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Organotin Compounds in the Three Gorges Reservoir Region of the Yangtze River

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Tributyltins (TBT) are known endocrine disrupting chemicals (EDCs). It was reported that TBT at concentrations of more than 7 ng Sn/l would induce juvenile *Buccinum undatum* to develop a penis and a *vas deferens*, i.e. imposex (Ten Hallers-Tjabbes et al. 2003). TBT in aquatic systems were also reported to be related to various symptoms such as thickening of shell and failure of spat in oyster (Alzieu et al. 1986), impotence of neogastropods and gastropods (Gibbs et al. 1991a), reduction of the dogwhelk population (Gibbs et al. 1991b), and immunological dysfunction in fish (Suzuki et al. 1992). Although TBT has been legislatively banned in antifouling paints since the late 1990s in most European and North American countries (Chau et al. 1997) due to its toxicity to aquatic life at low concentrations, there is still no specific legislation controlling the use of TBT in China. Fragmentary data about the occurrence of organotin compounds in China showed that some aquatic environments have been seriously polluted by butyltin compounds (Jiang et al. 2001; Gao et al. 2004). The construction of the Three Gorges Dam has drawn attention to the impact on the environment of the Three Gorges Reservoir region, which is controversial for several reasons. Up to now, there is still no knowledge about the occurrence of organotin compounds in this region, and a reliable investigation on the occurrence of organotins is useful in assessing the water pollution of the Three Gorges Reservoir Region.

Most analytical methods for the determination of organotin compounds are based on the use of hyphenated techniques that combine gas chromatography (GC) with an element-selective detector. Ionic organotin compounds in the environment generally have high boiling points and need to be derivatized into volatile forms prior to separation by GC. In this paper, the occurrence of butyltins and monphenyltin in the Three Gorges Reservoir region in China was first reported using solid-phase micro- extraction (SPME)-GC-MS combined with ethylation by tetraethylborate ($NaBEt_4$).

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MATERIALS AND METHODS

Monobutyltin trichloride (MBT, 97%) and monophenyltin trichloride (MPT, 98%) were purchased from ACROS ORGANICS (Belgium). Dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 95%), tripropyltin chloride (TPrT, 95%) and sodium tetraethylborate ($NaBEt_4$, 98%) were purchased from Wako (Japan). Tetrahydrofuran from DIKMA (USA) was HPLC grade. Acetic acid and sodium acetate were AR grade from Beijing Chemical Plant, and were used without further purification. Water was obtained by a compact ultrapure water system (EASY pure UV, USA). Individual stock solutions of organotins (1000 mg/l as Sn) were prepared in methanol. A mixed organotins working solution containing 200 mg/l (as Sn) for each compound was also prepared using methanol as solvent, and dilution in methanol was used as required. $NaBEt_4$ solution of 4% (w/v) was prepared with tetrahydrofuran every month. Acetate buffer (pH=4) was made from acetic acid and sodium acetate solution. All the solutions were stored at 4°C in the dark.

An SPME holder and fiber coated with 100 μm thickness polydimethyl- siloxane (PDMS) were obtained from Supelco (Bellefonte, PA, USA). An HP 5890 gas chromatograph equipped with a split/splitless injection port and coupled to a HP 5971 mass selective detector (Agilent Technologies Co., USA) using electron impact in the selected ion monitoring (SIM) mode were used. Separations were performed in a capillary column (HP-5MS, 30m x 0.32mm i.d.x0.25μm coating thickness) throughout the experiment. The carrier gas was helium of high purity (99.9999%).

An appropriate amount of TPrT internal standard was added into 22-ml water samples in 40-ml amber glass vials sealed with PTFE-lined silicon septa. After 2 ml acetate buffer and 0.1 ml 4% $NaBEt_4$ solution were added, the vial was immediately closed and stirred on the magnetic stirrer. Then the SPME fiber was exposed to the headspace over the vigorously stirred solution at room temperature to analyze TBT, DBT, MBT and MPT. After 20 min, the fiber was withdrawn into the needle of the holder and the SPME was placed in the GC injector. Desorption time was 3 min, and no carryover was observed after 3-min desorption time. The temperature programs used for the GC column were: 60°C for 2 min, 20°C/min to 130°C, 5°C/min to 250°C, then 20°C/min to 280°C, hold 1 min. The temperatures of the injector and detector were 270 and 280°C, respectively. The concentrations of organotins in samples were determined by selecting ions as shown in Table 1.

