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Assessment of Organotin Compounds in Coastal Sediments of Kuwait

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Abstract: The present study provides a baseline on organotin levels in sediments throughout the Kuwaiti marine environment. The study was designed to detect the organotin compounds including butyltin represented by mono (MBT), di (DBT), tri (TBT), tetra (TeBT) and total tin in surface and core sediments. A total of 76 grab and 19 core sediment samples were collected from 19 locations in the northern coast, Kuwait bay and around islands. The results revealed that only TBT compound has been detected in surface sediment samples at four locations; Rumaila shipwreck, Mubarak port, Failaka island and Shuwaikh port with an average of 0.991, 0.622, 0.736 and 1.242 µg/g, respectively. All levels were found to be exceeding the standards adopted by both EAC and EQS. However, no levels were detected in core samples neither for TBT nor for other organotin compounds. There are many sunken vessels in the NW Arabian Gulf just close to the borders with adjacent countries since the Iraq-Iran war during 1980-1988 in additions to others sunk during the Gulf war in 1991 and Iraq invasion in 2003. These vessels represent a potential source of TBT leakage from their paints driven by current regime in the area toward the Kuwaiti waters, in addition to dry-docks activities in the ports at neighbour countries. It is of great importance to initiate the salvage for the sunken vessels and to cooperate on transboundary effect of overall marine pollutants.

Introduction

Kuwaiti territorial waters are characterized as well-mixed year around with a maximum depth of 30 m (Al-Yamani et al., 2004). Tidal cycle and winds are the main factors controlling the water mass movement in the NW Arabian Gulf. The water circulation in the Arabian Gulf is known as a counter clock where the water mass enters the Arabian Gulf through Strait of Hormuz aligned the Iranian side on the east turning to the Arabian side on the west in the southward path as indicated by Reynolds (1993).

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Shatt Al-Arab river which is formed by the confluence of the Euphrates-Tigris rivers is considered as the major source of freshwater influx into the Arabian Gulf. The extent of the discharge is mostly within the northwest Arabian Gulf where the Kuwaiti territorial waters located and with lesser extent to the Saudi Arabian coast. The flow rate of the discharge was estimated by 1,456 m^3/s (Reynolds, 1993). Although the annual discharge is in a decrease trend along the last three decades as a result of constructions of dams at the upper reaches of Tigris and Euphrates basin and the diversion of Karun river, there is no recent estimation available indicating to which limit the discharge has been decreased. The previous estimation of the average of annual discharge was varied between 35 km^3/year (Saad, 1978) and 45 km^3/year (Reynolds, 1993). A large sediments load is transported by the river discharge of Shatt Al-Arab river and the Third river as well through Khor Al-Zubair and Khor Abdullah.

According to Alkuwairan (2013), Kuwait's coastal topography is characterized by high sediment load in the northern areas and Kuwait bay. On chemical basis, the northern Arabian Gulf and Kuwait bay exhibited a mix of dolomite [$CaMg(CO_3)_2$], carbonate and siliciclastic sediment and dolomitic cement was a major component due to the predominance of fine silt and mud silt.

Organotin compounds were widely used as antifouling substances. During 1950's and 1960's, the quantity was increased from 5000 tons to 60,000 tons (Ritsema et al., 1998). In 1970's, the toxicity of organotin compounds was reported as a result of marine mollucs populations decline in the coast of Plymouth sound, United Kingdom. Consequently, several regulations were developed and implemented to reduce the use of highly toxicity organotin compounds (Okoro et al., 2011). After recognition of the complexity, regulations concerning the use of TBT on a global scale were initiated in the 1980's, including a ban on its use since 1st January 2008 (Maguire, 2000).

Kuwait as a member of ROPME (The Regional Organization for the Protection of the Marine Environment) effectively implemented the protocol that controlled and managed the ship biofouling. The only study dealing with organotin compounds in the marine environment of the Arabian Gulf was carried by ROPME after IMO (International Maritime Organization) banned the use of TBT in antifouling paints in 2008 (ROPME, 2011).

The present study aims to estimate the concentration of organotin compounds by different fraction of butyltin represented by MBT, DBT, TBT, TeBT and total tin in sediments throughout Kuwaiti marine environment.

Materials and Methods

Samples were collected from 19 locations, as shown in Figure (1), including ports, marinas and islands. At each site, three replicates of four

surface sediment samples by Van Veen grab sampler and one core sample from the center by the Kajak core were collected between March and June 2015. In the laboratory, surface sediment samples were air-dried in a hood. The same procedure was applied to the core samples after cutting it in sections of 2.5 cm, 3 cm and 5 cm interval to the end of the core. Grab and core samples were grounded and stored in clean glass containers in dark.

Organotin compounds were extracted from sediment by acetate buffer to methanol (CH_3OH) and 5% sodium tetraethyl borate ($NaBEt_4$), and partitioned into n-hexane (David et al., 2003). To 1 gram of air dried samples, blank, or CRM in a centrifuge tube, 10 ml of acetate buffer, 7 ml of methanol, 4 ml of 5% $NaBEt_4$, 10 ml of hexane and 250 µl of 10 ppm internal standard were added. The mix was shaken for 20 minutes, then it was centrifuged for 10 minutes. The clear upper layer was used for TBT analysis.

