Science of the Total Environment 437 (2012) 196–199

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Short Communication

Characteristics of DDTs in fish from Lake Taihu: An indicator of continual DDTs input in China

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HIGHLIGHTS

► DDTs residue levels were examined in typical freshwater fish from Taihu, East China.
► Both historical usage of technical DDT mixture and dicofol-type DDT were simultaneously occurred in TH.
► Dicofol-type DDT is widespread and become an important continual source of DDT in China.

ARTICLE INFO

Article history:
Received 28 November 2011
Received in revised form 9 February 2012
Accepted 9 February 2012
Available online 30 August 2012

Keywords:
Dichlorodiphenyltrichloroethane
Dicofol
Fish
Lake Taihu
China

ABSTRACT

Four typical freshwater fish species in Lake Taihu (TH), China, were collected and analyzed for the residue levels of DDT and its metabolites DDD and DDE (sum of o,p′- and p,p′-DDT, DDD, and DDE is designated as DDTs). The DDTs concentrations ranged from 3.24 to 37.1 ng/g, and p,p′-DDE was the dominant isomer, followed by p,p′-DDD and o,p′-DDT. Source identification indicated that DDTs in TH was mostly stemmed from the historical usage of technical DDT mixture, but a new source of DDT, i.e., dicofol-type DDT, also occurred. The results from the present work, together with previously published data, clearly indicate that dicofol-type DDT was widespread and was an important continual source of DDTs in China.

1. Introduction

Dichlorodiphenyltrichloroethane (DDT) is an extensively used organochlorine pesticide. It plays an important role in the vector control and agriculture production. Due to its high persistence, toxicity, bioaccumulation, and long-range transport properties, DDT is ubiquitous in various environmental matrices and has been extensively investigated for several decades (Beard, 2006). To balance the potential adverse effects with the social benefits of DDT, many countries banned DDT in the 1970s, and so did China in the early 1980s (Qiu and Zhu, 2010). However, high DDT levels in various environmental media were still being observed recently in China (Liu et al., 2009; Qiu et al., 2004; Xu et al., 2007), indicating there might exist continual source of DDT (Jiang et al., 2009).

The historical usage of DDT in China began in 1950s. Considering the persistence and toxicity of DDT, Chinese government partly banned the agriculture usage of technical DDT in 1982. However, technical DDT is still produced and used in China for some non-agricultural purposes (e.g., export, malaria control, anti-fouling paint). Meanwhile, dicofol formulation, which was introduced as acaricide in the late 1970s in China, may be a continual source of DDT into the environment since it is synthesized from technical DDT and usually contains high proportions of DDT as an impurity (Qiu et al., 2005; Tao et al., 2007).

Lake Taihu (TH) is located in the Yangtze River Delta, East China. It is the largest freshwater lake in China, with an area of 2338 km^2 and the average depth of 1.9 m (Qiu et al., 2004). Historically, large amounts of organochlorine pesticides have been used in its catchment. Previous results in the sediment core of TH show that DDT concentrations increase recently (Liu et al., 2009) and a possible source of DDT was also identified (Qiu et al., 2004). This suggests that, in this area, DDT pollution is still a serious problem and deserves more concerns. Fish is a suitable indicator for environmental monitoring and is also one of the important pathways for human exposure. To better understand the current DDT pollution in TH, typical freshwater fish species from TH were collected in September 2009 and analyzed. The purposes of the present study are the following: (1) to reveal the residue level and characteristics of DDTs in fish from TH; (2) to provide critical information on the potential source of DDT in this area.

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0048-9697/$ – see front matter
doi:10.1016/j.scitotenv.2012.02.016

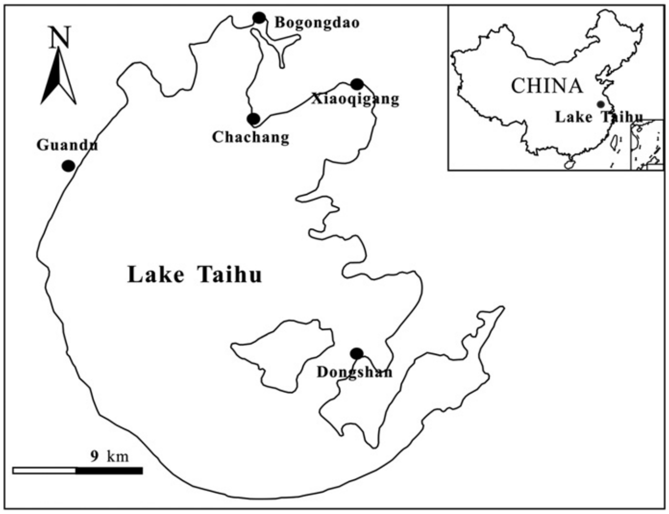

Fig. 1. Map of the sampling sites.

