

# Organotin Compounds in Marine Sediments

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## Abstract

Organotin compounds are widely used in almost all sectors of industry. Antifouling paints, which were applied to ship hulls to protect from fouling organisms, are the main source of TBT and TPhT derivatives loaded into the sea. The global ban on the use of these compounds in antifouling systems was introduced by the IMO in 2001. However, the ban did not solve the problem of the use of alternatives to TBT in the ship industry. Moreover, the issue of storing the organotins-containing dredged spoils at sea still remains unresolved. The pollution load deposited in port sediments may become an additional threat to the organisms that dwell in a given water basin. In such cases, it is necessary to establish appropriate norms for the quality classification of dredged spoils. Unfortunately, detailed guidelines concerning the disposal of dredged spoils are still lacking.

**Keywords:** organotin compounds, sediments, antifouling paints, dredged material

## Introduction

Due to their toxic properties, high propensity to accumulate in live organisms and slow degradation in the environment, organotin compounds constitute a group of pollutants of organic origin that is dangerous for the marine environment.

The first organotin compounds were synthesized in the mid 20th century. Since the 1960s they have been used in the global production of biocides, PCV stabilizers, industrial catalysts and wood preservatives [32]. Shortly afterwards, the toxic properties of these compounds were applied to protecting ship hulls, fishing nets and other elements submerged in water against fouling organisms. Antifouling systems based on TBT and TPhT were protecting with such efficiency that they became the main source of organotin compounds load into the sea (HELCOM

Recommendation 20/4, 1999) [26]. When it seemed that the ship building industry had found an effective means for antifouling protection, news about the negative impact of organotins on live organisms started to appear in the press.

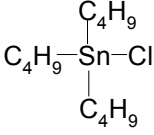
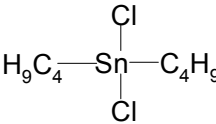
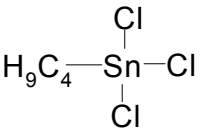
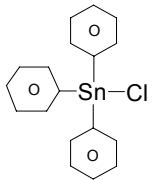
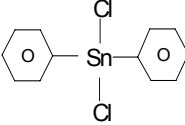
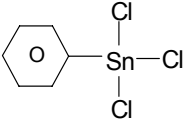
The development of the ship building industry resulted in a significant concentration of organotin compounds in the marine environment, including sediments. At present, because of numerous bans and legal sanctions a decrease in the inflow of additional organotin compounds to sediments was noted. However, the areas particularly exposed to pollution are still an exception. Such areas are shipyards, harbors and passenger ship terminals that constitute a potential pollution source for the marine environment via intensive shipping, reception of various wastes from the ships, cargo loading and unloading operations, and ship building and repairing/remodeling. Therefore, harbor sediments become a receptacle and storage compartment for many hazardous substances including organotins. This fact acquires a particular significance in the case of deepening harbor canals. The sediment enriched in chemical compounds is dredged

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Table 1. Physico-chemical properties and molecular and structural formulas of selected butyltin and phenyltin chlorides.

Derivative	Abbreviation	Molecular formula	Structural formula	Boiling point (°C)	Melting point (°C)	Solubility (mg/l <sup>3</sup> )*
Butyltin derivatives (BTs) Σ BTs = MBT+DBT+TBT						
Tributyltin chloride	TBTCl	Bu <sub>3</sub> SnCl		172	-16	5-50
Dibutyltin dichloride	DBTCl <sub>2</sub>	Bu <sub>2</sub> SnCl <sub>2</sub>		135	39-41	4-92
Monobutyltin trichloride	MBTCl <sub>3</sub>	BuSnCl <sub>3</sub>		93	na	na
Phenyltin derivatives (PhTs) Σ PTs = MPhT+DPhT+TPhT						
Triphenyltin chloride	TPhTCl	Ph <sub>3</sub> SnCl		na	106	1-5
Diphenyltin dichloride	DPhTCl <sub>2</sub>	Ph <sub>2</sub> SnCl <sub>2</sub>		333-337	42	50
Monophenyltin trichloride	MPhTCl <sub>3</sub>	PhSnCl <sub>3</sub>		na	na	na

\*solubility in seawater; na – not available (source: [27, 41])

from the harbor canals and then stored under specific conditions in the defined sea areas [51]. The load of hazardous substances deposited with the sediment may be a potential risk for the marine ecosystem. The increase of pollutants re-emission from the sediment into the water column can lead to the disturbance of the marine ecosystem’s equilibrium.

Sediments are a degraded and endangered habitat. They constitute a historical record of physico-chemical changes in the marine environment, and present a picture of environmental contamination by chemical compounds, including organotins. Sediments should be monitored and controlled in a detailed way, particularly for the content of organotin compounds.

In this work the characteristics of organotin compounds in regard to their origin, legal regulations and pathways in the marine environment are presented with a special emphasis on benthic sediments.

