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Monitoring the Organotin Contamination in the Taihu Lake of China by Bivalve Mussel *Anodonta woodiana*

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Abstract As a part of the pilot study on "Freshwater Mussel Watch", butyltin (monobutyltin, MBT; dibutyltin, DB; tributyltin, TBT), and phenyltins (monophenyltin, MPT; diphenyltin DPT; triphenyltin TPT) were analyzed in soft tissues of 15 bivalve mussels *Anodonta woodiana* sampled from five separate sites (Huzhou, Xueyan, Dapu, Sansandao, and Wulihu) around the Taihu Lake of China in 2004. The residue of total butyltins and total phenyltins in the all mussels ranged 142–1693 and 3.0–90 ng Sn g^{-1} dry weight, respectively. Except for the mussels from Xueyan, DBT and MBT accounted more than 60% of total butyltins in those from other four sites. In contrast, TPT were usually almost 100% of the mussels studied. The present study provides most recent information about the organotin contamination in the Taihu Lake, and suggests *Anodonta woodiana* can be used as a suitable bioindicator.

Keywords *Anodonta woodiana* · Butyltin · Contamination · Phenyltin · Taihu Lake

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The Taihu Lake, located in eastern China, is the third largest freshwater lake in China approaching 2,428 km^2 of water surface area. It is one of the most developed regions of China for agriculture, industry and commerce, playing a critical role on water supply, tourism, fishery and navigation. So far the lake has been seriously eutrophicated and the water quality has been greatly deteriorated by discharge of industrial and domestic wastewater (Shen et al. 2001; Wang et al. 2003). It is necessary to investigate the water contamination status of heavy metals and other pollutants, and to give an assessment environmental quality. "Mussel Watch" has been proven successful as a very applicable approach to monitor the status and temporal changes in metal and organic contaminants in estuarine and coastal waters using bivalve mussels as sentinel organisms (Goldberg 1986; Tanabe and Subramanian 2006). Consequently, a "Freshwater Mussel Watch" project in Taihu Lake has been under way first-hand by our laboratory, using the bivalve mussels *Anodonta woodiana* from the Taihu Lake as a unique bioindicator, to document reliable baseline levels of heavy metals (e.g., Zn, Cu, Pb, Cd, and As), and organochlorine chemicals (e.g., DDTs, HCHs) (Yang et al. 2005; Bian et al. 2007). The species is widely distributed across China and commonly used for food and cultivating pearl (Cai and Huang 1991).

Organotins (esp., butyltins and phenyltins) are typical endocrine disrupting chemicals (Fent et al. 1998; Vos et al. 2000; Santillo et al. 2001). To date, organotin contamination has been reported more widely in crustaceans, cephalopods, echinoderms, fish, birds, marine and terrestrial mammals, as well as human beings (Iwata et al. 1994; Takahashi et al. 1997, 1999; Harino et al. 2000).

In recent years pollution of organotins, used on plastic stabilizes, antifouling paints for vessel and aquatic cultivation, is paid attention in China gradually (Jiang 2001;

Yang et al. 2006a, b; Zhao et al. 2007). A few papers indicated the pollution in some bays of northern China and inland waters (Jiang et al. 2000; Yan et al. 2001). Tributyltin (TBT) concentration of water in Huangpu River in Shanghai was documented as high as 425.3 ng Sn L^{-1}, and those of Yangtze River in Jiangyin City and Dianchi Lake in Yunan Province were also high (10 and 37.6 ng Sn L^{-1}, respectively). Imposex can occur at as low as 0.1 ng Sn L^{-1} in gastropod (Vos et al. 2000). Therefore, the accumulation and toxicity of organotins in aquatic animals of Chinese water ecosystem should be got great concerned. However, there are neither countrywide surveys on contamination of organotins productions, nor national regulations on utilization of them in China.

Being integrating our above previous studies in heavy metals and organochlorine chemicals, the aim of this work was to further evaluate the extent of organotin (butyltin and phenyltin) pollution by *Anodonta woodiana* in the Taihu Lake.

