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Evaluation of Methyltin and Butyltin Pollution in Beijing Guanting Reservoir and Its Downriver Yongding River

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There is growing concern about the presence of organotin compounds in the environment due to their high bioaccumulation potential, persistence in sediments for periods of up to several years and high toxicities to non-target organisms. However, large amounts of anthropogenic organotin compounds still pose a toxicological risk and continue to be pollutants in environment because of their wide use in various fields in many countries without legislative regulations such as China. These compounds can be widely used as stabilizers for PVC, antifouling additives in paint formulations, fungicides and miticides in agriculture (Warren, 1973). The toxicities of these species definitely depend on their chemical forms. In general, the toxicities increase with the increase of the number of the alkyl substituents and decrease of the carbon chain (Dowling and Uden, 1993). Thereby it is necessary to make the speciation of organotin compounds. Wherein, methyltin and butyltin species, as two kinds of high toxic compounds, have been of great concern. The levels high at ngL^{-1} to μgL^{-1} have been reported in natural water (Jackson et al., 1982), marine and fresh water (Mueller, 1984), lakes and harbors (Maguire, 1984). As some water is or will be used as drinking water, which is closely linked with people's health, it is of special importance to investigate the pollution of methyltin and butyltin compounds and their sources in such water.

The preliminary survey on methyl- and butyltin compounds in Beijing Guanting reservoir in China was carried out by gas chromatography-flame photometric detector. Wide occurrence of butyltin and methyltin compounds was found, which reminded that it was imperative to take immediate action on the protection of aquatic environment of Guanting reservoir from further pollution. In addition, the pollution in the lower reach-Yongding river was also investigated to reveal the contamination status in the related aquatic system.

MATERIALS AND METHODS

The standards of trimethyltin chloride (TMT, 98%), dimethyltin dichloride (DMT, 97%), and monomethyltin trichloride (MMT, 97%) were obtained from Aldrich Chem. Co. (USA). The standards of tributyltin chloride (TBT, 90%), dibuthyltin

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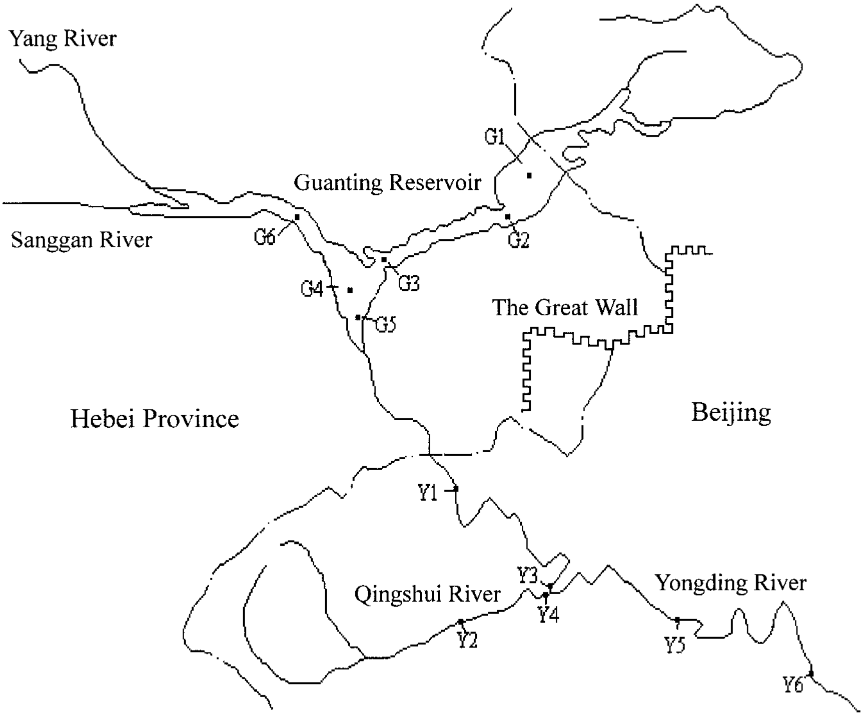

Figure 1. Sampling sites in the Guanting reservoir and its downriver Yongding river

dichloride (DBT, 97%), and monobutyltin trichloride (MBT, 97%) were obtained from Acros Organics (New Jersey, USA). Each compound was directly weighed and dissolved in methanol to form a concentration of 1mg mL^{-1} (as Sn) as the stock solution. Working standard solutions (10µg mL^{-1}) were newly prepared by diluting the stock solution with de-ionized water and the pH was adjusted to 2 using HCl to ensure their stabilities. Sodium tetrahydridoborate ($NaBH_4$, 99.7%) was also obtained from Acros Organica (New Jersey, USA) A fresh solution of 3% (w/v) was made daily with deionized water just before use. Buffer solution with a pH of 3.3 was prepared by mixing suitable amount of acetic acid and sodium acetate solutions. Small amount of HCl and NaOH were needed to adjust the pH of the water samples.

