

An improved activated carbon method to quantify dichlorodiphenyltrichloroethane (DDT) in surface water

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Received: 31 August 2006 / Accepted: 25 September 2006 / Published online: 15 November 2006
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Abstract Currently, South Africa is designing a strategy for surface water protection involving organic contaminants such as dichlorodiphenyltrichloroethane (DDT), which is currently used for malaria control in mosquito-infested areas. Here, we demonstrate the successful use of an improved activated carbon technique using dichloromethane instead of chloroform, and slower leaching rate of 15 mL/min to quantify DDT and its metabolites in surface water. The recovery tests for 2,4' DDT, 2,4' DDD, 2,4' DDE, and 4,4' DDT, 4,4' DDD, 4,4' DDE ranged from 75 to 84% and 87 to 96%, respectively (DDE: dichlorodiphenyldichloroethylene, DDD: dichlorodiphenyldichloroethane). The main advantages of this technique over conventional liquid–liquid extractions are reduced amount of organic solvent, little sample preparation, and larger sample throughput. Because activated charcoal is fairly cheap, the technique can be routinely used to quantify and monitor DDT and its metabolites in surface water samples.

Keywords DDT · Metabolites · Surface water · Activated carbon · South Africa

Introduction

Chlorinated pesticides are ubiquitous environmental contaminants (Lichtfouse et al. 2005). Among them dichlorodiphenyltrichloroethane (DDT) has received the most attention because of its earlier usage to eradicate malaria-carrying mosquitoes in several tropical and subtropical countries (Ngabe and Bidleman 2006). The use of DDT as pesticides has been restricted or discontinued in several developed countries because of its interferences with hormonal functions in mammals and wildlife (Colborn 1991, 1993). These compounds have been linked to breast, liver, and testicular cancers and lower sperm counts in humans (Davies and Barlow 1995; Cocco et al. 1997). Several studies have reported the detection of these compounds in human milk (Bouwman et al. 1994; Chikuni et al. 1997; Atuma et al. 1998; Okonkwo et al. 1999), water, sediment, and air (Iwata et al. 1994; Karlsson et al. 2000; Ngabe and Bidleman 2006).

Because DDT and its metabolites can occur in the environment at low concentrations, sensitive and inexpensive pre-concentration techniques are needed prior to analysis. Liquid–liquid and solid-phase extraction techniques appear to be very popular with water samples (Albanis et al. 1998). In a study designed to determine carbon adsorption–desorption efficiency and reproducibility in the recovery of organic pesticides, Eichelberger and Lichtenberg (1971) determined that carbon provided only 37% recovery rate for DDT compared to 70–85% for the other organochlorines. The low recovery rate for DDT may have been due to the solvent system used as well as the flow rate during analyte desorbing from the carbon. It has been suggested that maximum organic adsorption efficiency can be achieved with flow rates less than 120 mL/min. This study describes improved recovery rates of DDT and its metabolites using a

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different solvent system, dichloromethane (instead of chloroform) and slower leaching rate at 15 mL/min. In South Africa, studies using other extraction techniques to monitor water bodies for chlorinated pesticides, particularly, DDT has shown widespread detections in surface water and sediments (Naude et al. 1998; London et al. 2000; Fatoki and Awofolu 2003).

Although, various treatments (activated carbon, resins, inverse osmosis, chemical oxidation) have been employed to treat waters contaminated with pesticides, this study explores the adsorptive property of activated carbon in pre-concentrating DDT and its metabolites. The information gathered on the high persistence and toxicity of these compounds may give rise to public awareness and inclusion in South African legislation for drinking water. Such information is extremely important as South Africa is formulating a surface-water quality protection strategy, in relation to organic contaminants.

Experimental

The glassware used were thoroughly washed and rinsed with de-ionized water and acetone and then oven-dried at 100 °C. All solvents, *n*-hexane, dichloromethane, and standards used were spectrophotometric grade (99%). The silica gel (70–230 mesh), anhydrous sodium sulfate, and activated charcoal (50–100 mesh) used in the column clean up and adsorption studies, respectively, were also of analytical grade. The anhydrous sodium sulfate and activated charcoal were pre-heated in a muffle furnace between 350 and 400 °C for 4 h prior to use.

