**Research Articles**

**TBT-contaminated Sediments**

Treatment in a Pilot Scale

*Dedicated to Prof. Dr. Ulrich Förstner on his 65th birthday*

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**Abstract**

Background, Aims and Scope. Sediments in harbours and nearby shipyards demonstrate widespread contamination with tributyltin (TBT). Therefore, reuse and relocation of dredged material from these locations are prohibited. Even if the International Marine Organization (IMO) convention concerning TBT-based paints is ratified (Champ 2003) the TBT problem in sediments will continue to remain for many years due to the persistence of TBT.

Methods. An electrochemical process has been developed to treat polluted sediments. Dredged materials with high and low TBT-contents were studied on a technical and a pilot scale. The treatment process was assessed by chemical analysis and a biotest battery. Additionally, an economic analysis was performed to check the economic feasibility of the process to treat dredged material from two different locations at different operating conditions. Furthermore an up-scaling estimation was performed to evaluate treatment costs at a larger scale, i.e. for a plant having a capacity of 720,000 t/a.

Results and Discussion. Butyltin species and polycyclic aromatic hydrocarbons (PAH) were decomposed due to electrochemically-induced oxidation, while the treatment did not alter heavy metal and PCB concentrations. The bacteria luminescence test indicated a reduced toxicity after the electrochemical treatment, while the algae growth inhibition test and bacteria contact test did not confirm these results. Based on a small consumer price of € 0.12/kWh, treating the high-contaminated sediment in the pilot plant would cost € 21/m³ and € 31/m³ for the low contaminated sediment, respectively. Assuming an industrial consumer price of € 0.06/kWh for electricity in an up-scaled process with a capacity of 720,000 t/a, the total treatment costs for the low contaminated sediment would be € 13/m³.

Conclusion. The results of treating dredged material from Bremerhaven and the fine-grained fraction from the METHA plant show that the effectiveness of the process performance is more related to the binding form and sediment composition than to the initial concentration of TBT. The electrochemically treated material complies with chemical criteria for relocation of dredged material, but post-treatment, e.g. washing and/or reduction of remaining oxidants with Fe-III-salts, is needed to fulfil ecotoxicological criteria for relocation.

Economic investigations have shown that the electrochemical treatment might be a technical option to treat TBT contaminated, dredged material. However, the technique is not fully developed and cannot remove all chemicals of concern, e.g. heavy metals. The decision as to whether this technique can be applied is site-specific and should be taken based on the case-by-case approach.

**Recommendation and Outlook.** Since biotests integrate the effects of all contaminants present in a sample, process-accompanying evaluation procedures need additional assessment methods such as TIE (toxicity identification evaluation) as a second tier following ecotoxicological tests, in which the reasons for the effects are identified. For reasons of sustainability, a much more effect-oriented and long-term cost effective approach should be applied in future to avoid the release of harmful substances into the environment. Life cycle assessment should be carried out to identify and quantify impacts of sediment treatment processes in order to take into account both the distant effects of local actions and local effects of distant actions.

**Keywords:** Biotests; cost calculation; dredged material; electrochemical treatment; heavy metals; PAH; pilot plant; sediments; tributyltin

**Introduction**

TBT is used as an additive in antifouling paints to avoid growth of microorganisms and larger species on submerged ship surfaces. Due to reduced fuel consumption this, on one hand, is an economic and environmental benefit (Evans 1999); on the other hand, impacts on marine organisms such as intersex and imposex of snails are found as widespread phenomena caused by organotin compounds, in particular by TBT (Evans et al. 2000). Commercial cargo shipping and local ferry-traffic are important tributyltin (TBT) sources as well as untreated or insufficiently treated wastewater from shipyards, which are the most important point sources (Strand 2003).

TBT is one of the most toxic anthropogenic substances for aquatic organisms because of its endocrine properties, but also antibiotic effects are being discussed (Oehlmann 1996). Organotin compounds are distributed ubiquitously in the marine environment (Michel et al. 1999, Biselli et al. 2000).
TBT and other butyltin compounds are persistent (Ritsema et al. 1998), bio-accumulat-ing in the marine environment (Rouleau et al. 1999), and enriched in molluscs, fishes and mammals (Belfroid et al. 2000, Caricchia et al. 1991).

Human health risks due to consumption of contaminated seafood and the necessary length of exposure are still unknown. Due to their persistence organotin compounds accumulate in sediments and TBT is therefore mentioned as a priority hazardous substance in the European Water Framework Directive (WFD). Although the use of antifouling paints containing TBT has been banned since 2003, the problem of sediment contamination still remains and endangers the quality of marine and estuarine environments.