Water samples were collected at the late fall in 2000. The detailed sampling locations in this paper are indicated in figure 1. The water (5-10cm below the surface) was collected and immediately adjusted to pH 2-3 by 6mol L^{-1} hydrochloric acid. They were stored in the dark at 4℃ and analysis was usually carried out within a week.

Methyltin compounds in water samples were detected by the previous reported method of cryogenic purge and trap gas chromatography-flame photometric detection (PTI-GC-FPD) (Liu et al. 2001). The acidified water samples were adjusted to pH 5 with small amount of 6mol L^{-1} NaOH solution just before analysis. A 15mL of sample was placed into the reaction vessel and 1mL of of 3% $NaBH_4$ solution was added to form methyltin hydrides. The analytes was purged with 30mL min^{-1} of nitrogen for 12 minutes and trapped in the fused-silica capillary at –75°C by a Model CP-4010 purge and trap injector (Chrompack, Middleburg, the Netherlands). Then the trap was electrically heated to 200 °C quickly and the hydrides were released into the capillary column (HP-1, 30m×250μm×0.25μm). The analytes were base-lined separated in an HP Model 6890 series gas chromatograph (Agilent, USA) by a column temperature programmed at 50 °C for 2 minutes and then heated to 150 °C at 20 °Cmin^{-1}. The measurement was carried out in the flame photometric detector equipped with a 394nm cut-on interference filter. The detector temperature was maintained at 200 °C and a hydrogen-rich flame supported by a mixture of H_2 at 60mL min^{-1}, air at 70mL $min^{-1}$and N_2 at 20 mL min^{-1} offered the most sensitive detection.

Butyltin compounds in water samples were monitored by capillary gas chromatography with a laboratory-made flame photometric detector using quartz surface-induced tin emission after in-situ hydride derivatization and solid phase microextraction (SPME-GC-QSIL-FPD) (Jiang et al., 2000). A 50mL of water sample was first adjusted to pH 3.3 with a small amount of 6 mol L^{-1} NaOH solution. 1mL of 3% $NaBH_4$ solution was added to react with butyltin compounds. The corresponding more volatile butyltin hydrides was extracted and concentrated for 15 minutes by a manual SPME device (supelco, Bellefonte, PA, USA.) with the fiber coated with 100μm of polydimethysiloxane (PDMS). After a 10 minutes complete thermal desorption in 220°C injector, the butyltin hydrides were separated by a shimadzu GC-9A (Tokyo, Japan) equipped with a capillary column (HP-1, 25m×0.32mm i.d. × 0.17μm). The oven temperature was initially held at 55°C for 1 minute, programmed at 10 °C min^{-1} to the final temperature of 150°C for 3 minutes and high purity nitrogen was used as the carrier gas with the column head pressure kept at 0.26Mpa. The sensitive detection was realized in a 140 °C flame phometric detector, wherein hydrogen and air were maintained at flow rates of 260mL min^{-1} and 90mL min^{-1}.

RESULTS AND DISCUSSION

Guanting reservoir is located in the northwest of Beijing. The reservoir ranges about 230 km^2 and its total volume is approximately 2.27×10^9 m^3. It used to be an important drinking water source of Beijing in 1960s. With the development of industry and agriculture, many factories such as fur factories, paper mills, phosphate fertilizer factories have been built in the headwaters, which led to the high input of pollutants in the past few decades. Guanting reservoir has lost its use as drinking water source because of its bad water quality since 1997. As continuous droughts persist in north area in China and the population in Beijing keeps on quickly increasing, water supply deficiency is an urgent problem confronting Beijing. Thereby, it is determined that Guanting reservoir will resume

