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Reduction of Tributyltin (TBT) and Other Organic Pollutants of Concern in Contaminated Sediments by means of an Electrochemical Oxidation

In contaminated sediments butyltin compounds and PAH can be diminished by means of an electrochemical treatment. The butyltin concentrations of the fine fraction (particle size < 20 µm) of a mechanical separation unit were reduced from 350 µg/kg to < 10 µg/kg for tetrabutyltin (TeBT), from 2600 µg/kg to < 30 µg/kg for tributyltin (TBT), 380 µg/kg to < 100 µg/kg for dibutyltin (DBT), and from 570 µg/kg to < 100 µg/kg for monobutyltin (MBT), respectively. Furthermore the sum of PAH concentrations for 16 PAH descended approximately 90 % during a residence time in the electrolysis cell of 3 h, while in contrast PCB concentrations remained the same before and after the treatment. Apparently, the presence of PCB limited the application of this process, if the initial concentration exceeded guideline values for relocation. Further investigations have to be undertaken to clarify this point. Nevertheless the promising results obtained from a technical treatment unit have led to the construction of a pilot plant, which is installed in Bremen and operating since the beginning of 2002.

Research Paper

Verminderung der Konzentration von Tributylzinn (TBT) und anderen relevanten organischen Schadstoffen in kontaminierten Sedimenten mittels elektrochemischer Oxidation

Durch elektrochemische Oxidation können die Konzentrationen von Butylzinnverbindungen und PAK in kontaminierten Sedimenten vermindert werden. Die Konzentrationen von Butylzinnverbindungen aus der Feinkornfraktion (< 20 µm) einer mechanischen Sedimentbehandlungsanlage wurden von 350 µg/kg auf < 10 µg/kg Tetrabutylzinn (TeBT), von 2600 µg/kg auf < 30 µg/kg Tributylzinn (TBT), von 380 µg/kg auf < 100 µg/kg Dibutylzinn (DBT) und von 570 µg/kg auf < 100 µg/kg Monobutylzinn (MBT) verringert. Außerdem verringerte sich die Summe von 16 PAK um ca. 90 % innerhalb einer Verweilzeit von 3 h in der Elektrolysezelle. Im Gegensatz dazu blieb die Konzentration der untersuchten PCB konstant. Vermutlich begrenzt diese Schadstoffklasse die Anwendung des Verfahrens, wenn die Ausgangskonzentration im Sediment über den für eine Umlagerung relevanten Grenzwerten liegt. Weitere Untersuchungen sind notwendig, um die Grenzen der Anwendung dieses Verfahrens zu untersuchen. Aufgrund der vielversprechenden Ergebnisse mit der Technikumanlage ist eine Pilotanlage konstruiert und gebaut worden. Die Anlage wird seit Anfang 2002 in Bremen betrieben.

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1 Motivation

Tributyltin (TBT) is used as additive in antifouling paintings. Inhibition of microbiological growth on underwater ship surface reduces fuel consumption. This is a desirable economic and ecological benefit [1]. But the usually applied self-polishing paintings cause a permanent release of organotin compounds into the environment [2]. Therefore significant concentrations of TBT can be found in harbour and harbour navigation channel originated sediments but also in sediments from freshwater lakes [3]. TBT has endocrine properties [4, 5], and is like PCB and DDT persistent in sediments and accumulates in the food web [6, 7].

Hamburg and Bremerhaven are the most important harbours in Germany and located in the north of Europe. To ensure the depth of navigation channels in these both harbours 1.5...2 Mio m³ sediment have to be dredged every year and approximately 1.3 Mio m³ of this dredged material has an organotin contamination above 100 µg/kg. In Bremerhaven the dredged material is disposed on land and in Hamburg after mechanical separation, too.

Recently TBT has been defined as hazardous priority substance within the European water framework, which means that its emission has to be reduced to zero within one generation or approximately 20 years. At present there is no official limit value for TBT in sediments, but in practice nobody would get a permission for dredged material relocation in Germany with a TBT concentration above 100 µg/kg (related to dry weight).

