

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN ARIES RIVER WATER NEAR AN INDUSTRIAL DUMP USING SPE/HS-SPME/GC-ECD METHOD

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Abstract. In this study 19 organochlorine pesticides (OCPs) were determined in Aries River, upstream and downstream of an industrial dump near Turda town (Cluj County, Romania), where tons of hexachlorocyclohexane (HCH) wastes were deposited. For the analysis of OCPs, solid phase extraction (SPE) followed by headspace solid phase microextraction (HS-SPME) were used for analytes extraction and concentration and then gas chromatography with electron capture detection (GC-ECD) for separation and quantification. In the two water samples all the investigated OCPs were detected and registered values of 144.5 ng/l and 316.4 ng/l, respectively. The most predominant contaminants were HCH isomers, mainly γ -HCH which exceeded the maximum admissible concentration in the downstream water sample. The composition of HCHs showed that there was fresh input of lindane (γ -HCH).

Keywords: organochlorine pesticides, SPE, HS-SPME, GC-ECD, surface water

INTRODUCTION

Organochlorine pesticides (OCPs) are among the most widespread and persistent environmental pollutants. They are toxic, highly resistant to degradation and they tend to bioaccumulate through the food chain (Derouiche et al., 2007). Humans and animals exposed to OCPs can develop various health problems including cancer, genetic variation, diseases of the immune system, reproductive toxicity (Wang et al., 2009), being also potential endocrine disruptors (Zhang and Lee, 2012). Nowadays, these compounds are forbidden around the world, but due to their physicochemical properties they can still be found at trace levels in the environment (Neves Dias et al., 2015). OCPs can enter the aquatic environment through different pathways, including effluent discharge, agricultural runoff, atmospheric deposition and air/water exchange (Yuan et al., 2013). Monitoring the trace levels of organochlorine pesticides in water is important for human health protection and environmental control (Lu et al., 2011).

In the last years, the analytical methods tended towards miniaturisation, and improvement of sample extraction and cleanup methods with universal microextraction procedures. Among these extraction and cleanup methods, solid phase extraction (SPE) and solid phase microextraction (SPME) have become popular techniques. SPE represents a cost-effective alternative to/replacement for liquid-liquid extraction (productivity, solvent, waste). SPME is an inexpensive, environment-friendly and solvent-free technique with reliable and excellent sensitivity, as well as good selectivity (Merib, 2013). The SPME, prior to the GC analysis can be carried out by direct immersion of the fibre into the sample (DI-SPME) or via the exposure of the fibre in the headspace above a liquid or solid sample (HS-SPME) (Chai and Tan, 2009).

In this study, the surface water samples were collected from Aries River, near the industrial dump of “Poșta Rât”, located on the left side of the Aries River, in the

unincorporated territory of the Turda town, Cluj County, Romania, and occupies an approximately 10 ha area. The former Turda Chemical Plants deposited on the dump 18,500 tons of toxic substances, mainly hexachlorocyclohexane (HCH), a toxic waste resulting from the manufacturing process of lindane, a pesticide used in agriculture, during the period of 1954 - 1983 (<http://postaraturda.ro/?lang=en>).

The aim of this study was to determine the concentrations of 19 OCPs in two surface water samples collected from Aries River (Cluj County, Romania), upstream and downstream of “Poșta Rât” dump, using a combined extraction method (SPE and HS-SPME) followed by gas chromatography coupled with electron capture detector (GC-ECD). The used method was adapted from Qiu and Cai’s method (Qiu and Cai, 2010).

MATERIALS AND METHODS

Reagents and instrumentation. Solvents (methanol, n-hexane) were gas chromatography grade of quality (Merck, Darmstadt, Germany). Mix standard solution consists in α -, β -, γ -, δ -, ϵ - isomers of hexachlorocyclohexane (expressed as HCHs), 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, 2,4'-DDD, 2,4'-DDT and 4,4'-DDT (expressed as DDTs), aldrin, dieldrin, heptachlor, heptachlor epoxide (isomer A), heptachlor epoxide (isomer B), α -endosulfan, β -endosulfan and hexachlorobenzene (HCB), 10 $\mu\text{g/ml}$ each component (LGC Standards, Germany). Sodium chloride was obtained from Merck (Darmstadt, Germany). Ultrapure water was prepared using a Milli-Q water purification system from Millipore (Bedford, MA, USA). The instrumentation used consists in an Agilent Technologies 6890N gas chromatograph (GC) with electron-capture detector (μ -ECD). The used capillary column was a 30 m L \times 0.32 mm ID \times 3.0 μm film thickness, DB-1 (Agilent J&W, USA). High purity Helium was used as carrier gas at a constant flow rate of 1.6 ml/min. For SPE extractions, ISOLUTE C18 500 mg cartridges were used. For the SPME extraction, a manual fiber holder Supelco Inc. (Bellefonte, PA, USA) with an polydimethylsiloxane (PDMS) coated fiber (100 μm film thickness) Supelco Inc. (Bellefonte, PA, USA) were used. Prior to analysis, the fiber was conditioned in the GC inlet for 0.5 h at 250°C. To facilitate the evaporation a vacuum pump (Ilmvac, Germany) was used.