Figure 1: Location map of sediment samples.

Results and Discussion

The result indicates a presence of TBT in surface sediment samples at four locations (stations 3, 4, 5 and 9), i.e. 20% of the monitoring stations, three in the northern coast and one in Kuwait bay. The highest TBT concentration

detected was 1.242 µg/g dw at station 9 (Al-Shuwaikh port) and the lowest was 0.572 µg/g dw at station 5 (Failaka island) as presented in Table (1). The concentrations found to be variable within the subsamples of the four locations. However, no levels neither of TBT nor of other organotin compounds have been detected in core sediment samples throughout all sections examined down to depth of 50 cm.

Station 3: Rumaila Shipwreck

Rumaila is an Iraqi oil tanker which sunk in the north of Khor Abdullah in 1991 and settled horizontally (Figure 2) forming a barrier against the currents movements. The oil is still continuously leaking from the shipwreck as illustrated in Figure (3). Two of the four surface sediment subsamples were collected from the southern side (subsamples 1 and 2 representing the face side of the ship) and the other two subsamples were collected from the northern side (subsamples 3 and 4 representing bottom side of the ship). TBT was detected only in subsamples 1 and 2. The concentrations of TBT triplicates in subsample 1 were 1.118, 1.420 and 1.128 µg/g dw, with an average of 1.222 µg/g dw and in subsample 2, the concentrations were relatively lower estimated to be 0.805, 0.795 and 0.678 µg/g dw with an average of 0.759 µg/g dw (Figure 4). The levels detected in both subsamples 1 and 2 could be attributed to the ship's paint leaking into the sediment. The no TBT detection in the subsamples 3 and 4 could be due to the huge sedimentation accumulated on the bottom side where the shipwreck acts as a barrier against the current flow.

Table 1: TBT concentrations in surface sediment subsamples at the four polluted locations.

Stations	Location	Sample No.	Subsample 1	Subsample 2	Subsample 3	Average
St. 3	Rumaila: Iraqi wrecked ship	1	1.118	1.420	1.128	1.222
		2	0.805	0.795	0.678	0.759
		3	0	0	0	0
		4	0	0	0	0
St. 4	Mubarak port, Bobyan island	1	0.678	0.785	0.637	0.700
		2	0.591	0.588	0.555	0.578
		3	0.562	0.591	0.613	0.589
		4	0	0	0	0
St. 5	Failaka island	1	0.815	1.021	0.860	0.899
		2	0.609	0.557	0.551	0.572
		3	0	0	0	0
		4	0	0	0	0
St. 9	Al-Shuwaikh port	1	1.149	1.327	1.252	1.242
		2	0	0	0	0
		3	0	0	0	0
		4	0	0	0	0

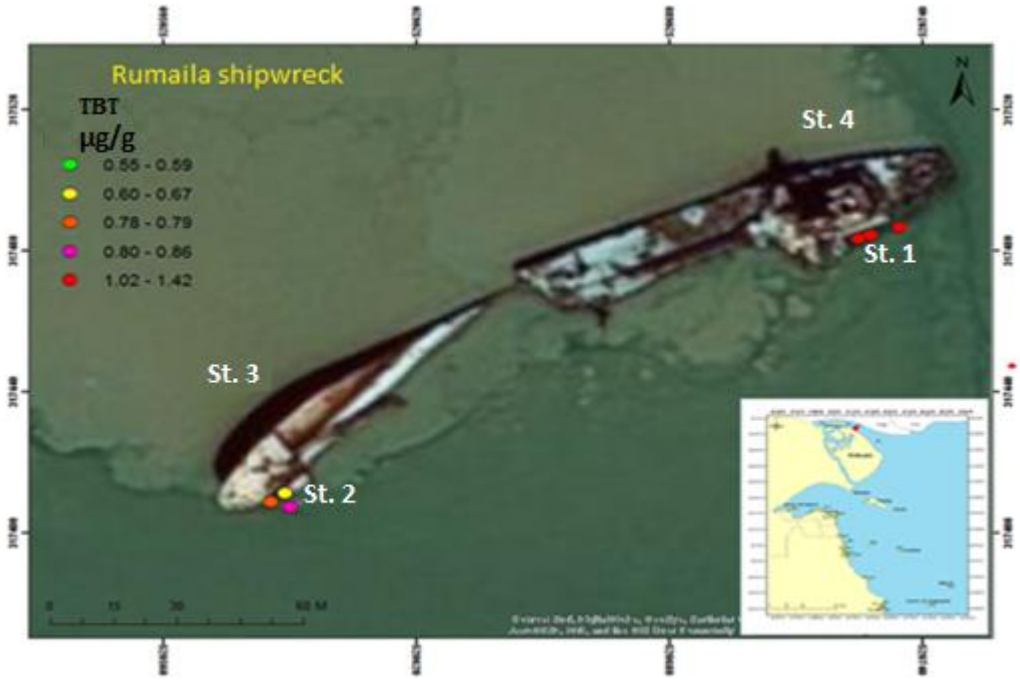

Figure 2: TBT concentrations in sediment samples at Rumaila shipwreck location.

