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Assessment of the Tributyltin Distribution in the Central Red Sea Coast of Saudi Arabia

Lafi Al Solami
Department of Marine Biology, Faculty of Marine Sciences, King Abdulaziz University, Jeddah, Saudi Arabia
lalsulami@kau.edu.sa

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ABSTRACT

Tributyltin (TBT) is one of the significant anthropogenic impacts on the coastal ecosystems throughout the world. The current study evaluated the status of TBT contamination in the central Red Sea coast of Saudi Arabia. In order to accomplish this, samples (water, sediment and gastropods) were collected from four locations from the Jeddah coast of the central Red Sea for the analysis of TBT. The findings showed that the levels of TBT level in the sediment and seawater were below detection limits in stations that were distant from the harbor. Sediment samples taken from the stations close to the harbor revealed a low-level (0.011- 0.021µg g-1) occurrence of TBT. TBT content was recorded in the gastropods collected from all the four stations. Overall, the findings showed that the TBT concentrations in sediment and gastropod samples were below the maximum allowable limits suggested by various international agencies.

INTRODUCTION

The monitoring of the pollutant concentration in the environment and organisms is one of the tools to assess its impact on the ecosystem. The pollutants from the anthropogenic sources pose adverse effects on marine ecosystems around the world **(Sharaf & Shehata, 2015)**. Tributyltin (TBT) is one of the most harmful substances released into the marine environment by antifouling coatings among other pollutants **(Maguire, 2000; Beyer *et al.*, 2022)**. Because of its affinity for organic molecules and membranes, TBT is readily absorbed by the marine creatures once it is released into the environment **(Pagliarani *et al.*, 2010)**. The impacts of TBT on marine organisms include endocrine disruption, mortality, and sex reversal (imposex) in gastropods **(Tabb & Blumberg, 2006; El Ayari & El Menif, 2019)**. The International Maritime Organization forbids the use of TBT in antifouling paints due to the negative effects on the environment **(Satheesh *et al.*, 2016)**. However, TBT may persist in the environment and in the organisms even if it is no longer released to the environment from the antifouling paints because of various transformation processes and long half-life **(Filipkowska &**

Lubecki, 2016). Moreover, the degradation of TBT may take months to years depending on the environmental conditions of the marine ecosystems **(Chen *et al.*, 2010)**.

Due to its high salinity and warmth, the Red Sea is renowned for its special qualities in the tropics **(Shaikh *et al.*, 1986)**. Approximately, 1,840km of the Saudi Red Sea shoreline makes up 79% of the eastern Red Sea coast **(Pan *et al.*, 2011)**. Saudi Arabia's fast industrialization has resulted in widespread pollution in the coastal areas due to trash disposal **(Pan *et al.*, 2011)**. Due to rapid industrialization in Saudi Arabia, the coastal regions are subjected to widespread pollution from the waste disposal **(Pan *et al.*, 2011)**. Further, the high shipping traffic in the Red Sea region has led to the discharge of numerous pollutants into the environment **(Gladstone *et al.*, 1999)**. Undoubtedly, TBT might be one of the pollutants due to intense the shipping traffic in this region, but monitoring studies on the present status of TBT and other organotin compound levels in the Red Sea are lacking. In Saudi Arabia, few studies were conducted after the ban of TBT in the Arabian Gulf to assess the organotin pollution status **(Al-Shatri *et al.* 2015; Ashraf *et al.*, 2017; Hassan *et al.*, 2019)**.

While sevearal previous studies reported the pollution status of the central Red Sea, the data on the present status of TBT pollution are lacking from this region. Monitoring of TBT levels in marine environment is essential to understand the pollution levels after restrictions **(Furdek *et al.*, 2012; Mikac *et al.*, 2022)**. Hence, in this study, the TBT content in the sediment, water, and gastropod (marine molluscs) samples gathered from the Jeddah shoreline were analyzed. The main objective of this investigation was to monitor the concentration of TBT along the shoreline of the central Red Sea. The results of this study was helpful to understand the pollution levels in the coastal ecosystems of Jeddah coast, Saudi Arabia.

MATERIALS AND METHODS

Study area

The research was conducted during September-November 2019 along the Jeddah shoreline in Saudi Arabia's central Red Sea. Sediment, water, and gastropod samples were collected from four different sites. Table (1) provides information about sampling stations. The rationale for the selection of these locations was based on the closeness to the Jeddah harbor. Among the four stations, station 4 is situated in the south of a harbor (southern corniche area), whereas sampling stations 1, 2 and 3 are situated to north of the harbor (Fig. 1).