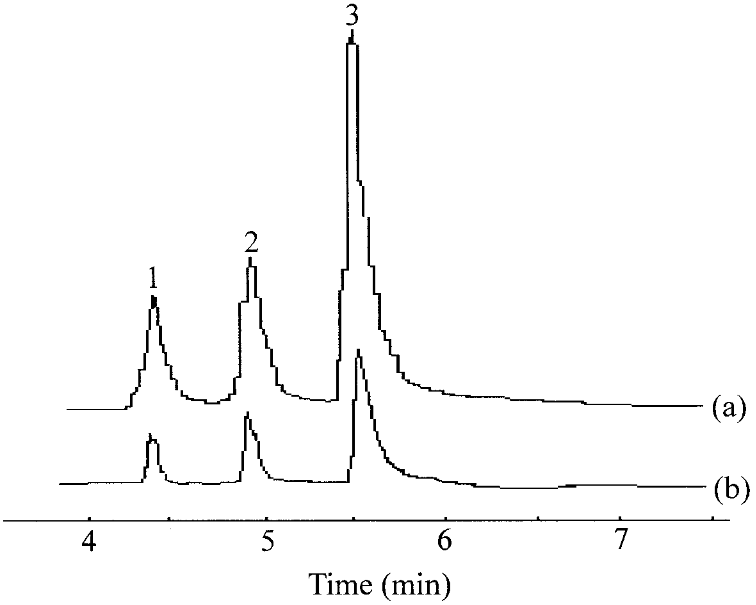

Figure 2. Chromatogram comparison of methyltin standards and a water sample 1. CH_3SnH_3, 2. $(CH_3)_2SnH_2$, 3. $(CH_3)_3SnH$ (a). Standard, 1ngmL^{-1} as Sn (b). Water sample collected in Guanting reservoir

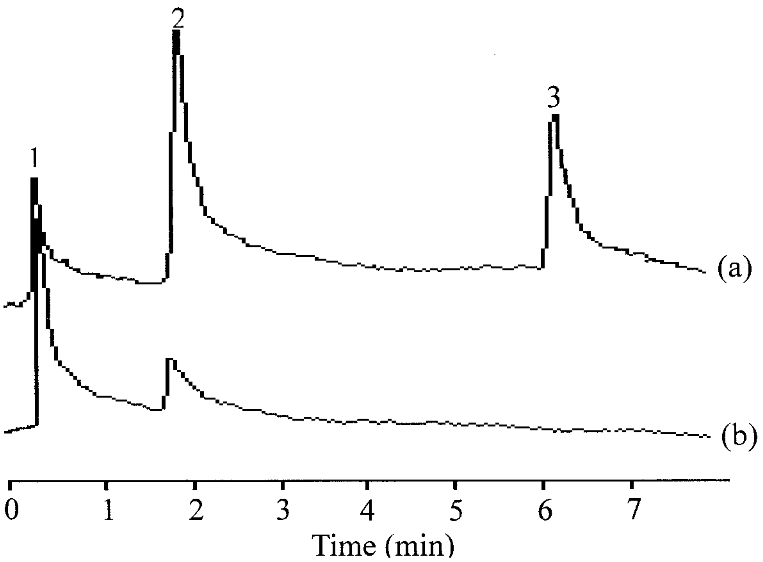

Figure 3. Chromatogram of water sample (a) collected in Guanting reservoir compared with butyltin standard chromatogram (b) Peaks identified as: 1. $BuSnH_3$; 2. Bu_2SnH_2; 3. Bu_3SnH

to be an important water supply source in 2005 after some pollution control steps are carried out. Some factories have now been or will be closed and some sewage farms have been or will be built. The pollution evaluation is thereby of much significance in the reservoir and its downriver, wherein methyltin and butyltin species, as a kind of important endocrine disruptor, have drawn much attention.

Methyltin compounds in water samples were sensitively detected by the method of PTI-GC-FPD, whose detection limits (3σ) of MMT, DMT, and TMT were 18 ng Sn/L, 12 ng Sn/L and 3 ng Sn/L respectively and the relative standard deviation was below 5 % for five repeated determinations. Recoveries from the water samples ranged from 91 to 106% for all species. Figure 2 showed the chromatogram comparison of the methyltin standards and a typical example of a water sample collected in Ganting reservoir, which definitely proved the existence of methyltin pollution.