Figure 3: Oil spill from the Rumaila shipwreck.

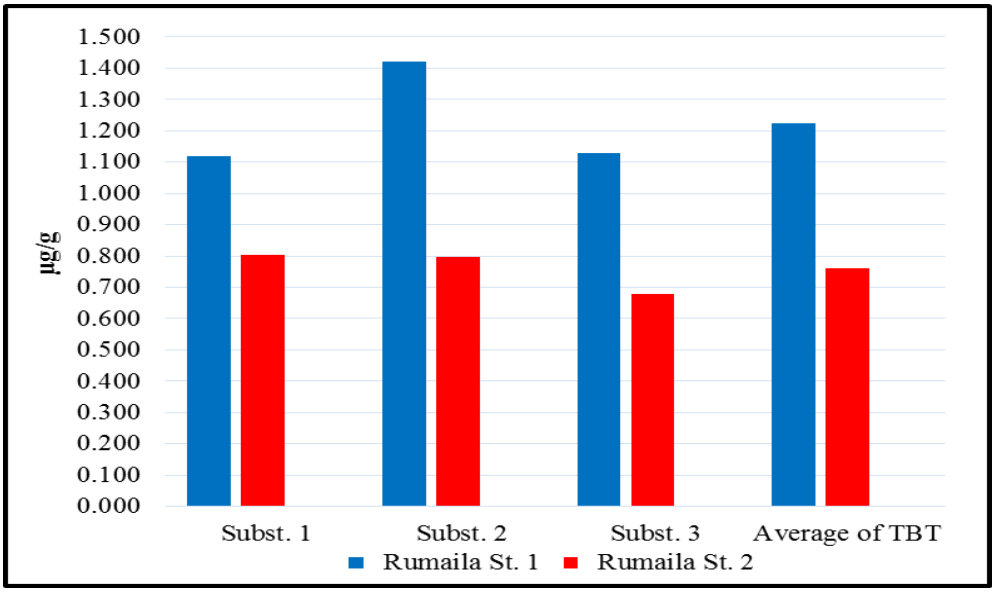

Figure 4: Average of TBT in sediment subsamples at Rumaila shipwreck location.

Station 4: Mubarak Port

Mubarak port is newly established on the east coast of Bobyan island (Figure 5). Out of the four surface subsamples collected from the port area, TBT was detected at three locations. The concentrations of TBT in subsample 1 were 0.678, 0.785 and 0.637 µg/g dw with an average of 0.700 µg/g dw representing the highest level in this location. In subsample 2, the TBT concentrations were 0.591, 0.588 and 0.555 µg/g dw with an average of 0.578 µg/g dw, which seem to be more or less similar to the TBT concentrations in subsample 3 those estimated to be 0.562, 0.591 and 0.613 µg/g dw with an average of 0.589 µg/g dw (Figure 6).

The highest levels of TBT observed at subsample 1 indicates trapping of pollutants potentially transported by the currents inside the port. The TBT detected could be sourced as a result of maintenance activity in the dry dock at ports in adjacent countries. Moreover, the paint leaked from the sunken vessels along Khor Abdullah since the Gulf war in 1991 probably represents a further source drifted by the currents.

Station 5: Failaka Island Marina

Failaka marina is characterised by a rocky shore with approximately 250 m intertidal zone. Of the four surface sediment samples collected, TBT was found in two samples those located at the marina's west side (Figure 7). TBT concentrations in these two sediment samples were 0.815, 1.021 and 0.860 µg/g dw in subsamples 1, with an average of 0.899 µg/g dw. In subsamples 2,

the TBT concentrations were relatively lower represented by 0.609, 0.577 and 0.551 µg/g dw, with an average of 0.572 µg/g dw (Figure 8). The high levels of TBT observed at the west side of the marina, particularly in the inner sample, could be attributed to trapping of pollutants transported by currents inside the marina. However, samples 3 and 4 were collected from the east side with no TBT levels. The samples were associated with new sedimentation noticeably accumulated on the east, thus no TBT were detected in the surface. Kuwait's Ministry of Communication and Touristic Enterprising Company maintained the marina by regular dredging to secure the navigation for passenger boats.

The source of TBT in Failaka marina could be attributed to the sunken boats in the lower reaches of Shatt Al-Arab river and many others scattered within the Iraqi territorial waters since the Iraq-Iran war (1980-1988) and as a result of the Gulf war (1991) as illustrated in Figure (9). Moreover, other sunken vessels at the entrance of Khor Bobyan (Figure 10) may also provide further source for TBT observed in this location where the water mass is drifting westerly toward the Kuwaiti territorial waters as a result of anti-clockwise current pattern in the Arabian Gulf (Figure 11).