Chemical and Physical Properties of Organotin Compounds

Organotin compounds belong to the group of organometallic substances. The chemical structure of such compounds can be described by the following molecular formula [37, 41]:

R<sub>n</sub>SnX<sub>(4-n)</sub> (1)

where:  
R - alkyl or aryl group (i.e. methyl (Me, CH<sub>3</sub>-), butyl (Bu, C<sub>4</sub>H<sub>9</sub>-), phenyl (Ph, C<sub>6</sub>H<sub>5</sub>-), octyl group (Oc, C<sub>10</sub>H<sub>21</sub>-),  
X - inorganic anion: O<sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, SH<sup>-</sup>, etc.,  
n - a consecutive number from 1 to 4.

- Organotin compounds are:
- lipophilic,
  - poorly soluble in water,

Table 2. Toxic effects of trisubstituted tin derivatives on selected species.

Live organisms	Toxic effect	Source
Snails (Neo-, Gastropodas)	TBT causes imposex, i.e. development of male characteristics in females (e.g. male sex organs) it leads to infertility, sterility and species dying off.	[14, 59]
Bivalves	BTs cause thickening and delamination of shells, enlargement of the mouth, endocrine disruptor, increased mortality and imposex or intersex.	[7, 18, 44]
Fishes	TBT and TPhT accumulate, among others, in heart, brain, blood and liver. TBT causes immunological disorders, loss of appetite, increased opaqueness of an eye, mitochondrial degeneration, lesions of gills and cornea, spasms, changes in gallbladder and bile system, and mortality of fry.	[8, 13, 31]
Mammals / Humans	TBT has a negative impact on eyes, skin, kidneys, liver, blood supply to lymph nodes, breathing processes (particularly TPhT), nervous system, enzymatic activities and hormone levels. In addition, TBT, TPhT and TPPrT* in humans disturbs the transport of calcium, magnesium, potassium and sodium ions through mitochondrial membranes by blocking ATPase activity in the brain. They cause disappearance of noradrenalin and dopamine in the brain and adrenal glands, and adrenaline in adrenal glands. Trimethyl- and triethyltin derivatives inhibit oxidative phosphorylation in mitochondria. Organotins have a toxic effect on thymus and gallbladder and bile system. TBT can cause headaches, weakening, fever, convulsions and lack of motor coordination, irritation of eyes and skin, and neurological disorders. In both humans and marine mammals TBT inhibits catalytic activity of cytochrome P450 aromatase that catalyzes the conversion of androgens into estrogens. TBT is also involved in such basic processes as mitochondrial respiration, ion channels, receptor activation, and gene transcription. It should, however, be stated that the causative mechanisms behind the toxic effects of organotin compounds are not completely known.	[4, 21, 34, 36, 44, 46, 56]

\*TPPrT abbreviates tripropyltin

- easily degradable by UV, light or gamma ( $\gamma$ ) radiation,
  - susceptible to nucleophilic or electrophilic attacks.
- Physico-chemical properties of butyl- and phenyltin derivatives are presented in Table 1.

### Toxicity of Organotin Compounds

Tin in its inorganic form is accepted as being non-toxic, but the toxicological pattern of organotins is very complex. The biological effects of the substances depend on both the nature, number and type of organic groups R (alkyl or aryl group) bound to the Sn cation [27]. Inorganic anion X plays a secondary role.

It has been established that the toxicity of organotin compounds is the highest for  $n=3$ . Therefore, eco-toxicity increases dramatically in the order MBT < DBT < TBT for certain endpoints or modes of action [59, 60]. It has to be noted that TBT is more toxic than TPhT.

Toxicity of the butyl- and phenyltin derivatives in live organisms depends, inter alia, on dose, time of exposure, the type and specificity of a given species, the age and resistance of an individual and, lastly, on physiological processes (e.g. metabolism) undergoing in a given organism. It should be pointed out that mollusks and snails accumulate the most organotins, and are the main source of pollutants delivered to the remaining links in the food chain. Next, crustaceans and fish should be mentioned. Lipophilicity of organotins results in their propensity to persist and bioaccumulate in the sequential links of the food chain. This may lead to the spread of toxic substances in the food web, and in particular cases, to the poisoning of specific organisms.

According to HELCOM LAND (12/2007) [23], several organotins are strongly immunosuppressive, display developmental and reproductive effects, and are neurotoxic. Tributyltin is harmful to snails and oysters at concentrations ranging from 1 to 10 ng/l [39], while at 1-2 ng/l causes chronic and acute toxicity in algae, zooplankton, bivalves and fry [17]. Tributyltin is an endocrine disruptor in certain marine and freshwater mollusk species at such low concentrations in water as 1 ng/l [59, 60]. The most sensitive to the toxic effect of TBT are male individuals [4]. Tributyltin and triphenyltin may be classified as substances of high risk according to the assessment of substances in the European Union [12]. Both TBT and TPhT cause imposex which complicates reproduction [67]. In mollusks tributyltin causes imposex below the concentration of 2.0 ng/l, and intersex above 2 ng/l [44]. Dibutyltin may actually be more toxic than TBT to certain enzyme systems. Immunotoxic and developmental effects in mammals may also be more sensitive to DBT than to TBT [59, 60]. The lethal dose for a rat ( $DL_{50}$ ) is 9-500 mg/kg b.w. in the case of  $R_3SnX$ , 120-2300 mg/kg b.w. for  $R_2SnX_2$  and 9-15 mg/kg b.w. for  $R_4Sn$  [56]. Data on toxicity of trisubstituted tin derivatives in selected species has been summarized in Table 2.