TBT ban will pose a legacy problem after transferring the framework into national laws or guideline values. At present no economically acceptable treatment method apart land filling is available. Efforts were undertaken by Belgium [8] and Germany [9] to reduce organotin and especially TBT applications by national laws. Belgium wanted to ban all organotin antifouling paintings from 2003, which stays in agreement to international negotiations through the international marine organisation (IMO). Both efforts are rejected by the EU [10]. It seems that to realise a ban of TBT takes some time and an interim solution is needed until TBT release into the environment disappears.

Our approach is to use an electrochemical sediment treatment process, which might become an alternative to the common practice. For the investigations we used fine fraction from a mechanical sediment separation unit in Hamburg. After separation of coarse material like bikes, cars, stones, or tires, the dredged material is classified into three main fractions within this plant:

1. Sand
2. Fine sand
3. Silt/fine silt

The silt fraction is usually relatively highly contaminated with all kinds of pollutants and therefore the most challenging material for a decontamination process. This fraction is chosen to verify former results from laboratory experiments and to ensure that those results are transferable in the up-scaling process. Due to the abrasive properties of sediments special requirements for the electrode materials are needed:

– Mechanical stability
– High yield of oxidising species
– No dissolution as anodes
– The material itself must be non-toxic.

Titanium modified metal oxide electrodes can perform such requirements [11]. New developments with doped carbon electrodes are very promising [12], but these electrodes are just recently commercially available in a larger scale.

The principle of the electrochemical treatment is to generate highly reactive radicals, or oxidising species at the electrodes, which are able to destroy the bonding between the central tin atom and the butyl ligands. This is possible on an oxidative as well as on a reductive pathway [13]. As probable products inorganic tin, butanol, and/or butane will be formed. Also organics, especially aromatic compounds, are oxidised by electrochemically generated radicals [14, 15].

The electrochemical process for sediment treatment has been mentioned by Stichnothe et al. [16]. Further investigations by the same authors have shown that the main process parameters are current density and chloride concentration [17]. This is in agreement with results from Comninillis [18], who investigated the oxidation of phenol in presence of chloride, and from Kraft et al. [19] concerning drinking water disinfection. Besides butyltin decomposition, behaviour of organics, e.g. PAH, PCB, and mobility of heavy metals influenced by the electrochemical treatment are of great interest for the application and assessment of the process, because these parameters are also relevant for the relocation of treated sediments. As neither the concentration of heavy metals nor their mobility behaviour change due to the treatment [17], only PAH, pesticides, and PCB will be discussed in this paper.

Mailhot et al. [20] described the photo-induced degradation of TBT in water, identified most of the photoproducts, and proposed a hydroxyl-radical based mechanism. In the early stage of the degradation of TBT, DBT and MBT occur as intermediate products. After long irradiation time they just detected inorganic tin, mainly SnO_2, remaining in solution, besides determination of carbon dioxide formed by oxidation of butyl groups was in very good agreement to theoretical calculations.

2 Materials and methods

2.1 Samples

The sample was taken from a mechanical sediment separation unit in Hamburg (METHA) and originated from a location

in Hamburg Harbour. The size fraction < 20 μm was selected for further treatment.

2.2 Analytical procedure

For organotin and organic analysis the samples were centrifuged and freeze-dried. The analysis of organotin species was conducted by in-situ derivatisation of the organotin cations with sodium tetraethylborate (NaBEt$_4$) after acidifying and extraction with *n*-hexane. The hexane extract was cleaned up with silica gel and concentrated to a small volume. Tripropyltin and tetrapropyltin were used as internal standards. A GC-AED (HP 6890 GC-HP G 2350 AED) system was used for determination of organotin species. Analyses were conducted in duplicates and average values were denoted. Detection limits according to DIN 32645 for the butyltin analysis are shown in Table 1.

Table 1: Detection limits for butyltin analysis.

Nachweisgrenzen der Butylzinnverbindungen.