Table 1. Details of stations selected for the sample collection for this study

Station	Name	Location
Station 1	Dhaban	21°50′39″N, 38°59′42″E
Station 2	Jeddah beach	21°38′58″N, 39°06′01″E
Station 3	Al-Baghdadiyah	21°29′42.0″N, 39°10′13.2″E
Station 4	South Corniche	21°16′45″N, 39°06′39″E

Collection of water and sediment samples

The Van Veen grab sampler was used to collect the sediment samples (in replicate, n=3 for each station) from every location. Surface water samples from the study area were collected in 1L amber bottles. The collected samples were kept in cool boxes and taken to the laboratory. Prior to further analysis (which took place within 48 hours), the sediment samples were stored in the laboratory at -20°C, while the water samples were kept at -4°C in dark environment.

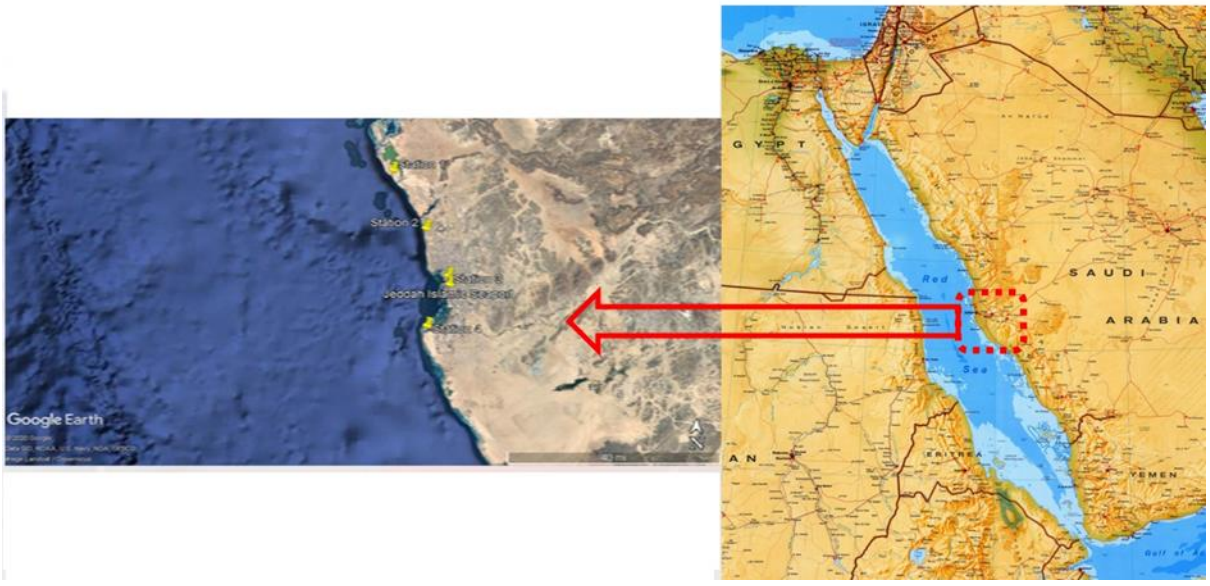

Fig. 1. Study area marked with four sampling locations along the Jeddah coast of the central Red Sea

Collection of gastropods

We collected the common mud-snail *Nassarius* sp. from the study sites by hand-picking. Five gastropods (in replicates, n=3) were collected from each station to get adequate tissue samples for the analysis. The collected samples were immediately placed in polythene bags and kept in a cool box.

Chemical and reagents

All chemicals and reagents (analytical grade) were purchased from Sigma-Aldrich. Tributyltin chloride (95%) was used as a standard and tripropyltin chloride as an internal standard. The stock solution of the internal standard was prepared in dichloromethane (2mg ml^{-1}) and diluted with methanol before usage. Tributyltin standard solution was prepared in distilled water. The stock solutions were stored at -4°C until further analysis.

