LIFE02 ENV/B/000341

Development of an integrated approach for the removal of tributyltin (TBT) from waterways and harbors: Prevention, treatment and reuse of TBT contaminated sediments

Layman's Report

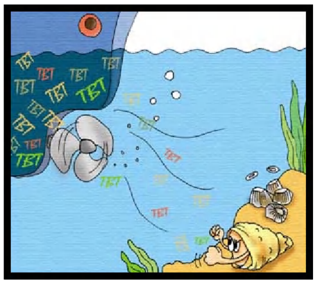
TBT CLEAN

THE INTEGRATED APPROACH

Introduction

Tributyltin (TBT) is probably the best known type of organotin compounds, a class of man-made chemicals composed of a central tin ion (Sn^{4+}) with one (mono-), two (di-), three (tri-) or four (tetrasubstituted) bonds with a carbon group. Due to its strong biocidal properties, it was soon discovered (1960`s) as a very effective and economical additive in ship paints to prevent the adhesion of aquatic organisms to ship hulls, known as fouling.

However, several years after its first use as an anti-fouling agent in paints, the environmental impact of TBT was revealed (late 1970`s – 1980`s): shell deformations in crustaceans, hormone disruptions in molluscs and dogwhelks, growth inhibition of algae, a.o. The latter effects are the result of TBT`s high toxicity, persistence in nature and tendency to adsorb onto sediment particles or be taken up by aquatic organisms. Despite several legal restrictions on its application, ships painted with TBT before the 1^{st} of January 2003 are still allowed to sail the international waters until 2008. At that moment, all TBT-paints must be removed and its use will be absolutely forbidden. However, banning the use of TBT will not entirely solve the problem …



The TBT-Clean project

Along busy ship traffic routes and especially in harbors and marinas, a large amount of TBT has accumulated in the sediments. As such, these sediments have acted as a sink and are a possible source for re-entry of TBT in the environment.

As one of the busiest European ports, the Port of Antwerp inevitably also has to face the sediment TBT-issue inside the harbor docks. In order to find the best ecological and economical solution to handle this problem, the **Antwerp Port Authority (APA)** decided to submit a European LIFE-Environment project proposal entitled `Development of an integrated approach for the removal of tributyltin from harbors and waterways: prevention, treatment and re-use of TBT-contaminated sediments`, in short `TBT-Clean`.

To have all aspects of the project covered, the APA gathered a number of partners with different fields of expertise. The **APA** was responsible for a screening of possible remediation techniques in literature, for contact with other port authorities and ship owners/yards, for dredging within the docks, …
To handle the dredged material and explore different remediation technologies for TBT-removal and reuse of treated material, two world-leading dredging companies - environmental contractors signed up in the project: **Envisan (Group Jan De Nul) and DEC (DEME group)**.

To carry out all the chemical analyses and perform lab-scale feasibility experiments for the different sediment and water remediation techniques, the **Environmental Research Center (ERC)** was also part of the team.

Finally, **APEC- Antwerp Port Consultancy (APEC)** took care as general project manager of e.g. coordination between partners, preparation of the TBT-Clean website and CD-ROMS with project reports, organization of the meetings of the scientific advisory committee, organization of a special session during an international congress on environmental biotechnology and of visits to other European ports as part of the project dissemination …
As an external project manager, responsible for budget survey, planning, task coordination, reporting of project meetings, cost-benefit analysis, ... **Environmental Resources Management (ERM)** was selected, being one of the largest environmental consultants in the world.

Results of the different tasks of the project

Fouling of ship hulls has major financial consequences for sea-going vessels, e.g. increased drag causing ships to slow down, higher fuel costs, regular visits to the shipyards for hull cleaning, ...

Fouling on a tug's hull in the Port of Antwerp

Ever since the negative environmental impact of TBT was proven and its use was restricted, both the shipping and the paint industry have been experimenting with alternative ways to prevent fouling. In order to learn about the current use of TBT-alternatives in other ports, the APA sent out a questionnaire to shipyards, ship owners and paint manufacturers all around the world (**Task 3543: State of the art on TBT-alternatives**).
A statistically sufficient number of answers were received, which clearly showed that the whole industry is aware of the need to switch to other additives in ship paints.

