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

Task 3550
Treatment of sediment

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EXECUTIVE SUMMARY

In Task 3550 Treatment of Sediments various commercial and experimental technologies were applied in order to reduce the organotin concentrations. For any technology used however the important boundary condition 'on-land sediment reuse' was kept in mind, with both respect to chemical (environmental acceptable) and geotechnical quality of the treated sediment. Both chemical and geotechnical quality of the treated materials will be discussed in the report of Task 3553 'Reuse of sediments'.

Basically two main types of treatment have been looked at. First of all the separation of the organotin compounds via its associated phases in the sediment without actual destruction of the organotins, secondly the destruction of the organotin compounds within the sediments. DEC studied the latter options, however via a wide variety of techniques and a wide variety of destruction principles. First of all, biological degradation of organotin compounds was studied in three techniques: simple aerobic biological degradation by means of autotrophic micro-organisms, enhanced aerobic biological degradation by means of addition of selected micro-organisms, plant enhanced aerobic biological degradation. Secondly, chemical destruction of organotins in the sediments was applied in two ways: direct chemical oxidation by injection of oxidants, indirect chemical oxidation by electrolysis.

As all techniques showed promising results on the laboratory scale, field pilot trials have also been carried out. The pilot trials dimensions give the opportunity to estimate the full scale possibilities such as: technical feasibility, operational costs, complexity and safety.

From all tests it can be concluded that the 'soft' techniques (bioremediation) have a promising potential as they can be applied in conventional treatment centers (lagooning fields), however they require longer treatment times compared to classical pollutants, need regular follow-up, and the residual non-degradable concentrations are difficult to estimate. In addition, these techniques are primarily one-step operations, and they result in a good sediment quality.

The 'strong' techniques such as chemical oxidation have the potential of a total destruction of organotins and organic pollutants. However these techniques are complex to apply as many steps are involved, require high capital and operational costs, and result in sediment with poor quality.

GENERAL TABLE OF CONTENTS

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

Task 3550 Treatment of sediment
Chapter 1: Characterisation of the sediment
Final report october 2004

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CHAPTER 1: CHARACTERISATION OF SEDIMENTS.

Table of contents

List of figures

List of tables

CHAPTER 1: CHARACTERISATION OF SEDIMENTS.

1.1. Introduction.

For the technologies assessed in this report, and based on the findings in Task 3546 Sediment characterization two dredging locations were selected for recovery of test material. Location 2.1 near Antwerp ship repair showed very high organotin concentrations (in the order of 10's of mg/kg DW) while location 1.5 showed a more typical organotin pollution in the order of 1 mg/kg DW. These sediments will be further referred to as 'batch 1.5' and 'batch 2.1'.

1.2. Dredging of the sediments.

First dredging campaign.

Early May 2003 about 100 m^3 were dredged from each of the above locations using a crane dredger on a pontoon (see figures 1.1 & 1.2). They were separately transported over water via barge to the DEC Sediment Recycling Centre at Ruisbroek. The sediments were unloaded; part of each batch was stored in small lagoons specially constructed for the project. On these sediments the effect of lagooning on organotin breakdown, and phytoremediation was studied.

Figure 1.1: Dredging of sediment at location 1.5.

Figure 1.2: Transport of the sediments in a barge.

The remaining sediment of these batches (about 15 m³ per location) was kept in anoxic conditions in two separate containers covered by a tarpaulin and kept airtight by about 20 cm of water on top of the tarpaulin (see figure 1.3). Subsamples were from these containers for all chemical oxidation and electrochemical oxidation tests.

Second dredging campaign.

During the second dredging campaign on the same locations about 150 m³ on each of the locations were dredged. These batches were separately transported over water via barge to the DEC Sediment Recycling Centre at Ruisbroek. The sediments were transferred into a separately lined lagooning/bioremediation field within an existing lagooning field. These sediments were only used for the large scale lagooning and bioremediation test.

1.3. Characterisation of the sediments.

Although a thorough sediment characterization has been carried out within Task 3546 Sediment Characterisation, extra basic characterization has been done on every of the batches

during the two sampling campaigns. For each of the specific treatment options, as will be outlined further, extra parameters were analysed in function of that treatment option.

Figure 1.3: Storage containers for sediment from both locations.

First dredging campaign May 2003.

As the sediments from both locations were thoroughly mixed during the various handlings (dredging, loading in the barge, unloading, truck transport, loading in the containers or small lagoons) it was supposed that the sediments were well homogenized. Therefore a composite sample from each of the storage containers was considered as representative and sent for analysis.

