

Three Bench-scale Tests Designed to Destroy Tributyltin (TBT) in Marine Sediments from North Queensland, Australia

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Abstract

Organotin compounds, such as tributyltin (TBT), were used as antifouling biocidal agents in ship maintenance throughout the world prior to 2000. As a consequence, TBT has accumulated in marine sediments of some harbours, rivers and ports, and in and around shipyards, dry-docks and marinas. Organotin-contaminated marine sediments, when left undisturbed, pose little risk to the local environment or society, however, due to its toxic nature, TBT can pose a significant risk to the marine environment, groundwater, and potentially human health if contaminated marine sediments are dredged and left untreated on land or disposed to landfill, and disturbance through dredging can liberate TBT into the water column. Both scenarios can provide pathways for dissemination and contamination.

Given the low allowable concentrations of TBT in marine sediments, the need for sustainable management and treatment of TBT is imperative. However, despite a worldwide effort to find effective treatment strategies for TBT in marine sediments, few examples exist which actually destroy the TBT molecule. For this reason, TBT is considered one of the world's most persistent organic pollutants and is stable when in-situ sediments are left at the bottom of ports and harbours.

Two samples of contaminated marine sediment were excavated from a slipway in far North Queensland and analysed for TBT and other contaminants. Each sample was then subjected to one of three bench-scale tests: Test 1 a treatment of six oxidising and/or immobilizing chemical agents; Test 2 thermo-chemical treatment; and Test 3 thermal treatment only. The six agents in Test 1 had little or no impact on total TBT, leachable TBT, water soluble TBT, or total petroleum hydrocarbons (TPH), however, the combined thermal and chemical treatment used in Test 2 and the thermal treatment used in Test 3 reduced total TBT, leachable TBT, water soluble TBT, and TPH by >99%.

Keywords: Organotin; Tributyltin; Marine sediments**Introduction**

For four decades prior to 2000, shipyards and dry-docks throughout the world used organotin-based, anti-fouling paints (commonly called "bottom paints") to protect the outer hulls of ocean-going ships and floating structures. These paints were distributed under various product names, including Alumacoat, Bioclean, TinSan and Fungitrol. During routine annual maintenance, dry-docks hydro-blast hulls with freshwater to remove biofouling slime, encrustations (such as the adhesion of barnacles, which inhibit the speed of ships and reduce fuel consumption by up to 15%), and flaking paint. Organotin-based paints were preferable over other paint formulations, such as those based on copper sulfate (CuSO_4), because they increased the periodic episodes of hydro-blasting from one to three years and did not promote the bimetallic corrosion of hulls.

However, rather than collecting and treating the large volumes of wastewater generated from high-pressure hydro-blasting prior to discharge to the environment, organotin-contaminated wastewater was routinely discharged into waterways such as ports, harbours and rivers, where liberated paint particles accumulate and concentrate in marine sediments after settling [1]. It has also been suggested that organotin compounds can enter the food chain due to the simple leaching of organotin contaminants from fresh and exposed paint in seawater, as occurs with zinc when used as an anti-corrosive agent in ship maintenance [2]. For these reasons, organotin compounds have translocated and accumulated in sediments around slipways, marinas, dry-docks and shipyard maintenance facilities throughout the world [3].

Organotin compounds consist of organic molecules attached to a tin atom (or atoms) via carbon-tin covalent bonding. The organotin cation species tributyltin (TBT) has the formula $[\text{C}_4\text{H}_9]_3\text{Sn}^+$ and has a

half-life greater than ten years under reducing conditions. TBT has been used as a biocide (i.e., as a fungicide, bactericide and insecticide) in the form of TBT oxide and TBT methacrylate, and naturally decomposes to the less toxic breakdown products dibutyltin (DBT, $[\text{C}_4\text{H}_9]_2\text{Sn}^{2+}$), and subsequently monobutyltin (MBT, $[\text{C}_4\text{H}_9]\text{OSn}^+$); Al-rashdi has conducted the most thorough investigation into the chemistry of TBT and debutylisation [1]. Organotin compounds have been used as stabilizers in the manufacture of plastic products, specifically as an anti-yellowing agent in clear plastics and as a catalyst in polyvinylchloride products. In addition to the application of organotins in anti-fouling paint, organotins have also been used as preservatives in wood, textiles, paper, leather and electrical equipment. In 1996, the total worldwide production of organotin compounds was estimated at 50,000 tons per year [4], with >5,200 tons deposited to landfill annually in the U.S. in 1976; however the amount of TBT disposed on soil and in sediment, both in the past and present, is unknown.

