

# Tributyltin and its Derivative in Water Samples of National Inland Water Way Authority Harbour of Warri, Delta State, Nigeria

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## Abstract

Surface water samples were collected and analyzed to evaluate the fate of tributyltin (TBT) and its derivatives dibutyltin (DBT) and monobutyltin (MBT) from National Inland Waterway Authority (NIWA) Harbour, using gas chromatography coupled with flame ionization detection (GC-FID) with detection limit of 0.001 µg/l. The concentrations were in the range of TBT (0.01 µg/l to 0.05 µg/l), DBT (0.01 µg/l to 0.03 µg/l) and MBT (0.01 µg/l to 0.02 µg/l). The total butyltin concentration ranged from 0.04 µg/l to 0.09 µg/l. TBT was generally dominant in most of the samples, suggesting fresh inputs of tributyltin compounds and/or less degradation of TBT. The measured mean concentrations in surface water samples exceeded the ecotoxicological benchmark of 0.01 µg/l recommended by US Environmental Protection Agency (USEPA) indicative of potential environmental risk. This survey provides baseline data on tributyltin compound contamination in National Inland Waterway Authority (NIWA) Harbour and suggests further environmental monitoring of other Nigeria harbours.

**Keywords:** Tributyltin; Dibutyltin; Monobutyltin; Inland waterway; Warri

## Introduction

The environmental concern about organotins has remarkably increased due to the large use of the compound as active components in antifouling paints. Organotin compounds have been used as stabilizers in the manufacture of polyvinylchloride [1], as biocides in agriculture [2], as a fungicidal component in wood preservation [3] and in anti-fouling systems [4,5]. They are routinely found in both estuarine and marine waters, sediments and biota [6]. The most prominent of this organotin compounds are the trisubstituted forms tributyltin (TBT) which have been extensively used as biocides in antifouling paints for the past few decades [1,4]. Tributyltin (TBT) an antifouling paint additive is a highly toxic biocide that has been used extensively to protect the hulls of large ships and boat, sewage pipe systems, docks, fishnets, and buoys to prevent the attachment of fouling organisms [7]. The large-scale utilization of TBT has resulted in the occurrence and high abundance of TBT and other organotins in many aquatic and marine environments [4,8]. Commercial shipping and dry-docking activities in harbours and shipyards are possible input sources of TBT in recent times. Ship building, repairing and anti-fouling paint applications are conventional sources of TBT pollution [8-10]. TBT has been considered the most hazardous compound to marine organisms and it is perhaps the most toxic xenobiotic compounds ever been introduced deliberately into the marine environment by man [11-13]. It is a problem in the aquatic environment because it is extremely toxic to non-target organisms [14]. TBT in the marine environment is very persistent and causes a pseudohermaphroditic condition known as imposex in female prosobranch gastropods. Imposex is characterized by the presence of a penis and/or vas deferens in females and has been identified in over 140 species of snails worldwide [15]. This condition may lead to reproductive failure and consequential population decline [16,17]. Due to the persistent nature and bioaccumulative potential, TBT has been classified as a persistent organic pollutant (POP) [18] which also has a high toxicity on organisms [19]. Although many countries have banned the application of TBT containing anti-fouling paints on smaller boats, larger sea-going vessels have continued its use. TBT is now regarded as a global pollutant, as a result, European Union (EU) and other countries worldwide have banned the application of

TBT-based paints to small vessels (<25 m). Moreover, the International Maritime Organization (IMO) proposed a global prohibition on the application of TBT as biocide in antifouling systems on ships by January 1, 2003 and a complete prohibition of its presence by January 1, 2008 [20]. Despite this commitments by European Union (EU) and International Maritime Organization (IMO), TBT compounds are still been used as antifouling agents in marine paints in Africa and Nigeria in particular. In spite of its widespread usage and biological effects, no studies on the fate and distribution of butyltin contamination in shipyards have been documented in Nigerian waters. Therefore, the purpose of this study was to determine the concentrations of tributyltin and its derivatives in National Inland Waterway Authority harbour in Warri River, Delta State of Nigeria.

