Bull Environ Contam Toxicol (2009) 82:690–693
DOI 10.1007/s00128-009-9677-9

Persistent DDE in the Mesopotamian Wetlands of Southern Iraq

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Received: 13 May 2008 / Accepted: 26 February 2009 / Published online: 18 March 2009

Abstract Screening of potential pollutants in surface sediments revealed that almost all persistent organochlorine pesticides were not detected in the newly flooded Mesopotamian wetlands of southern Iraq. This observation suggests that there has been minimal input of organochlorine pesticides recently except for *p,p′*-DDE which was the only pesticide residue detected (0.29–2.33 μg/kg). It was found in all samples indicating its ability to persist under severe drying of previously exposed surface sediments, high temperature, and intensive solar radiation. *p,p′*-DDE appears to have a negative relationship with wetland biota, such as zooplankton.

Keywords DDE · Mesopotamian wetlands · Pesticide residues · Sediment

The Mesopotamian wetlands of southern Iraq derive most of their water from upstream streams and rivers and the surrounding watershed. Water entering the wetlands contains high suspended sediment loads and organochlorine pesticides (DouAbul et al. 1988; Saeed et al. 1999). Among such pesticides, DDT (dichlorodiphenyltrichloroethane) was one of the most predominantly used pesticides in the watershed. As the wetlands contained the threat of malaria, DDT had been used also within the area of wetlands as a way of controlling mosquitoes and the spread of malaria (Habib 2005). In mid-1980s, mean concentrations of DDT and its metabolites dissolved in water were: 98 for *p,p′*-DDE (*p,p′*-1,1,dichloro-2,2 bis (4,-chlorophenyl) ethylene); 8 for *o,p′*-DDD; 28 for *p,p′*-DDD; 16 for *p,p′*-DDT; 30 for aldrin; 66 for dieldrin; 57 for *cis*-chlordane; 15 for *trans*-chlordane and 10 for heptachlor (in ng/L). Mean concentrations in suspended particulates were: 76 for *p,p′*-DDE; 67 for *p,p′*-DDT; 154 for endrin; 11 for *cis*-chlordane, and 68 for heptachlor (in μg/kg, dry weight). Mean concentrations in wetland sediment were: 19 for *p,p′*-DDE; 4 for *p,p′*-DDD; 3 for *p,p′*-DDT; 7 for endrin and 14 for dieldrin (in μg/kg, dry weight) (DouAbul et al. 1987a, b). These values exceed any acceptable concentration in the environment (WHO 2003; US EPA 2003).

The Mesopotamian wetlands were nearly completely dried during the 1990s as a result of large-scale water diversions. Consequently, the wetlands changed from serving as important biogeochemical sinks to becoming sources of sediments through wind erosion and remobilization of biogeochemical elements, such as DDT, that previously would have been held in the accumulated sediments (Saeed et al. 1999).

As a consequence of exposure and drying out of the wetlands, pesticide residues in the wetland sediments were subjected to harsh weathering processes including exposure to solar radiation and extremely high summer temperatures for more than 10 years (DouAbul et al. 2006; Richardson and Hussain 2006; USAID 2006). In 2003, the new Iraqi government allowed river waters to resume flow through their natural courses again into the Mesopotamian wetlands. Since then, the wetlands are beginning to show the first signs of ecological recovery (DouAbul et al. 2005;

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Salim et al. 2005; Richardson et al. 2005; Rushdi et al. 2006; USAID 2006). It might also be expected that the newly flooded wetlands are almost pesticides-free. This hypothesis is based upon the following assumptions: (1) exposure to high temperature (i.e., in excess of 50°C in summer) and solar radiation for more than 10 years could have activated bacterial degradation of organochlorine residues under aerobic conditions, and (2) obliteration of the river water inflows to the wetland would have limited upstream pesticide inputs via drainage from the surrounding watershed to the new flooded wetlands.

The present study was conducted to test the above hypothesis and to investigate the levels of organochlorine pesticides in the new flooded wetland areas. This information serves as an important baseline for monitoring the impacts of DDT on the restored wetlands and formulating management priorities aimed to protect human health and the quality of the environment in the Mesopotamian wetlands in the future.