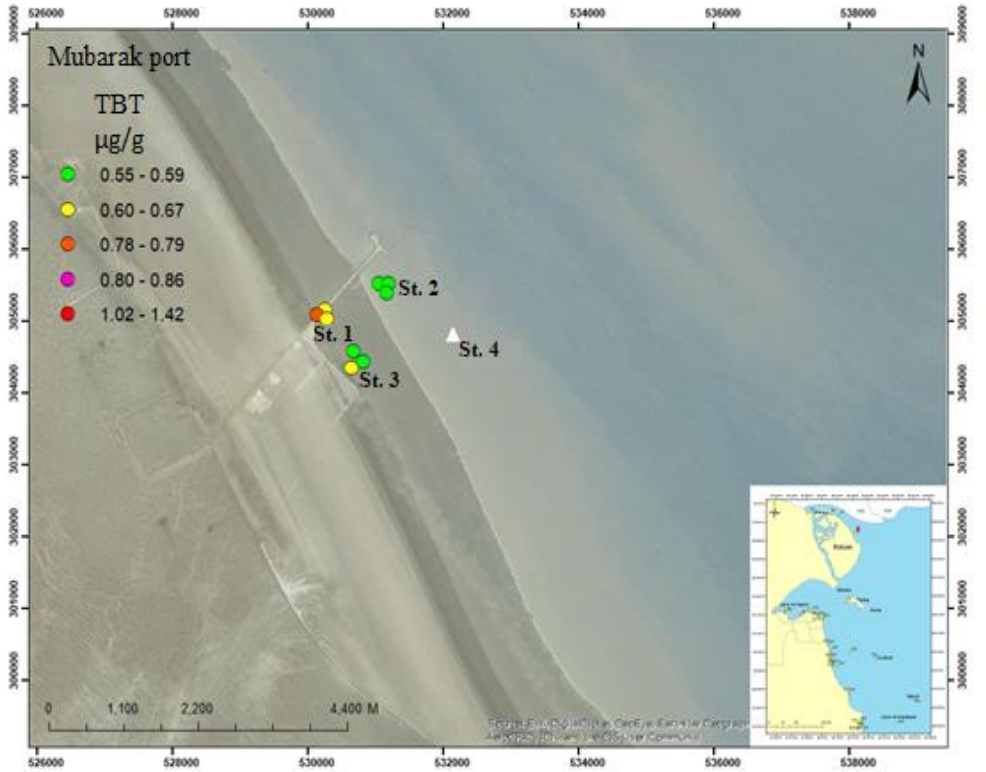

Figure 5: TBT concentrations in sediment samples at Mubarak port location.

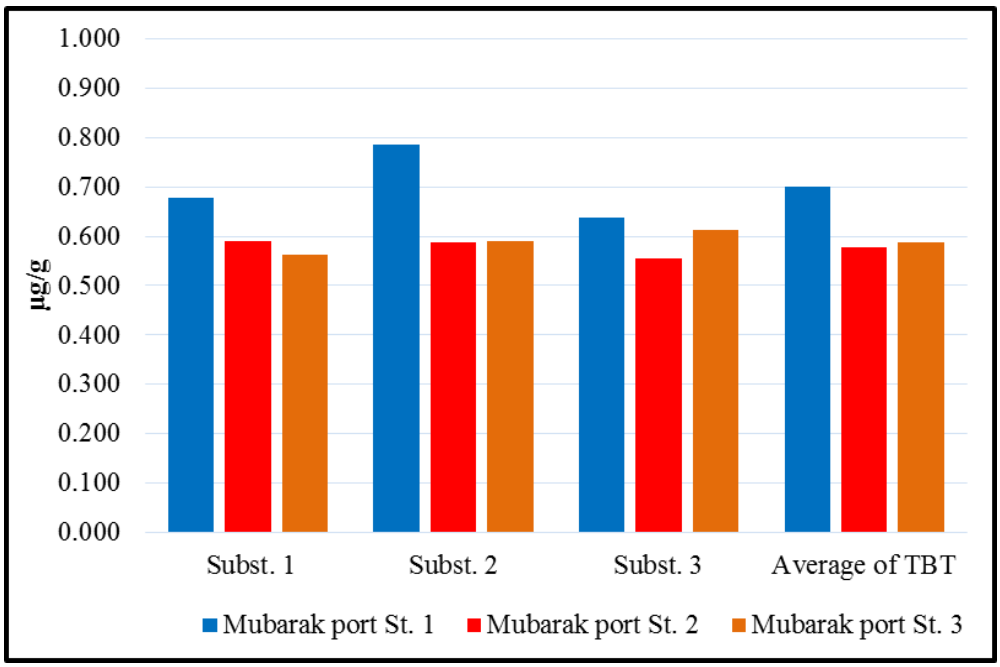

Figure 6: Average of TBT in sediment subsamples at Mubarak port location.