## Materials and Methods

### Sampling area

National Inland Waterway Authority (NIWA) is located between 05°31.297'N latitude and 005°46.054'E longitude. The station is located in Warri, Delta State which is a coastal area (Figure 1). The station handles more than 90% ship repair and construction. It receives the inflows of the metallurgical waste, paint and oils wastes from ship construction and repairs.

### Collection of samples

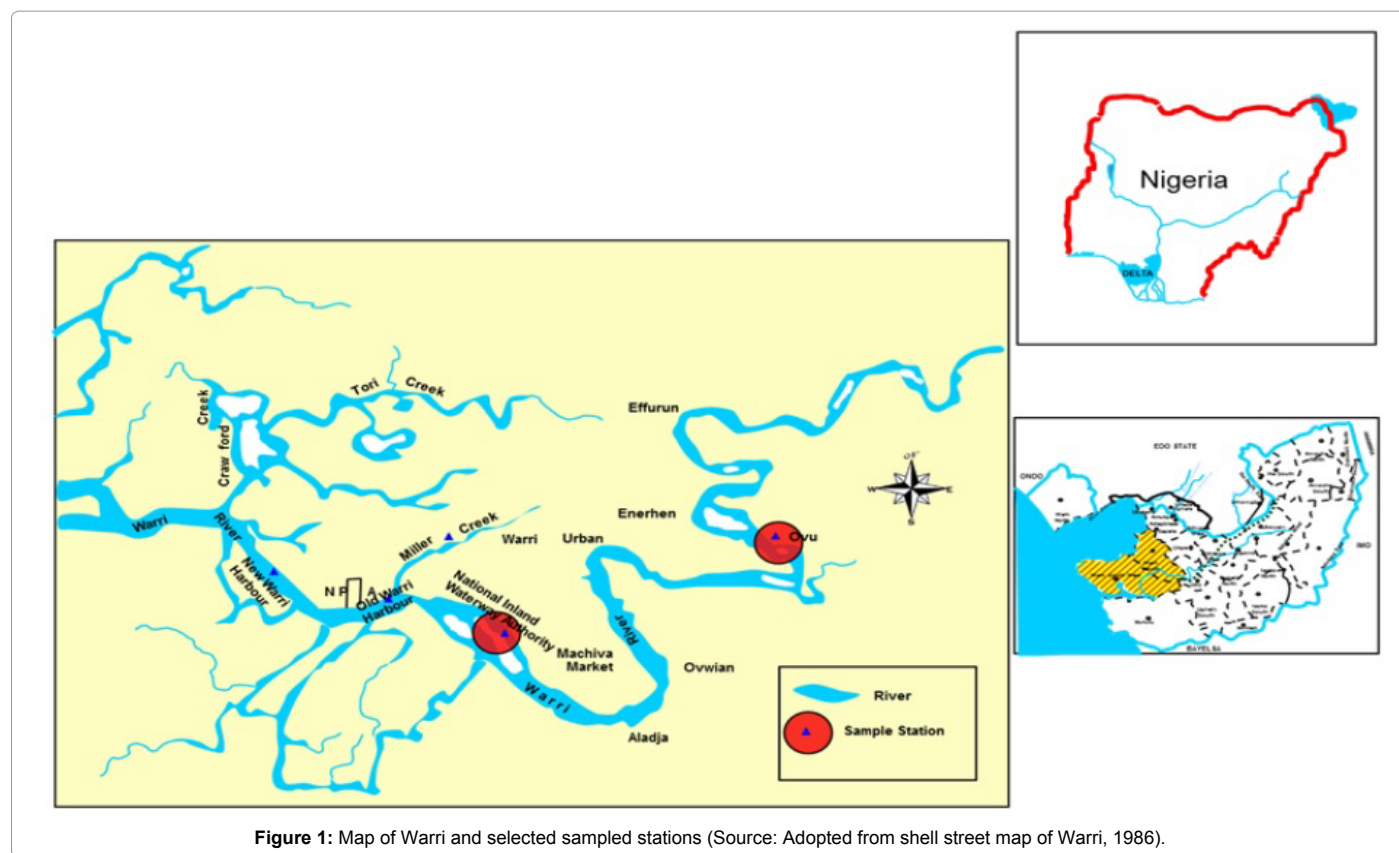
Water samples were collected twice monthly between April 2010 to March 2011 using pre-cleaned amber glass bottles that had been

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washed with 5% nitric acid solution in ultra-pure deionized water. The samples from the harbour in Warri River Delta State were collected by submersing the amber glass bottles at a depth of 0.5 m using a close-open-close sampler. The samples were then acidified on-site to pH 2 using suprapure HCl, to increase the solubility of the organotins and thereby avoid adsorption to the glass walls, and stored in a refrigerator at 4°C in the laboratory.