Organotin compounds get easily absorbed through the skin, which may manifest itself by a skin rash. Particularly, the  $R_3SnX$  type compounds bind quickly to proteins, most likely via sulphur of the amino acids cysteine and histidine. Interactions with mitochondrial functions through various mechanisms are probably the biochemical pathways that lead to toxic responses [58].

Most information dealing with the toxicity of organotin compounds in humans originated in 1950 due to the fact that people in France were exposed to stannous chloride used for treating dermatological disorders, bone marrow inflammation and anthrax. The active ingredient of this pharmaceutical preparation was diethyltin iodide, but the toxicity could have been caused by tainting with triethyltin iodide. In this case, the most sensitive target turned out to be nerve tissue. The victims suffered from nerve tissue swelling, brain and spinal cord swelling and cerebral hemorrhage. The effects of poisoning were tragic as 100 Frenchmen suffered from it [58].

### History of Organotin Compounds

The use of mono- and dialkyltin derivatives in the production of polyvinyl chloride products started only in 1940. Intense development of industrial production based on organotin compounds started in 1960 [32] and coincided with the discovery of the lethal effect of TBT derivatives in bivalves. In less than 20 years, global production of biocides based on these compounds has already reached 30 thousand tons annually [64]. At present, organotin compounds are used in practically all sectors of industry, inter alia, pharmaceutical industry, dyeing, chemical production, shipbuilding, wood processing and agriculture. It has been estimated that the EU produces 3 thousand tons of TBT per annum [43].

The use of TBT in HELCOM countries during 2000-05 is presented in Table 2.

The problem of the negative impact of TBT on marine organisms was encountered for the first time in 1970 in France [2]. Since 1980 many countries have introduced legal sanctions in regard to the use of antifouling paints based on organotin compounds for the protection of ships longer than 25 m.

The main legal regulations that were passed later, i.e. the Helsinki Convention of 9 April 1992 on the Protection of the Marine Environment of the Baltic Sea Area [3] and resolution 46 (30) issued during the 30<sup>th</sup> meeting of the Marine Environment Protection Committee (MEPC) in 1990, significantly reduced the use of organotin compounds in the shipbuilding industry. However, only during the 21<sup>st</sup> Assembly meeting of the International Maritime Organization (IMO) in 1999 resolution A.895 [53] was adopted that has banned the use of TBT in new antifouling systems from January 1, 2003 and required to take action to render harmless or remove the old systems until January 1, 2008 [53]. In October 2001, at the IMO headquarters, the International Convention on the Control of Harmful Anti-fouling Systems on Ships (the AFS Convention) was adopted [33]. The convention was signed by the following states: Antigua and Barbuda, Bulgaria, Denmark, Japan, Latvia, Nigeria, Norway, Poland, Romania, Spain, Sweden, Cyprus, Greece, Luxembourg, Saint Kitts and Nevis, and Tavalu.

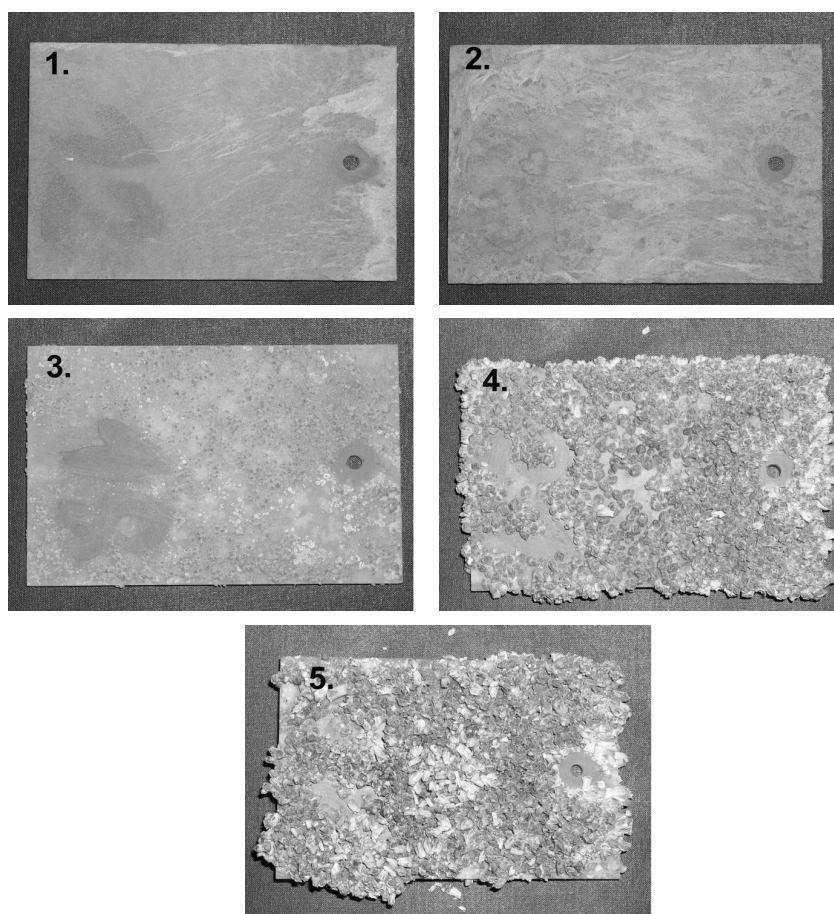


Fig. 1. Growth of barnacles on polymethacrylic, i.e. plexiglass plate (a lighter than steel and non-corrosive substratum was used in testing). Numbers 1, 2, 3, 4 and 5 stand for consecutive months of growth (Photo: Cezary Kania, Ship Design and Research Centre S.A.).