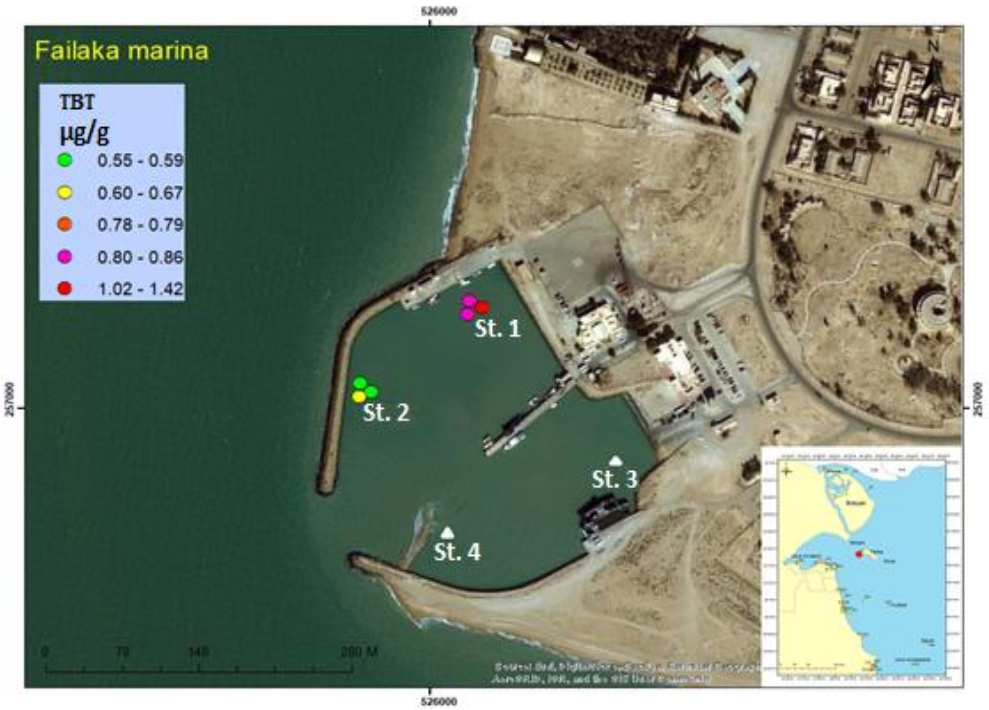

Figure 7: TBT concentrations in sediment samples at Failaka marina location.

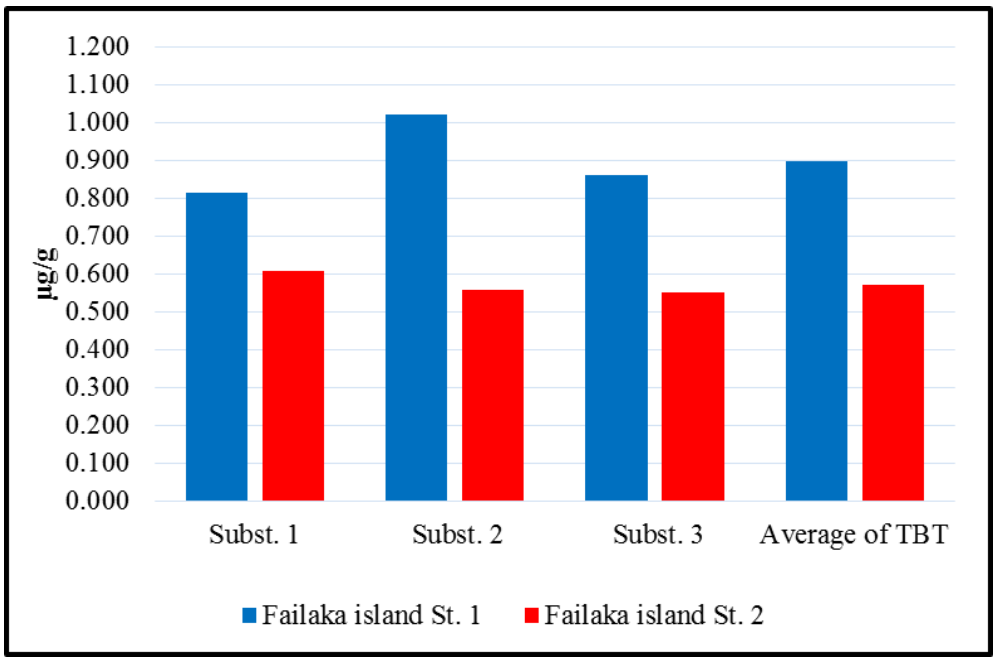

Figure 8: Average of TBT in sediment subsamples at Failaka marina location.