	Detection limit, μg/kg	Confidence interval, μg/kg	
		lower	upper
MBT	3.0	1.8	7.2
DBT	11.2	6.9	27.4
TBT	6.6	4.1	10.0
TeBT	7.8	4.8	19.0

For PAH analysis 4 g dry sediment were treated with *n*-hexane/dichloromethane (ratio 1 : 1) 6 h in a Soxhlet extractor. The extract volume was reduced to 2 mL by a rotary evaporator. The samples were analysed in duplicates with a GC-MS (HP5890II – MSD 5971A) system.

For PCB analysis 4 g dry sediment were extracted with *n*-hexane in a Soxhlet extractor for 6 h. The extract was cleaned up with silica gel and silver nitrate. After concentration to 2 mL with a rotary evaporator, measurements were conducted as duplicates using a GC-ECD system of Perkin Elmer.

Chlorobenzenes and pesticides were analysed after extraction similar to the procedure for PCB, but using *n*-hexane/diethyl ether instead of just *n*-hexane. The determination was conducted with the same system as for PCB.

2.3 Electrolysis

Based on experiments in a laboratory cell the experiment was conducted in a technical scale. The storage tank had a volume of 2 m^3 and the electrolysis cell a free volume of 30 L. IrO$_2$ anodes and steel cathodes with approximately surface ratio of 1 : 2 were used (anode area 2 m^2). The power supply could deliver a current of maximum 300 A and a voltage of 20 V. To maintain the sediment in suspension a stirrer was needed. The process scheme is shown in Figure 1.

In order to enhance conductivity NaCl addition is needed for freshwater sediments, while marine sediments usually contain sufficient electrolytes. After suspension in 0.5 M NaCl solution the sediment was transferred upwards into an electrochemical cell and circulated by pumping in the electrolysis cell to examine different residence times. The experiments were carried out with current density at the anodes of 80 mA/cm^2.

3 Results and discussion

Only butyltin species were found in the fine-grained sediment from the mechanical separation unit in Hamburg, phenyl tin and cyclohexyltin compounds could not be detected. This clearly indicated the origin of the contamination which was
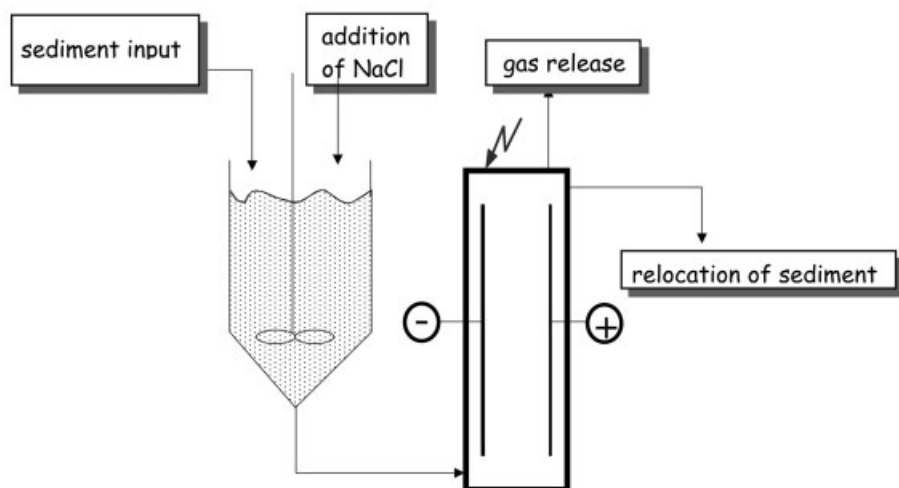

Fig. 1: Scheme showing the process for slurry electrolysis.

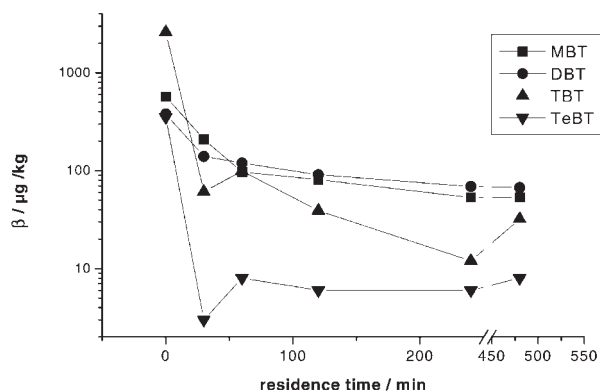Prozessschema der Suspensionselektrolyse.