The portion of the Yangtze River Basin between Chongqing and Yichang City where the Three Gorges Dam is located is generally referred to as the Three

Table 1. Ions monitored in SIM mode.

Time window (min)	Analyte	Molecular weight	Ion monitored
6.50-7.90	MBT	282.18	121,149,177,179
7.90-9.00	TPrT	282.91	193,191,163,149
9.00-10.50	DBT	303.83	121,177,149,179
10.50-11.90	MPT	302.17	197,195,120,255
11.90-16.00	TBT	325.51	177,149,121,207

Gorges Reservoir Region (Fig. 1). Twelve water samples collected at 12 monitoring stations (Daxigou, Wanglongmen, Qingxichang, Mishiquan, Lianerqi, Shaiwangba, Xiayanshi, Baidicheng, Daninghe, Wuxiakou, Baqian and Xiangxihe) in the Three Gorges Reservoir Region were studied. Water samples were manually collected in the middle of the river from just beneath the surface in October of 2003 using amber glass bottles. To avoid microlayer contamination, the bottle cap was carefully removed under the water surface. The unacidified and unfiltered samples were stored at 4°C. Geographical coordinates were determined with a mobile GPS at each sampling station.

RESULTS AND DISCUSSION

Fig. 2 shows the extraction GC-MS chromatographs of a standard sample (a) and the water sample from Xiangxihe (b). A baseline separation was easily achieved for organotins studied under the GC conditions used in this study as shown in Fig. 2 (a). An internal standard quantification strategy was employed to minimize the response variation. The isotope pattern created by the contribution of ten tin isotopes is particularly useful for recognition of any organotin compounds occurring in a sample. Peaks in the chromatograms were assigned to individual organotin compounds on the basis of retention time, and peak areas were used for quantitative calculation. The detection limits of MBT, DBT, TBT and MPT in SIM mode by this method were 0.95, 1.23, 1.67, and 2.16 ng Sn/l, respectively. The average recoveries based on the standard spiking method were between 88 and 112(n=5) for each compound.

Fig. 2 (b) shows the chromatogram of the water sample from Xiangxihe in selective ionization mode (SIM), which compared with that of standards. From this figure, it can be found that MBT, DBT and MPT were detected. Fig. 3 (a) and (b) show the extraction chromatograms of MPT at m/z 195, 197, 255 and 120 for a standard sample and the water sample from Xiangxihe, respectively. It can be