#### Extraction of tributyltins

Water samples were extracted using a solid phase extraction (SPE) technique according to the method of Ref. [21]. 750 ml of harbour water sample was taken in a Teflon separatory funnel, to which 100 ml of 5% NaCl in deionized water was added and the sample pH adjusted to 2 with HCl. The sample was then spiked with internal standard tripropyltin and extracted twice for 15 minutes with 20 ml of 0.03% of tropolone in dichloromethane by shaking vigorously in a separatory funnel. The extracted organic phase was dewatered with sodium sulphate, to which 1 ml of Isooctane was added and then reduced to almost dryness under a stream of nitrogen, and treated with the Grignard's reagent pentyl magnesium chloride for 5 minutes at room temperature. The excess Grignard's reaction was destroyed by adding carefully, drop-by-drop 2 ml of deionized water. The derivatized tributyltins were subsequently extracted twice with 2 ml of n-hexane and 5 ml of 1M sulphuric acid. Then as a clean-up step, the sample was reduced to 0.5 ml under a stream of nitrogen, and eluted with 10 ml of 1:1 hexane-toluene through a 6 g column of activated flurosil. The eluate was finally evaporated to 0.5 ml under gentle stream of nitrogen and analyzed with gas chromatography.

#### Analysis

Separation and quantification of tributyltin (TBT) compounds and its derivatives dibutyltin (DBT) and monobutyltin (MBT) were

carried out using gas chromatographic system equipped with flame ionization detector (GC/FID) (Hewlett-Packard 6890 Series, Little Falls, Delaware, USA) according to the method of Ref. [22]. Sets of blanks and standards were also processed following the same method as for samples. The injection mode was split less and the temperature was set at 250°C. The column was a 30 m × 0.32 mm i.d. × 0.25 μm film thickness HP-5 (Agilent Technologies). Helium was used as the carrier gas at a constant flow of 1 ml/min. The temperature was programme at 55°C for 1 min, then 20°C/min to 200°C, which was held for 5 min. The oven was programmed from 40°C (1 min) at 20°C/min to 220°C (3 min) and the carrier gas was at a constant pressure of 80 kPa.

#### Results

Tributyltin (TBT) and its derivatives dibutyltin (DBT) and monobutyltin (MBT) were detected in surface water samples. Total TBT concentration was  $0.0292 \pm 0.01240 \mu\text{g/l}$ , DBT  $0.0200 \pm 0.00739 \mu\text{g/l}$  and MBT  $0.0175 \pm 0.00622 \mu\text{g/l}$ . The monthly trend of TBT levels in water was significantly high in November and February and low in May. TBT was generally predominant in all the samples (Figure 2). Butyltin degradation index (BDI) which was used to predict whether contamination of tributyltin was recent or not showed that total BDI was highest in April and lowest in October (Figure 3). When BDI value is less than 1 it indicate fresh input of TBT and low degradation rate while less than 2 indicate moderate degradation.

#### Discussion

The levels of TBT in water appeared to reflect the activities performed at National Inland Waterway Authority (NIWA) Harbour. The highest concentration of tributyltin in NIWA harbour was recorded in November and February. This could be attributed to high

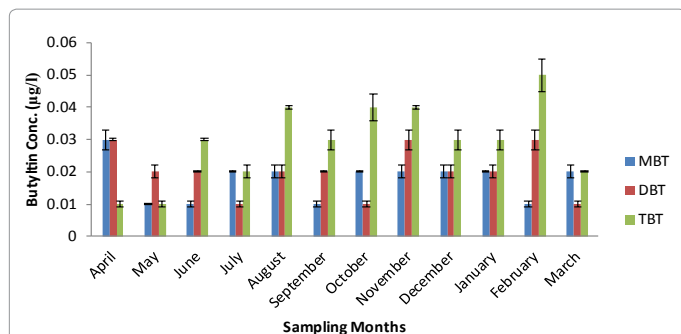


Figure 2: Tributyltin and its metabolites concentration in water samples of National Inland Waterway Authority (NIWA) Harbour.