Fig. 2: Electrochemical decomposition of butyltin compounds in sediments.

Elektrochemische Zerstörung von Butylzinnverbindungen in Sedimenten.

not caused by agricultural input in the Elbe River or any other diffuse sources, but based on the use of antifouling paintings on submerged ship surface. In non-optimised experiments conducted in a technical scale, the butyltin concentrations could be reduced in the dredged material from 350 µg/kg to

< 10 µg/kg TeBT, from 2600 µg/kg to < 30 µg/kg for TBT, 380 µg/kg to < 100 µg/kg for DBT, and from 570 µg/kg to < 100 µg/kg for MBT, respectively. All butyltin compounds could be destroyed by means of electrochemical sediment treatment below the relocation criteria in Germany of < 100 µg/kg.

TeBT and TBT, which show a stronger +I-effect are decomposed faster than DBT and MBT. The decomposition of the pollutants occurs due to electrophilic attack of oxidising species, e.g. hydroxyl radicals, hypochloride, ozone which are generated electrochemically. It is well known that those generated species react favourably with electron-rich compounds [20, 21 and cited publications therein]. So our hypothesis stays in good agreement with the common knowledge of electrochemical oxidation of organic compounds. The real mechanism cannot be investigated in such multi-component systems. Further investigations with model systems will have to be undertaken to elucidate the mechanism. The results of the electrochemical butyltin decomposition are depicted in Figure 2.

Next to TBT, we have investigated 16 PAH in the sediment before and after electrochemical treatment. All PAH are present in the dredged material. An overall decomposition rate of approximately 90% could be achieved; this is reflected by the sum of all PAH, which are reduced from 4.1 mg/kg to

Table 2: Mass fractions of PAH in the sediment.

Massenanteil der PAK im Sediment.

Mass fraction, mg/kg	Residence time			
	$t = 0$ min	$t = 30$ min	$t = 60$ min	$t = 120$ min
Naphthalene	0.23	0.67	0.54	0.18
Acenaphthylene	0.05	<0.03	<0.03	<0.03
Acenaphthene	0.06	<0.03	<0.03	<0.03
Fluorene	0.13	0.03	0.03	<0.03
Phenanthrene	0.48	0.10	0.08	0.05
Anthracene	0.16	0.04	0.03	<0.03
Fluoranthene	0.60	0.13	0.10	0.06
Pyrene	0.51	0.08	0.06	0.04
Benz[*a*]anthracene	0.28	0.06	0.04	<0.03
Chrysene	0.34	0.08	0.06	0.04
Benzo[*b*]fluoranthene	0.41	0.10	0.07	0.04
Benzo[*k*]fluoranthene	0.17	0.09	0.05	<0.03
Benzo[*a*]pyrene	0.26	0.05	<0.03	<0.03
Indeno[1,2,3-*cd*]pyrene	0.15	0.04	<0.03	<0.03
Dibenzo[*a,h*]anthracene	0.09	<0.03	<0.03	<0.03
Benzo[*ghi*]perylene	0.17	0.04	<0.03	<0.03
Sum PAH	4.1	<1.6	<1.2	<0.53

0.53 mg/kg. The concentrations of the PAH are shown in Table 2. The electrochemical degradation is not uniform for the single PAH and for most of the compounds degradation occurs within the first 30 min of the treatment. Naphthalene is an exception, which is perhaps due to its occurrence as intermediate product of the electrochemical degradation process of other PAH. At the beginning of the treatment, the naphthalene concentration increases from 0.23 mg/kg to 0.67 mg/kg but decreases afterwards to 0.18 mg/kg. So not just TBT but all PAH are decomposed during the electrochemical sediment treatment.

Table 3: Mass fractions of PCB in the sediments versus treatment time.

Massenanteil der PCB im Sediment in Abhängigkeit von der Behandlungszeit.