Water samples were collected using thoroughly cleaned 2.5 L Winchester bottles from different sampling areas in March, July, and October 2004. Prior to use, the bottles were first rinsed with the water samples and then immersed to about 5 cm below the surface. After collection, the water samples were preserved, by adding about 5 mL analytical grade HNO₃, sealed, and kept in the dark at 4 °C before use. About 1 L of pre-filtered water samples was passed at a flow rate of 15–20 mL/min through a column packed with 10–15 g of activated charcoal which had been activated with 5 and 10 mL methanol and double-distilled water respectively. After the column was rinsed with double-distilled water, its contents were eluted with dichloromethane. The extracts collected were subjected to column chromatography and then reduced to 2 mL after adding an internal standard. The procedure was repeated with 1 L of double-distilled water spiked with a mixture of DDT, dichlorodiphenyldichloroethylene (DDE), and dichlorodiphenyldichloroethane (DDD) at concentrations ranging from 0.1 to 100 µg for a recovery test.

Table 1 Percentage recoveries of dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), and dichlorodiphenyldichloroethane (DDD) standards obtained from spiked water samples

2,4' DDD	2,4' DDE	2,4' DDT	4,4' DDD	4,4' DDE	4,4' DDT
75	80	84	87	90	96

Results and discussion

Recovery test

Table 1 shows the extraction ability of the improved technique using spiked double-distilled water. The high percentage values recovered suggest its effectiveness in absorbing such chlorinated compounds as DDT. The recovered values are comparable to such extraction techniques as liquid–liquid, solid-phase, and microwave-assisted solvent elution (Chee et al. 1996).

The total DDT concentration values are given in Table 2. Compared to the World Health Organization (WHO) guideline value (2 µg/L) in drinking water, values for the middle-stream in this study are marginally higher. There is a cause for concern, considering the fact that some inhabitants close to this river use the water for various domestic purposes.

Concentrations of DDT and metabolites in water samples

The technique was also applied to some collected water samples. The mean DDT concentrations and its metabolites are shown in Table 3.

Dichlorodiphenyltrichloroethane, DDE, and DDD were detected in the water samples collected in March and July for all the sampling points. The samples collected in October showed DDT, DDE, and DDD detected in the middle- and down-stream sampled areas.

The values for the middle-stream were consistently higher than the other sampled areas for all the months. The concentrations obtained are higher than the values (0.055–0.45 µg/L) reported by Fatoki and Awofolu (2003) in Eastern Cape water bodies. Higher concentrations (0.032–0.6210 mg/kg) have been reported in sediments sampled from the Pongolo floodplain in KwaZulu-Natal and the

Table 2 Total dichlorodiphenyltrichloroethane (DDT) concentrations (µg/L) along the Jukskei River

Sampled point	Collection dates (2004)		
	March	July	October
Middle-stream	2.2	2.8	1.9
Down-stream	1.8	2.1	nd
Upper-stream	0.5	0.46	0.3

nd, no detection.

Table 3 Mean concentrations ($\mu\text{g/L}$) in water obtained from the Jukskei River ($n = 3$)

Sampling point	March			July			October		
	DDT	DDE	DDD	DDT	DDE	DDD	DDT	DDE	DDD
Middle-stream	0.75	0.93	0.52	0.80	1.21	0.79	0.65	0.75	0.50
Down-stream	0.56	0.82	0.52	0.62	1.00	0.48	nd	nd	nd
Upper-stream	0.11	0.21	0.18	0.17	0.14	0.15	0.14	0.06	0.10

nd, no detection.

Letaba River in Mpumalanga Province (Naude et al. 1998). This is not surprising because sediments act as sinks to a wide range of pollutants. Also, DDT like most chlorinated pesticides has low water solubility. The values obtained in the study are within similar ranges (0.20–3.86 $\mu\text{g/L}$) reported by London et al. (2000) in water sampled from rural parts of Western Cape. The lower metabolites concentrations obtained in this study could be an indication of reduced uses of DDT. However, high concentrations of DDE and DDD may also suggest a more prolonged use and contamination, resulting in the break down of DDT into its subsequent metabolites.

Conclusion

This study demonstrates that using the technique to extract DDT and its subsequent metabolites is an adoptable technique. Over 70% recovery was obtained for all the organic compounds in this study. The main advantages of this technique over the conventional liquid–liquid extraction techniques are reduced uses of organic solvent, little sample preparation, and larger sample throughput. Also, little or no emulsion problem was encountered with the sampled water, compared to the conventional liquid–liquid extraction. Because activated carbon is fairly cheap, the technique can be routinely used in monitoring programs to detect and quantify DDT and its metabolites in surface water samples.

Acknowledgements The authors are indebted to Water Research Commission, South Africa for financial support.

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