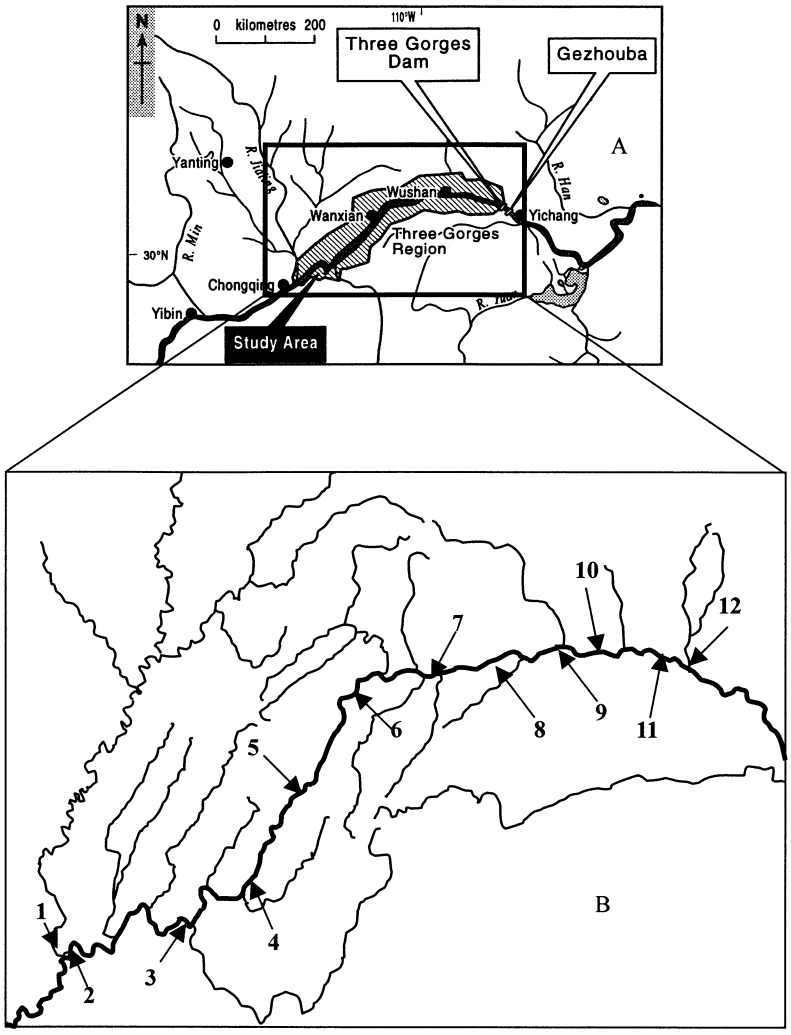

Figure 1. The Yangtze Three Gorges (A comes from reference Lu and Higgitt, 2000). Numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 denote sampling stations at Daxigou, Wanglongmen, Qingxichang, Mishiquan, Lianerqi, Shaiwangba, Xiayanshi, Baidicheng, Daninghe, Wuxiakou, Baqian and Xiangxihe, respectively.

found that retention time and four fragment ions of MPT in the water sample were all in agreement with that in the MPT standard, which further demonstrates the occurrence of MPT in Xiangxihe. This is the first report that MPT was found in the Three Gorges Reservoir Region. The concentrations of four organotins in unfiltered water samples from the Three Gorges region are given in Table 2 and

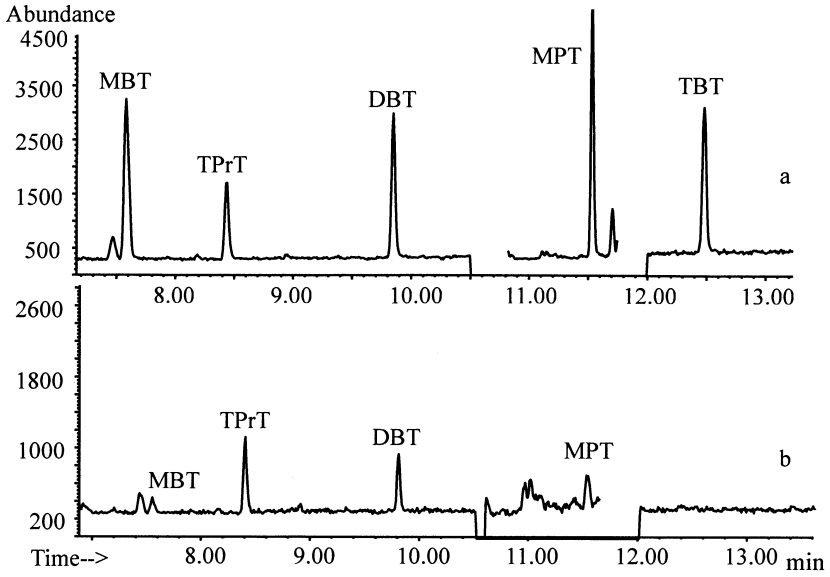

Figure 2. Extraction chromatograph of standard sample (a) and water sample from Xiangxihe (b) The extraction ion: 149 for MBT, DBT, TPrT and TBT, 197 for MPT.

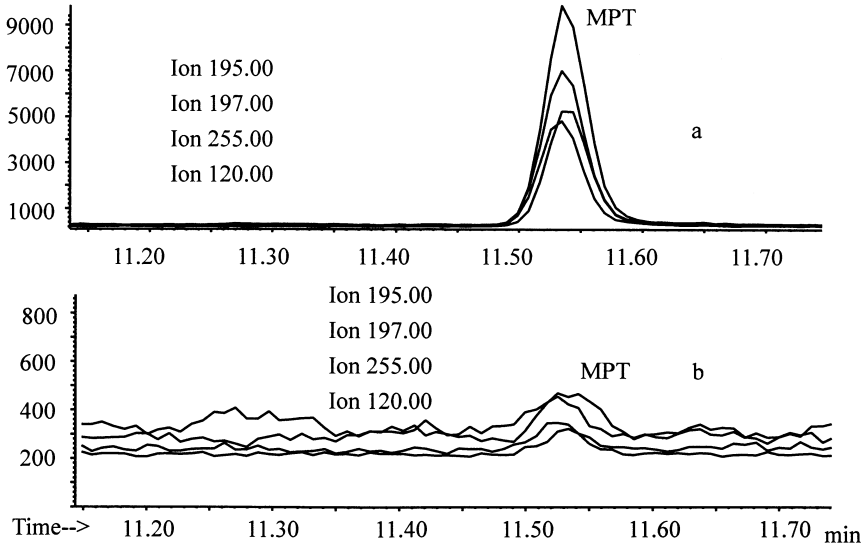

Figure 3. Extraction chromatograph of MPT standard sample (a) and water sample from XiangXi River (b).