2. Materials and methods

2.1. Sampling

Eighty-two wild fish samples, consisting of four typical species in TH, i.e., Crucian carp (*Carassius auratus*), Common carp (*Cyprinus carpio*), Bighead carp (*Aristichthys nobilis idellus*), and Topmouth culter (*Erythroculter ilishaeformis*), were collected from the main fish port around TH, including Guandu, Bogongdao, Chachang, Xiaoqigang, and Dongshan in September 2009 (Fig. 1). Upon collection, all the samples were kept in ice, and brought back immediately to the laboratory, where they were stored at −20 °C until analyzed.

2.2. Extraction and instrumental analyses

DDTs analytical procedure followed those described in our previous work (Guo et al., 2007). Briefly, an aliquot of each sample, spiked with surrogate standards PCB-30, PCB-65 and PCB-204, was Soxhlet extracted for 48 h with 200 ml of acetone:*n*-hexane (1:1, v:v). A portion (approximately 20%) of the extract was removed for gravimetrical lipid determination, and the remaining extract was subjected to a gel permeation chromatography (50 cm length × 2.0 cm i.d.) packed with 40 g of SX-3 Bio-Beads (Bio-Rad). The column, loaded with an extract, was eluted with 50% dichloromethane in *n*-hexane for lipid removal. The fraction from 110 to 280 ml containing DDTs was collected and concentrated. The subsequent cleanup and fractionation were performed with a multilayer alumina/silica column packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (12 cm, 3% deactivated), and anhydrous sodium sulfate (1 cm). The defatted sample was pre-washed with 15 ml of *n*-hexane and eluted slowly with 70 ml of *n*-hexane:dichloromethane (7:3, v:v), and only the latter portion was collected. The eluent was concentrated, quantitatively transferred into a 2-ml vial, and further concentrated to the final volume of 500 μl under a gentle nitrogen stream. An internal standard, PCB-82, was added to the extract prior to instrumental analysis.

Analyses of DDTs were performed on an Hewlett-Packard (HP, Avondale, PA, USA) Agilent 6890 gas chromatograph system equipped with an Agilent 5975B mass selective detector operating in selective ion monitoring mode using a DB-5 capillary column (60 m length × 0.25 mm i.d. × 0.25 μm film thickness). Splitless injection of 1.0 μl of sample was conducted with an auto-sampler. The GC oven temperature was programmed from 80 to 200 °C at a rate of 12 °C/min, to 220 °C at a rate of 1 °C/min, and then to 290 °C at a rate of 15 °C/min (hold for 30 min). The quantified compounds included DDT, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE) (sum of o,p′- and p,p′-DDT, DDD, and DDE is designated as DDTs).

2.3. Quality control and quality assurance

For each batch of 20 field samples, a procedural blank, a spiked blank, and a spiked matrix sample were processed. The mean percent recoveries of the surrogate standards were 109.3 ± 9.8% for PCB-30, 104.8 ± 10.9% for PCB-65 and 78.2 ± 22.4% for PCB-204, respectively. Recoveries of DDT isomers in triplicate spiked blanks and triplicate spiked matrix ranged from 78.2 ± 5.7% to 102.7 ± 17.4% and 81.1 ± 1.3% to 92.3 ± 1.9%, respectively. The limits of detection (LOD) of DDT isomers ranged from 0.01 to 0.05 ng/g wet weight (defined as signal-to-noise ratio > 10). Besides, zero was taken if the residue level was less than LOD. No target compounds were found in the procedural blanks. All the results were expressed on a wet weight basis and were not corrected for surrogate recoveries.

3. Results and discussion

3.1. Concentrations, characteristics and source identification of DDTs in fish from TH

Concentrations and diagnostic ratios of DDT measured in four fish species are reported in Table 1. Overall, the DDTs concentrations in fish from TH ranged from 3.24 to 37.1 ng/g, with the mean value of 10.6 ± 6.18 ng/g. If different fish species is taken into accounted, the DDTs levels in Common carp and Bighead carp were similar to each other, but significant differences were found among other species (*t*-test, $p<0.05$). The highest level was found in Topmouth culter with the mean value of 15.6 ng/g, followed by that of Crucian carp, Bighead carp, and Common carp, with the mean value of 11.6 ng/g, 7.91 ng/g, and 7.21 ng/g, respectively.

All DDT isomers were detected in all the samples except that p,p′-DDT. This compound was detected in 44% of the fish samples analyzed. The relative abundance of each DDT isomers in each fish species are

Table 1
Concentrations (ng/g, wet weight) and diagnostic ratios of DDT in fish from Lake Taihu.