TBT is considered highly toxic to animals and humans [5,6], although Al-rashdi claims no known adverse effects on humans have been documented [1]. In fact, TBT is considered one of

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the most acutely toxic and harmful chemical substances deliberately introduced into the natural environment anthropogenically [7], on a par with other persistent organic pollutants (POPs), such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenols (PCBs), and dioxans [8]. TBT can enter the human body through ingestion of contaminated seafood, and Al-rashdi has documented daily TBT intakes of 6.7 µg/person in Japan and up to 2.1 µg/person in Asia [1]. However, cooking does not remove organotin molecules from foods but potential adverse effects of TBT in humans have yet to be fully investigated.

Concerns associated with adverse reactions in rats, mice and hamsters to reproductive organs, teratogenic markers (i.e., developmental abnormalities associated with birth defects, cleft palate, irregularities in rib cage development and fetal birth weights, for example), organ toxicity, and indications of carcinogenic mutations have been observed [9-13]. Boyer cites TBT and DBT as food chain bio-accumulators and bio-concentrators, having demonstrated their ability to accumulate and concentrate in crabs, oysters, mussels, carp, mullet, silver bream and salmon [10]; according to Boyer, in mammalian species TBT can metabolize to DBT [10], and the U.S. EPA has associated TBT with imposex and immuno-suppression in snails and bivalves, such as dog whelk (*Nucella lapillus*) and sea snails (*Thais orbita*) [4,14], which can continue long after the destruction of TBT through natural degradation processes [15]. Reports from the United Kingdom indicate that dog whelk communities have become extinct due to TBT, with eel grass, maerl and mussel beds are at risk [16].

TBT has therefore been classed as a persistent toxic substance (PTS) in most jurisdictions, and products containing TBT must carry the signal words “danger” and “warning”; a typical safety data sheet for TBT lists a range of potential human health risks, including hazards to eyes and skin, and dangers associated with ingestion and inhalation potentially leading to death. Negative effects of TBT in marine and coastal environments include changes in reef community structure, such as decreases in live coral cover and increases in algae and sponges, and damage to seagrass beds and other aquatic vegetation [16].

From a regulatory point-of-view, in the United States organotins generally (and TBT specifically) became regulated under the Organotin Antifouling Paint Control Act of 1988, and subsequent worldwide bans on the use of organotin compounds including TBT were introduced in 2000-2001, to be phased in over five to ten years (for example, the International Maritime Organisation’s “Control of Harmful Anti fouling Systems for Ships”, which came into effect in 2001) by most jurisdictions. However, in 2003 it was noted that because of its effectiveness, TBT-based anti-fouling paints were still in use in less regulated jurisdictions [8].

In Australia, there is evidence that TBT can be found in water and has accumulated and concentrated in marine sediments and animals around many of the country’s ports, slipways, harbours and rivers. For example, samples of water, sediment and oyster tissue at several locations between Brisbane and Karumba in north Queensland found total TBT concentrations of up to 174 ngSn/L in water, 790 µgSn/kg in sediments, and 34 µgSn/kg in oyster tissues.

Similarly, at the Port of Mackay, TBT concentrations in dredged harbour spoil were 84 µgSn/kg in 1996, 300 µgSn/kg in 1997, and 3,200 µgSn/kg 1998, suggesting both accumulation and concentration over time; a sample at Hay Point coal terminal indicated TBT concentrations of 8.2 µgSn/kg. A Queensland EPA survey of TBT in the lower Brisbane River downstream of a major ship repair facility

indicated TBT in sediments of up to 22,100 µgSn/kg; on the Sunshine Coast, concentrations of TBT in sediments associated with a boatyard were up to 8,300 µgSn/kg, and concentrations in oysters up to 30 µgSn/kg [17].