Materials and Methods

Surface sediment samples were collected in May and November 2005, from 6 locations within the wetlands of southern Iraq (two locations in the north, three in the west, and two in the southeast of the wetlands). The sampling locations were selected based on proximity to local villages where the use of pesticides might be more intensive compared to more remote parts of the wetlands. A van Veen grab sampler was used to collect samples. A sample of the surface 5 cm was kept for pesticide analysis. Samples were stored in coolers for transport to the laboratory at the University of Basra. They were freeze-dried and shipped to TDI-Brooks International, Texas, USA for the analysis of organochloride pesticide residues. Subsamples of 15 g of dried sediment were pre-treated with pesticide grade *n*-Hexane. A gas chromatograph/electron capture detector (GC/ECD) coupled to two capillary columns was used to resolve, detect and quantify organochlorine pesticide residues in sediments. Samples are injected into a temperature-programmed GC/ECD, operated in splitless mode. The capillary columns are DB-5 (30 m × 0.25 mm ID and 0.25 μm film thickness) and DB-17HT (30 m × 0.25 mm ID and 0.15 μm film thickness). The DB-17HT column is used for analyte confirmation. Surrogate recoveries ranged between 65% and 112% with both mean and median at 88%. Further details on laboratory procedures are available on the TDI-Brooks International web site (http://www.tdi-bi.com/analytical_services/analytical_services_main.htm). The data acquisition system continuously acquires and stores all data.

Water samples were also collected at the same field locations at five different times over the study period for phytoplankton and zooplankton analyses. For analysis of total phytoplankton, 1 L of surface water was collected in a plastic bottle, and 5 mL of Lugol's solution was added in the field as a preservative. Samples were also collected using a 20 μm mesh size phytoplankton net to aid species identification. For total zooplankton analysis, a volume of 40 L of surface water was filtered through a 20 μm mesh size net and collected in a 1 L plastic bottle. 10 mL of 10% formaldehyde was added in the field as a preservative. In the laboratory, the samples were concentrated and examined under a microscope to identity and count phyto- and zooplankton taxa.

Results and Discussion

Although several organochlorine pesticide residues were detected during the 1980s in sediments in the Mesopotamian wetlands (DouAbul et al. 1987a, b; 1988), the present study showed virtually no trace of the pesticides except for 4,4′-DDE. Concentration of DDE was significantly variable among sampling locations (Table 1). Variations in DDE concentrations between sites within the wetlands may be attributed to different inputs of DDT and variable nature of degradation processes at the individual sampling sites. The pesticide residues that were not detected include: aldrin, dieldrin, endrin, heptachlor, heptachlor-epoxide, oxychlordane, alpha-Chlordane, gamma-Chlordane, *trans*-nonachlor, *cis*-nonachlor, alpha-HCH, beta-HCH, delta-HCH, gamma-HCH, DDMU, 2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 2,4′-DDT, 4,4′-DDT, 1,2,3,4-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, hexachlorobenzene, pentachloroanisole, pentachlorobenzene, endosulfan II, endosulfan I, endosulfan sulfate, mirex and chlorpyrifos in the new flooded wetland areas. The detection limit for those pesticides were 0.07,

Table 1 Concentration of DDT and its metabolites in sediment samples at six sampling stations

Station	DDT		DDD		DDE	
	2,4′-	4,4′-	2,4′-	4,4′-	2,4′-	4,4′-
1	–[a]	–	–	–	–	1.09±0.01*d*
2	–	–	–	–	–	1.16±0.02*c*
3	–	–	–	–	–	0.77±0.01*e*
4	–	–	–	–	–	2.33±0.01*a*
5	–	–	–	–	–	2.06±0.02*b*
6	–	–	–	–	–	0.29±0.01*f*
Detection limit	0.09	0.06	0.05	0.08	0.06	0.06

Samples were collected in 2005. Mean ± SE (μg/kg) are shown (n = 6). Means followed by different alphabetic letters are significantly different (one-way ANOVA: $p < 0.001$, Tukey HSD: $p < 0.05$)

[a] Below detection limit

0.06, 0.06, 0.06, 0.08, 0.07, 0.06, 0.06, 0.06, 0.07, 0.12, 0.06, 0.06, 0.05, 0.05, 0.08, 0.06, 0.09, 0.06, 0.07, 0.06, 0.07 and 0.08 μg/kg, dry weight sediment respectively.