Fish species	Crucian carp	Common carp	Bighead carp	Topmouth culter
o,p′-DDE	0.53 ± 0.34 [a]	0.37 ± 0.25	0.47 ± 0.22	1.45 ± 2.41
p,p′-DDE	7.46 ± 3.44	3.97 ± 1.60	4.41 ± 1.60	7.97 ± 3.13
o,p′-DDD	0.30 ± 0.24	0.22 ± 0.16	0.29 ± 0.22	0.55 ± 0.28
p,p′-DDD	2.11 ± 1.68	1.17 ± 0.91	1.32 ± 0.50	1.91 ± 0.90
o,p′-DDT	1.07 ± 0.88	1.43 ± 1.34	1.79 ± 0.98	3.36 ± 4.50
p,p′-DDT	0.20 ± 0.27	0.11 ± 0.11	0.24 ± 0.31	0.22 ± 0.28
DDTs	11.6 ± 4.57	7.21 ± 3.08	7.91 ± 2.90	15.6 ± 8.44
p,p′-DDT/p,p′-DDE + p,p′-DDD	0.04 ± 0.04	0.03 ± 0.03	0.05 ± 0.03	0.04 ± 0.02
o,p′-DDT/o,p′-DDE + o,p′-DDD	1.75 ± 1.98	3.82 ± 4.14	4.00 ± 4.20	1.72 ± 1.49
o,p′-DDT/p,p′-DDT	5.22 ± 2.83	7.13 ± 2.55	5.80 ± 2.92	3.28 ± 1.94

[a] Arithmetic mean value ± standard deviation.

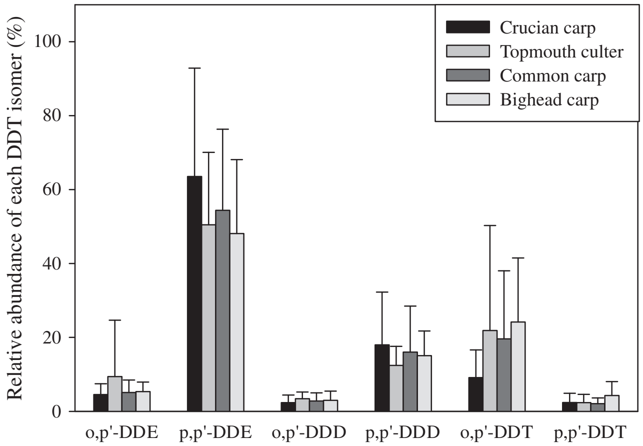

Fig. 2. Relative abundance of each DDT isomers in different fish species.

shown in Fig. 2. In all the samples, p,p′-DDE was the dominant isomer, with the average abundance of 48.1–63.5% in different fish species, followed by p,p′-DDD and o,p′-DDT, with the average abundance of 15.1–18.0% and 9.1–24.2%, respectively, while the average abundance of the rest isomers were generally less than 5%. The predominance of p,p′-DDE and to a less extent of p,p′-DDD in fish samples suggests that the p,p′-DDT in TH was mostly degraded. In addition, relatively high levels of o,p′-DDT indicate that new input of o,p′-DDT into TH might occur recently.

The ratios of the parent compound to its metabolite can provide useful information on the pollution source. A ratio of DDT/DDE + DDD higher than one is generally pointed to fresh input of DDTs. Otherwise, aged DDTs is suggested. There are two known sources of DDTs characterized by the o,p′-DDT/p,p′-DDT ratio of 0.2–0.3 in technical DDT mixture and ~7.0 in dicofol products in China, respectively (Qiu et al., 2005). Therefore, the ratio of o,p′-DDT/p,p′-DDT ($R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$) is usually used to distinguish technical DDT from dicofol-type DDT (Qiu et al., 2005; Yang et al., 2008b; Zheng et al., 2010), and an elevated $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$ is an indicative of the dicofol-type DDT. The diagnostic ratios of DDT in fish from TH are shown in Table 1. The ratios of p,p′-DDT/p,p′-DDE + p,p′-DDD were much less than one, with the mean value of 0.03 to 0.05 in different species. This indicates that p,p′-DDT, which primarily originated from the technical DDT mixture, was mostly stemmed from the historical input. On the contrary, most of the o,p′-DDT/o,p′-DDE + o,p′-DDD ratios (more than 70%) were higher than one, with the mean value of 1.72 to 4.00 in different species. This suggests that fresh o,p′-DDT was introduced into TH recently. Moreover, elevated $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$, with the mean value of 3.28 to 7.13 in different fish species, were also observed. This clearly demonstrates that the new input of o,p′-DDT was from dicofol-type DDT. In summary, mixed sources of DDTs, i.e., both historical input of technical DDT and new input of dicofol-type DDT, were obvious in TH.