Moreover, TBT has been found in the marine sediments and mussels growing in sediments in and around the Swan Yacht Club in the Swan River, Western Australia [2]. For example, the highest total concentrations of TBT were >5,000 µgSn/kg, concentrations of DBT were >5,000 µgSn/kg, and concentrations of MBT were >810 µgSn/kg in some marine sediments; similarly, the highest TBT concentrations recorded in mussel tissue in and around the Yacht Club were 140 ngSn/g, with DBT at 39 ngSn/g and MBT at 4.9 ngSn/g.

TBT has also been documented in marine sediments around marinas, shipyards and slipways in Canada, France, Japan, Spain, UK and USA, and has even been found in river sediments upstream from point-sources of contamination [1,4,18,19]. In Australia, safe TBT concentrations in marine sediments are considered to be <5.0 µgSn/kg; in the U.S., the water soluble criterion to protect saltwater aquatic life from the chronic toxic effects of TBT is 0.0074 µg/L [4], which is comparable to Australia’s <0.002 µg/L for the same purpose [20].

By far the largest commercial operation to dredge, treat and reuse organotin-contaminated marine sediments was carried out in Finland between 2007 and 2009 [21]. Conducted at Finland’s second largest port, the Port of Turku at the mouth of the River Aura where about four million tonnes of cargo and more than four million passengers pass each year, this project dredged 40,000 m³ of TBT-contaminated marine sediments, removing the sediments to an on-site treatment area where they were treated with a combination of cement, fly ash and pulverised blast-furnace slag. However, the highest concentrations of TBT recorded in this sediment averaged a relatively low 200 µgSn/kg (in a range of 28-1,200 µgSn/kg) with leachable TBT of 0.005 µg/L, far less than many of the reported TBT concentrations in Australia’s ports and marinas, as cited above. However, the use of cement, fly ash and pulverised blast-furnace slag as “binders” in the immobilisation of TBT at Turku did not result in the complete immobilisation or destruction of leachable TBT, with levels actually rising to 0.03-0.07 µg/L over a 60-day period.

Without providing specific data, Howard and Gkenakou also reported that a variety of materials, including activated carbon, organically modified clays, iron, fly ash, and cement, had demonstrated promising results in immobilising TBT in sediments, but that ultrasonic destruction of TBT had only reduced TBT by 40%; the authors cite incineration as a viable method of destroying the TBT molecule, but dismiss it as being commercially impractical [22]. The adsorption capacity of TBT, DBT and MBT to kaolin under a range of acidic conditions was also investigated by Yvon, Le Hécho and Donard, with modest results [23].

Similarly, Wardell Armstrong proposed that chemical oxidation, phytoremediation and bioremediation may be viable treatment options, but that steam stripping and thermal desorption would “likely” be required for higher concentrations of TBT [16]; Wardell Armstrong also noted that few treatments of TBT have been experimentally or commercially proven. In laboratory scale tests, Envisan reported that bioremediation reduced TBT in marine sediments by 70% (although it is not immediately apparent how the energy generated from biological digestion could account for a molecule with covalent bonds as tightly formed as those in TBT), no effect was observed using phytoremediation, chemical oxidation using potassium permanganate

“theoretically” had the potential to destroy TBT, and electrochemical oxidation was viable, but the researchers also discovered the last process generated toxic chlorinated compounds [19].

Goethals and Pieters reported that dissolved air flotation (DAF) had little or no effect on TBT removal rates from marine sediments, but showed how varying the length of time in soil washing (including adding activated carbon in some wash cycles) had a salutary effect [24]; however, the authors also define “highly contaminated” marine sediments as those with an average TBT concentration of 60 µgSn/kg, not the higher levels cited above for Australia. Perhaps more concerning was Goethals and Pieters’ observation that soil washing, even with the greatest agitation for the longest time, only reduced TBT by 30%, or from 60 µgSn/kg to 43 µgSn/kg. However, Goethals and Pieters also reported that high temperature thermal desorption “debutylated” TBT-, DBT- and MBT-contaminated marine sediments by >97% at 400°C [23]. Al-rashdi [1] suggested that nanoscavenging (using a chemically modified mesoporous silica) can reduce TBT, DBT and MBT in water, and Luan, et al. reported 90% degradation of TBT at concentrations of 10, 50 and 100 µgSn/L by alginate-immobilized *Chlorella vulgaris* beads during six, four-day treatment cycles [25].

