Effects of endocrine disrupting chemicals on China's rivers and coastal waters

Wei An and Jianying Hu*

In the past decade, many studies have investigated the occurrence, and associated biological effects, of endocrine disrupting chemicals (EDCs) in China's aquatic environments. Here, we summarize the exposure levels of butyltins and other EDCs in major Chinese river watersheds and coastal waters and review their biological consequences. High concentrations of butyltins were found in seawater from the coasts of Dalian, Tianjin, Qingdao, Shanghai, and the Guangxi North Sea, and in sediments from Daya, Haimen, and Guangao Bays. In areas with high butyltin concentrations, there was an increased incidence of imposex (in which male sexual characteristics are found in female gastropods). We discuss the effects of EDCs on other wildlife, including night herons, Chinese sturgeon, and crucian carp, and propose a number of ways to limit the release of EDCs and reduce their effects.

摘 要：近十年来，中国科学家就内分泌干扰物质在水生环境中的污染状况及其生物危害性方面开展了研究。本文重点总结了有机锡和其他几种内分泌干扰物质在中国主要流域和海洋水体以及沉积物中的浓度水平及相应的生物危害。其中，有机锡，在水体中，大连、天津、青岛、上海和广西北海(平均浓度 128 ng.Sn/L，范围 3.1-1273 ng.Sn/L)的浓度较高；在沉积物中，珠江、大亚湾、海门湾和广澳湾的浓度较高(平均浓度 84 ng Sn/g 干重，范围 0.16-380 干重)。这些化学物质已经对野生生物产生了明显的危害。例如，在有机锡浓度较高的地区，出现了大量的雌性腹足类的雌雄同体；在太湖地区，发现了夜鹭鸟蛋内滴滴涕类物质的高残留和该区夜鹭幼鸟存活率的明显下降；在长江，发现了中华鲟的雌雄同体；在海河流域，雄性鲫鱼体内检测出了卵黄蛋白原。为了降低内分泌干扰物质对野生生物的影响，本文还就中国削减内分泌干扰物质排放的可能措施提出了建议。

中國的環境

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In recent years, a number of papers have highlighted the potentially detrimental effects of certain anthropogenic compounds on the reproductive processes of both wildlife and humans. There has been increasing evidence that these compounds can alter endocrine function and disrupt growth, development, and reproduction by interfering with the production, release, transport, metabolism, and elimination of endocrine hormones. The regulation of developmental processes is also affected (IPCS 2002; Van der Kraak 1998).

In a nutshell:

- Environmental pollution is increasing in China as a result of industrialization and the rapid development of both urban and rural economies
- Endocrine disrupting chemicals (EDCs) are ubiquitous in water, sediment, and aquatic organisms in major rivers, lakes, and coastal waters
- Typical detrimental effects of EDCs, such as malformation of sex organs, have been observed in marine gastropods and fish and birds
- High concentrations of tributyltin (TBT) have been found in large Chinese seaports, and DDT has been found in the Hai River, Tai Lake, Min River, Jiulong River, and Pearl River

Authors' contact details are on p386

To date, the effects of endocrine disruptors on aquatic wildlife have been linked primarily to particular compounds, such as butyltins, natural (Estrone [E1], 17β-estradiol [E2]) and synthetic (nonylphenol [NP]) estrogens, atrazine, dichlorodiphenyltrichloroethane (DDT)-related compounds, polychlorinated dibenzo-*p*-dioxin/dibenzofurans (PCDD/F), and coplanar polychlorinated biphenyls (co-PCBs; IPCS 2002). Several examples of the biological impacts of endocrine disrupting chemicals (EDCs) on wildlife have been documented (Miyamoto and Burger 2003). One of the best-known cases is tributyltin (TBT), which has been shown to cause male sex characteristics to form on normal females, in a range of marine gastropod mollusks (Matthiessen *et al.* 1998), including the dogwhelk (*Nucella lapillus*). Imposex, as it is called, effectively prevents these animals from reproducing and leads to changes in population levels. Evidence of intersexual characteristics among male frogs exposed to atrazine (Hayes *et al.* 2002) and of eggshell thinning in birds as a result of exposure to DDT and its metabolites