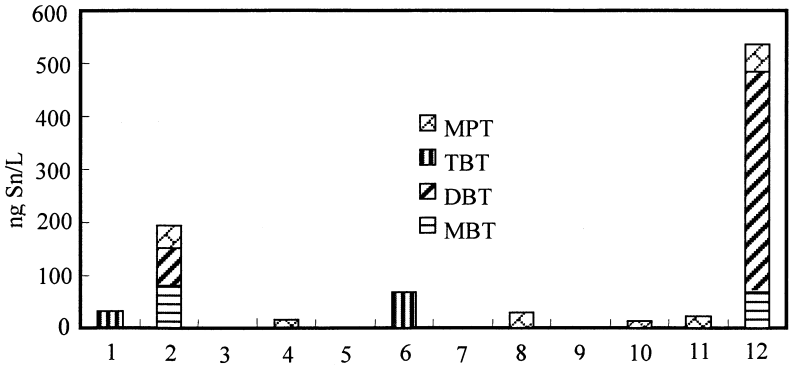

Figure 4. Organotin contamination in the waters of the Three Gorges region, Yangtse River. Numbers 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 indicate Daxigou, Wanglongmen, Qingxichang, Mishiquan, Lianerqi, Shaiwangba, Xiayanshi, Baidicheng, Daninghe, Wuxiakou, Baqian, and Xiangxihe, respectively.

Table 2. Concentrations of organotins in unfiltered waters from the Three Gorges, Yangtze River.

Sampling station	Position coordinate		Concentration（ng Sn/L）				
	North latitude	East longitude	pH	MBT	DBT	TBT	MPT
Daxigou	29°33.22 ′	106°26.80 ′	8.0	ND*	ND	33.4	ND
Wanglongmen	29°34.32 ′	106°34.25 ′	8.3	79.1	71.8	ND	43.2
Qingxichang	29°43.97 ′	107°21.02 ′	7.7	ND	ND	ND	ND
Mishiquan	29°54.23 ′	107°45.08 ′	7.9	ND	ND	ND	15.9
Lianerqi	30°18.64 ′	108°3.60 ′	8.7	ND	ND	ND	ND
Shaiwangba	30°49.91 ′	108°27.08 ′	8.6	ND	ND	68.9	ND
Xiayanshi	30°56.51 ′	108°55.74 ′	8.7	ND	ND	ND	ND
Baidicheng	30°1.43 ′	109°29.88 ′	8.3	ND	ND	ND	29.6
Daninghe	31°3.10 ′	109°50.97 ′	8.3	ND	ND	ND	ND
Wuxiakou	31°1.49 ′	110°6.32 ′	8.6	ND	ND	ND	13.3
Baqian	30°59.01 ′	110°38.12 ′	8.7	ND	ND	ND	21.9
Xiangxihe	30°57.93 ′	110°46.12 ′	8.4	66.4	416.8	ND	52.0

* ND indicates that the concentration was below the detection limit.

Fig. 4, which show that no organotins were found in Qingxichang, Lianerqi, Xiayanshi and Daninghe, and only MPT was found in Mishiquan, Baidicheng, Wuxiakou and Baqian with the concentrations of 15.9, 29.6, 13.3, and 21.9 ng Sn/L, respectively. Interestingly, MBT, DBT and MPT were simultaneously detected in Wanglongmen and Xiangxihe, and their concentrations in