Mass fraction, μg/kg	$t = 0$ min	$t = 30$ min	$t = 60$ min	$t = 120$ min	$t = 240$ min
PCB 31	3.9	5.2	3.4	2.4	2.4
PCB 28	3.4	3.7	4.0	2.8	2.0
PCB 52	7.1	7.4	9.4	6.2	4.0
PCB 10	17.4	10.8	9.7	8.0	n.d.
PCB 153	11.6	16.2	17.1	16.3	14.1
PCB 138	12.2	16.1	17.9	16.2	15.6
PCB 180	7.9	12.7	13.0	12.7	11.2

Table 4: Pesticides and chlorobenzenes before and during the treatment.

Massenanteil an Pestiziden und Chlorbenzolen vor und während der Behandlung.

Mass fraction, μg/kg	$t = 0$ min	$t = 30$ min	$t = 60$ min	$t = 120$ min
1,3,5-Trichlorobenzene	3.2	5.7	6.1	3.3
1,2,4-Trichlorobenzene	5.8	17.3	1.4	2.6
1,2,3-Trichlorobenzene	4.6	20.3	18.3	7.5
1,2,4,5-Tetrachlorobenzene	2.8	n.d.	n.d.	n.d.
1,2,3,4-Tetrachlorobenzene	0.7	n.d.	n.d.	n.d.
Pentachlorobenzene	3.4	5.5	4.3	3.1
Hexachlorobenzene	16.1	31.4	29.4	19.1
α-HCH	0.2	0.2	0.2	0.2
β-HCH	0.6	0.6	0.6	0.6
γ-HCH	0.4	0.4	0.4	0.4
Heptachlor	0.9	5.7	2	0.8
Aldrin	0.4	0.4	0.4	0.4
Heptachlorepoxid B	0.5	0.4	0.4	0.4
α-Endosulphone	13.1	2.2	1.8	1.7
β-Endosulphone	17.8	25.6	26	23
Dieldrin	0.6	0.8	0.6	0.6
Endrin I	8.5	12.6	13.5	10.1
Endrin II	7.6	9.6	9.2	9
2,4-DDE	1.9	n.d.	n.d.	n.d.
4,4-DDE	13.1	5.5	3.7	3.7
2,4-DDD	8.5	16.2	11.5	11.5
4,4-DDD	0.6	0.6	0.6	0.6
2,4-DDT	0.9	0.8	0.8	0.8

n.d.: not determined.

PCB are another important pollutant class in sediments. Seven PCB are investigated in agreement with the list of orientation values for sediment relocation. The results are presented in Table 3. Auxiliarily chlorobenzenes and pesticides are analysed. The results are shown in Table 4.

Significant change in concentrations of pollutant compared with naturally occurring variations due to sediment heterogeneity in the investigated area could not be observed. Furthermore the presence of elementary sulfur in the samples causes overlaps in the spectra. Therefore 2,4-DDE, 1,2,3,4-tetrachlorobenzene and 1,2,4,5-tetrachlorobenzene could not be detected in the treated sediments. There are weak indications that α-endosulphone will be decomposed too and that perhaps chlorinated benzenes, like trichloro- and hexachlorobenzene will be formed and afterwards decomposed within the treatment process (see Table 4).

4 Conclusions

The target value for relocation of sediments in Germany of < 100 µg/kg TBT is achieved with the presented process. Furthermore other chemical criteria like PAH and PCB concentrations are investigated. While the PAH are decomposed simultaneously as well as organotin compounds the PCB concentrations remain the same. The degradation rate for PAH is approximately 90 %. Former studies have shown that the concentrations of heavy metals and their mobility are not influenced by the treatment. Process conditions have to be controlled very carefully, because simultaneously to the electrochemically induced pollutant degradation other sediment ingredients can react with the electrochemical generated radicals and form by-products which might be undesirable.

In addition to the chemical analysis bioassays should be applied to prospect undesired effects. Chemical analysis is a strong tool in assessing the main target of decontamination processes, but advanced process optimisation should also include effect studies if the treated material is supposed to release into the environment again.

A pilot plant was installed and is operated in Bremen in co-operation with the harbour authorities of Bremerhaven.

Acknowledgements

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