3.2. *Dicofol-type DDT source in China: evidence in other environmental matrices*

Dicofol, an acaricide with high DDT impurity, has been extensively used in China since the 1970s (Qiu et al., 2005; Tao et al., 2007). Although few studies on the dicofol in the environment were reported, evidences shown that dicofol-type DDT occurred in various environmental matrices in China, such as air (Qiu et al., 2004; Ding et al., 2009; Zheng et al., 2010), water (Qiu et al., 2008; He et al., 2011), soils (Wang et al., 2008; Yang et al., 2008b; Jiang et al., 2009), and sediments (Li et al., 2011), as well as other environmental media (Li et al., 2008; Yang et al., 2008a) (Table 2). Dicofol products used in China usually contains high proportion of o,p′-DDT as impurity compared to that of technical DDT (Qiu et al., 2005). This facilitates us to distinguish dicofol-type DDT from technical DDT.

Qiu et al. (2004) firstly reported high $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$ (6.3 ± 3.7) in air from TH. Those ratios were close to that of dicofol products (7.0 ± 2.2) used in China, indicating a dicofol-type DDT pollution appeared in TH. Similar results were also reported in air from South China Sea (Zhang et al., 2007), Guangzhou (Yang et al., 2008c), and Tianjin (Zheng et al., 2010). Recently, high levels of o,p′-DDT were observed in cotton topsoil from Jiangsu Province (16.9 ± 14.4 ng/g) (Yang et al., 2008b) and school yard soils from Beijing (mean: 42.4 ng/g) (Wang et al., 2008), showing relatively high $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$ compared to that of technical DDT. This was also the case to the agriculture soil from Shanghai (Jiang et al., 2009). In water, DDT in samples from TH (Qiu et al., 2008) and Lake Chaohu (He et al., 2011) was also characterized by relatively high $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$, with the values of 3.6 ± 2.0 and 0.81 ± 0.28, respectively. Meanwhile, high $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$ ratios were also reported in other environmental media, such as fishpond sediments from Pearl River Delta (Li et al., 2011), conifer needles from Tibetan Plateau, Southwest China (Yang et al., 2008a), and fish from Lake Gaobeidian, Hebei Province (Li et al., 2008). If all studies mentioned above were site-specific, a national-wide investigation clearly suggests that the dicofol-type DDT was widespread in China (Jaward et al., 2005).

Table 2
Ratios of o,p′DDT/p,p′-DDT in different environmental matrices in China.

Samples	Sampling sites	Sampling time	o,p-DDT/p,p-DDT	References
Air	Lake Taihu	2002	6.3 ± 3.7	Qiu et al. (2004)
Air	Lake Taihu	2004	5.9 ± 3.4	Qiu et al. (2008)
Air	South China Sea	2005	5.6 ± 2.8	Zhang et al. (2007)
Air	Urban, Guangzhou	2005–2006	1.96 [a]	Yang et al. (2008c)
Air	Rural, Guangzhou	2005–2006	3.32 [a]	Yang et al. (2008c)
Air	Tianjin	2006–2007	1.38 ± 0.28	Zheng et al. (2010)
Air	Tianjin	2007–2008	1.36 ± 0.36	(Zheng et al., 2010)
Air	32 sites in China	2004	3.2 ± 2.3	Jaward et al. (2005)
Water	Lake Taihu	2004	3.6 ± 2.0	Qiu et al. (2008)
Water	Lake Chaohu	2009	0.81 ± 0.28	(He et al., 2011)
School yards soil	Beijing	2006	2.42 [a]	Wang et al. (2008)
Cotton topsoil	Jiangsu Province	2006	0.64 [a]	Yang et al. (2008b)
Vegetable topsoil	Jiangsu Province	2006	0.57 [a]	Yang et al. (2008b)
Agriculture soil	Shanghai	2007	0.51 [a]	Jiang et al. (2009)
Fishpond sediment	Pearl River Delta	2005	2.1 [a]	Li et al. (2011)
Conifer needle	Tibetan Plateau	2006	0.94 ± 0.55	Yang et al. (2008a)
Fish	Gaobeidian, Hebei Province	2006	2.41 ± 1.98	Li et al. (2008)

[a] Ratios were from the mean value of o,p-DDT and p,p-DDT.

4. Conclusion

The present study examined the residue levels of DDTs in typical freshwater fish species from TH, East China. The DDTs concentrations in fish ranged from 3.24 to 37.1 ng/g. The predominance of p,p′-DDE in fish suggests that the DDTs in TH was mostly stemmed from the historical usage of technical DDT. However, significantly high values of $R_{o,p'\text{-DDT}/p,p'\text{-DDT}}$ were found in fish, strongly suggesting a new source of DDT, i.e., dicofol-type DDT occurred in TH. The results from the present work, together with previously published data, clearly indicate that the dicofol-type DDT was widespread and was an important continual source of DDT in China.

Acknowledgements

The authors are grateful for the financial support from China's National Basic Research Program: "Water environmental quality evolution and water quality criteria in lakes" (2008CB418200) and the National Natural Science Foundation of China (40973087).

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