## Antifouling Paints

Antifouling paints are the main source of TBT and TPhT load into the sea [42]. They are used in the ship-building industry for protecting ship hulls against fouling by marine organisms. The intensity of barnacle growth on a plexiglass plate is shown in Fig. 1.

Direct emission of toxins from antifouling paints takes place during the stay of ships in harbors and repairs and remodeling operations of the hulls in shipyard docks (washing and removal of old paint, utilization of paint containers).

A ship that is not protected with an antifouling system can collect about 150 kg/m<sup>2</sup> of fouling organisms during a six-month stay at sea. This means that a tanker of 300 thousand tons cargo carrying capacity would carry about 6 thousand tons of fouling organisms on the 40 thousand m<sup>2</sup> of the submerged hull [9]. Such additional weight would result in the increased use of fuel necessary to overcome hull drag and the increased emission of pollutants into the atmosphere (among others, NO<sub>x</sub> and SO<sub>x</sub>) from the burnt fuel. Therefore, a lot of attention in the shipbuilding industry is being paid to antifouling systems, and the utmost efforts are being made to secure their high efficiency and long protection against fouling organisms. Next, the suitability of a given paint is considered in regard to the exploitation conditions, ship's speed and the area in which the ship stays. Antifouling systems that fulfill the above-mentioned conditions are self-polishing acrylic copolymer paints based on TBT. The first antifouling paints, i.e. Free Association Paints (FAP) were releasing biocides from the resin matrix into the water column in an uncontrolled manner, meaning that the release was uneven and decreasing with the decreasing thickness of the paint layer (Fig. 2A). The introduction of Self Polishing Copolymer Paints (SPC; Fig. 2B) has become a big success of the shipyard industry. Ships after 60 months of exploitation were coming to the docks without any fouling growth [9]. Moreover, the efficiency of hull protection increased from 2 years in the case of FAP system type to 5 or even 7 years in the case of SPC-TBT system [27]. Unfortunately, because of the high toxicity of antifouling systems based on organotin compounds in live organisms these paints have been withdrawn from the shipyard industry.

Under these circumstances, it has become necessary to introduce to the ship building industry the alternative antifouling systems that would be as effective as the TBT-based ones, but much more environment friendly. The available antifouling systems fall into two basic types: those with biocides other than tin, and without biocides. The alternative antifouling strategy is presented in Fig. 3.

The marine antifouling systems without organotins (TBT) contain organic (Diuron, Zineb), inorganic (copper oxides, zinc etc) or natural antifoulants. Copper compounds, e.g. copper oxide, copper thiocyanate and elemental copper are the basic biocidal agents in new antifouling paints that are reinforced with a selected biocide booster [63] such as Irgarol 1051, dichlofluanid, chlorothalonil [1],

diuron, [63] and Kathon 5287 (Sea Nine 211). This allows the protection of the hull against a spectrum of fouling organisms, e.g. algae. Based on the press releases, the first results of toxicity testing of biocide boosters such as Sea Nine 211, diuron, and Irgarol 1051 indicate that they have negative impact on selected marine organisms [15, 43, 47, 48].

Alternative non-TBT antifouling paints (for example biocide-free types on the basis of silicone or fluoro-polymer) do not seem completely safe either. The potential threats to ecosystems and the ecotoxicological profiles of these alternatives have to be carefully evaluated.

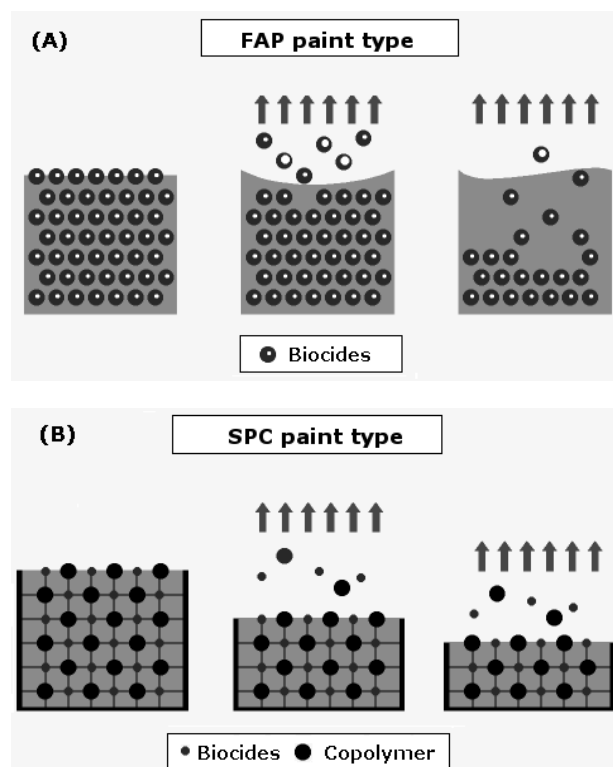


Fig. 2. Release of biocides from paint type (A) - FAP and type (B) - SPC [50].