Belgian Navy minesweeper coated with a lining technology incorporating glass platelets into a resin vehicele

Alternatives that seem to be widespread are copper-based anti-foulings and different types of biocides that are less toxic than TBT. These products are commercialized under different names such as Irgarol 1051, Sea-Nine 211, diuron ... However, as more and more studies are published on the presence and (negative) impact of these copper and biocide alternatives in the aquatic environment, a continuous effort is undertaken to propose components that are less persistent and thus can be detoxified in a short period of time after they are released from the hull paint.

Other commercial paints are totally free of chemical agents, and aim at a weaker adherence of the organisms to the ship paint layer by making the latter 'non-sticky' (e.g. by use of silicones). The lower mechanical strength and resistance to damage by rough contact with e.g. quay walls, as well as the difficulties encountered when repairing the damage are aspects of these paints that are currently under study. Most recently, a paint containing small glass flakes in an epoxy matrix showed very promising results and is completely neutral for the environment.
Clearly, this market of anti-foulings is still in great motion to find an ecologically safe and economically sound TBT-replacement.

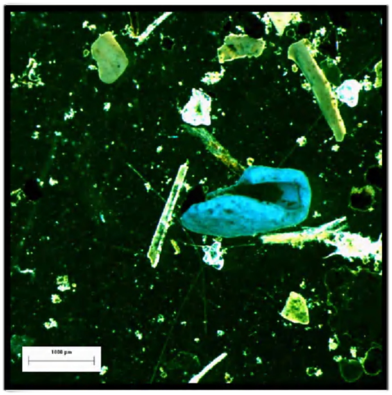
Despite the search for and application of other additives in ship paints, TBT still poses a problem because it is present in harbor and freshwater sediments from where it can either be taken up directly by benthic organisms or indirectly after desorption from the sediment to the water phase by e.g. fish. Therefore, clean up of these sediments is also necessary.

Before actually starting with the remediation tests, a literature review of existing technologies for TBT-removal from sediment and water was made (**Task 3544: Screening of technologies**). A broad range of sediment treatment technologies were described, however most of them were only tested on lab- or pilot-scale: physico-chemical treatment, land farming, thermal treatment, electrochemical oxidation, bio- and phytoremediation.

Of these sediment treatment technologies, thermal treatment and mainly electrochemical oxidation seemed to be promising. On a pilot-scale, the latter degradation process was running quickly (a few hours) and a TBT-removal efficiency of up to 99% or higher was achieved. Based on these experiments, a treatment cost of 15 €/tonne was

For the water phase, treatment techniques were mainly applied to ship repair discharge water loaded with TBT or TBT paint flakes due to high pressure hosing of the ship hull during cleaning. Techniques cited in literature included activated carbon adsorption/filtration, activated sludge treatment, ultraviolet-light oxidation and solvent extraction. The latter two were very promising, being tested on a full-scale: a few hours treatment time resulted in a removal efficiency of 99.9%, with a cost that might be as low as 7 €/m³.

In order to make a decision on which techniques to be used in the TBT-Clean project, the sediment in the port of Antwerp needed to be characterized in detail (**Task 3546: Sediment characterization**). A sampling campaign was organized, during which sediment surface samples were collected at different locations with a Van Veen grab. Prior to analysis, ERC developed a new analytical technique to accurately measure TBT and other organotin compounds, to a level of about 1 mg/kg dry weight (DW) in sediments and 1 ng/L in water samples. All samples were screened for these organotins and for a diversity of other important environmental parameters and contaminants. Average TBT-concentrations in most areas of the harbor were found to be 50-300 µg/kg DW.