Sample preparation. Standard water samples (prepared by spiking 2 l ultrapure water with a certain amount of mix standard solution) and the surface water samples (2 l) were concentrated on ISOLUTE C18 cartridges, previously conditioned with methanol and equilibrated with ultrapure water, then air dried under vacuum (Mmualefe et al., 2009). Retained analytes were eluted with 10 ml n-hexane (Qiu and Cai, 2010). The elute was collected in 20 ml SPME glass vials, evaporated under nitrogen current until 1 ml. The concentrated elute (1 ml) was transferred to a 10 ml SPME glass vials, where a magnetic stirrer bar was previously added and then 1 ml pH buffer solution (pH 10) was pipetted. The vial was placed on a magnetic stirrer plates. The vial was connected to the PTFE connector to the vacuum pump through a condenser tube and the evaporation was carried out until no visible layer of organic solvent could be seen in the vial (Qiu and Cai, 2010). For the SPME step, 0.10 g NaCl was then added in the vial and it was sealed with Al/PTFE septum and the extraction was performed by immersing the PDMS SPME fiber in the vial’s headspace, at 50 °C during 20 min, under stirring conditions.

GC- μ ECD analysis. After the extraction, the fiber was desorbed in the GC injector at 280°C for 8 min. The GC- μ ECD was operated in splitless mode and the oven temperature program consists of 4 stages: from 80°C to 196°C (rate 4°C/min, 2 min), from

196°C to 224°C (rate 4°C/min, 2 min), from 224°C to 240°C (rate 4°C/min, 2 min) and from 240°C to 275°C (rate 4°C/min, 2 min). Detector temperature was set at 300°C with nitrogen makeup gas at a rate of 30 ml/min.

RESULTS AND DISCUSSION

Method validation. For the SPE/SPME/GC-ECD method, calibration was performed using external standard calibration curve with different concentration levels of OCPs, spiked in n-hexane (10 ml) using the same procedure for SPME extraction and chromatographic determination, starting with solvent conversion. The working standard solutions were prepared by diluting accurate volumes of mix standard solution of OCPs in n-hexane. The method linearity was studied in the range 0.0010 - 50 µg/l, and the correlation coefficients were higher than 0.985 for all the investigated compounds.

The blank test was performed using 2 l ultrapure water passed through the entire procedure. The detection limits of the entire method varied between 0.0050 ng/l and 0.150 ng/l. Because the analytes are concentrated on the cartridge and fiber, and then are rapidly delivered to the column, minimum detection limits are achieved. The accuracy of the method was determined in terms of recovery experiments by extracting the OCPs from spiked water samples, prepared by adding adequate volumes of mix standard solution to 2 l of blank matrix. The precision, expressed as the repeatability (% RSD) was determined by three consecutive extractions of OCPs from spiked water samples. The values obtained for recovery and for RSD ranged between 36.5 - 112.2% and 6.7 - 20.4%, respectively.

Determination of organochlorine pesticides in water samples. In September 2014, two surface water samples were collected from Aries River, near Turda town, Romania, just below the water surface in 2 l pre-cleaned brown glass bottles with glass stoppers. One sample was collected upstream (sample 1) and one sample downstream (sample 2) of the industrial dump. The geographic coordinates of sampling points were recorded using a Global positioning system (GPS) unit and they are shown in the Table 1. Upon arrival at the laboratory the samples were filtered through 0.45 µm filter membranes and preserved at 4 °C prior to analysis.