To ensure the depth of rivers and navigation channels for harbour access, large amounts of TBT-contaminated sediments have to be dredged in Hamburg, but also in other important harbours in Europe such as Rotterdam, Antwerp and Bremen. Usually sediments from navigation channels show relatively low TBT values compared to sediments in harbour areas, especially close to dockyards. The preferred (cheapest) option is to relocate those sediments, but this praxis is frequently prohibited by its TBT-content. So other technical methods must be developed to treat such polluted material.

The aim of the described electrochemical process is to decompose TBT. Initial experiments were conducted in a laboratory cell, followed by investigations on a technical scale and later on in a pilot plant. Here, results for two sediments from different scales are discussed. A high-contaminated sediment originated from the METHA-plant, a mechanical separation plant operating on a large scale in Hamburg. This material was treated on a technical scale. The second, lower contaminated sediment originated from Bremerhaven and was treated in the pilot plant.

Cost calculations were conducted to evaluate the economical suitability of this technique. For quality assessment, chemical sediment analyses which have been done to a large extent during the last years cannot be used exclusively because there is still only little information on the toxicological effect of surface bound contaminants, of cross contamination and modes of action on organisms. For integrated assessment, Chapman et al. (1992) proposed a ‘Sediment Quality Triad’, a combination of data about sediment chemistry, ecotoxicity and resident community alterations. Biotest combinations are suitable to assess the quality of sediments by considering major uptake routes, i.e. direct uptake from the water column during relocation and uptake by contact with sediments and/or ingested sediments.

1 Electrochemical Oxidation

1.1 Principle

Organotin compounds have a central tin atom linked to four or less organic groups like phenyl or butyl with hydroxyl or chloride as an anion. The principle of the electrochemical treatment is to generate highly reactive radicals or oxidizing species at the electrodes which are able to destroy the linkage between the central tin atom and the organic substituents. Water is decomposed by electrolysis, and hydrogen and hydroxyl radicals are formed contributing to the decomposition of organic and metal organic compounds. Additionally, chloride is oxidized at the anode to chlorine that reacts to hypochlorite with hydroxyl ions formed at the cathode. Hydrogen peroxide and ozone are also formed in lower concentrations.

The most important reaction mechanisms are:

\[
2 \text{(C}_4\text{H}_9\text{)}_3\text{Sn}^+ + 3 \text{OCl}^- + 2 \text{O}_2 + 3 \text{H}_2\text{O} \\
\rightarrow 2 \text{SnO}_2 + 6 \text{C}_4\text{H}_9\text{OH} + 3 \text{Cl}^- \quad \text{oxidative reaction}
\]

\[
(C_4H_9)3Sn^+ + 4 Cl^- + H_2 \\
\rightarrow SnCl_4 + 3 C_4H_{10} + 2 HCl \quad \text{reductive reaction}
\]

1.2 Technical realisation

1.2.1 Technical plant

The storage tank had a volume of 2 m³ and the electrolysis cells a free volume of 30 l. IrO₂-anodes and steel cathodes with approximately 1 m² surface area were used. The power supply could provide a current with a maximum of 300 A and a voltage of 20 V. The operating conditions in the technical plant are summarized in Table 1.

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Technical plant</th>
<th>Pilot plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density [A/m²]</td>
<td>76</td>
<td>66</td>
</tr>
<tr>
<td>Anodic area installed [m²]</td>
<td>3.3</td>
<td>68</td>
</tr>
<tr>
<td>Voltage [V]</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Sediment residence time [h]</td>
<td>1.14</td>
<td>0.85</td>
</tr>
<tr>
<td>Electricity consumption of peripheries [kW]</td>
<td>5.5*</td>
<td>6.77</td>
</tr>
</tbody>
</table>

* Calculated from the pilot plant without degassing unit

1.2.2 Pilot plant

The plant was placed in two standard-containers (each 12.0 m x 2.3 m x 2.4 m). A longitudinal wall was removed from one site of each container and the remaining pieces welded together. This allowed a compact construction. The layout of the pilot plant is shown in Fig. 1.

The dredged material was mixed with water to get a pumpable suspension in a 4 m³ mixing tank. After separation of coarse material, the suspension was pumped into a reaction tank. The feeding was time-interval controlled and additionally secured by level sensors. The three electrolysis cells were fed from the mixing tank. Each cell contained 15 anodes and 16 cathodes aligned alternately. The suspension was pumped up-stream into the electrolysis cells, treated, and left the cells through a free overflow. The electrodes were contacted with copper bars and connected with a power supply. Decomposition of TBT occurred within the cells. After the electrochemical treatment, the suspension was transferred into a tapered sedimentation basin, where solid/