Microscopic picture of paint flakes (about 1-2 mm long) in the sand fraction

However, in the vicinity of the former ship repair site, black spots with TBT-concentrations of more than 40 mg/kg DW were found. Three classes of TBT-contamination were composed: low (50-300 µg/kg DW), moderate (1-5 mg/kg DW) and high (30-50 mg/kg DW). Grain size distribution of representative samples of these classes was determined, and they all consisted to a large extent of particles smaller than 63 µm (clay and silt). The sand fraction, and especially the fraction >250 µm was relatively small. However, the latter fraction was highly concentrated in TBT, which was suspected to be due to paint flakes from the dry dock cleaning water. A microscopic examination confirmed this hypothesis: colored particles of about 1-2 mm were clearly distinguished from the inorganic sediment particles. No 'TBT-free' fraction was found, however we did find a correlation between TBT and the content of total organic carbon (TOC) and heavy metals in the fractions. The latter is an indication of a possible adhesion or chemical bond of TBT^+-ions to clay particles and sediment organic matter. The work carried out for this task gave a solid base for later decisions on the possibility of using certain remediation techniques.

In addition, depth profiles of the highly TBT-contaminated sediment near Antwerp ship repair were obtained with a vibrocorer device. The aim was to collect some more information about the sediment characteristics and the contamination (especially TBT, but also other contaminants) along the total depth of the sediment layer and of the original subsoil below the sediment. Since no dredging activities took place at this location during the last 10 years, this extra information could give an idea about the historical contamination of the sediment, degradation processes and possible migration of contaminants from the sediment to deeper layers. In a typical vibrocorer sample of 2.5 meter deep (1.75 meter sediment and 0.75 meter subsoil), the highest TBT-concentration was found at the top of the sediment (~30 mg/kg DW) while at 1 meter deep a concentration of about 7 mg/kg DW was found and at 1.75 meter no more TBT was detected. Also the subsoil was free of TBT. The presence of organotin compounds in the deeper layers most probably originates from his toric pollution.

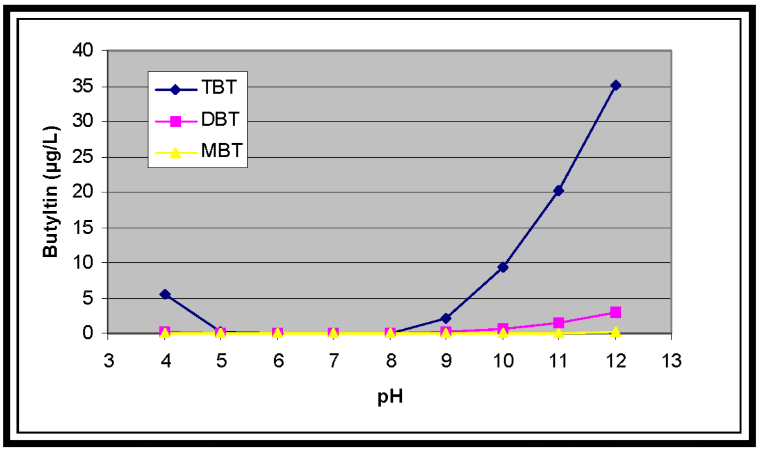
Vibrocorer device and sediment sample showing contaminated upper layer.

The Antwerp Port Authority's precision grab dredger "The Nose" equipped with valves to minimize resuspension, taking a sediment sample.

The TBT-gradient with depth could be an indication that TBT is slowly degraded to dibutyltin (DBT), monobutyltin (MBT) and inorganic tin over time. TBT-migration to deeper sediment layers seems to be very unlikely, theoretically, because of the strong adsorption capacity of TBT to organic material and clay, and in practice, because this would cause a depth profile with a TBT-peak beneath the top layer. Migration of the degradation products however cannot be excluded as they show a different pattern compared to TBT.

In order to obtain contaminated sediment for remediation tests, several dredging operations were carried out. This is one of the activities that poses a potential threat of bringing adsorbed TBT back into the water phase, besides resuspension of sediment material during passage of large ships and dumping of contaminated material e.g. at sea. As one of the goals of the TBT-Clean project was to estimate the release of TBT from the sediment to the water phase **(Task 3545: Release of TBT)** and its relation to the amount of resuspended sediment particles, water samples were taken during dredging and analysed for suspended solids and TBT-content. During a first dredging operation in May 2003, we found elevated TBT-concentrations in the water up to 500 ng/L at suspended solids levels of 150-200 mg/L. However, during three later dredging activities these results could not be confirmed, as no elevated TBT-levels were then found. Also a difference in TBT-remobilisation between two types of dredging equipment (grab dredger versus suction dredger) could not be demonstrated. Despite the significantly higher amounts of suspended solids caused by grab dredging, no TBT-release was measured.