Wanglongmen were 79.1, 71.8 and 43.2 ng Sn/L, respectively, while in Xiangxihe, they were 66.4, 416.8 and 52.0 ng Sn/L, respectively. Furthermore, in all of the samples, TBT was detected only in Daxigou (33.4 ng Sn/L) and Shaiwangba (68.9 ng Sn/L). The concentrations of butyltins in the Three Gorges Reservoir Region of the Yangtze River except for Xiangxihe were similar with that in Lake Westeinder, Netherlands (Stab et al. 1996), and in Lake Lucerne, Switzerland (Fent et al. 1995), but their detection rates were lower than those in Lake Westeinder and Lake Lucerne. In addition, MPT was detected in half of the samples, and the detection rate was higher than butyltins, which showed different spatial distributions of MPT and butyltins in the Three Gorges Reservoir Region of the Yangtze River. It should be noted that the concentrations of TBT in Wanglongmen and Xiangxihe were all higher than the criterion (63 ng/L) for protecting freshwater aquatic life from chronic toxic effects (EPA-822-B-02-001, 2002). In short, from the above results, it can be concluded that Wanglongmen and Xiangxihe are the two hotspots for organotin contamination in the Three Gorges Reservoir Region.

Generally, TBT in the aquatic environment is a result of leaching from anti-fouling paints, although it also has been found as a result of other uses, such as its use as preservative for timber. MBT and DBT are usually a result of TBT degradation. However, because MBT and DBT are both common stabilizers for PVC and catalysts for polyurethane foams, silicones, etc. (Fent 1996), there is a possibility of leaching from PVC and other materials. The fact that no TBT but MBT and DBT were detected simultaneously in Wanglongmen and Xiangxihe suggested that the MBT and DBT contamination in theThree Gorges Reservoir Region was mainly due to leaching from PVC or other materials. The main source of TBT contamination in Daxigou and Shaiwangba was mainly due to shipping activities, because there are some boats at the two sites. Furthermore, MPT that was found at Mishiquan, Baidicheng, Wuxiakou, Baqian, Wanglongmen and Xiangxihe may mainly come from the degradation of TPT, and further investigation is needed to understand the occurrence of DPT and TPT.

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REFERENCES

Alzieu C, Sanjuan J, Deltreil JP, Borel M (1986) Tin contamination in Arcachon Bay: effects on oyster shell anomalies. Mar Pollut Bull 17:494-498

Chau YK, Maguire RG, Brown M, Yang F, Batchelor SP (1997) Occurrence of organotin compounds in the Canadian aquatic environment five years after the regulation of antifouling uses of tributyltin. Wat Qual Res J Canada 32:453-521

EPA-822-B-02-001 (2002) Ambient aquatic life water quality criteria for Tributyltin (TBT)–draft, United States Environmental Protection Agency, Office of Water 4304T, Washington, DC, U.S.A.

Fent K, Hunn J (1995) Organotins in freshwater harbors and rivers: temporal distribution, annual trends and fate. Environ toxicol chem 14:1123-1132

Fent K (1996) Organotin compounds in municipal wastewater and sewage sludge: contamination, fate in treatment process and ecotoxicological consequences. Sci Total Environ 185:151-159

Gao JM, Hu JY, Wan Y, An W, An LH, Zheng ZG (2004) Butyltin Compounds Distribution in the Coastal Waters of Bohai Bay, China. Bull Environ Contam and Toxicol 72:945-953

Gibbs PE, Pascoe PL, Bryan G.W (1991a) Tributyltin-induced imposex in stenoglossan gastropods: pathological effects on the female reproductive system. Comp Biochem Physiol 100C:231-235

Gibbs PE, Bryan G.W, Pascoe PL (1991b) TBT-induced imposex in the dogwhelk, *Nucella lapillus*: geographical uniformity of the response and effects. Mar Environ Res 32:1-5

Jiang GB, Zhou QF, Liu JY, Wu DJ (2001) Occurrence of butyltin compounds in the waters of selected lakes, rivers and coastal environments from China. Environ Pollut 115:81-87

Lu XX, Higgitt DL (2000) Estimating erosion rates on sloping agricultural land in the Yangtze Three Gorges, China, from caesium-137 measurements. Catena 39:33-51

Stab JA, Traas TP, Stoomberg G (1996) Determination of organotin compounds in the foodweb of a shallow freshwater lake in the Netherlands. Arch Environ Contam Toxicol 31:319-328

Suzuki S, Matsuda R, Saito Y (1992) Molecular species of tri-n-butyltin compounds in marine products. J Agric Food Chem 40:1437-1443

Ten Hallers-Tjabbes CC, Wegener JW, Hattum BV (2003) Imposex and organotin concentrations in *Buccinum undatum* and *Neptunea antiqua* from the North Sea: relationship to shipping density and hydrographical conditions. Mar Environ Res 55:203- 233.