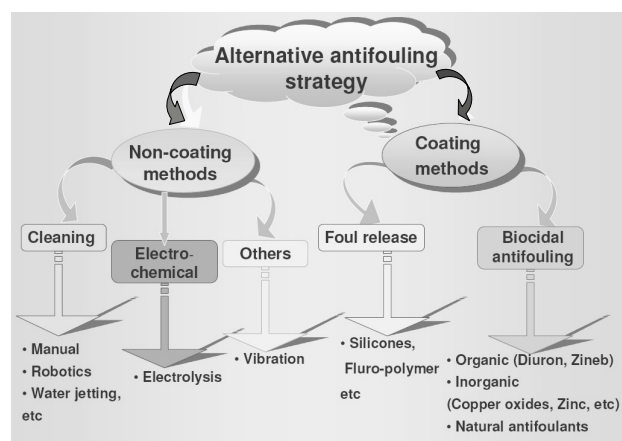


Fig. 3. Scheme of alternative antifouling strategy [57].

On the other hand, the presently used antifouling systems have a limited strength and act selectively on specific fouling organisms which results in only partial protection of the submerged ship parts. This seems to be an economical solution of low value. Moreover, the novel tin-free substitutes are much more expensive than the traditional TBT-based system. Considering the above-mentioned issues, it should be stated that the appropriate alternative antifouling systems capable of successfully replacing TBT-based paints are presently lacking.

This unsolvable problem creates specific threats, such as [57]:

- Increased introduction of alien species in tropical waters,
- Increase in fouling organism on ship hulls,
- Increase in emission of greenhouse gases and VOCs,
- Shift of local pollution problem to global pollution.

Therefore, the present research should be conducted with the aim to elaborate new technological solutions that are environment-friendly and more economical.

### Dredged Soils

The majority of harbors are located in the river mouth areas as such natural conditions are preferable. The shallowing of harbor canals resulting from sediment transport via river can render safe navigation impossible. Therefore, it is necessary to conduct dredging (deepening) of the canals.

According to the law, alluvial deposits and mud removed from the bottom of the harbor canals (so-called dredged spoils) should be treated as waste. Legal procedures in regard to dredged spoils are described in a number of regulations to protect the environment against contamination.

In the case of the Baltic Sea, the legal conditions of such actions are regulated by Article 11 and Annex V of the Helsinki Convention (1992) [3], HELCOM Recommendation 13/1 (1992) [25] and the HELCOM Guidelines (2007) [22].

In accordance with the HELCOM Recommendation 13/1 (1992) [25] and HELCOM Guidelines (2007) [22], the assessment of dredged material should be based on physical, chemical and biological studies of the collected sediment.

Evaluation of physical properties of sediments helps to determine potential impacts and the need for subsequent chemical and biological testing. Therefore it is strongly recommended to carry out the following assessment:

- sediment characteristics by grain size analysis or exceptionally on the basis of visual determination (i.e. clay/silt/sand/gravel/boulder),
- content of organic matter as total organic carbon,
- density/specific gravity of sediment

The information for chemical characterization allows the measurement of potential impact, and interpreting of available existing sources of contamination (point source or diffuse sources). Chemical analysis should be carried out on the whole sediments (fraction <2.00 mm), or in fine frac-

tion (<0.063 mm). It should be mentioned that fine fraction is recommended for assessing the content of organotin compounds in benthic sediment samples, too [68]. In such cases, the results of analysis of fine grained fraction should be appropriately converted to whole sediment concentrations for establishing total loads in the dredged material. Generally, the analyses of dredged material required the following list of substances:

Primary list:

- trace metals – in all cases,
- polychlorinated biphenyl (PCB), polycyclic aromatic hydrocarbons (PAHs), arsenic – not in all cases (for example, when there are no significant sources of contamination, and sediments are coarse and the content of total organic carbon is low).

Secondary list (it is required in cases when local information about point or diffuse sources of contamination, or historic inputs is available):

- other chlorobiphenyls, organochlorine and organophosphorus pesticides,
- tributyltin compounds, their degradation products, other organotin compounds, and other anti-fouling agents,
- petroleum hydrocarbons, polychlorinated dibenzodioxins (PCDDs)/polychlorinated dibenzofurans (PCDFs).

The biological testing should be conducted on appropriately sensitive and representative species. The required tests were as follows:

- acute toxicity,
- chronic toxicity,
- the potential for bioaccumulation,
- the potential for tainting.

In order to classify the pollution level in dredged spoils actually three cases are used (Recommendation 13/1, HELCOM, 1992) [25].

Case 1. Concentrations of harmful substances are equal or lower than the index values. Such material is considered not contaminated or contaminated at low level. The spoils should not be monitored more frequently than every three years.