Lab-scale simulation experiments of sediment resuspension in harbour water showed that environmental conditions such as pH, salinity, temperature … have a major influence on TBT-partitioning. Mainly pH is a determining factor whether TBT will remain adsorbed to sediment organic matter and clay particles, or be desorbed to the water phase. Acidic (pH < 5) and alkaline (pH > 8.1) conditions favoured TBT-release, while in between these values TBT remained adsorbed. Also increased temperature and salinity favoured TBT-release. The values obtained during this research are however subject to local sediment characteristics and cannot be extrapolated to other ports with different characteristics.



pH as the main determining factor for desorption of TBT from sediments.

Harbor water characteristics in the port of Antwerp also tend to change quite significantly, due to seasonal variations of temperature and salinity: during summer a smaller amount of fresh canal water enters the docks and more brackish water from the tidal river Scheldt penetrates through the locks, this in comparison with winter conditions. These variations were shown to have a marked effect on TBT-release during resuspension, probably causing the differences in measured TBT-concentrations during the dredging operations.

As a precautionary advice, we concluded that dredging of highly TBT-contaminated sediment in the port of Antwerp when the water pH is above 8.1 in combination with elevated temperature and/or salinity (e.g. during summer), should be avoided. These conditions were only met during the very first dredging campaign of the project (pH 8.3), resulting in a high TBT-release.

The dredged material was subsequently transported to the treatment facilities of both Envisan and DEC for remediation tests. At the start of the project, the applicable treatment techniques were split into two parts: Envisan carried out experiments on physico-chemical treatment and thermal treatment, while DEC concentrated on bio- and phytoremediation and (electro)chemical oxidation **(Task 3550: Treatment of the solid phase)**.

Sediment characterization showed that the sand fraction (>63 µm) in the sediment was fairly limited, but still represents about 35-45% of the volume and furthermore is heavily contaminated with TBT. So, physico-chemical separation of this sand fraction with a subsequent washing step was still considered worthwhile to examine, also because sand is the first fraction that is qualified for reuse. To separate the sand, a ***hydrocycloning*** step was executed. The fraction with a diameter smaller than the 63 µm cut-off point of the cyclone (silt and clay particles) still contained most part of the TBT, however in a reduced volume to be treated afterwards. The sand fraction, also containing the paint flakes, was further treated with two different techniques: pilot-scale ***density separation*** and lab-scale ***flotation***. Clean-up efficiencies of 60 to 65% were achieved.

Since the lab-scale experiments on TBT-release to the water phase showed that elevated pH results in TBT-desorption, this characteristic was used as a possible remediation technique. On a lab-scale, this ***'chemical washing'*** worked very well at low suspended solids concentrations of only a few grams per liter (>80% desorption at pH 12). At higher amounts of suspended solids, this efficiency rapidly decreased. Pilot tests where the pH of the sediment-water mixture was increased to 12 and higher by addition of lime, confirmed these lab-scale results. Mixing intensity and duration were varied for several dry matter contents, with the aim of maximum transfer of TBT from the sediment to the water phase (being easier to treat). However, the highest TBT-release achieved only amounted 30% and therefore this technique was not sufficient for remediation.

Other techniques that were tested aimed at breaking down and removal of TBT. Lab-scale tests confirmed the theory of stepwise debutylation, which was postulated also in literature. During this breakdown process the TBT molecule loses one butyl group at a time, and is converted to DBT, MBT and finally harmless inorganic tin. One of the methods to accomplish this conversion is ***chemical oxidation***. In this technique, a strong oxidizer is added to a sediment-water mixture, which reacts with TBT to form inorganic tin. One example of such a chemical is potassium permanganate ($KMnO_4$), a well-known and often-used chemical oxidizer for soil treatment. Despite the fact that TBT was indeed removed from the mixture, this technique was not considered appropriate due to unpredictable side reactions with the organic matter present in the sediment. The latter is a consequence of the non-selectivity of such a chemical oxidizer. Furthermore, the resulting sediment-water mixture proved difficult to dewater and the sediment can not be reused.