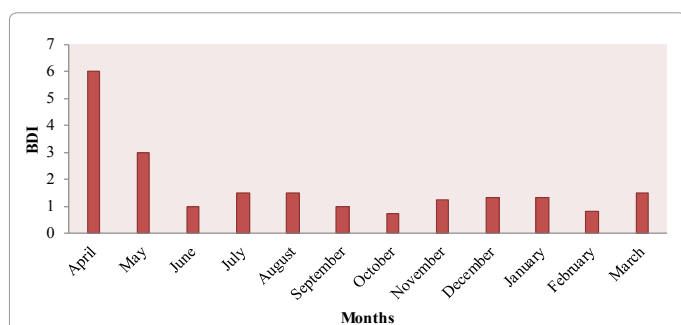


Figure 3: Butyltin Degradation Index in water samples of National Inland Waterway Authority (NIWA) Harbour.

shipping and boating activities during these months. It could also be as a result of leaching of TBT from the hulls of mooring vessels, barges, and ferry boats. NIWA harbour is one of the busy stations for ferry boats, repair and maintenance of small ships and barges, construction and painting of barges slipway and oil jetty. These activities could have impacted on the elevated TBT levels [23]. NIWA harbour has no technical means of disposing paint waste rather they are discharge into the harbour. The results showed that the levels of TBT in the NIWA harbour are likely to pose a threat to aquatic organisms. These results are supported by studies of Ref. [24] and Ref. [25]. The observed TBT levels in NIWA are comparable to those reported from other coastal areas of the world subject to shipping activity. The metabolites DBT and MBT of TBT were detected in NIWA harbour. Degradation TBT could be caused by microbial activity and/or photochemical reactions, but recently evidence for direct input of DBT and MBT was found by leaching from polyvinyl chlorides (PVC). Rates of photodegradation and biodegradation of organotin in water are also dependent upon environmental conditions. The concentrations of TBT and its derivatives detected in NIWA harbour were lower than those reported by Ref. [26] in SW Spain and Ref. [27] in SW and N-SW coasts of Spain. TBT degradation process may be explained as a sequential loss of alkyl group from TBT to form non-toxic inorganic tin. The degradation ratio is used to determine whether the discharge is recent [28]. The quantitative importance of TBT degradation was evaluated using TBT degradation index {(Butyltin degradation index) (BDI)}.  $BDI < 1$  indicates recent input of TBT. In NIWA harbour, the BDI calculated ranged from 0.75 to 6 indicating fresh TBT inputs or slow degradation. The degradation rate of TBT in NIWA harbour may be due to warmer ambient temperature and the intense sunlight in the tropics [26,29,30]. This could be most probable reason for high value of MBT and DBT in the surveyed harbour. Nigeria is a typical tropical country with hot

and humid coastal areas. Most parts of the country have a very sunny climate with an average of seven to ten hours of sunshine a day. The warm ambient water and intense sunlight in the coastal areas could be the main causes of the rapid degradation of TBT in water to other metabolites DBT and MBT. But recent evidence for direct inputs of DBT and MBT into the aquatic system has been reported [4] as a result of leaching from PVC materials. TBT exhibits both lipophilic and ionic properties. This means TBT levels will be influenced by the concentrations of organic carbon [31-33].

## Conclusions

The monitoring programme was the first assessment of tributyltin and its derivatives in the aquatic environment of Nigeria. The results of the study showed that tributyltin compounds were detected in significant concentrations in National Inland Waterway Authority (NIWA) Harbour with high boating and dry dock activities. The high concentrations were mainly due to the use of TBT as antifouling agent. In all the TBT concentrations were higher compared to its derivatives DBT and MBT. Consequently, continuing research on the occurrence and fate of TBT in the aquatic environment of Nigeria is needed in order to recognize potential sources and evaluate the effects of this contaminant on the biota.

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