Case 2. Concentrations of harmful substances exceed the index values up to five times. Such material is classified as medium contaminated. In this case, full spectrum monitoring should be conducted three years after the previous assessment.

Case 3. Concentrations of harmful substances in dredged spoils are higher than the fivefold index values. Such material is significantly contaminated. Full monitoring should be conducted annually.

Sediment can be stored at sea or on land if it does not pose a threat to the environment (Case 1). In such cases, it is used for beach nourishment and enforcement, enlargement of islands, parks and ports, and for filling roads [51].

Slightly contaminated sediments (Case 2) that do not pose a risk to fauna and flora can also be dumped at sea. In such a case, the quality of both the dumped and receiving sediment is considered. The quality of either the dumped or the receiving sediment can not deteriorate as this could possibly have a negative impact on the living conditions of marine organisms. Moreover, the chemical (pH, redox

Table 3. Uses of TBT in EU countries during 2000-05 [23].

Type of business (NACE or other) and/or mode of application	HELCOM country of confirmed use	Remarks
Antifouling paints / active substance (biocide)	Historical use in all / many HELCOM countries	<b>Main emission source</b> is leaching from ship hulls (still continuing); related main activities that cause emissions are sea ship traffic, shipyards (during removal of old antifouling paints), contaminated harbour sediments/dumping of dredged material (OSPAR, 2000 WFD-EAF 2004)
Diapers (probably as impurity), PVC flooring and vinyl wall-papers (probably as impurity), Earplugs (probably as impurity)	Denmark	Study originates from 2000
Manufacture of regular (non-antifouling) paints / fungicide	Finland	Year 2004, TBT naphtenate, both industrial and consumer use possible
Manufacture of aircraft / marking agent	Finland	Year 2004, TBT oxide, industrial use
Silicon-sealings in buildings	Germany	
Chemical industry/production and wide application of chemical preparations containing TBT	Poland	Year 2003, TBT-naphtenate, -benzoate and chloride, probably mainly industrial use
Rain clothes, glues and sealants used in construction industry	Sweden	Study originates from 2000
Impregnation of wood / biocide	Possible in all EU countries except - use ceased in 1999 in Finland - use ceased in 1990 in Germany	Industrial use more probable than private use (WFD-EAF 2004), biocide use banned in EU in autumn 2006 (Directive, 98/8/EC)
Biocidal (antiseptic or disinfecting) use in applications such as - pillows (RPA, 2005) - canvas, carpets, cuttings (OSPAR, 2000 RPA, 2005) - pharmaceuticals (WFD-EAF 2004) - sponges and shoe insoles (KEMI, 2005 RPA, 2005) - preservative for textile (in back-coating of textiles used in upholstery and in treatment of feather), paper, leather and glass	Possible in all HELCOM countries	Industrial use and consumer end-use possible, biocide use banned in EU in autumn 2006 (Directive 98/8/EC)
Use as intermediate in the production of other chemicals	Possible in all HELCOM countries	Industrial use

potential, etc.) as well as physical (wave action, tides, currents and bottom dynamics) and geological properties (bottom characteristics, sediment type and material transport) of the storage area are also considered. For example, in Great Britain the sediments dredged from the bottom are stored 12 nautical miles away from the coastline if they fall within the defined index values [51]. It should be mentioned that the sediment classified as Case 2 can be cleaned or partially cleaned.

The sediment classified as Case 3 undergoes total remediation. Material whose chemical composition exceeds the allowable index values is dumped at the specially controlled and contained areas, e.g. in The Netherlands at Slufter and Papagaaiabek dumping sites. Under no circumstances should such material be used for environmental improvement projects without a previous removal or reduction of contaminating substances.

In recent years, increasing attention has been paid to highly toxic organotin compounds accumulated in harbor sediments. The significant amounts of these compounds got

– and are still getting – into the harbor water and sediments, particularly during repair and remodeling works, i.e. production and sandblasting of hulls, hull painting and removal of old antifouling paint, and during the regular harbor stays of ships and boats protected with paints based on organotins. The report of HELCOM MONAS (8/2005) [24] provided the information that Danish threshold values for TBT vary from 10 to 250 µg/kg. In Germany TBT contents vary widely, maximum concentrations being 20,000 µgTBT/kg near docks and wharves, and < 5 µg/kg at some coastal sites. In Lithuania the maximum TBT concentration of 82,000 µg/kg was observed near a shipyard. In Finland maximum (normalized) concentration observed was 15,000 µg/kg at a shipyard.

Being aware of the gravity of the problem, some EU countries took the initiative to individually propose the criteria in regard to the admissible TBT content in the dredged spoils (Table 3). Moreover, in Norway the concentrations of organotins in sediment (fraction <2.00 mm) were measured by using the following classification [66]:

Table 4. Classification criteria for the dredged spoils containing TBT [40].

Country	Critical value 1 (target value) (NG SN/G)	Critical value 2 (limit value) (NG SN/G)
Belgium*	3	7
Finland*	3	200
The Netherlands*	7	240
Great Britain**	200	500
Germany**	20	600 (since 2001) 300 (since 2005) 60 (from 2010)

Limit values were established in different ways; however, critical value 1 corresponds to the detection limit. Critical value 2 was determined from the background values of marine samples, and multiplied by 5.