As an alternative, ***electrochemical oxidation*** was considered to decompose TBT. Aggressive chemical radicals containing a.o. chlorine and oxygen are produced on the electrodes of the reactor by sending an electrical current through the watery suspension of sediments. This technique was already tested in another LIFE-Environment project by a research group in Hamburg, and showed promising results. Pilot-scale testing on sediment from the port of Antwerp confirmed these results, but due to the inherent production of toxic chlorinated compounds from oxidation of chlorides in the electrolysis reactor and major safety issues, this technology was not considered to be economically and technically feasible on a commercial scale.

Lagooning of sediments: test field

Another class of remediation techniques that was tested is based on (micro)biological breakdown of organotins, also referred to as ***bio- and/or phytoremediation***. In this technique, dredged sediment is spread out over a large area and is first dewatered by ***lagooning*** (natural removal of water by drainage and evaporation). As the sediment gets more and more oxidized, aerobic bacteria actively oxidize organic material in the sediment, including TBT. If needed, extra nutrients such as nitrogen and phosphorus are supplied to stimulate the indigenous bacteria. External bacterial inocula with known TBT-degradation capabilities can be added.

The advantage of such a technique is its low investment cost and the large quantities (thousands of cubic meters) that can be treated at once and simultaneously in a layer of about 1 meter thick). Disadvantages are the required land space and long treatment times as a period of about six months of West-European summertime weather conditions are needed. Both lab-scale as field experiments showed promising TBT-removal efficiencies of up to 70%. Higher efficiencies can be obtained in warmer and drier climates, making this technique very interesting in (sub-)tropical areas.

Bioremediaton: test field

Test site of phytoremediation

Phytoremediation is the use of plants to remediate soil or sediment (e.g. willow trees for metal extraction). In the TBT-framework, a diversity of plants (barley, sorghum, grasses …) was tested. In order to get the plants growing, the sediment needed to be lagooned first. Some plants grew very well on the TBT-contaminated sediment, however TBT-extraction and accumulation in the plants was not observed. The only measurable effect of the plants was an enhanced microbiological activity around the plant root system, improving bioremediation.

A last technique that was considered is ***thermal treatment***. Lab-scale orientation tests showed that elevated temperatures rapidly remove TBT from the sediment via stepwise debutylation. At 450°C, a residence time in the oven of 15 minutes was already sufficient for complete removal of TBT and its breakdown products. Dewatering prior to heating significantly improved the TBT-removal. Indeed, the moisture content of the sediment is a determining factor for the kinetics of the process as water needs a lot of heating energy to be vapourized and temperature will only rise to temperatures above 100°C once all water has been removed. Because the dredged sediment from the port of Antwerp contained about 50 to 70% water, a dewatering step prior to thermal treatment was absolutely necessary. This was done by mechanical dewatering with a filter press. The resulting cake had a dry matter content of around 65-70 % and was treated in a full-scale thermal desorption unit at a rate of 22 tonnes per hour at different temperatures between 300 and 450°C. Removal efficiencies of more than 99 % were achieved at 450°C, with also complete degradation of other organic contaminants such as mineral oil. For the highest contaminated sediments (concentrations of 50 mg TBT/kg DW and more), this technique proved to be the only applicable remediation technology to obtain very low residual TBT.

At least two classes of remediation technologies needed a dewatering step to improve the kinetics of the process. Especially mechanical dewatering where lime (CaO) is added to improve dewaterability, resulted in a filtrate water with a high pH (>12) and strongly enriched in TBT.

Full-scale thermal treatment installation

A number of water treatment techniques were tested (**Task 3551: Treatment of the aqueous phase**), such as ***activated carbon (AC)*** filtration/adsorption and chemical oxidation. The effectiveness of AC was shown both on lab-scale and on full-scale. TBT is readily adsorbed from the water phase, with a higher efficiency around neutral pH and higher surface area (smaller sized AC particles). However, the AC technique still needs post-treatment for complete removal of TBT, which is also the case for the gas phase when TBT is stripped out of the water with air.