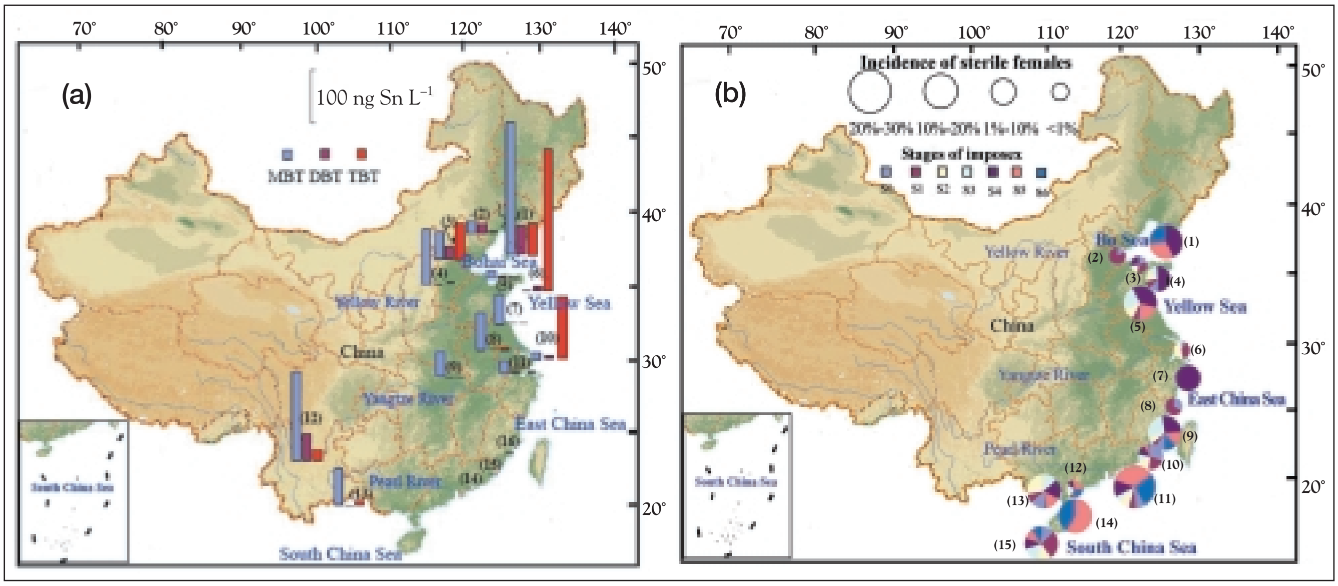

Figure 1. *(a) Concentrations of tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) in surface waters of the main rivers and seas in mainland China. Sampling locations: (1) Dalian new shipyard; (2) Qinghuangdao coast; (3) Tianjin coast; (4) Baiyangdian Lake; (5) Yantai coast; (6) Qingdao coast; (7) Lianyungang Port; (8) Yangtze River (Jiangyin); (9) Yangtze River (Wuhan); (10) Huangpu River (Shanghai); (11) Qiantang River (Hangzhou); (12) Dianchi Lake; (13) Guangxi North Sea; (14) Daya Bay; (15) Haimen Bay; (16) Guangao Bay. (b) Relative proportions of imposex stages (S0–S6) and predicted incidence of sterile females in coastal waters of mainland China. The radius represents the predicted incidence of the sterile prosobranch female population on the basis of imposex stages. Sampling locations: (1) Dalian; (2) Tianjin; (3) YanTai; (4) Qinghuangdao; (5) Lianyungang; (6) Hangzhou Bay; (7) Ningbo; (8) Fuzhou; (9) Xiamen; (10) Shantou; (11) Shenzhen; (12) Zhanjiang; (13) Beihai; (14) Haikou; (15) Dongya.*

has also been observed. The abovementioned EDCs, with the exception of PCDD/F, are widely used in agricultural, industrial, and household products. Because of the general lack of standards and regulation, many sources of EDCs exist in developing countries, including China (Table 1). As a result, Chinese scientists have carried out numerous studies on EDCs during the past decade. Most of the early studies focused on the occurrence of typical EDCs, including TBT, NP, atrazine, DDT, PCDD/F, and co-PCB in the environment, but new evidence regarding the adverse effects of EDCs on wildlife has been increasingly reported in recent years.

Occurrence and biological impacts of EDCs

This paper summarizes most of the studies that have been published about EDCs in China. The study areas encompass the major watersheds in China, including the Liao, Yang, Luan, Hai, Yellow, Huai, Yangtze, Huangpu, Qiantang, Min, Jiulong, and Pearl Rivers, as well as the Bohai, East China, Yellow, and South China Seas. These studies report on the occurrence of EDCs (butyltins, NP, atrazine, DDT, PCDD/F, and co-PCB) in the river watersheds and the biologically adverse effects observed among wildlife, including imposex in marine gastropods and decreased survival of young night herons, both resulting in declining population, vitellogenin induction in male crucian carp (this egg yolk precursor protein is normally only expressed in female fish), and an intersex condition known as testis–ova in anadromous Chinese sturgeon.

Butyltins

Butyltin compounds are used widely as stabilizers, catalysts, and biocides. They were first marketed in 1936 and have been used in antifouling paints for ships since the 1960s. The total production of butyltin compounds worldwide was about 50 000 tons in 1992. In China, these compounds have been produced since 1964, with maximum annual production as high as 7500 tons (Li *et al.* 2003). TBT has been regulated in antifouling paints since the late 1980s in most European countries and North America, owing to its extreme toxicity to aquatic life, even at low concentrations. However, there are currently no laws limiting the use of TBT in China.

Butyltin compounds were found to be widespread in aquatic environments in China (Figure 1a; Jiang *et al.* 2001; Shi *et al.* 2003; Gao *et al.* 2004). Since concentrations of butyltins are often related to shipping activities, much higher concentrations of butyltin were consistently detected in the large harbors of Qingdao, Dalian, Shanghai, and Tianjin. Here, TBT concentrations ranged from 10–977 ng Sn L^{-1} (Jiang *et al.* 2001). High concentrations were found mostly in seaports, because of frequent shipping activities and minimal exchange of seawater in seaports. Gao *et al.* (2004) studied butyltin in the open waters of Bohai Bay, where the concentrations (0–14.7 ng Sn L^{-1}) were much lower than those found in seaports around Bohai Bay (TBT: 17–322 ng Sn L^{-1}; Jiang *et al.* 2001). Two other butyltin compounds, dibutyltin (DBT) and monobutyltin (MBT), are the degradation products of TBT. A higher ratio of TBT to DBT in the