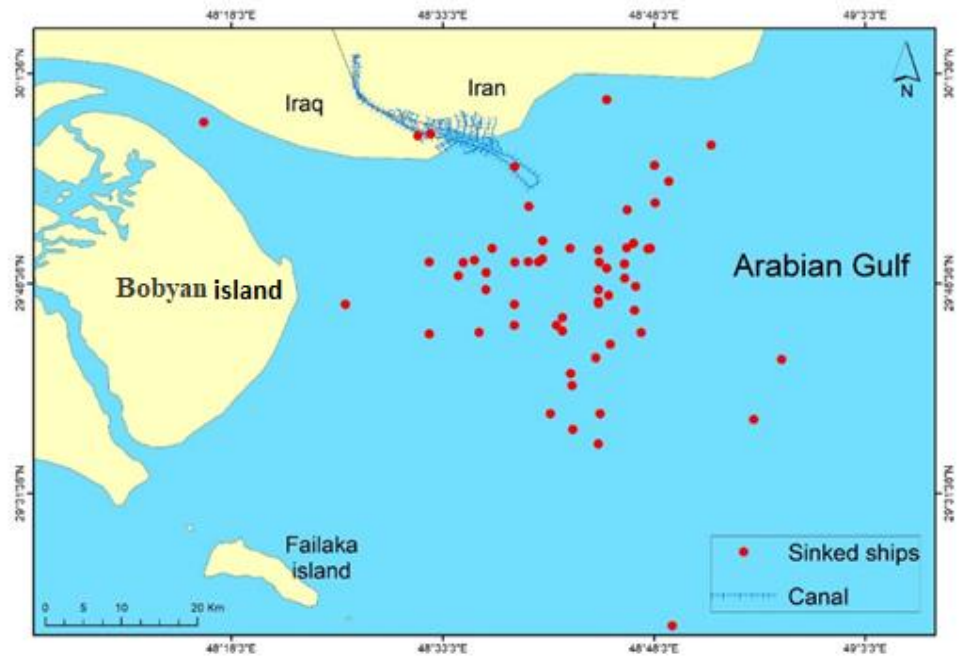

Figure 9: Locations of sunken vessels in the northwest Arabian Gulf (Qasim & Ali, Unpublished).

Figure 10: Locations of sunken vessels in the Kuwaiti territorial waters (Al Turkeit & El Kandary, 2003).

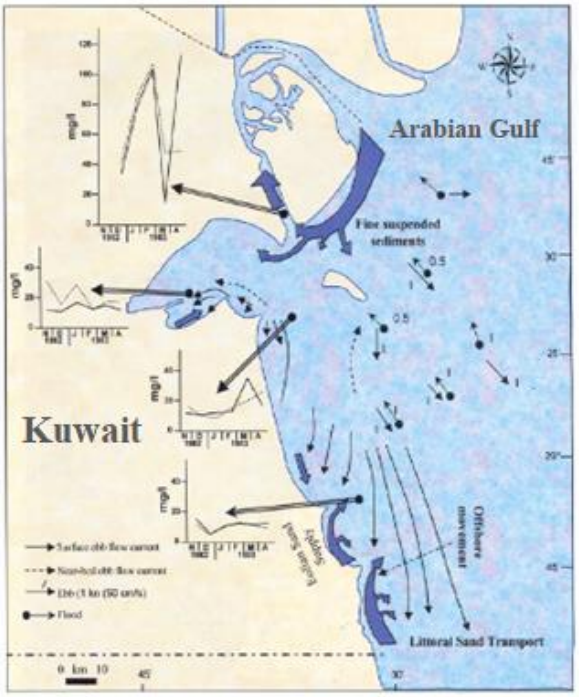

Figure 11: Currents regime along the Kuwait coast (Al-Ghadban, 2004).

Station 9: Shuwaikh Port

Shuwaikh port is the largest commercial port located in the eastern part of Kuwait bay. Out of the four sediment surface samples taken from this location, only sample 1 at the dry dock was found to be contaminated by TBT (Figure 12). The TBT concentrations in the subsamples of this site were 1.149, 1.327 and 1.252 µg/g dw, with an average of 1.242 µg/g dw (Figure 13) indicating the highest levels throughout the stations surveyed. The dry dock at Shuwaikh port was constructed in 1974 for both large and small ship maintenance. Accordingly, the main source of TBT at this site could be the result of antifouling paints escaping during the maintenance activity in the dry dock.

TBT Levels in Comparison with Regional and Global Scales

Compared to TBT concentrations in other Gulf Cooperation Council (GCC) countries, the concentrations found in the present study are less than those reported by Hasan & Juma (1992) in Bahrain in early 1990 (128-1,930 µg/g dw) and in 1992 (352-1330 µg/g dw). However, the TBT concentrations determined by de Mora et al. (2003) during 2000-2001, indicated that the levels in the United Arab Emirates were < 0.08-0.13 µg/g dw, which are less than those obtained in the present study while the range of levels in Qatar (<0.06-1.7 µg/g dw), Bahrain (< 0.39-40 µg/g dw) and Oman (0.1-60 µg/g dw) were higher than the range of the present study. The recent assessment carried out by ROPME (2011) indicated that TBT concentrations in the GCC countries including Kuwait, Saudi Arabia, Bahrain, Qatar and Oman were < 0.3 µg/g dw during 2011 and in the United Arab Emirates was 0.4-2.2 µg/g dw, confirming substantial elevation in comparison with the levels found in the present study. Recently, the study conducted by Al-Shatri et al. (2014) revealed a noticeable decrease of TBT in Saudi Arabia where the levels were ranged between 0.051 µg/g and 0.695 µg/g. Based on the TBT standard adopted by the OSPAR (0.00001 µg/g) and the EU Environmental Quality Standards EQS (0.00002 µg/g) as reported by Nyberg et al. (2013), all TBT concentrations determined in the Arabian Gulf are substantially beyond these two standards.