\* per dry weight of sediment, \*\* per sediment mass, \*\*\*sum of TBT, DBT and MBT

class I (good) <1;  
class II (fair) 5;  
class III (poor) 5-20;  
class IV (bad) 20-100  
class V (very bad) >100 (µg/kg d.w.).

Unfortunately, the Polish Regulation of the Minister of the Environment on the types and concentrations of substances causing the contamination of dredged material [11] does not contain indicator values for organotins.

The quality assessment of dredged spoils that contain organotin compounds still remains problematic for many countries. On one hand, it requires detailed physico-chemical and biological studies, and on the other hand, the financial means necessary to implement the system of quality assessment for the organotin-containing spoils. The dredged material classified according to Recommendation 13/1 [25] as low, medium or highly contaminated has to be cleaned of the hazardous substances (Cases 2 and 3). Considering the present remediation process, it is understandable that it raises strong emotions, and is slowly implemented by the governments of specific countries.

High costs of the remediation process are the main reason. At first, contaminants other than TBT are removed from the dredged material; TBT is next. Thermal decomposition takes place in rotating ovens at 450°C. Moreover, the furnace exhaust gases have to be purified and cleaned of sulphur. It has been estimated that removing TBT from 1 m³ of dredged sediment costs from 80 to 100 Euro. In the repair shipyards of Western Europe and the United States the removal of TBT from wastewater is successfully practiced. The treatment results in a significant reduction of TBT concentration from 1 mg·dm<sup>-3</sup> (wastewater concentration after washing the hull) to about 50 ng·dm<sup>-3</sup> (amount in groundwater admissible by US EPA) [40]. If remediation could be improved and additionally the costs

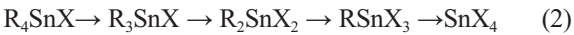
could be lowered the problem of managing the sediments enriched with organotin compounds would be solved, and the implementation of the dredged spoils quality assessment would be facilitated.

Pathways of Butyl- and Phenyltin Derivatives in Marine Environment

Because dredged spoils can be stored at sea it is necessary to pay attention to the behavior of these compounds in the environment under changed conditions. In the case of organotins, salinity, pH value and insolation have significant effect. These factors determine processes in the sea, for example, sorption and desorption, hydrolysis, photolysis, bioconcentration, biodegradation and sedimentation.

Degradation

A sequential removal of the consecutive organic groups from the organotin molecule until reaching a complete metamorphosis into inorganic and non-toxic Sn (IV) can be transcribed as follows [16]:



Degradation takes place under the influence of radiation (light, UV, gamma) and biological as well as chemical factors.

Photolysis is considered the fastest degradation process of organotin compounds in the aquatic environment. It decreases with decreasing light intensity in the water column and sediments [27]. It has been established that photolysis is faster in phenyltin derivatives as compared to butyltin compounds.

The degradation of organotins may also occur as a result of interactions among molecules of nucleophilic and electrophilic character (e.g. organic and inorganic acids and non-metallic ions) and the polarized Sn-C bond of an organotin compound.

The most important mechanism of TBT elimination from sediment is biodegradation [16]. It has been established that biochemical degradation due to microbial activity (i.e. activity of bacteria, algae and fungi) is faster in the water column as compared to sediment. This results from the higher light intensity and better oxygenation of the water column in comparison to sediment. The half-life time of organotin compounds in seawater ranges from a couple of days to a couple of weeks. In the case of TBT, it may reach 15 days, while for DBT and TPHT 10 up to 60 days, respectively [20]. Degradation of organotin derivatives under anoxic conditions occurs at a slower rate so that the half-life time of TBT in benthic sediments has been estimated at 4 months to 8 years [61].

The reversal process to degradation is methylation. Methyltin derivatives form in the marine environment via biomethylation, e.g. biomethylation of inorganic tin by sulphur bacteria which results in the presence of mono- and dimethyltin in benthic sediments [69].

## Physico-Chemical and Geochemical Factors Influencing the Pathways of Organotin Compounds in Sediments

### *Water pH*

Water pH is a controlling factor in the processes of speciation, bioavailability, sorption, desorption and hydrolysis. Depending on pH, organotin compounds may occur in seawater in three different forms, i.e. neutral ion pair, complex or cation [55]. Butyl- and phenyltin derivatives undergo hydrolysis due to pH.

In general, cations form when pH is less than  $pK_a$  of a given derivative ( $pK_a$  - acid dissociation constant), while neutral hydroxyl-complexes (i.e. TBTOH) when  $pH > pK_a$  [28]. The  $pK_a$  value for TBT equals 6.3, while for TPhT 5.2 [6]. This phenomenon plays a significant role in bioconcentration processes in zooplankton. Bioconcentration is at its highest at pH 8 because then 98% of TBT and TPhT occur as neutral molecules, i.e. TBTOH and TPhTOH that have a propensity to accumulate in live tissues [70]. According to Fent and Looser [13], neutral TBTOH molecules can much easier penetrate cellular membranes than the hydrophilic  $TBT^+$  cations. However, in the case of TPhT, the difference is less perceptible. It has been established that the intake of  $TPhT^+$  cation by live organisms is almost the same as that of TPhTOH [70].