In order to examine a range of treatment options for the destruction of TBT in highly contaminated Australian marine sediments, this study therefore asked: 1) do *ex-situ* chemical, thermo-chemical, and thermal treatments destroy the TBT molecule in highly contaminated marine sediments; and 2) is TBT leachable and water soluble as a result of these treatments?

Methods

Three regulatory guidelines govern safe levels of TBT in Australia: 1) National Environment Protection Council [26,27] Assessment of Site Contamination and Amendment of the Assessment of Site Contamination NEPM 1999, the so-called NEPM guidelines; 2) Australian and New Zealand Environment Conservation Council [20] Guidelines for fresh and marine water quality, volume 1, the so-called ANZECC guidelines; and 3) Environment Australia [28] National ocean disposal guidelines for dredged material, the so-called NODG guidelines. Each regulatory framework provides different criteria about acceptable levels of TBT concentrations as they relate to seawater and marine sediments. For the purposes of this study, these three criteria were used as benchmarks of effective treatment of TBT and have been summarised in Table 1.

Two separate 17 kg samples of marine sediment were collected one month apart from under a wharf adjacent to a slipway located in North Queensland. Samples 1 and 2 were a blackish-brown, moist but spadable sludge with little or no obvious odour. Prior to treatment, a 500 g sub-sample of each sample was analysed for pH, moisture content, total TBT, DBT and MBT (for Sample 2 only), leachable TBT and tin (Sn) as measured by TCLP, water soluble TBT, total metals, polycyclic aromatic hydrocarbons (PAH), benzene, toluene, ethylbenzene and xylene (BTEX), and total petroleum hydrocarbons (TPH). Total TBT was measured on a dry base and represents the total concentration of TBT present in the marine sediment on a parts per billion basis; leachable TBT was analysed using the Toxicology Characteristic Leaching Procedure (TCLP) of the U.S. EPA [29] and is reported in a parts per trillion basis; water soluble TBT was measured by mixing one part sediment to five parts dionized (DI) water and then analysing the total TBT concentration in the liquid phase; water soluble

Parameter	NEPM	ANZECC	NODG
Total TBT	No criteria	<5.0 µgSn/kg	<70 µgSn/kg for ocean disposal
Leachable TBT	<0.002 µg/L (i.e., <2.0 ngSn/L)	No criteria	No criteria
Water Soluble TBT	<0.002 µg/L (i.e., <2.0 ngSn/L)	<0.005 µg/L (80% level of protection); <0.0004 µg/L (99% level of protection)	No criteria
Total Sn	No criteria	No criteria	No criteria
Leachable Sn	No criteria	No criteria	No criteria
Total petroleum hydrocarbons (TPH)	No criteria	No criteria	No criteria

Table 1: Australian regulatory frameworks for TBT, Sn and TPH. Concentration limits for marine sediments

TBT is reported in a parts per trillion basis; leachable Sn was also analysed using TCLP and is reported on a parts per million basis.

Analytical results for Samples 1 and 2 are presented in Table 2. From this data it can be concluded the sediment in Sample 1 had a near-neutral pH, had a solids content of 47%, had a total TBT concentration of 1,550 µgSn/kg with leachable TBT of 802 ngSn/L, water soluble TBT of 534 ngSn/L, but no detectable leachable Sn, 220 mg/kg of total petroleum hydrocarbons (all of it in the heavy C16-C34 fraction on a dry base), but did not contain any detectable PAH or BTEX (in other words, total PAH and BTEX in Samples 1 and 2 were below the detection limit of 0.5 mg/kg).

The measure of total petroleum hydrocarbons (TPH) represents the total amount petroleum-based hydrocarbons present in the sediment, and is a measure of the gross amount of hydrocarbons without reference to its constituent petroleum “fractions”. However, in this study, the fractions of TPH were also measured, and the analyses showed that there were no hydrocarbons present in the lighter C6-C9 and C10-C16 fractions (normally associated with compounds such as benzene, toluene and naphthalene) or in the heaviest C34-C40 fraction (normally associated with crude oil), but were concentrated in the C16-C34 fraction (normally associated with mineral oils). Both samples were tested using gas chromatography–mass spectrometry (GC-MS) for TBT, DBT, MBT, PAH, TPH and BTEX, and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for leach ability.