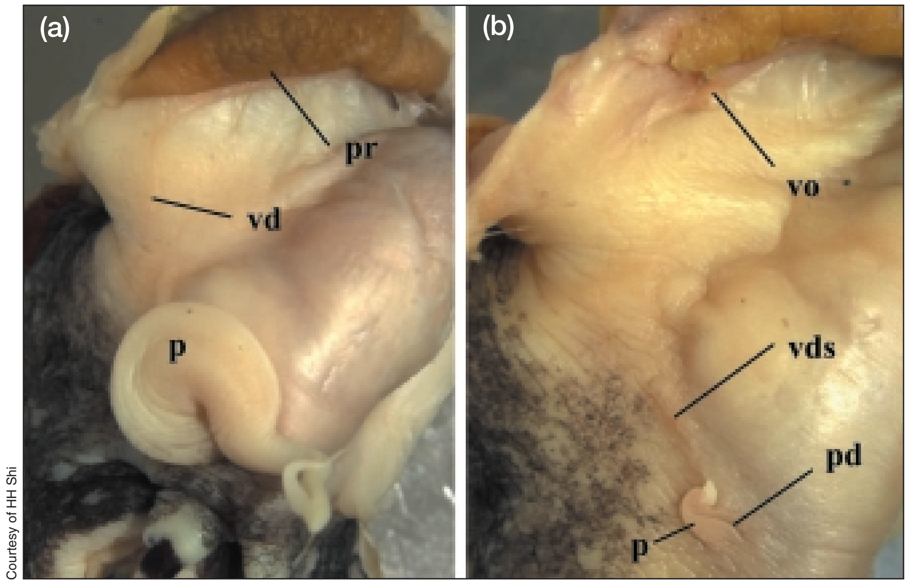

Figure 2. *Photos of (a) a normal male and (b) an imposex (the development of male sex organs on female gastropods) female of* Thais clavigera *collected from large ports along the southeast coast of China. The penis of the female is similar to that of the male. Key: p: penis; pd: penis duct; pr: prostate; vd: vas deferens; vds: vas deferens section; vo: vaginal opening (Shi* et al. *2003).*

water suggests more recent contamination by the active compound TBT in the area. The concentration ratios between TBT and DBT in Qingdao, Shanghai, Yantai, and Dalian were 1:35, 1:26, 1:2.70, and 1:1.08, respectively, suggesting that there are new sources of TBT pollution in these regions. Several studies have reported on the occurrence of butyltins in sediment from the Pearl River, Western Xiamen Harbor, and Minjiang Estuary. The concentrations in Pearl River (16–380 ng Sn g^{-1} dry weight [dw]) are higher than those in Western Xiamen Harbor and Minjiang Estuary (0.16–24 ng Sn g^{-1} dw; Yuan *et al.* 2001; Fu *et al.* 2003; Dong *et al.* 2004). Butyltin concentrations in seafood in most coastal cities were found to be between 40 and 160 ng Sn g^{-1} wet weight (ww; Li *et al.* 2003), lower than concentrations measured in Taiwan (36–11473 ng Sn g^{-1} ww; Dong *et al.* 2004).

The main adverse effects of butyltins on aquatic life have been malformations in marine gastropods. The most serious of these, imposex, can lead to sterility and local extinctions of affected species in the most severe cases of contamination (Oehlmann *et al.* 1998). In China, a number of reports of imposex in mollusks have been published in recent years (Shi *et al.* 2001, 2003, 2005). The morphological characteristics of imposex were found in marine gastropods along the southeast coast of China (Shi *et al.* 2001; Figure 2). Shi *et al.* (2005) reported in detail the occurrence of various stages and types of imposex in gastropods along the coastlines of mainland China from 1999 to 2004 (Figure 1b) by dividing the morphological expression of imposex in gastropods into seven stages (S0–S6).

Different gradations (stages) of imposex are described by the vas deferens sequence (VDS), determined by examining female gastropod genitalia using a stereomicroscope. We have attempted to predict the percentage of sterile females along the coasts of mainland China using this scale and the following equation, developed by Oehlmann *et al.* (1998):

(1) $y = 100^{1+e-0.529*(V-4.52)} + 0.0018$
(n = 438, r = 0.922, $P < 0.0005$)

where *y* is the incidence of sterile females, and *V* is the VDS index. As shown in Figure 1b, the coastlines around Dalian, Lianyungang, Xiamen, Shenzhen, the Pearl River, Beihai, Haikou, and Dongya were predicted to

Table 1. Annual release quantities and main sources of typical EDCs in China

Chemicals	*Annual quantities released*	*Sources*	*References*
Butyltins	7500 tons	Stabilizers, catalysts, biocides	Li *et al.* 2003
Nonylphenol ethoxylate (NPEOs)	93 000 tons	Synthetic scour (80%), agricultural industry (8%), textile industry (6%), construction engineering (2%), leather industry(2%), paper industry (2%)	Feng 2005; Huang *et al.* 2002
Atrazine	5000 tons	Herbicides	Ren *et al.* 2002
Dichloro-diphenyl-trichloro-ethane (DDT)	8000 tons (1950–1983)	Insecticides	Qiu *et al.* 2004
Dioxins	1.51 kg I-TEQ*	Bleached chemical wood pulp and paper mills	Jin *et al.* 2004
	0.013–1.256 kg I-TEQ	Municipal solid waste and crematoria incinerators	
	0.375–3.5 kg I-TEQ	Coke production, sinter plant, iron and steel, non-ferrous metal, cement kilns	
	4.4–6.6 kg I-TEQ	Chloralkali industry	
	0.066–0.122 kg I-TEQ	Coal combustion	
	0.6 kg I-TEQ	Pentachlorophenol/phenate	

*I-TEQ: International toxicity equivalents have high percentages of sterile individuals (10–27%). The highest incidences of female sterility were found along the coast between Shantou and Shenzhen, where high concentrations of TBT in surface water (0.35–3.35 ng L^{-1}) and sediment (1.7–6.31 ng g^{-1}) were also detected (Shi *et al.* 2003). The VDS for the ivory shell (*Babylonia formosae habei*) was also found to be related to the concentration of TBT along southern China coastlines (4 at 1.19 ng L^{-1} of TBT and 5 at 3.35 ng L^{-1}). Some local gastropod populations will become extinct if the current high incidence of female sterility continues, indicating an urgent need to prohibit the use of butyltins in antifouling paints in China.

