) | 12.20 | 40.67 | | 98 ± 2 (100) | 7.55 | 25.17 |
| p,p'-DDE | | 87 ± 6 (80) | 10.89 | 36.30 | | 93 ± 1 (100) | 7.54 | 25.13 |
| dieldrin | | 78 ± 7 (80) | 4.06 | 13.52 | | 90 ± 7 (100) | 7.36 | 25.43 |
| endrin | | 70 ± 7 (80) | 21.92 | 73.08 | | 132 ± 1 (100) | 6.78 | 22.60 |
| End II | | 86 ± 7 (80) | 3.42 | 11.41 | | 122 ± 3 (100) | 7.60 | 25.33 |
| p,p'-DDD | | 70 ± 8 (80) | 9.68 | 32.26 | | 70 ± 2 (100) | 6.26 | 20.87 |
| o,p'-DDT | | 78 ± 10 (80) | 8.81 | 29.38 | | 82 ± 5 (100) | 6.11 | 20.37 |
| methoxychlor | | 70 ± 14 (80) | 12.75 | 42.51 | | 112 ± 7 (100) | 7.51 | 25.03 |

LOD ($\mu\text{g kg}^{-1}$) – limit of detection; LOQ ($\mu\text{g kg}^{-1}$) – limit of quantification; 5 g of soil.

for **dieldrin**. This can constitute a threat to the human consumer. The other studied pesticides were not detected in the samples.

The results obtained with this study reveal the importance of monitoring on a regular basis the levels of OCPs.

In Portugal, at the present moment, there are no limits established for OCPs in soil. In Swiss legislation there is a guide value of 2 mg kg⁻¹, but this value refers to the sum of aldrin, dieldrin, endrin or DDT isomers and its degradation products (Hilber, Mader, Schulin *et al.* 2008). So a potential health risk for humans is indicated by this trigger value, according to the Swiss legislation (Hilber, Mader, Schulin *et al.* 2008). None of the sampled soils exceeds this value.

The contamination seems to be independent of the farming system as the percentage of positive samples is similar in conventional and organic farming.

CONCLUSIONS

The results obtained showed that some of

these 14 compounds OCP tend to be very persistent, as they are still found although they were banned decades ago. Positive findings were found for HCH isomers and dieldrin.

From the 11 Portuguese soils studied only one soil sample obtained a concentration of dieldrin higher than the LOQ

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