Table 1

| | Geographic coordinates of sampling points | |
|----------|---|---------------|
| | Latitude | Longitude |
| Sample 1 | 46°33'53.97"N | 23°49'4.61"E |
| Sample 2 | 46°33'43.25"N | 23°48'46.73"E |

The samples were subjected to the SPE, HS-SPME extractions and then to the GC-ECD analyses, respecting the conditions described above. Fiber blanks were measured before each sample in order to check the carry-over effect. The results of OCPs concentrations in the studied surface water samples are shown in Table 2. OCPs were detected in both samples at the concentrations of 144.5 ng/l and 316.4 ng/l, respectively. In the European Union (EU), the maximum admissible concentrations (MACs) of OCPs in both the environment and drinking water is 0.1 µg/l for a single compound and 0.5 µg/l for the total concentration of all OCPs (Zhang and Lee, 2012). In the downstream water samples, the concentration of γ -HCH (0.125 ng/l) exceeded the MAC.

In the analysed samples, the major contaminants were hexachloro- cyclohexane (HCH) isomers and dichlorodiphenyltrichloroethane (DDT) and its metabolites. Among

HCHs, the dominant isomers were β - and γ -HCH and are consistent with β -HCHs environmental degradation difficulty and the large deposit of γ -HCH (lindane) in the vicinity. Moreover, losses by volatilization are higher for the α isomer (Rissato et al., 2006).

Table 2

| Concentrations of OCPs in Aries River water samples (ng/l) | | | |
|--|-----------------------------|----------|----------|
| Crt. No. | Compound | Sample 1 | Sample 2 |
| 1 | α -HCH | 8.34 | 24.10 |
| 2 | β -HCH | 9.61 | 46.90 |
| 3 | γ -HCH | 13.8 | 125.1 |
| 4 | δ -HCH | 2.07 | 3.60 |
| 5 | ϵ -HCH | 0.86 | 4.01 |
| 6 | Hexachlorobenzene | 18.90 | 14.40 |
| 7 | Heptachlor | 2.44 | 3.16 |
| 8 | Aldrin | 12.60 | 9.75 |
| 9 | Heptachlor epoxide β | 3.17 | 1.45 |
| 10 | Heptachlor epoxide α | 0.065 | 0.036 |
| 11 | 2,4'-DDE | 4.58 | 1.29 |
| 12 | α -Endosulfan | 0.096 | 0.041 |
| 13 | 4,4'-DDE | 10.80 | 15.00 |
| 14 | 2,4'-DDD | 6.41 | 8.07 |
| 15 | Dieldrin | 0.103 | 0.421 |
| 16 | β -Endosulfan | 4.08 | 1.13 |
| 17 | 4,4'-DDD | 9.07 | 11.06 |
| 18 | 2,4'-DDT | 1.84 | 4.25 |
| 19 | 4,4'-DDT | 35.70 | 42.60 |

The α -HCH/ γ -HCH ratio can be used to identify the source of HCHs in water. The α -HCH/ γ -HCH ratio in areas where lindane has been used, typically ranges from 0.2 to 1, due to the photochemical transformation of γ -HCH into α -HCH (Rissato et al., 2006). In this study, the α -HCH/ γ -HCH ratio in the two studied surface water samples, were 0.60 and 0.19, respectively, indicating lindane as the HCH source. DDE and DDD are products formed from DDT in aerobic and anaerobic condition, respectively, thus, the ratio of (DDE + DDD)/DDT and DDE/DDD could reflect the input and degradation of DDT (Zhi et al., 2015). In the analysed water samples, the ratio of (DDD + DDE)/DDT were both below 1 (0.82 and 0.76, respectively), indicating that DDTs are still used in the adjacent area, and might also have a new input to the environment (Zhi et al., 2015). The obtained results underline that the sources of contamination are closely related to human activities, such as industrial discharge and domestic use of agricultural pesticides.

CONCLUSIONS

The used method for determination of OCPs in surface water samples, SPE/HS-SPME/GC-ECD is simple and highly sensitive due to the enrichment on SPE cartridge and SPME fiber. The method requires low volumes of organic solvents.

In the two water samples investigated, collected from Aries River, upstream and downstream of an industrial dump, near Turda town, Romania, OCPs were detected and registered values of 144.5 ng/l and 316.4 ng/l, respectively. The most predominant

contaminants were HCH isomers (mainly γ -HCH), DDT and its metabolites. In the downstream water sample, the concentration of γ -HCH exceeded the MAC. The ratio of α -HCH/ γ -HCH was smaller than unit, indicating that there has been a recent input of lindane.

Washing out of HCHs from the industrial dump and DDTs from weathered agricultural soils, were the mainly processes which caused the increasing concentrations of these chemicals in the investigated area.

Acknowledgement. This work was supported by Romanian financing authority UEFISCDI, Capacities, Romania-Austria bilateral cooperation project, project number 751/2014.

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