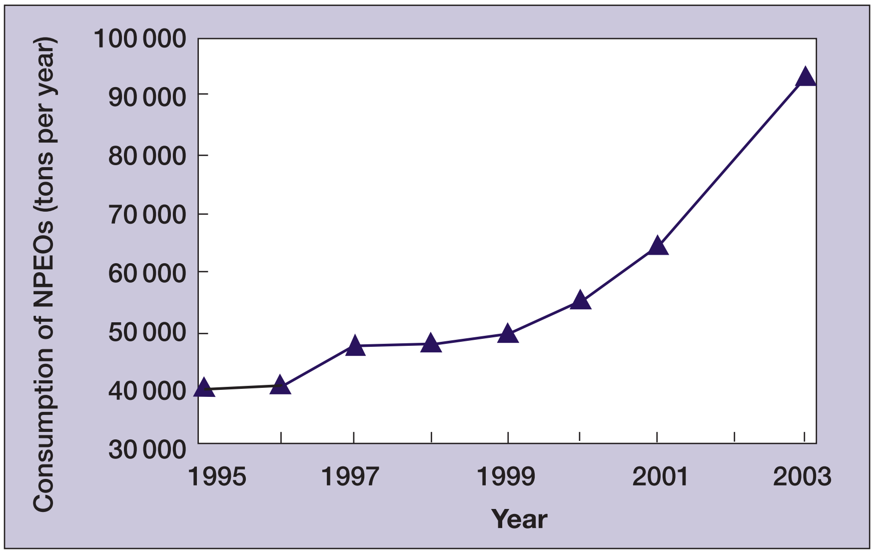

Figure 3. *Annual nonylphenol ethoxylate (NPEOs) usage in China, from 1995 to 2003.*

NP and natural estrogens

Nonylphenol (NP) is a metabolic byproduct of nonylphenol ethoxylate (NPEOs) found in aquatic environments. NPEOs have been used widely in industry and agriculture (eg in textile manufacturing, petroleum refining, and pesticide formulations) since they were first synthesized in 1940. The total annual quantity of NPEOs used in China increased from 40 000 tons in 1995 to 93 000 tons in 2003, an annual increase of 11% (Figure 3). This represents about 10% of global usage (Huang *et al.* 2002; Feng 2005).

The NP concentrations in the Yangtze River (1.55–6.85 μg L^{-1}) near the city of Chongqing in July 2001 (Shao *et al.* 2002) were higher than those measured in the Pearl River between July and September 2002 (0.1–0.16 μg L^{-1}; Duan *et al.* 2004), in the Yellow River in August 2003 (near the city of Lanzhou: 0.240–2.10 μg L^{-1}; Hou *et al.* 2005), and in the Hai River in August 2003 (0.031–0.553 μg L^{-1}; Jin *et al.* 2004). However, concentrations of NP in surface waters are closely linked to seasonal variations in usage as well as temperature-dependent biodegradation rates. For example, while NP concentrations in the Yangtze River in April ranged from 0.01 to 1.12 μg L^{-1}, the concentrations increased to 1.55–6.85 μg L^{-1} in July (Shao *et al.* 2002).

The NP concentrations in the Yangtze River are higher than those found in the Detroit River (0.269–1.19 μg L^{-1}) in the United States (Snyder *et al.* 1999). NP concentrations of 151.4 ± 50 to 677.8 ± 136 ng g^{-1} lipid were also detected in organisms throughout the marine aquatic food web, including 14 species of marine plankton, benthic invertebrates, fish, and marine birds in Bohai Bay (Hu *et al.* 2005a).

The adverse biological effects of NP have been linked to the induction of vitellogenin in male fish, intersex conditions, and abnormal sex ratios in fish. In China, Hu *et al.* (2003) developed a high performance liquid chromatography assay and enzyme-linked immunosorbent assay kit to test for vitellogenin, and used it to detect the protein (0.284–5.971 mg mL^{-1}) in wild male and female crucian carp (*Carassius auratus*) taken from the Beijingpaiwu River, part of the Hai River watershed. The group also detected NP concentrations of about 30–1510 ng g^{-1} ww in the tissues of these fish, suggesting that NP concentrations are related to vitellogenin induction (Jin *et al.* 2004). In fact, intersexual testis–ova, declining sperm activity, and a substantial decline in the male to female ratio have been reported in populations of anadromous Chinese sturgeon (*Acipenser sinensis gray*) in the Yangtze River (Wei *et al.* 1997). Chinese sturgeon, which spawn and hatch mainly in the Yangtze River, are close to extinction and are high on the list of protected species in China. Zhang *et al.* (2005) investigated the effects of NP on vitellogenin gene expression in Chinese sturgeon and found concentrations of 2.78–2.41 μg g^{-1} ww in the liver of these fish, following short-term exposure to NP. Because NP concentrations of 0.8 to 1.92 μg g^{-1} ww were detected in wild fish in the Yangtze River (Shao *et al.* 2005), Zhang *et al.* (2005) suggested that potentially high NP residues could exist in Chinese sturgeon and that this could induce vitellogenin gene expression following long-term exposure. It should be noted that NP has the potential to mimic estrogen, but this is approximately 100 000 times weaker in eliciting estrogenic responses than natural estrogen (17β-estradiol). In fact, naturally produced estradiol and synthetic estrogens from human or pig excreta are probably of greater importance in this respect than NP. However, there is little data on the occurrence of natural and synthetic estrogens in China. The amounts of natural estrogens (estrone [E1] and 17β-estradiol [E2]) excreted by humans and released into different river watersheds were estimated using the following equation:

$$I = 365 * q * n/f \quad (2)$$

where I is the amount of natural estrogen released into the river; q is the amount released per individual (E1: 10.2 μg day^{-1}; E2: 6.6 μg day^{-1}; Johnson *et al.* 2004); n is the total