Materials and Methods

Bivalve mussels *Anodonta woodiana* were collected from five sites around the Taihu Lake in August–November 2004, i.e., Huzhou city, Xueyan of Changzhou city, Dapu of Yixing city, Sansandao and Wulihu of Wuxi city (Fig. 1). The a total 15 mussels of similar size were selected and kept without food in laboratory for several days in continuously aerated tap water in order to empty digestive tracts as much as possible. After measurement of the biological parameters (Table 1), the mussels were dissected, and all soft tissues were stored immediately at −20°C until chemical analysis.

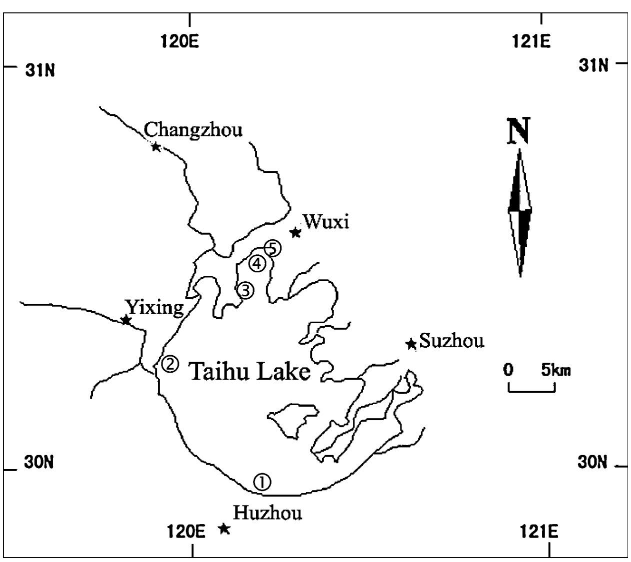

Fig. 1 The map of sampling locations in the Taihu Lake, China. ① Huzhou city, ② Dapu of Yixing city, ③ Xueyan of Changzhou city, ④ Sansandao of Wuxi city, ⑤ Wulihu of Wuxi city

All the mussel samples were freeze-dried and homogenized before analysis. The procedures for analyzing butyltins [including monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT)] and phenyltins [including monophenyltin (MPT), diphenyltin (DPT), triphenyltin (TPT)] were mainly followed the method of Harino et al. (2005). Briefly, about 0.2 g of the homogenate samples were treated. After the addition of deuterated organotins ($MBTCl_3$-d_9, $DBTCl_2$-d_{18}, TBTCl-d_{27}, $MPTCl_3$-d_5, $DPTCl_2$-d_{10}, TPTCl-d_{15}) (Hayashi Pure Chemical Ind. Ltd, Osaka, Japan) as surrogate standards to the samples, organotin compounds were extracted with 1 M HCl–methanol/ethyl acetate (1:1). After the centrifugation, a saturated NaCl solution added to supernatant and analytes were then extracted with ethyl acetate/hexane (3:2). The extract was mixed with hexane. After the removal of aquatic layer, the organic layer was dehydrated with sodium sulfate anhydrous and then concentrated to about 1 mL. The concentrate was mixed with an acetic acid–sodium acetate buffer solution (pH 5.0) and $NaBEt_4$ solution in order to derivatize target organotins. Then, 1 M KOH–ethanol was added to the derivatized sample solution. Left overnight, the mixture was shaken for 1 h to decompose any fat. After saponification, the ethylated organotins were extracted with hexane, and the extract was dehydrated with sodium sulfate anhydrous and then concentrated. The sample was cleaned using a florisil cartridge column (Water Association Co. Ltd., MA, USA) and TeBT-d_{36} and TePT-d_{20} (Hayashi Pure Chemical Ind. Ltd, Osaka, Japan) as an internal standard was added to it. Determination by selected ion monitoring was carried out by an Agilent 6890 series gas chromatography equipped with a mass spectrometry (5973 N). The organotins detect limits were 1 ng Sn g^{-1} dry weight at a signal-to-noise ratio of three duplicates in this study. When 1 mg of each organotin were spiked to 5 g of soft tissues, recovery rates of MBT, DBT, TBT, MPT, DPT and TPT were 98%, 92%, 90%, 109%, 97% and 90%, respectively and the standard deviation of MBT, DBT, TBT, MPT, DPT and TPT were 10%, 12%, 8%, 9%, 8% and 12%, respectively. In this study, concentration is presented as ng Sn g^{-1} dry weight basis, and the results can be converted to wet weight basis by a general moisture content 86% of *Anodonta woodiana* (Yang unpublished).