Contrary to activated carbon, which causes a shift of TBT from the water to a solid phase, ***chemical oxidation*** destroys TBT to less toxic products in one single step. High-energy ultraviolet (UV) light, ozone, $KMnO_4$ and combinations of these oxidants were applied to remediate the contaminated water. Ozone and a combination of $KMnO_4$-UV proved to be the most efficient method to remove TBT. Factors such as safety, economics, residuals … should be taken into account when deciding on which treatment technique to use.

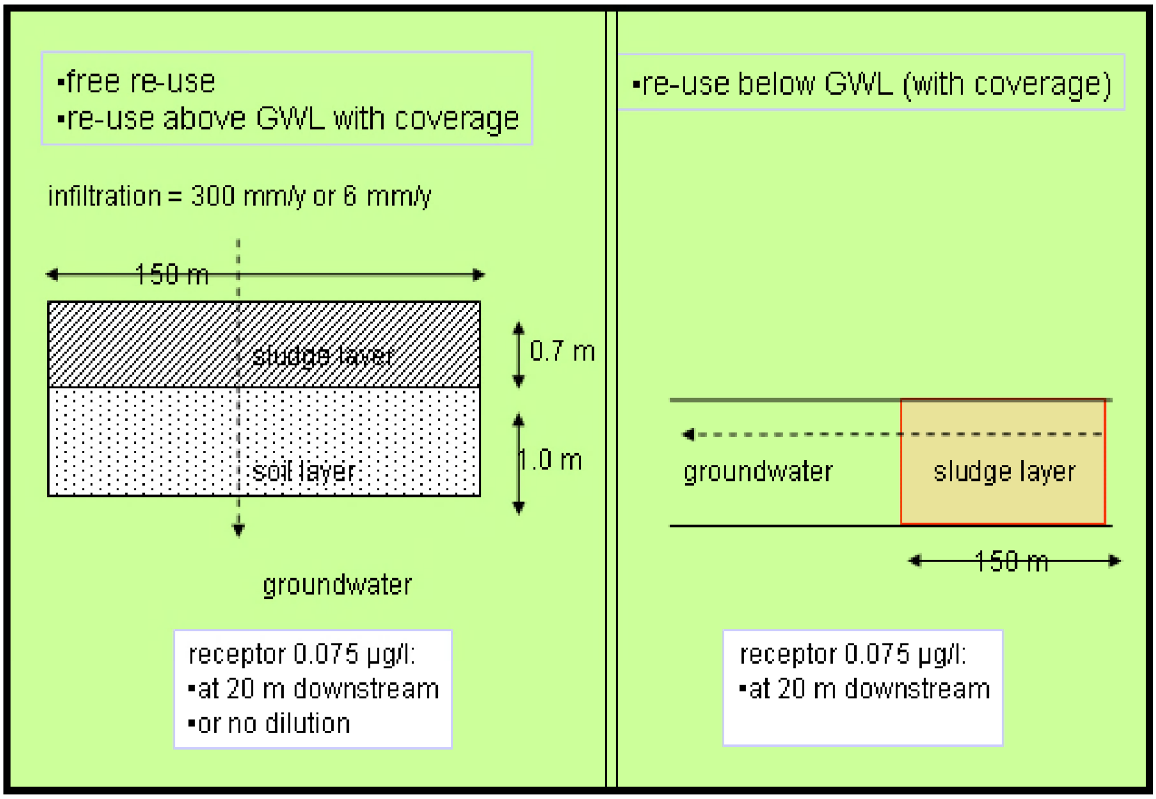
Re-use of treated sediments

Treated sediments need to meet certain criteria before they can be reused as construction material according to the Flemish Regulation for Waste Management (VLAREA). In the last technical task of the project (**Task 3553: Reuse of cleaned sediments**), thermally treated and lagooned/bioremediated sediments were evaluated for their mechanical properties, such as optimal moisture content for compaction, shear strength, plasticity … A series of lab-scale and on-site field tests were performed, and the thermally treated sediment was shown to be easily reusable for land raise, without any need for stability-improving additives. The bioremediated sediment seemed to be immediately applicable e.g. as backfill material.