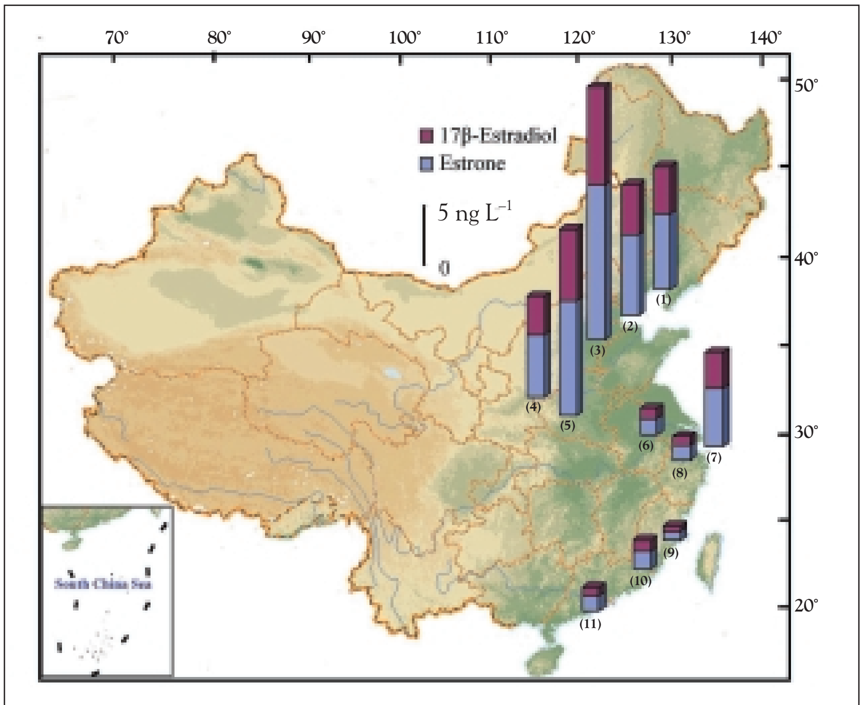

Figure 4. *Estimated levels of natural estrogens released by human into the main rivers in China: (1) Liao River; (2) Luan River; (3) Hai River; (4) Yellow River; (5) Huai River; (6) Yangtze River; (7) Huangpu River; (8) Qiantang River; (9) Min River; (10) Jiulong River; (11) Pear River.*

population in the river watershed; and *f* is the water flow (tons per year) of the river. These parameters (*n* and *f*) are listed in Table 2 (Wu *et al.* 1999), and the estimated amounts of natural estrogens released into China's main rivers are shown in Figure 4. It can be seen that the concentrations of estrogens in northern rivers are much higher than those in the southern river watersheds, due to the low flows of the northern rivers. More adverse biological effects of estrogens are therefore observed in northern China than in southern China.

Atrazine

Atrazine was first synthesized in Switzerland in 1955, and first licensed in the US in 1959 as an herbicide that inhibited photosynthesis. It was registered for the control of broadleaf weeds and some grassy weeds in crops such as corn, sorghum, sugarcane, wheat, guava, macadamia nuts, and hay. Laboratory observations showed that a low concentration of atrazine (0.1 μg L^{-1}) can cause hermaphroditism in male frogs (Hayes *et al.* 2002); feminization of wild frogs is found throughout the US, and has been correlated with widespread usage of atrazine. This has triggered concerns about the biological effects of environmental atrazine on amphibians. To date, however, there have been no reports of feminization of male frogs in China, even though atrazine usage is relatively high.

In China, atrazine has been produced and used since the 1980s, and the quantities have increased each year since then. The total quantity of atrazine produced in China has reached 5000 tons per year (Ren *et al.* 2002). Although its use has been restricted in Switzerland for 10 years and was recently banned in Italy and Germany, atrazine is still one of the most common herbicides in the world. This, together with its persistence in the environment, has contributed to widespread water contamination. Atrazine has been detected in the surface water in the Liao River, Guanting Reservoir, and the Yang River in China. The highest concentration found in the Yang River was 6.7 μg L^{-1}, higher than both the Liao River (0.3 μg L^{-1}; Marion *et al.* 2002) and the Guanting reservoir (1.5 μg L^{-1}; Ren *et al.* 2002). This, in turn, is slightly higher than the 1.29 μg L^{-1} found in the Patuxent River estuary in the United States (McConnell *et al.* 2004). In fact, the high concentrations of atrazine in the Yang River and Guanting reservoir have been linked to discharges from factories manufacturing pesticides (Ren *et al.* 2002).

Table 2. Population size and flux in major river watersheds of China (Wu *et al.* 1999)

River watershed	*Population size (10^6)*	*Flux ($10^9 m^3$)*
Daliao River	15.1	8.9
Luan River	16.3	9
Hai River	79.7	22.8
Yellow River	80.7	58
Huai River	160	62.2
Yangtze River	351	960
Huangpu River	13	10
Qiangtang River	15	44.4
Min River	11.37	58.6
Jiulong River	5.43	13.7
Pearl River	110	341.2

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Dichlorodiphenyl trichloroethane (DDT)

DDT was first synthesized in 1873 by Othmar Ziedler, and has been used as an organochlorine insecticide since 1940. It is still used today for disease vector control (mostly malaria) in 25 or more developing countries. This is primarily because of its high performance and low cost. DDT was widely used in China from 1950 to 1983. During this period, China produced 270 000 tons of DDT, representing 20% of the total world production (Qiu *et al.* 2004). Although DDT was banned in China at the beginning of the 1980s, one of its metabolite residues, dichlorodiphenyldichloroethylene (DDE), can still be detected in aquatic environments due to its extended persistence and the use of other sources, such as the organochlorine pesticide dicofol, which contains small quantities of DDT. Runoff from fields treated with these chemicals has resulted in high concentrations in the sediments of freshwater, estuarine, and marine environments in China (Figure 5; Hong *et al*., 1995; Wu *et al*. 1999; Hu *et al*. 2005b).