The results obtained at the four contaminated locations in the present study are extremely higher than the standards of TBT levels in sediment adopted by EAC and EQS as illustrated in Figure (14).

The temporal satellite image showed many shipwrecks in the Shatt Al-Arab river as a result of the Iraq-Iran war (1980-1988) and Khor Abdullah and Khor Al-Zubair as a result of both the Gulf war (1991) and the US invasion of Iraq (2003). At least 80 ships remained as wrecks in and on the sides of the main navigation channel, which potentially threatened the marine environment due to the spills of petroleum products, unexploded ordnance

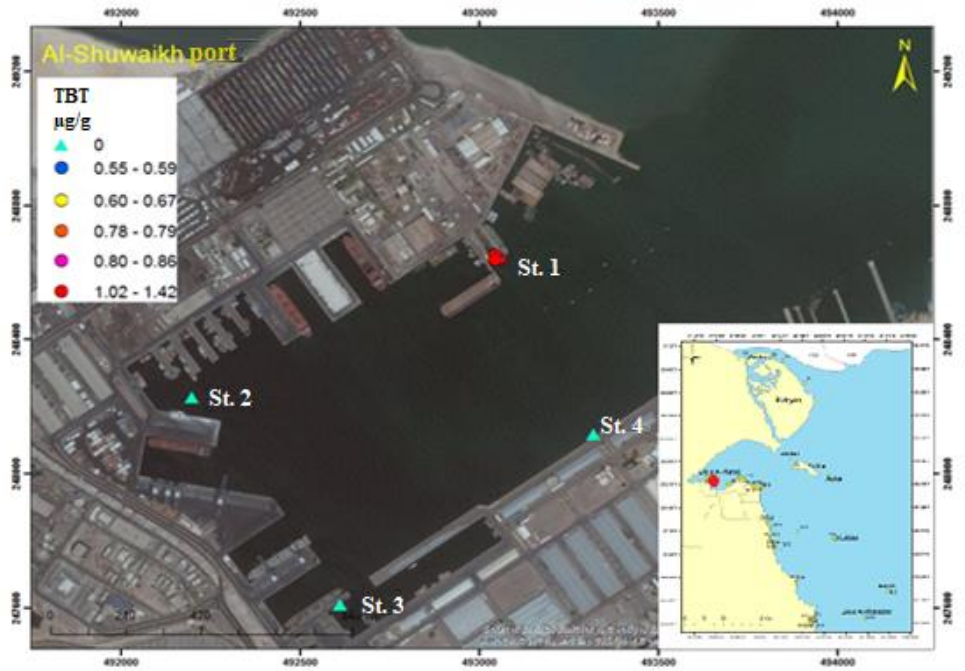

Figure 12: TBT concentrations in sediment samples at Shuwaikh port location.

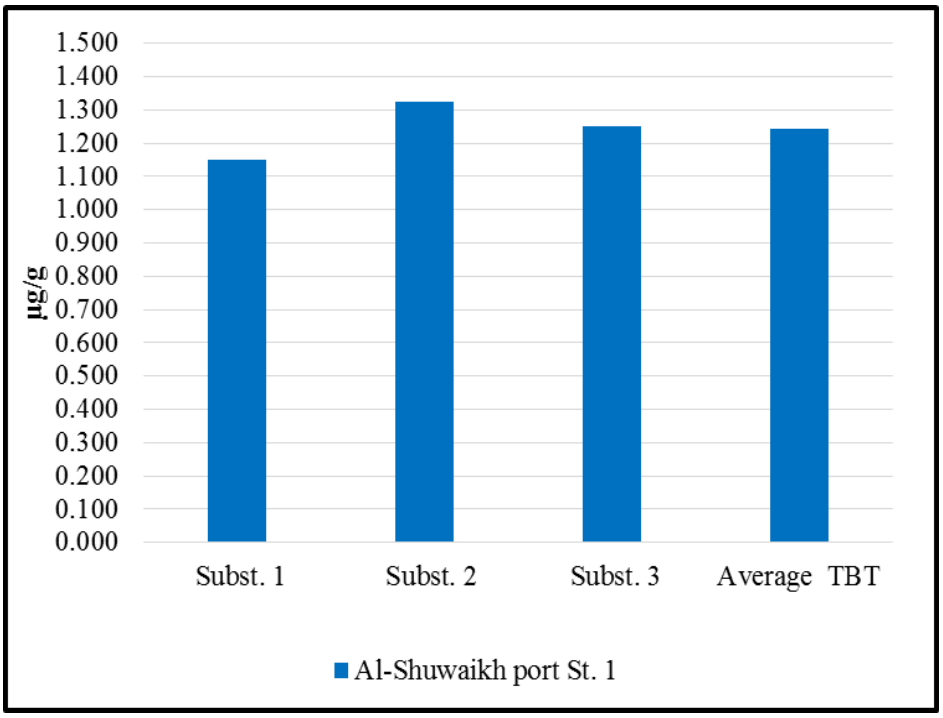

Figure 13: Average of TBT in sediment subsamples at Al-Shuwaikh port location.