From this data it can also be concluded the sediment in Sample 2 had a near-neutral pH, had a solids content of 43%, and had a total TBT concentration of 4,140 µgSn/kg, DBT concentration of 450 µgSn/kg, and MBT concentration of 3.0 µgSn/kg with water soluble TBT of 597 ngSn/L, but no detectable leachable Sn. Therefore the two samples were largely congruent except for the marked difference in total TBT concentrations, indicating that marine sediments from North Queensland were heterogeneous in nature.

Test 1

Chemical Treatment

Six, 1.0 kg sub-samples of Sample 1 were treated using a combination of four oxidising and immobilising agents and two immobilising agents in isolation. Use of oxidising agents was designed to provide the necessary chemical energy to destroy the TBT molecule by breaking it down into its constituent atoms, while immobilising agents used in combination with oxidising agents or in isolation

Parameter	Sample 1	Sample 2	Detection Limit
pH	8.5	8.4	—
Moisture content (%)	53	57	—
Total TBT (µgSn/kg)	1,550	4,140	0.5
Total DBT (µgSn/kg)	—	450	0.5
Total MBT (µgSn/kg)	—	3.0	0.5
Leachable TBT (ngSn/L)	802	953	2.0
Water soluble TBT (ngSn/L)	534	597	2.0
Leachable Tin (mg/L)	<0.1	<0.1	0.1
Total Tin (mg/kg)	10	8.0	5.0
Polycyclic aromatic hydrocarbons (mg/kg)	<0.5	—	0.5
BTEX (mg/kg)	<0.5	—	0.5
TPH C6-C10 fraction (mg/kg)	<10	—	10
TPH C10-C16 fraction (mg/kg)	<50	—	50
TPH C16-C34 fraction (mg/kg)	220	—	100
TPH C34-C40 fraction (mg/kg)	<100	—	100
Total petroleum hydrocarbons (mg/kg)	220	—	50

Table 2: Pre-treatment analysis of two marine sediments from North Queensland.

were designed to bind Sn into non-bioavailable forms. When applied oxidising and immobilising chemical additives are designed to provide synergistic oxidation and ionic binding, with each additive enhancing the performance of the other. The following treatments were applied to the sediment sub-samples:

Treatment A = a combination of 97% high-grade soluble potassium permanganate (KMnO₄) (also called permanganic acid, potassium salt, or permanganate of potash), an inorganic salt crystal for oxidation, and ElectroBind reagent, a clay-like material derived from modified alumina refinery residue for immobilisation. The primary constituents of ElectroBind are hematite (Fe₂O₃), boehmite (γ-AlOOH), gibbsite (Al[OH]₃) and sodalite (Na₄Al₃Si₃O₁₂Cl), but also contains anatase (TiO₂), argonite (CaCO₃), brucite (Mg[OH]₂), diaspore (β-Al₂O₃·H₂O), ferrihydrite (Fe₂O₃·[OH]₄·4H₂O), gypsum (CaSO₄·2H₂O), hydrocalumite (Ca₂Al[OH]₇·3H₂O), hydrotalcite (Mg₃Al₂CO₃[OH]₁₆·4H₂O), and p-aluminohydrocalcite (CaAl₂[CO₃]₂[OH]₄·3H₂O). The physical and chemical properties of ElectroBind reagent and its preparation have been discussed in detail elsewhere [30,31].

Treatment B = a combination of 98% high-grade soluble sodium persulphate (Na₂S₂O₈), an inorganic compound for oxidation, and ElectroBind reagent for immobilisation.

Treatment C = a combination of ascorbic acid (C₆H₈O₆), also called threoscorbic acid or antiscorbutic factor, for oxidation and ElectroBind reagent for immobilisation.

Treatment D = a combination of industrial-grade hydrogen peroxide (H₂O₂), an inorganic Fenton's compound for oxidation, and ElectroBind reagent for immobilisation.

Treatment E = ElectroBind reagent for immobilisation.