Hu *et al*. (2005b) reported the presence of DDT-related compounds in Bohai Bay and the adjacent Hai River watershed in northern China. They found that 2,2-bis-chlorophenyl-aceticacid (p,p'-DDA), a major degradation product of DDT, accounted for 52–93% of the total DDT concentration in the water. In sediment, dichlorobenzophenone (p,p'-DBP; range: 0.60–3.30 ng g^{-1} dry weight [dw]) is a major metabolite, comparable with DDE (range: nondetectable–1.80 ng g^{-1} dw) and DDD (2,2-bis-(chloro-phenyl)-1,1-dichloroethane, range: nondetectable–2.86 ng dw). Wu *et al*. (1999) also recorded concentrations of DDT and its metabolites (p,p'-DDE, p,p'-DDD, and p,p'-DDT) in sediments collected from major rivers and seas in China (Figure 5). These concentrations were relatively low in sediments from rivers in the north of China, with the exception of the Hai River (9.5–11.5 ng g^{-1} dw), while the values for DDTs were high at different locations in South China, including Tai Lake (0.97–12.66 ng g^{-1} dw; Yuan *et al*. 2003), the Minjiang River (6.9–13.1 ng g^{-1} dw; Zhang *et al*. 1996), the Jiulong River (4.1–6.1 ng g^{-1} dw; Zhang *et al*. 1996), and the Pearl River (6.5–14.5 ng g^{-1} dw; Liao *et al*. 1983). Compared with other rivers around the world (Iwata *et al*. 1994), the residual concentrations of DDTs in sediments in this region were relatively low, although large quantities of organochlorines have been produced and used in China.

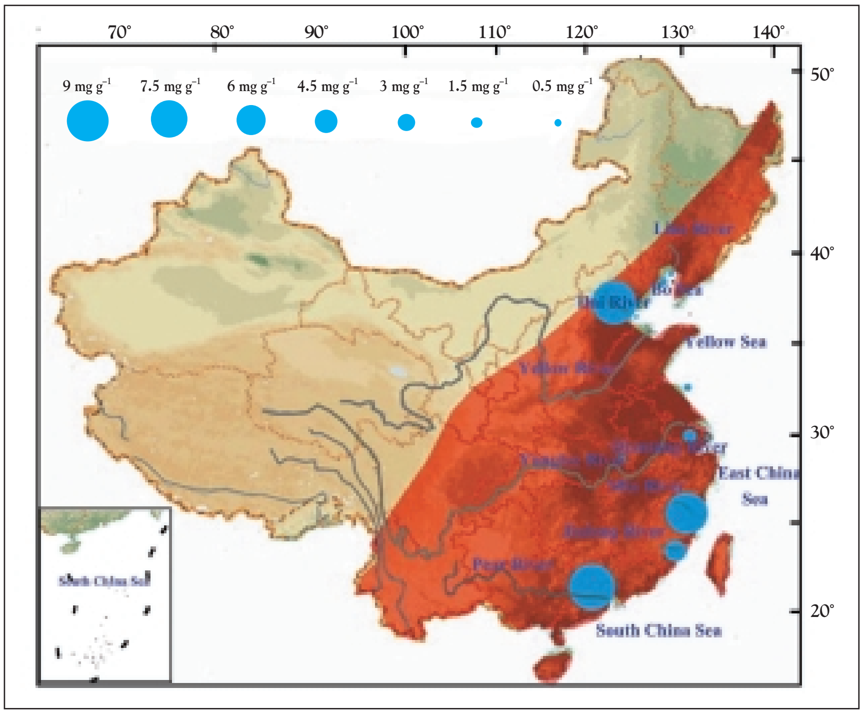

Figure 5. *Distribution of DDT concentrations in sediments of the main rivers and seas (circle radius represents the exposure level of DDT) and night heron habitat in China. Red shadow reprinted with permission from Oxford University Press.*

It is well known that DDT and its metabolites accumulate in waterfowl and raptors. Dong *et al*. (2004) detected DDTs in the eggs of black-crowned night herons (*Nycticorax nycticorax*), little egrets (*Egretta garzetta*), cattle egrets (*Bubulcus ibis*), and Chinese pond herons (*Ardeola bacchus*) from a colony near Tai Lake. While quantities of DDE found in the eggs of night herons from Tai Lake (mean concentration 1103 ng g^{-1} ww; range: 196–5837 ng g^{-1} ww) are higher than those from a colony near Hong Kong (mean concentration 491 ng g^{-1} ww; range: 200–1200 ng g^{-1} ww), the concentration in the eggs of little egrets around Tai Lake (mean concentration 397.41 ng g^{-1}; range: 77.18–2151.4 ng g^{-1} ww) was lower than that from the Hong Kong colony (mean concentration 941 ng g^{-1}; range: 530–1700 ng g^{-1} ww). This may be due to differences in the egrets' diet. However, in both colonies, DDE accounted for 85–95% of the total DDTs in these species.