DDE (1,1,dichloro-2,2 bis (4,-chlorophenyl) ethylene) is the major dead-end, lipophilic product formed through restricted transformation of the pesticide 1,1-trichloro-2, 2-bis (4-chlorophenyl) ethane (DDT). Most often, the enhanced level of DDE in the natural environment is a direct consequence of incomplete microbial biotransformation of DDT, and this product is more recalcitrant compared to the parent compound (Pfaender and Alexander 1972; Jablonski and Ferry 1992; You et al. 1996; Kale et al. 1999). Half-life of DDE in tropical and temperate soils is usually in the range of 10–30 years (Hwang et al. 2006). Although the parent compound of DDE, which is DDT, was not detected in any of the samples, residues of *p,p′*-DDE were present in all samples (Table 1). The presence of DDE in the sediment of the newly flooded areas likely indicates its historical origin rather than being of recent origin (Pinkney and McGowan 2006; Zeng and Venkatesan 1999). The apparent absence of DDT suggests the lack of new sources of DDT in recent years reaching the flooded areas. Contrary to our hypothesis, *p,p′*-DDE has survived the dry period, and is the sole pesticide showing persistence despite severe environmental conditions, including aerobic degradation, high temperature (>50°C in summer), and intensive solar radiation for more than 10 years. This persistence of DDE to degradation in the soil agrees with previous studies (US EPA 2006). The fact that DDMU residue was not detected in any of the sediment samples suggests no reductive dechlorination of DDE in the Mesopotamian wetlands (Quensen et al. 1998).

In order to examine the potential effects of DDE residues on biota in the newly flooded wetlands, distribution and abundance of phytoplankton and zooplankton were also monitored. Correlation coefficients between 4,4′-DDE residues and species richness, Shannon–Wiener diversity, and the 1st axis scores of Principal Component Analysis (PCA) were all negative, suggesting that both diversity and distribution of phyto- and zooplankton species are negatively affected by 4,4′-DDE residues. In particular, the relationship between the residues and the PCA scores of zooplankton data was statistically significant. Negative effects of DDE residues on zooplankton communities agree with some previous studies (Bengtsson 1978; Barber et al. 2003) (Table 2).

Further work is needed on other biotic groups in the wetlands to determine potential impacts of DDE. For example, fishes collected in the 1980s from the wetlands typically contained high levels of DDE (DouAbul et al. 1987a). Up to 180,000 of bioconcentration factors (BCF) have been reported for fish elsewhere, suggesting that bioconcentration in aquatic organisms is effective (US EPA 2006). DDE is known to disturb the metabolic functions of living organisms, as well as act as an antiandrogen, binds to the androgen receptor, and inhibits transcriptional activation, causing sexual abnormalities (WHO 2003).

Table 2 Pearson correlation coefficients between 4,4′-DDE concentration and species richness, Shannon–Weiner diversity index, and the first axis scores of principal component analysis (PCA) of phytoplankton and zooplankton data (n = 6)

	Phytoplankton	Zooplankton
Species richness	−0.252	−0.129
Shannon–Wiener diversity	−0.189	−0.314
PCA axis score	−0.226	−0.767*

* $p < 0.05$

In summary, we conclude the following from our present work:

(1) There is no recent input of organochlorine pesticides to the new flooded wetland areas.

(2) *p,p′*-DDE residue has survived the drying of the wetlands that took place during the 1990s despite harsh environmental conditions in the intervening period to the present.

(3) *p,p′*-DDE residue is negatively controlling the distribution of some biota including zooplankton.

Acknowledgments We are grateful to the Canada-Iraq Marshlands Initiative, University of Waterloo and the Canadian International Development Agency (CIDA) for support. TDI-Brooks International, Texas graciously performed all laboratory analyses. We thank the local wetland dwellers for field assistance, without whose involvement, this study would not have been possible.

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