Treatment F = Ordinary Portland cement (OPC) for immobilisation.

In stage one, each oxidant in Treatments A-D was thoroughly mixed into sediment for approximately one hour before the stage two addition of ElectroBind and OPC in powdered form, which were mixed for a further ten minutes; immobilising agents in stage one Treatments E-F were mixed for 15 minutes. (Table 3) presents the protocols for each treatment. After treatment, all sub-samples were sent for analysis within 24 hours of mixing.

Test 2: Thermo-chemical Treatment

Test 2 utilized a combined thermal and chemical treatment. A 2.0 kg sub-sample of Sample 1 was mixed with approximately 10% w/w ElectroBind for ten minutes and then placed in an incinerator and heated to 1,000°C for ten to fifteen minutes. The specially designed incinerator used in test 2 featured sequential heating zones to control volatilization and the elimination of inherent interwoven and interstitial compounds such that an open lattice structure to the sediment would be created. Using sequential heating, including pre-heaters and smoke and fuel recycling to reduce carbon emissions to zero, and the addition of ElectroBind to act as a vitreous powder, porous matrices within the sediment were bonded into self-supporting structures. Liquid spray, gas and vapour nozzles within the thermal process were controlled to apply so-called surface or interstitial active coatings to the sediments; these coatings imparted catalytic, ion-exchange capacity, electronic capacitance, conductivity and gas storage porosity to the heated sediment.

Test 3: Thermal Treatment

Test 3 utilized a rotary half kiln to heat a 2.0 kg sub-sample of Sample 2 to 400°C. Rotary half kilns, which are typically used for small batch experiments, perform the same basic function as a rotary or cement kiln, but do not employ a continuous feed. As would have been the case with a rotary kiln, the rotary half kiln used in this test 3 was a slightly inclined cylindrical vessel, which rotated slowly about its axis.

However, unlike the standard rotary kiln which would have fed the sediment into the upper end of the cylinder, which with stirring and mixing would have allowed the sediment to gradually move down towards the lower end of the kiln, the rotary half kiln liberated the sediment from the same upper end of the cylinder. However, hot gases pass through the rotary half kiln in the same direction as the “co-current” sediment, but in a rotary kiln these gases would pass in the opposite or “counter-current” direction to the treated material.

Results

Test 1: Chemical Treatment

Results of test 1 are presented in Table 4. Analysis of total Sn was not carried out because Sn does not change unless it is removed from the substrate, which was not designed to occur in these treatments; similarly, total BTEX and PAH were not analysed because they were not present in the initial analysis.

The data in Table 4 show that chemical addition had a significant impact on post-treated sediment pH, ranging from as low as 3.5 for Treatment B to 11.8 for Treatment F; however, moisture content was unaffected for all treatments (while moisture content was not tested for Treatment F, it can be to have changed by was <5%). Only Treatment A had any significant impact on total TBT concentrations, with a 43%

Treatment	Stage One		Stage Two	
	Additive	Dose Rate	Additive	Dose Rate
A	Potassium permanganate	10%w/w	ElectroBind	3%w/w
B	Sodium persulphate	10%w/w	ElectroBind	3%w/w
C	Ascorbic acid	10%w/w	ElectroBind	3%w/w
D	Hydrogen peroxide	10%w/w	ElectroBind	3%w/w
E	ElectroBind	10%w/w	—	—
F	OPC	40%w/w	—	—

Table 3: Treatment protocols for six chemical additions.

Parameter	Untreated Sediment	A	B	C	D	E	F
pH	8.5	9.7	3.5	5.8	8.2	7.4	11.8
Moisture content (%)	53	49	47	47	51	49	—
Total TBT (µgSn/kg)	1,550	890	1,360	1,460	2,220	1,720	1,450
Leachable TBT (ngSn/L)	802	—	—	1,340	—	2,190	<2.0 [†]
Water soluble TBT (ngSn/L)	534	—	—	666	—	351	—
Leachable Tin (mg/L)	<0.1 [†]	—	—	<0.1 [†]	—	<0.1 [†]	<0.1 [†]
Total petroleum hydrocarbons (mg/kg)	220	110	110	<50	120	150	—

[†] Below limit of detection

Table 4: Results for test 1.

reduction from 1,550 µgSn/kg to 890 µgSn/kg. Leachable TBT was reduced by 100% from 802 ngSn/L to <2.0 ngSn/L by Treatment F, but actually increased 65% and 180% respectively as a result of Treatments C and E, and water soluble TBT was reduced 35% from 534 ngSn/L to 351 ngSn/L by Treatment E, but also increased as a result of Treatment C. Leachable Sn was unaffected by all treatments, and TPH was reduced by an average of 50% for all treatments.