As a persistent lipophilic metabolite of DDT, DDE can cause thinning of eggshells and decreases in bird population sizes. DDE concentrations in birds, particularly waterfowl and raptors, are greatly increased through bioaccumulation. Night herons, for instance, are susceptible to persistent organic chemicals. These birds are common in China, and their habitats are associated with swamps, streams, rivers, marshes, muddy flats, and the edges of lakes from the north to the south of eastern China (Ramsay 2000; Figure 5). Zhang *et al*. (2003) found that reproductive success (76%) in the night heron colony near Tai Lake, where high DDE concentration residues are detected in the eggs (Dong *et al*. 2004), was much lower than in a reference area (95%; Zhu *et al*. 2000). The probability that DDE concentrations in the eggs of night herons inhabiting Tai Lake exceed the threshold concentration (1 μg g^{-1} ww per egg) where there are no effects on reproductive success (Connell *et al*. 2003) was estimated to be 56.5% (An *et al*. 2005). This high probability of reproductive impairment has lead to serious concern about the risk of negative effects of DDE in the night heron population. Using the intrinsic rate of population increase as an assessment endpoint, the effects of exposure to DDE on the night heron population at Tai Lake was calculated as a decrease in population size of 2.56% every year. In other words, about five individuals in a population of 100 pairs would be lost each year due to DDE exposure (An *et al*. 2006).

Fortunately, there have been many studies on DDT exposure, covering most of the river and lake watersheds where night herons are found (Figure 5). It is therefore possible to predict that the potential impacts on night

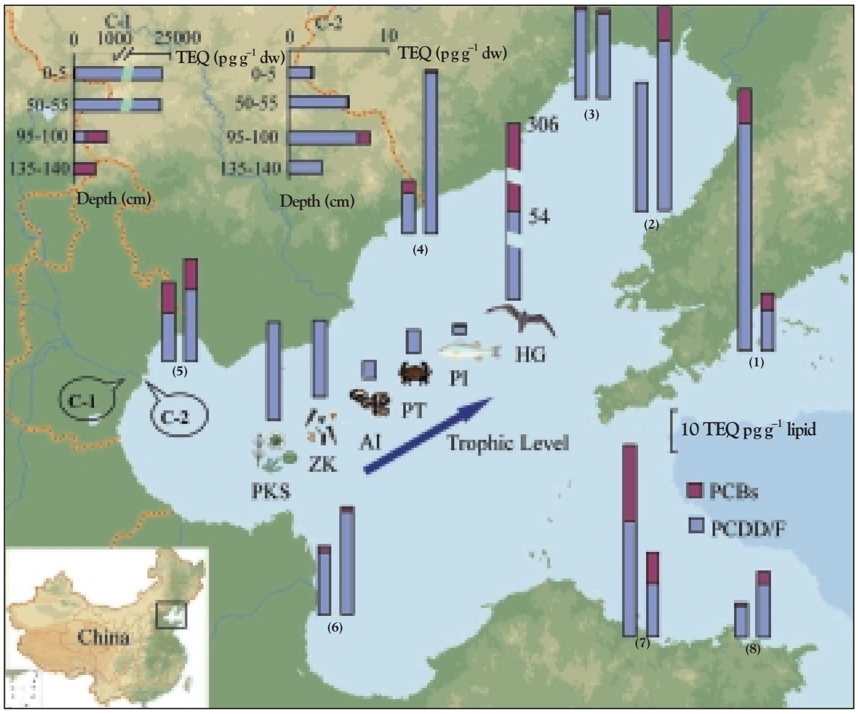

Figure 6. *TEQ of PCDD/F and co-PCB concentrations in slices of sedimentary cores (horizontal bars: C–1 and C–2), marine species at different trophic levels in Bohai Bay, and mollusks (vertical bars from 1–8) along the Bohai coastline. Marine species: PKS: phytoplankton; ZK: zooplankton; AI: bay scallop (*Argopecten irradians*); PT: crab (*Portunus trituberculetus*); PI: bartail flathead (*Platycephalus indicus*); HG: herring gull. The double vertical bars represent TEQ concentrations in whelks (left) and scallops (right). Sampling locations: (1) Dalian; (2) Yingkou; (3) Huludao; (4) Qinghuangdao; (5) Tianjin; (6) Yangkou; (7) Yantai; (8) Weihai.*

heron populations will occur in regions with high levels of organochlorine residues, for example the Hai, Pearl, Min, and Jiulong Rivers, where high concentrations of DDT residues exist in sediment. This calculation does assume that the bioaccumulation factor from sediment to eggs is constant in these regions.

PCDD/F and co-PCBs

PCDD/F and co-PCBs have attracted the attention of scientists and the public, because these compounds not only disrupt endocrine function, but have also been shown to have dermal toxicity, immunotoxicity, and carcinogenicity. Their toxic equivalency quantity (TEQ) is always calculated using the World Health Organization toxic equivalency factors (WHO- TEFs) and the international toxicity equivalency factor (I-TEF). Furthermore, due to the hydrophobic nature of these compounds, and their resistance to metabolism, they are ubiquitous in the environment, leading to human exposure. High rates of cancer mortality and chloracne have been reported in several groups of people exposed to dioxin compounds (PCDD/F) during herbicide production (Steenland *et al.* 2001).

Paper mills and the chloralkali industry, which produce chlorine for bleaching wood pulp, are the main sources of dioxins in China, producing about 5.9–8.1 kg I-TEQ. The domestic and industrial combustion of coal accounts for about 0.4–3.6 kg I-TEQ, because China relies mainly on coal for its energy production. Municipal solid waste incinerators and crematoria produce only 0.01–1.3 kg I-TEQ, and cement kilns and asphalt mixing also emit a relatively small amount of dioxins (about 0.2 kg I-TEQ). Other important sources of dioxins include the production and usage of pentachlorophenol (PCP), which is used widely as a biocide to control snail-borne schistosomiasis and also as a wood preservative. The emission of dioxins from PCP is about 0.6 kg I-TEQ. We found no peer-reviewed papers on the occurrence of co-PCBs in China. However, our own unpublished results indicate that the total amount of dioxins in PCP is 7420 ng g^{-1}, 130 ng g^{-1} in co-PCBs, and 7290 ng g^{-1} in PCDD/F (Hu *et al.* unpublished).