Results and Discussion

The present monitoring study by *Anodonta woodiana* suggests that butyltin and phenyltin contaminations were obvious in the Taihu Lake, because the detection rate was 100% for both pollutants in all mussels from five separate sites (Table 2), probably reflecting that recent inputs of these

Table 1 Biometric characteristics for *Anodonta woodiana* from the Taihu Lake of China

Sample code	Sampling site	Shell wide (cm)	Shell height (cm)	Shell length(cm)	Wet weight of soft tissue (g)	Dry weight of soft tissue[a] (g)
AW-12	Huzhou	3.6	6.0	9.9	17	2.4
AW-31	Huzhou	4.0	6.4	9.5	20	2.8
AW-32	Huzhou	3.9	6.1	9.2	20	2.8
AW-43	Xueyan, Changzhou	3.7	6.0	9.9	22	3.1
AW-58	Xueyan, Changzhou	3.7	6.8	9.7	21	2.9
AW-63	Xueyan, Changzhou	4.7	8.1	13	24	3.4
AW-78	Sansandao, Wuxi	4.2	6.9	9.1	20	2.8
AW-82	Sansandao, Wuxi	5.4	8.1	12	45	6.3
AW-83	Sansandao, Wuxi	3.7	6.0	9.2	16	2.2
AW-96	Dapu, Yixing	4.1	7.4	11	22	3.1
AW-106	Dapu, Yixing	4.5	7.0	10	21	2.9
AW-113	Dapu, Yixing	4.1	6.6	9.4	20	2.8
AW-184	Wulihu, Wuxi	4.0	9.9	10	35	4.9
AW-185	Wulihu, Wuxi	5.0	11	11	43	6.0
AW-186	Wulihu, Wuxi	4.5	10	10	38	5.3
Mean ± SD		4.2 ± 0.52	7.5 ± 1.6	10 ± 1.0	26 ± 9.6	3.6 ± 1.3

[a] Dry weight of soft tissue was calculated using a general moisture content 86% of *Anodonta woodiana* (Yang, unpublished)

pollutants have been available around the Taihu Lake. The residue of total butyltin (ΣBTs) in all mussels *Anodonta woodiana* ranged 142–1693 ng Sn g^{-1} dry weight. The highest concentration of ΣBTs (1172 ± 657 ng Sn g^{-1} dry weight) was found in the mussels from Dapu water area, while the lowest concentration of ΣBTs (142 ± 0.6 ng Sn g^{-1} dry weight) was noted in those from Huzhou. DBT and MBT accounted more than 60% of total butyltins in the mussels from Huzhou, Sansandao, Dapu and Wulihu waters, and MBT concentration usually accounted higher percentage than that of DBT in the most mussels (Table 2). Contrastly, TBT showed a slightly higher percentage than those of breakdown products DBT and MBT in the mussels from Xueyan water.