Test 2: Thermo-chemical Treatment

Results of test 2 are presented in Table 5. This table shows that pH was increased from 8.5 to 10.5 and total TBT was reduced from 1,550 µgSn/kg to <0.5 µgSn/kg (i.e., below the level of detection). This finding represents a reduction of 99% from 1,550 parts per billion to less than 0.5 parts per billion. Similarly, Table 5 shows that leachable TBT was reduced from 802 ngSn/L to <2.0 ngSn/L (i.e., below the level of detection of 2.0 ng Sn/L). This represents a reduction of >99% from 802 parts per trillion to less than 2.0 parts per trillion. Initial analysis had shown that water soluble TBT in untreated sediment was 534 ngSn/L but was reduced to <2.0 ngSn/L as a result of test 2. This finding is consistent with the fact that solubilising TBT with water is not as harsh on sediment as leaching of TBT under TCLP acid conditions (i.e., due to a pH of ±7.0 in the water test versus a pH of 2.88 in the TCLP leach test). Leachable Sn was below the level of detection in the sediment both before and after treatment, but TPH was reduced by 100% from 220 mg/kg to 0.0 mg/kg.

Of interest was the finding that moisture content in the sediment was reduced by 98% and sediment after treatment was not only dry but extremely hard as a result of test 2. The process transformed the sediment from a wet “sludge” into a dry, gravel-like material; of note also was the distinct change of colour in the sediment from a blackish-brown to a light brown colour. An examination of the beneficial reuse potential of this gravel-like material would be warranted, specifically how it might be used in road or building construction or as solid fill in land reclamation; reuse in cementitious materials might also prove viable.

Test 3: Thermal Treatment

Results of test 3 are presented in Table 6. This table shows that pH was increased from 8.5 to 10.5. Similarly, total TBT was reduced from 4,140 µgSn/kg to <0.5 µgSn/kg (i.e., below the level of detection). This finding represents a reduction of >99% from 4,140 parts per billion to less than 0.5 parts per billion. Similarly, Table 6 shows that leachable TBT was reduced from 953 ngSn/L to <2.0 ngSn/L (i.e., below the level of detection of 2.0 ngSn/L). This represents a

reduction of >99% from 953 parts per trillion to less than 2.0 parts per trillion. Initial analysis had shown that water soluble TBT in untreated sediment was 597 ngSn/L but was reduced to <2.0 ngSn/L as a result of test 2. This finding is consistent with the fact that solubilising TBT with water is not as harsh on sediment as leaching of TBT under TCLP acid conditions; leachable Sn was below the level of detection in the sediment both before and after treatment. Observations in test 2 related to changes in colour (although not as pronounced in test 3) and beneficial reuse options also apply to the treated solids from test 3.

Discussion and Conclusion

Despite reports in the literature that chemical oxidation destroys and chemical immobilisation binds [22] TBT in marine sediments, no evidence was found to support this claim in test 1. As the 10% w/w addition rate of oxidant used in this study exceeds those rates typically associated with the commercially viable chemical treatment of soils and sediments (i.e., ±3% w/w), and given that chemical oxidants are at the high end of the industrial chemical cost scale, it is unlikely that further testing with higher addition rates would prove technically or commercially worthwhile. Nevertheless, it was unexpected that such large amounts of chemical energy brought to bear on breaking the ionic bonds of TBT were not more effective.