Analysis of TBT in water and sediment samples

The water samples were processed for TBT analysis according to the protocol outlined by **Matthias *et al.* (1986)**. The sample volume and reagents for each step of the extraction process were adapted according to the method of **Bhosle *et al.* (2004)**. In brief, the water samples (750ml) were taken in a 500ml flask with a lid and 2ml of dichloromethane was added. To this mixture, 15ml of 6% sodium borohydride ($NaBH_4$) and the internal standard tripropyltin chloride (100µl containing 129ng) were added. The flask was shaken well initially by hand and after that for 20 minutes on a stirrer. The resulting organic layer was collected in a glass bottle. The extraction procedure was repeated with the addition of 10ml of dichloromethane. Following this, the organic layers obtained from the extraction process were combined and added with anhydrous sodium sulphate for drying. After that, the organic layer was concentrated to 1ml initially and again to 100µl with nitrogen gas before analysis. The TBT concentration was analyzed using Gas Chromatography. Additionally, the blank solution (129ng tripropyltin chloride) and standard solution (121ng TBT) were prepared using double distilled water (750ml). The blank and standard solutions were processed similarly to the seawater samples.

The sediment samples were freeze-dried and used for extraction. The procedure described by **Thomas *et al.* (2000)** was used for the processing of sediment samples. About 5g of sediment sample was taken in a flask with lid along with 10ml of NaOH (0.1%) in methanol. This was combined with tripropyltin chloride (129ng) as an internal standard. The mixture was vortexed for one hour, and then added with 5 hexane (5ml) and $NaBH_4$ (100mg). After that, it was vortexed for 15 minutes, and the hexane layer was collected. The extraction procedure was repeated by adding hexane and the hexane layers were pooled. The pooled hexane layers were added with sodium sulphate for drying and concentrated to 100µl with nitrogen. The extracted sample was used for TBT analysis.

Additionally, blank solution (added with 129ng triprophyltin chloride) and standard solution (121ng TBT chloride) were added with 10ml of NaOH (0.1%) in methanol and extracted similarly to the sediment samples.

The shells of the gastropod samples were removed, and the tissue was collected for analysis. The tissue sample was first homogenized in a tissue homogenizer and centrifuged at 3000rpm for 10min at 4°C. Afterward, the supernatant was collected in a test tube and extracted twice using 10ml of ethyl acetate and hexane (3: 2 ratio). The mixture was kept in a shaker for 1h and centrifuged again. The resulting organic layer was collected and concentrated to 1ml by passing nitrogen gas flow at 32°C. To this concentrated extract, 0.5ml of deionized water and 0.5ml of tetraethylborate solution were added. The contents were kept in the shaker for 30 minutes, and 10ml potassium hydroxide (1M) was added. The mixture was again kept in the shaker for 1h and centrifuged as described above. The supernatant was collected and passed through a column. The elute was collected and used for TBT analysis.

The TBT concentration in the samples was determined using a GC-MS (Gas Chromatography-Mass Spectrometry, Shimadzu QP 2010). A capillary column with 30m (length) x 0.25mm (inner diameter) x 0.25µm (film thickness) was used for the analysis. The GC analysis was carried out using helium as a carrier gas (flow rate: 1ml $min.^{-1}$). The GC operating conditions reported previously for organotin compounds by **Mukhtar *et al.* (2019)** were used for the analysis. The limits of detection (LOD) for the TBT were 0.01µg L^{-1} and 0.01µg g^{-1}, respectively, for water and sediment samples. The TBT recovery rates from the spiked water (0.1µg L^{-1}) and sediment (0.1µg g^{-1}) samples were 91 and 93%, respectively.

RESULTS AND DISCUSSION

Table (2) shows the TBT content of water, sediment, and gastropod tissue samples collected from the Jeddah coast. TBT concentration was below the detectable limit (BDL, <0.01µg L^{-1}) in all the water samples collected from four stations. In sediment samples, TBT level was below detectable limits in stations 1 and 2. A TBT content range of 0.011-0.021µg g^{-1} (dry weight) was recorded in the sediment samples collected from stations 3 and 4. The marine gastropod samples recorded very low to moderate concentrations (0.012 – 0.028µg g^{-1} dry weight) of TBT in all stations (Table 2). Among the three replicate gastropod samples, TBT was detected in all the replicates from stations 1, 3, and 4. Only one sample (sample 2) recorded a TBT level of 0.014µg g^{-1} (dry weight) from station 2.

Table 2. TBT concentration in water, sediment and gastropod samples collected from the Jeddah coast.