To date, only Yang et al. (2006a, b) reported the contamination of butyltin in Taihu Lake by samples of water,

Table 2 Concentrations (ng Sn g^{-1} dry weight) of butyltins (BTs) and phenyltins (PTs) in soft tissues of *Anodonta woodiana* from the Taihu Lake of China

Sample code	Water area	MBT	DBT	TBT	Total BTs (ΣBTs)	Area ΣBTs mean ± SD	MPT	DPT	TPT	Total PTs (ΣPTs)	Area ΣBTs mean ± SD
AW12	Huzhou	80 (56)[a]	28 (20)	34 (24)	142		<1 (0)	15 (59)	11 (41)	26	
AW31	Huzhou	105 (74)	16 (11)	22 (15)	143		<1 (0)	13 (69)	6 (31)	19	
AW32	Huzhou	117 (82)	14 (10)	11 (8)	142	142 ± 0.6	<1 (0)	<1 (0)	10 (100)	10	18 ± 8.2
AW43	Xueyan, Changzhou	223 (42)	76 (14)	236 (44)	535		<1 (0)	<1 (0)	32 (100)	32	
AW58	Xueyan, Changzhou	324 (27)	174 (14)	722 (59)	1220		<1 (0)	<1 (0)	13 (100)	13	
AW63	Xueyan, Changzhou	220 (37)	114 (19)	258 (44)	592	782 ± 380	<1 (0)	<1 (0)	7 (100)	7.0	17 ± 13
AW78	Sansandao, Wuxi	191 (58)	36 (11)	103 (31)	329		<1 (0)	<1 (0)	13 (100)	13	
AW82	Sansandao, Wuxi	140 (57)	30 (12)	77 (31)	248		<1 (0)	<1 (0)	5 (100)	5.0	
AW83	Sansandao, Wuxi	168 (54)	43 (14)	97 (32)	308	295 ± 42	<1 (0)	<1 (0)	21 (100)	21	13 ± 7.6
AW96	Dapu, Yixing	691 (41)	610 (36)	392 (23)	1693		<1 (0)	<1 (0)	90 (100)	90	
AW106	Dapu, Yixing	427 (31)	435 (31)	529 (38)	1390		<1 (0)	<1 (0)	66 (100)	66	
AW113	Dapu, Yixing	302 (69)	59 (14)	74 (17)	434	1172 ± 657	<1 (0)	<1 (0)	15 (100)	15	57 ± 38
AW184	Wulihu, Wuxi	159 (82)	26 (13)	10 (5)	194		<1 (0)	<1 (0)	3 (100)	3.0	
AW185	Wulihu, Wuxi	195 (83)	32 (13)	9 (4)	236		<1 (0)	5 (32)	10 (68)	15	
AW186	Wulihu, Wuxi	146 (85)	18 (10)	8 (5)	172	201 ± 33	<1 (0)	<1 (0)	6 (100)	6.0	8.0 ± 6.5

[a] Numbers in parentheses indicate the percentage data of MBT, DBT, and TBT or MPT, DPT, and TPT in total butyltins and phenyltins (%)

sediment, five fish muscle and one mussel soft tissue. The ΣBTs concentrations in their biota samples ranged 25–181 ng Sn g^{-1} dry weight, and the maximum data was detected in the muscle of a common carp (*Cyprinus carpio*). The source of butyltin was inferred from antifouling paints applied on aquaculture cages and vessels (Yang et al. 2006a, b). Except for the mussels (142–143 ng Sn g^{-1} dry weight) from Huzhou, ΣBTs concentrations in soft tissues of all *Anodonta woodiana* (172–1693 ng Sn g^{-1} dry weight, ca. 24–237 ng Sn g^{-1} wet weight) in the present study were usually much higher than the maximum level in the above previous literature (Table 2). Yang et al. (2006a, b) found, by *Mytilus edulis* and *Pema viridis*, the contamination of butyltins was relatively higher in the Bohai coast of China by comparison of many coastal waters worldwide, and the levels of ΣBTs in the bivalves ranged <23–162 ng Sn g^{-1} wet weight. Our results were comparable to the levels above and suggested that the contamination of butyltin in the Taihu Lake was much more obvious than those previously reported and butyltin residues in the Taihu Lake should be of primary concern.