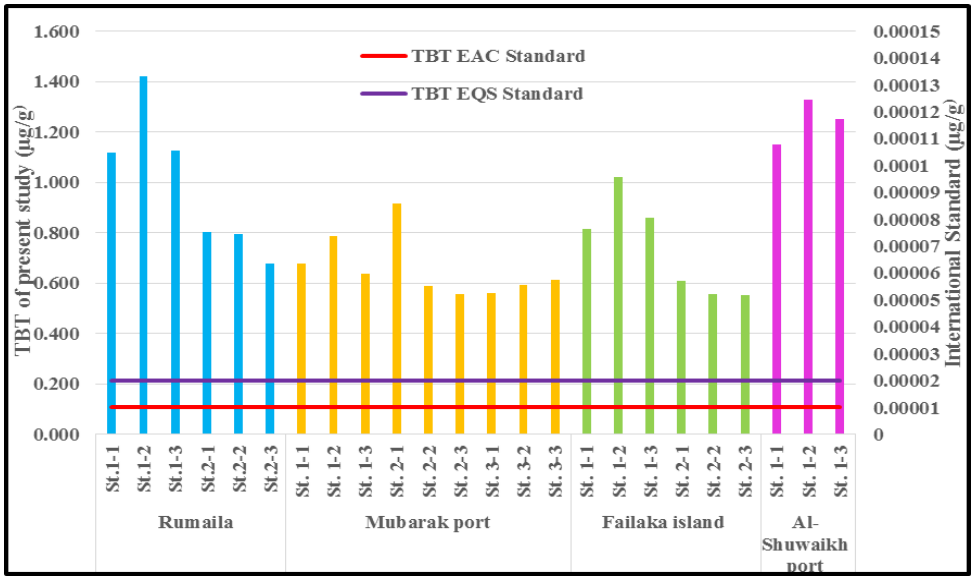

Figure 14: TBT concentrations in the study area in comparison to international standards.

and possibly rocket fuel, propellants and toxic chemicals (UNEP, 2003). A report published by the UN Development Programme identified 280 shipwrecks weighing more than 34 million tons, 260 of which are commercial and 40 of these shipwrecks need immediate removal (Valerie, 2005). A total of 61 sunken vessels of different sizes were located at the northwest Arabian Gulf, mostly at the entrance of Khor Abdullah as presented in Figure (9). According to Kuwaiti Ministry of Communication, further 34 sunken vessels of different sizes, most of them are a barge, were located within the Kuwaiti territorial waters along off the Kuwaiti coast as a result of the Gulf war (1991) as illustrated in Figure (10). These sunken vessels are considered as potential sources of different pollutants including TBT that might be drifted by the current regime towards the Kuwaiti territorial waters particularly during ebb cycle. Both petroleum and antifouling substances are the two critical problems posed by shipwrecks (UNEP, 2003; Valerie, 2005). TBT sorption in the natural sediment depends on pH, salinity and biotic and abiotic degradation and increase at pH 6 particularly in muddy and clay sediment (Adelman et al., 1990; Meador, 2000; Landmeyer et al., 2004; Kirli, 2005). Degradation of organotin compounds might be accelerated by UV radiation, increasing temperature and biological activity. The shallow depths throughout the Kuwaiti coasts (<10 m during high tide) provide an opportunity for irradiation by ultraviolet sunlight to degrade the TBT concentrations adsorbed onto surface sediments despite the complexity of the bottom texture.

Banning TBT as a component of antifouling paints in Kuwait since 2008 was obviously reflected on the marine environment, where the levels observed are mostly resulted due to transboundary effect that need to be regionally focus on to identify potential preventive and remedial actions to promote long-term sustainable development in the region.

Conclusions

The transboundary effect of maintenance activities practiced in the dry docks in adjacent countries formed potential source of antifouling compounds transported by freshwater discharge. The banning of TBT as a component of antifouling paint in Kuwait since 2008 obviously reflected on the quality of marine sediments, where the levels observed were very likely to be of transboundary sources, beyond the territorial waters.

The anti- clockwise currents system at the northern Arabian Gulf is the most factor controlling the movement of the water mass discharged from the Shatt Al-Arab river and Khor Abdullah to drift westerly toward the Kuwaiti territorial waters with sediment loads associated with anticipated pollutants. On the other hand, the shallow depths throughout the Kuwait's coasts (< 10 m during high tide), provide an opportunity for irradiation by ultraviolet sunlight to degrade the TBT concentrations adsorbed onto surface sediments by photoreaction despite the complexity of the bottom texture.

The northwest Arabian Gulf, where the sunken vessels are scattered, plays an important biological role as spawning, feeding and nursery grounds for broad scale of fishery species. Consequently, it is of great importance to initiate a regional survey to assess the levels and types of pollutants in this area and to take a cooperation action on the salvage of the sunken vessels.

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