Besides the mechanical properties, the chemical properties will mainly determine the possible destination of the treated sediment when brought on land. As no Flemish regulation exists regulating the reuse TBT-contaminated sediment on land, the TBT-Clean partner DEC asked VITO (Flemish Institute for Technological Research) to perform an ecotoxicological study and derive a set of threshold ***reuse criteria***. Additionally, specially designed leaching tests were carried out to estimate the TBT-leaching from the clean(ed) sediment samples. Re-use criteria were determined for the following applications:

- free re-use of sediments;
- restricted re-use, with a coverage of clean material and above ground water level;
- restricted re-use, below ground water level

As VITO is the official institute for determination of quality criteria in Flanders, this study could serve as a baseline for the development of a European regulatory framework regarding quality assessment for organotin in sediments with respect to their reuse on land.



Scenario's for which re-use criteria have been determined.

To finalize the project, all remediation techniques were compared with respect to their efficiency, treatment time, treatment space, costs … in a **cost-benefit analysis (Task 3554)**. The preferred technology will mainly be determined by the initial TBT-content and the required final clean-up level. Sediment dewatering and disposal in a landfill, being the current remedy for dredged sediment impacted with TBT, served as a baseline reference for costs. When highly TBT-contaminated sediments need to be cleaned, or when sediments need to be cleaned to very low residual TBT-levels, dewatering and thermal treatment seem to be the only available option. A valuable advantage of this technique is that it also removes other organic pollutants that may be present in the sediment. However, the elevated cost of this technology may be a limiting factor when large amounts of sediment need to be treated.

When low or moderately contaminated sediments need to be treated, lagooning/bioremediation seems to be a promising and cost-effective technique. However, disadvantages are the long treatment times and needed land area for spreading the sediment. In case these low or moderately contaminated sediments have a high sand fraction and low concentration of inorganic compounds in the fine fraction, a combination of hydrocycloning, chemical washing of the sand fraction and thermal treatment of the fine fraction could be an alternative. In case the fine fraction is polluted with e.g. heavy metals, dewatering and disposal of this fraction is required instead of thermal treatment.
Other 'hard' treatment techniques such as chemical or electrochemical oxidation with mechanical dewatering are potential alternatives for treating low and moderately contaminated sediments but have considerable disadvantages. Chemical oxidation in most cases requires a large amount of chemicals to be added and safety measures to be taken. Electrochemical oxidation generates highly toxic chlorinated organic compounds, especially when treating harbor sediments with considerable amounts of chloride. As the end-product could be even more toxic then the original material, this technique is not considered an applicable alternative.

Cost per ton (€/t) and Remedial Efficiency (%)

	Thermal	HC & Thermal	Dumping	Electrochemox	Chemox	Lagooning/Bio
Cost (€)	180	150	140	115	95	80
Efficiency (%)	99	80		80	90	70
Re-use suitability of end product	Yes	Yes	?	No	No	Yes

Comparision of cost, remedial efficiency and reuse possibility of end product for each remediation technique.
If a 70 % remedial efficiency is required, all techniques meet this criterium. If more than 95% is required, only the thermal treatment complies

Transferability of projects results

Port authorities and other authorities responsible for rivers, canals, bays and other water surfaces will read the final report with utmost interest in order to adapt the concept of maintenance dredging.

They can furthermore optimise the remediation techniques to implement in order to realise an overall treatment procedure of contaminated sediments.

Nevertheless, it has to be stressed that the obtained results apply mainly to the specific environment of the Port of Antwerp (e.g. brackish water, high content of organic material in sediment, small sand fraction) and that certain results (e.g. release of TBT as a function of pH) depend of this composition. These kinds of sediments, partly sand, partly silt, are to be found in a large area of river deltas in western and northern Europe and also in parts of the Mediterranean and the Black Sea.

Depending on the characteristics of the sediment to be treated (grain size distribution, organic content, salt content, pH) and the proposed reuse, an appropriate combination of the different techniques that have been investigated can lead to an adequate method of treatment. The present study provides numerous elements in order to select an optimised combination of treatment methods.

Discussion of project results with other port authorities

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