Yang et al. (2006a, b) reported that the main species of total butyltin was TBT by limited number of fish and mussel samples from the Taihu Lake. Contrastly, our results suggested that the composition of butyltin compounds in *Anodonta woodiana* is much more complex. The TBT in the mussels at Huzhou, Sansandao, Dapu and Wulihu waters have been metabolized obviously into its breakdown products DBT and especially, MBT (e.g., >80% in the mussels from Wulihu). In contrast, almost half of butyltins was still kept as TBT in the mussels from Xueyan water area, implying a probability of recent TBT sources. These phenomena indicated that the composition of butyltin species in the mussels presented geographic variation, being similar to the tendency of ΣBTs residue levels in the mussels among five sampling sites.

Concerning the phenyltins, the residue of total phenyltins (ΣPTs) in all mussels of *Anodonta woodiana* ranged 3.0–90 ng Sn g^{-1} dry weight. The highest concentration of ΣPTs (57 ± 38 ng Sn g^{-1} dry weight) was observed in the mussels from Dapu water area. In contrast, the lowest ΣPTs level (8.0 ± 6.5 ng Sn g^{-1} dry weight) was observed in those from Wulihu water area. So far there have been no data on contamination of phenyltins in the Taihu Lake. The present study is the first time to document the availability of phenyltin chemicals in the lake using the bivalve mussels *Anodonta woodiana*. Noteworthy, TPT was the only phenyltin compound detected in all mussels except for AW12, AW31, and AW185 (Table 2). These phenomena might be caused by (1) TPT is the dominant phenyltin species assimilated into the mussels from ambient water and food through gill and viscera (Shindo and Otsuki 1999); and/or (2) a low capability to degrade TPT

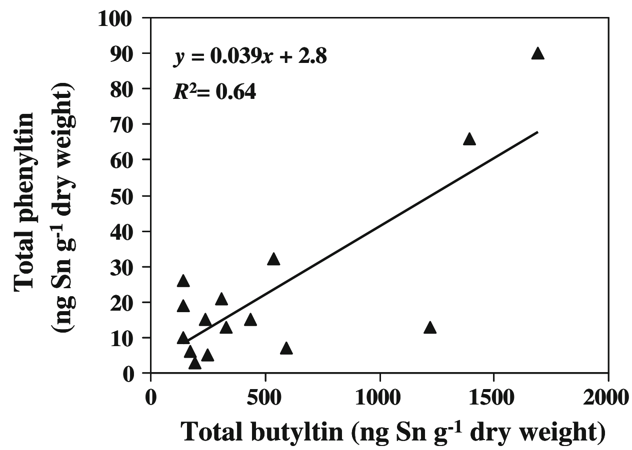

Fig. 2 Relationship between total butyltin (ΣBTs) and total phenyltin (ΣPTs) concentrations in Bivalve mussels *Anodonta woodiana* from the Taihu Lake of China

into its metabolites in the body of *Anodonta woodiana*, being similar to the phenomena found in zebra mussel (*Dreissena polymorpha*) (Stäb et al. 1996). Further study is required to confirm these possibilities. The breakdown product DPT could be found in an obvious level in the individual AW185, and especially AW12 and AW31.Geographic variation was also found among five sampling sites, but this tendency was only significant in ΣPTs residue levels of mussel rather than the composition of phenyltin species, showing a different characteristic from butyltin.

Significant positive correlation ($R = 0.80$) was observed between ΣBTs and ΣPTs concentrations in the mussels (Fig. 2), which is an indication of the possibility that small amounts of TPT might be used as the antifouling paints together with TBT (Regoli et al. 1999) in the Taihu Lake.

The present study provides most recent information about the organotin contamination in the Taihu Lake, and suggests *Anodonta woodiana*, an abundance and wide distribution mussel in inland waters of China, can be used as a suitable bioindicator to monitor the environmental baseline levels and their geographic variation of organotins and, therefore, will greatly facilitate our undertaking "Freshwater Mussel Watch" project in Taihu Lake.

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