Station	Sample	Water (μg L^{-1})	Sediment (μg g^{-1})	Gastropod tissue (μg g^{-1})
Station 1	Sample 1	BDL	BDL	0.019
	Sample 2	BDL	BDL	0.014
	Sample 3	BDL	BDL	0.012
Station 2	Sample 1	BDL	BDL	BDL
	Sample 2	BDL	BDL	BDL
	Sample 3	BDL	BDL	0.014
Station 3	Sample 1	BDL	0.013	0.028
	Sample 2	BDL	0.011	0.021
	Sample 3	BDL	0.015	0.02
Station 4	Sample 1	BDL	0.021	0.02
	Sample 2	BDL	0.018	0.017
	Sample 3	BDL	0.02	0.026

Samples 1, 2, and 3 are replicates in each station. TBT content in sediment and gastropod values are expressed for dry weight

The study revealed that TBT concentrations in water and sediments of the Jeddah region were below the detection limit in two stations. The gastropod *Nassarius* sp. samples collected from all the four stations recorded TBT levels in the tissues. The stations near the harbor showed higher TBT levels in sediment and gastropod tissues. The detection of TBT in stations in the proximity to harbor might be due to the accumulation before the restrictions of TBT in antifouling coatings. After being released to the environment, TBT may occur for a longer duration due to its long-term stability in the sediment **(Matthiessen, 2013)**. While no recent studies are available regarding this study area for the comparison, previous studies conducted on the Arabian Gulf coast of Saudi Arabia (Table 3) after the international total ban for the usage of TBT indicated a decrease in organotin levels **(Hassan *et al.*, 2019; Yoon *et al.*, 2019)**.

Table 3. Comparison of TBT levels in marine sediment and water samples analyzed from different locations in Saudi Arabia

Study area	Sediment (µg g^{-1})	Water (µg L^{-1})	Sampling year	Reference
Abu Ali Island, Arabian Gulf, Saudi Arabia	0.008-0. 112	--	2017	Yoon et al., 2019
Western Arabian Gulf, Saudi Arabia	BDL	--	2015	Hassan et al., 2019
Eastern Province, Saudi Arabia	--	0.14-1.9	2010	Al-Shatri et al., 2015
Southern coast of Arabian Gulf, Saudi Arabia	0.441-0. 695	--	NA	Al-Shatri et al., 2014
Jeddah coast, Central Red Sea, Saudi Arabia	0.011-0.21	BDL	2019	Present study

Numerous previous studies from other regions indicated that the TBT concentration in marine environment and organisms has been decreasing after the international restrictions **(Lahbib *et al.*, 2018; Laranjeiro *et al.*, 2018)**. However, occurrence of organotin in marine sediment and tissues of marine organisms are detected from many regions even after the restrictions on TBT **(Anastasiou *et al*., 2016; Castro *et al.*, 2018; Younis, 2020)**. In marine waters, the organotin compounds are present in low quantities (ng L^{-1}), and previous studies reported the ecotoxicological impacts on marine organisms at the range of 3- 10ng L^{-1} **(Gibbs *et al.*, 1998)**. Furthermore, as per the

environmental quality standard recommendations of the United Kingdom, the TBT concentration of 0.02µg L^{-1} is considered to cause ecotoxicological effects on marine organisms **(Cleary & Stebbing, 1987)**. Hence, the TBT levels detected in the sediment and gastropod tissue samples in the present study indicated the possibility of ecotoxicological impacts on marine organisms.

One of the impacts of TBT on marine creatures is the incidence of imposex in gastropods **(Abidli *et al.*, 2012)**. Hence, in this study, the gastropod *Nassarius* sp. was selected to analyze the TBT concentration in the tissues. *Nassarius* sp. is a popular model organism for measuring the TBT levels in marine environment **(Couceiro *et al.*, 2009)**. This snail is inhabiting the benthic zone of the marine ecosystems. The creatures living in or on the sediment are likely to accumulate the pollutants due to their feeding behavior. The results of this study indicated the occurrence of TBT in the tissues of *Nassarius* sp. collected from all the four stations. It is noteworthy to mention here that the stations 1 and 2 upon addressing the BDL of TBT in sediment and water samples also showed the occurrence of TBT in gastropod samples. This indicates that even very low content of TBT in the sediment or water may accumulate in the marine organisms. Furthermore, the harmful impacts of TBT on marine molluscs, such as bivalves and gastropods, were observed at 0.001- 0.06µg L^{-1} **(Eisler, 1989; Meador, 2000)**.

In conclusion, this study indicated that TBT concentration in the shoreline of the central Red Sea was below the detection levels in the seawater samples considering all the study stations. A low-level TBT was detected in sediment and gastropod samples. Though the TBT levels were below the international guidelines, further studies are needed to understand the distribution of TBT in coastal environments. Moreover, assessments of imposex in gastropods inhabiting coastal areas will provide additional insights into the impacts of TBT and other organotin compounds on marine organisms.

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