Butyltin compounds in water samples were measured by the method of SPME-GC-QSIL-FPD. This method offered a detection limits (3σ) of MBT, DBT, and TBT low to 28 ng Sn/L, 1.5 ng Sn/L and 0.5 ng Sn/L separately. The relative standard deviation was below 15 % for five repeated determinations and the recoveries from the water samples ranged from 95 to 109% for all species. The chromatogram comparison of the butyltin standards and a typical water sample from Guanting reservoir displayed in figure3 confirmed the presence of MBT and DBT compounds.

Table 1 summarizes the results of methyltin and butyltin compounds in six water samples collected from Guanting reservoir. Widespread occurrence of methyltin and butyltin compounds in the Guanting reservoir was clearly indicated here, wherein MMT, DMT and TMT pollution reached rather high levels. It is well known that anthropogenic inputs as well as methylation synthesis in the aquatic environment are possible sources of methyltin species (Ridley and Dizikes, 1977; Donard and Weber, 1988). Anthropogenic sources mainly come from their use as polyvinyl chloride stabilizers or catalysts. Chemical and biological methylation of naturally occurring tin or inorganic tin usually leads to the formation of MMT. Biotic and abiotic dealkylation processes can cause the transformation between different organotin species. For example, demethylation of anthropogenically discharged trimethyltin can yield DMT and MMT (Schebek et al., 1991). As for butyltin compounds, relative high levels of MBT and low levels of DBT were detected, while no TBT was found. This was probably due to the low anthropogenic inputs of TBT because there rarely existed boat vessels. Trace level of TBT could also quickly decompose as it had a short residence time, with a half-life in the range from several days to several weeks (Dirkx et al., 1993). The wide occurrence of DBT and MBT probably come from anthropogenic sources because they are familiar stabilizers in PVC.

Yongding river, which passes through Beijing, is the downriver of Guanting reservoir. The pollution status may reflect the upriver condition and it can also affect the groundwater of Beijing. As the results depicted in Table 2 showed that

Table 1. Concentrations of methyltin and butyltin species (ng L^{-1}) in Guanting reservoir (n=5)

Sampling sites	MMT	DMT	TMT	MBT	DBT	TBT
GT-1	290±9	315±10	381±11	178±6	3±1	nd
GT-2	328±10	345±11	256±7	243±7	3±1	nd
GT-3	374±11	357±10	361±11	121±4	3±1	nd
GT-4	234±7	187±6	209±7	117±4	2±1	nd
GT-5	170±6	116±4	193±6	134±5	2±1	nd
GT-6	159±6	114±4	156±5	37±2	3±1	nd

*nd = not detected.

Table 2. Concentrations of methyltin and butyltin species (ng L^{-1}) in Yongding river (n=5)

Sampling sites	MMT	DMT	TMT	MBT	DBT	TBT
YD-1	205±7	88±4	10±1	977±30	3±1	nd
YD-2	433±13	171±6	14±1	1683±44	4±1	nd
YD-3	194±7	80±4	12±1	72±4	4±1	nd
YD-4	499±14	180±6	15±1	1539±86	4±1	nd
YD-5	233±7	86±4	11±1	30±1	3±1	nd
YD-6	252±8	162±7	12±1	37±1	3±1	nd

*nd = not detected.

the pollution of methyltin and butyltin compounds was universal in six water samples collected from Yongding river. The pollution in Yongding river might come from the water flow from Guanting reservoir or anthropogenic inputs such as stabilizers in PVC drain pipes in downstream.

It is well know that there are considerable variations in the toxicity of different organotin compounds to different biotas, for example, trimethyltin compounds are most toxic to insects, while Gram-positive bacteria, fish, and fungi are most sensitive to tributyltin compounds (Davies and Smith, 1980). The acute or sublethal effects (eg. growth inhibition) of organotin compounds including methyltin and butyltin species on aquatic biota such as freshwater algae were available (Hall and Pinkney, 1985), which clearly showed the high toxicity of this species. Although some of the contamination levels detected here weren't high enough to cause acute poisoning, they will definitely affect the ecosystem and peope's life in the long-term view.

This investigation revealed the wide occurrence of methyltin and butyltin compounds in Guanting reservoir and its downriver-Yongding river. It is well known that Beijing is one of lacking-water cities and Guanting reservoir is planned to be an important drinking water resource in near future. However the pollution status is really worrying. In order to provide enough clean water to people in Beijing in future, it is urgent to take effective action to purify the water and control the further pollution of organotin compounds in the Guanting reservoir and its related valleys.

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