However, results from this study do confirm that both thermo-chemical and thermal treatment of organotin-contaminated marine sediment destroys the TBT molecule. This finding is consistent with those suggested by Goethals and Pieters [23]. Treated TBT concentrations of <0.5 µgSn/kg observed in tests 1 and 2 are lower than allowable under ANZECC and NODG guidelines in Australia [20,27], meaning that the treated marine sediments were safe for disposal or reuse. As a consequence, research question 1 was only partially answered in the affirmative, in that chemical oxidation and immobilisation methods did not result in the effective treatment of TBT, but thermo-chemical and thermal treatments did destroy the

Parameter	Untreated Sediment	Post-Treatment Sediment
pH	8.5	10.6
Moisture content (%)	53	1.0
Total TBT (µgSn/kg)	1,550	<0.5 [†]
Leachable TBT (ngSn/L)	802	<2.0 [†]
Water soluble TBT (ngSn/L)	534	<2.0 [†]
Leachable Tin (mg/L)	<0.1 [†]	<0.1 [†]
Total petroleum hydrocarbons (mg/kg)	220	0.0

[†] Below limit of detection

Table 5: Results for test 2.

Parameter	Untreated Sediment	Post-Treatment Sediment
pH	8.4	10.5
Moisture content (%)	57	1.5
Total TBT (µgSn/kg)	4,140	<0.5 [†]
Total DBT (µgSn/kg)	450	<0.5 [†]
Total MBT (µgSn/kg)	3.0	<0.5 [†]
Leachable TBT (ngSn/L)	953	<2.0 [†]
Water soluble TBT (ngSn/L)	597	<2.0 [†]
Leachable Tin (mg/L)	<0.1 [†]	<0.1 [†]

[†] Below limit of detection

Table 6: Results for test 3.

TBT molecule in highly contaminated marine sediments.

This study also demonstrated that Treatments C and E in test 1 did not significantly reduce either leachable or water soluble TBT. In fact, leachable TBT increased in both cases (from 802 ngSn/L to 1,340 ngSn/L and 2,190 ngSn/L respectively) while soluble TBT declined slightly in both cases (from 534 ngSn/L to 666 ngSn/L and 351 ngSn/L respectively). However, Treatment F in test 1 did significantly reduce leachable TBT (from 802 ngSn/L to <2.0 ngSn/L). Similarly, tests 2 and 3 reduced leachable TBT by >99% (from 802 ngSn/L and 953 ngSn/L to <2.0 ngSn/L in both cases) and soluble TBT by >99% (from 534 ngSn/L and 597 ngSn/L to <2.0 ngSn/L in both cases). These concentrations of leachable and soluble TBT are less than those required by NEPM (2013) for the marine environment (i.e., <2.0 ngSn/L), and are also less than the 80% level of protection in the marine environment as specified by the ANZECC guidelines of <0.005 µgSn/L, but were higher than the required <0.0004 µgSn/L for protection at the 99% level. Therefore, research question 2 was also only partially answered in the affirmative. Furthermore, tests 2 and 3 resulted in a significant reduction of moisture content and a slight increase of pH; the total destruction of petroleum hydrocarbons was observed in test 2, and an average 52% reduction of petroleum hydrocarbons was observed in test 1.

It is reasonable to conclude that some or all of the marine sediments sampled in this study have been, or are likely to be, dredged and disposed as spoil in ocean outfalls near the Great Barrier Reef, despite TBT concentrations present in the sediments at levels higher than those allowable under NODG. As North Queensland harbours expand to accommodate larger cruise ships and other uses, such as those planned for bulk handling coal exports at Abbot Point in Mackay, it is feasible that more TBT contaminated marine sediments will be dredged and disposed in ocean outfalls thereby making the need for sustainable management of TBT even more imperative. The present findings mean that such sediment can now be treated and disposed without future harm to the environment or society.

One of the limitations of thermal treatment of marine sediments cited in the literature is its high cost. It has been proposed that the cost of energy requirements in particular, be they supplied by gas or electricity to efficiently operate an incinerator, rotary kiln or other thermal device such as a thermal desorption unit, makes such applications for high volumes of marine sediment commercially impractical. However, a preliminary cost-benefit analysis for the marine sediments treated in these bench-scale tests indicate that treatment operating costs are no greater than disposal costs to regulated landfill, although may be higher than bulk disposal by barge to ocean outfall. Therefore, further attempts to optimise the thermal treatments described in this study may prove beneficial in driving future commercial outcomes.

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