In China, data on dioxin concentrations in the environment are very limited. However, the toxic equivalency quantity (TEQ-WHO) of PCDD/F and co-PCBs in sediment, as well as in aquatic organisms and seabirds, is often used to assess the ecotoxicological risks to high trophic level animals. Wu *et al.* (1997) investigated PCDD/F and co-PCBs pollution in the sediment of Ya-Er Lake in Hubei province; they found that concentrations of PCDD/F and co-PCBs were 0.10–857 pg TEQ-WHO g^{-1} dw and 0.03–64.1 pg TEQ-WHO g^{-1} dw, respectively. Hu *et al.* (2005b) reported on historical variations in PCDD/F and co-PCBs by analyzing the slices of sedimentary cores in the Nanpaiwu River and Bohai Bay (Figure 6). They found that the highest concentration (22000 pg TEQ-WHO g^{-1} dw) in the Nanpaiwu River was about 125 times higher than in a sedimentary core from Beaver Lake in Washington State (Lorber *et al.* 2002). The source of dioxins in the Nanpaiwu River was found to be the production of PCP, a pesticide that is manufactured in this area.

A few studies have been conducted on the occurrence of dioxins in various organisms in China. Wan *et al.* (2005) reported the trophodynamics of PCDD/F and co-PCBs in all organisms in the Bohai Bay food chain; there, concentrations ranged from 2.3 to 306 pg TEQ-WHO g^{-1} lipid (Figure 6). The highest TEQ concentration (306 pg TEQ-WHO g^{-1} lipid) was detected in herring gulls, which is 13–132 times higher than in other aquatic species. It is interesting that in aquatic organisms (excluding birds) 60–93% of the TEQ was co-PCBs, while in birds, over 85% of TEQ was contributed by PCDD/F. The authors concluded that this was due to differences in bioaccumulation within the food web between PCDD/F and co-PCBs. Zhao *et al.* (2005) studied a wide sweep of coastline around the Bohai Sea, measuring concentrations of PCDD/F and co-PCBs in mollusks, and reported that while the highest TEQ concentration of PCDD/F (51 pg TEQ-WHO g^{-1} lipid) was found along the Dalian coastline, the highest concentration of co-PCBs (17 pg TEQ-WHO g^{-1} lipid) was detected along the Yantai coastline (Figure 6), suggesting that there are different sources of dioxins in different locations. Using the reference dose (RfD) of 1–10 pg TEQ-WHO g^{-1} per kg d^{-1} for dioxin proposed by Greene *et al.* (2003), the ingestion rate ($IR = 6.5$ g) of consumed contaminated marine shellfish and fish tissue per day, and absorption efficiency ($AE = 1$; Barron *et al.* 1994), the adult burden (AB) of TEQ per day can be calculated using the following equation:

$$AB = AE \times IR \times C/70 \quad (3)$$

where C is TEQ normalized by lipid in shellfish and fish. The default weight in adult humans is 70 kg (154 lbs). Using equation 2, the mean TEQ burden for an adult seabird eating marine fish and shellfish from the Bohai Bay was estimated to be 0.085 pg TEQ-WHO g^{-1} per kg d^{-1} (range 0.025–0.35); this is much lower than the RfD of 1 pg TEQ-WHO g^{-1} per kg d^{-1} recommended by Greene, indicating that shellfish contaminated by dioxin (PCDD/F) and dioxin-like compounds (coplanar PCBs) would not cause an adverse response in humans.

Conclusions

Here, we have summarized the occurrences in Chinese aquatic environments of typical EDCs, together with related adverse biological effects. First, based on the high concentrations of butyltins in the rivers, lakes, and coastal waters of China, and the high incidence of sterility in gastropods along the mainland coasts of China, there is an urgent need to quantify new sources of butyltins and to reduce the concentrations of these harmful compounds in the environment.

Second, high concentrations of atrazine have been linked to detrimental effects in frogs in some rivers (eg the Yang River); greater attention needs to be focused on atrazine use and its potential impacts on wildlife, particularly amphibians, in China.

Third, although DDT was banned at the beginning of the 1980s in China, high concentrations of DDE residues are still detected in the environment and in tissues of various species. To protect bird populations, it is essential to control new sources of DDT pollution.

Finally, although the main sources of dioxins in China are reported to be from the chloralkali industry and the paper industry, other sources, such as pesticides and wood preservative, as well as emissions from municipal solid waste incinerators and crematoria should also be of major concern, due to the rapid increase in numbers of these installations in China.

Although recent studies have revealed the sources and fates of various EDCs in the environment, in China there are few regulations limiting production and dissemination of EDCs. For example, TBT antifouling agents have been banned in many developed countries, but remain unregulated in China. Although DDT has been banned as a pesticide in China, it is still used as a raw material in the manufacture of other pesticides. While NP is commonly found in rivers in China, the concentrations do not generally approach threshold levels for action. However, the increasing usage of NP in recent years necessitates continued control and monitoring. A similar strategy should be implemented for another important EDC, dioxin. Further research is also needed on the intersex effects observed in fish in China, as it is still unclear which chemicals caused these abnormalities.

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*College of Environmental Science, Peking University, Beijing, 100871 China *(hujy@urban.pku.edu.cn)*