### *Salinity*

Salinity is an important factor that determines sorption and desorption processes in the aquatic environment. The salinity increase results in decreased adsorption of organotin compounds onto sediment. The maximal values of TBT adsorption onto clay and other minerals were observed in the freshwater environment [28].

### *Organic Matter*

Both TBT and TPhT adsorb strongly to suspended matter in aquatic environment and end up in sediment [27]. In seawater from 10 to 70% of trisubstituted organotin derivatives are bound to such forms of matter [27]. Sorption of TBT and TPhT onto dissolved organic matter strongly depends on pH and is the most efficient at pH 6 and low salinity. Moreover, it is a fast but reversible process [55]. On the other hand, dissolved organic matter has a propensity to adsorb onto the surfaces of minerals - particularly clay - which helps the TBT transport into the sediment [45]. In general, the increase of organic matter content in sediment results in the increased adsorption of organotin compounds. The sediment-water partition coefficient ( $K_d$ ) assumes very low values for pure minerals with low organic matter content, e.g.  $K_d$  for pure kaolinite is 51 l/kg, while an admixture of 5% organic matter causes the abrupt increase of  $K_d$  up to 2700 l/kg [29].

Sorption of organotins onto dissolved humic substances (DHS) leads to the diminished bioavailability which, in turn, results in a lowered level of bioaccumulation in live organisms. It has been speculated that "TBT-humic acids" complexes are formed during sorption onto humic acids, and that because of their large size and polarity such complexes are not able to cross the biological membranes of live organisms [13].

### *Grain-Size*

Grain-size distribution of sediment significantly influences the distribution of organotins in sediments. As the grain-size decreases, the sediment's surface proper increases the latter being a ratio of total surface area of grains to their mass [52]. This results, inter alia, in the increased adsorption of chemical compounds, including organotin compounds, onto small grain-size material, i.e. grains with a diameter  $<0.063$  mm (increased adsorption onto small grain-size material [38, 62]. This phenomenon plays a significant role in the case of benthic organisms that are not capable of feeding on sediment fractions larger than muddy silt, i.e.  $>0.063$  mm.

Water pH determines, in a significant way, sorption of organotin compounds onto the particles of clay minerals. In the case of tributyltin, adsorption onto montmorillonite and kaolinite is most efficient at pH 6 and 7, respectively [28, 30]. For such pH values, the concentration of TBT ions ( $TBT^+$ ) is the highest because  $pH < pK_a$ . The TBT cations ( $TBT^+$ ) can be easily adsorbed onto negatively charged surface of minerals due to electrostatic interactions.

At pH between 7 and 9 ( $pH > pK_a$ ) adsorption of TBT decreases because of the hydrophobic character of TBT compounds that is less effective than the electrostatic interaction. At  $pH < pK_a$  the adsorption process of  $TBT^+$  is governed by electrostatic attraction, and the decreasing nature of TBT adsorption at pH 4 and 5 is largely attributed to the decreasing negative charge of the clay surface [29].

### *Landscape*

Landscape (bottom profile of the water basin) and hydrodynamics are the other criteria that define the distribution of chemical compounds, including organotins, in sediments. In a natural water basin theoretically there are areas characterized by erosion, transport and accumulation. According to Håkanson [19], the lowest concentrations of chemical compounds are found in the erosion type areas where no noticeable deposition occurs and the processes of washing out dominate. The bottom in such an area is hard and has no propensity for sorption of chemical compounds because of the presence of large grain-size fractions (sand, gravel and rock). Deposition of small grain-size material in the transport type area is temporary. However, the time period in which the material remains may be extended. The bottom of such an area undergoes seasonal changes, and due to redox conditions it is a place of fast reactions of the mobile chemical substances, e.g. phosphorus, nitrogen, magnesium

and iron. The transport type bottom dominates in the open sea part of the Baltic. The terminal deposition of the material occurs in the accumulation type area. It is a place characterized by the increased concentration of pollutants resulting from the accumulation of small grain-size material. Resuspension is a natural phenomenon in this area. Moreover, it should be remembered that in the regime of intensive bottom dynamics the erosion as well as accumulation processes may take place in such an area.

## Conclusions

The development of the shipbuilding industry has led to a significant concentration of organotin compounds in the marine environment. With progressing time, antifouling paints based on organotin compounds have become the main source of TBT and TPhT derivatives loaded into the sea. Thanks to numerous legal sanctions, the inflow of new amounts of these compounds into the marine environment was reduced. However, they still pose a threat to marine organisms. As a result of physico-chemical changes in the water basin the pollutant load accumulated in benthic sediments may undergo diffusion from sediment into the water column, and therefore again become bioavailable. This fact plays a particular role in the case of benthic sediment that originated from dredging of harbor canals. The dredged spoils are stored at sea, where physico-chemical properties of water are different than those in the harbor. In this case, the change in physico-chemical characteristics of water may accelerate the release of harmful chemical species into the sea. Until now, the widely available regulations in regard to managing dredged spoils are still lacking.

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