Location 2.1

Table 1.1: Basic parameters of location 2.1 (first campaign)

Parameter	
Dry matter content (%)	45.3
Lutum content (% of DW)	18
Sand fraction > 63 µm (% of DW)	17
LOI (% of DW)	8.6
TOC (% of DW)	2.07

Location 1.5

Table 1.2: Basic parameters of location 1.5 (first campaign)

Parameter	
Dry matter content (%)	38.8
Lutum content (% of DW)	13
Fraction < 63 µm (% of DW)	35
LOI (% of DW)	13.5
TOC (% of DW)	3.17

As was already illustrated in other TASK reports of TBT Clean, organotins were the only pollutants of concern. Typical other sediment pollutants such as PAHs were so low that they will not be systematically followed during the tests.

1.4. Characterisation of heterogeneity in the batches.

1.4.1. Introduction.

Over time, during the experiments and after several analyses of the initial batch samples, it was noticed that in particular for the heavy organotin pollutant batch (location 2.1) a wide dispersion occurred in the detected organotin values.

As the evaluation of the various sediment treatment options is primarily based on evaluation of the removal efficiency of the pollutants, it is of course extremely important to know the dispersions that can occur during sampling, lab sample pretreatment and analysis. After all, the removal efficiency of organotins is calculated by dividing the removed fraction with the initial concentration. Deviations in this initial concentration will extremely affect the efficiency figures.

1.4.2. Sampling and analysis.

In order to get a better idea on the dispersion of organotin values over the two batches from the first dredging campaign 10 composite samples per container were taken and analysed for organotins.

The results are shown below in table 1.3.

1.4.3. Discussion.

The dispersion of all organotin values for batch 2.1 is enormous. The standard variation is about 38 % of the average for TBT, and even much higher for MBT and the phenyltincompounds.

For batch 1.5 the dispersion is more limited for TBT, however it is considerable again for MBT and the phenyltincompounds.

1.4.4. Conclusion.

The following conclusions can be drawn from these findings:

- The high dispersion in organotin values for batch 2.1 are probably due to the association of organotins (especially TBT) with paint flakes, as was shown during the sediment characterisation. After all location 2.1 is situated near the outfall of the drydock of Antwerp Ship Repair.
- The high dispersions illustrate that extensive sampling is needed to evaluate the 'average' organotin content of the sediment, probably at any time during any treatment process, in particular in treatment processes where the sediment is not thoroughly homogenized. It is therefore dangerous to draw conclusions from a limited amount of samples.
- Probably the effect of dispersion is most expressed during subsampling in the analytical laboratory. From quite macroscopic samples in the field (order of few kilograms) very small subsamples are taken (order of few milligrams). On this level of milligram subsamples it is probable that e.g. the presence or absence of only one paint flake in this subsample can change the organotin concentration drastically. For example 1 paintflake of 1 mm^2 and 100 µm thick, containing 1 % TBT, in a sample of 1 mg dry matter, will contribute 1000 µg/kg DW to that subsample.
- The dispersion noticed on the MBT and phenyltincompounds is probably due to analysis variations that can occur at the lower concentration levels of these compounds.

Table 1.3: Organotin analyses of both batches from the first dredging campaign.

	Organotin (µg/kg)					
Batch 2.1	**TBT**	**DBT**	**MBT**	**TPhT**	**DPhT**	**MPhT**
2.1 /1	31371	1458	578	147	73	<DL
2.1 /2	25053	1117	202	53	37	<DL
2.1 /3	28872	1291	355	51	27	<DL
2.1 /4	39093	1520	442	62	38	<DL
2.1 /5	23840	1321	269	72	34	<DL
2.1 /6	48755	1904	448	69	41	<DL
2.1 /7	24458	1046	66	187	107	<DL
2.1 /8	39158	1493	585	50	27	<DL
2.1 /9	59182	1824	529	392	211	<DL
2.1 /10	17625	1040	126	92	61	<DL
Mean	**33740,7**	**1401,4**	**360**	**117,5**	**65,6**	
Standard Deviation	**12820,93**	**300,6128**	**187,2728**	**106,6367**	**56,85694**	
Minimum	**17625**	**1040**	**66**	**50**	**27**	
Maximum	**59182**	**1904**	**585**	**392**	**211**	
Standard Deviation (%)	38,00%	21,45%	52,02%	90,75%	86,67%	

	Organotin (µg/kg)					
Batch 1.5	**TBT**	**DBT**	**MBT**	**TPhT**	**DPhT**	**MPhT**
1.5 /1	3381	512	143	<DL	10	<DL
1.5 /2	3585	501	181	<DL	28	<DL
1.5 /3	3676	576	164	<DL	11	<DL
1.5 /4	3918	442	178	<DL	32	<DL
1.5 /5	3186	519	191	<DL	10	<DL
1.5 /6	3252	471	202	214	100	<DL
1.5 /7	2904	334	43	<DL	24	<DL
1.5 /8	3256	433	82	44	18	<DL
1.5 /9	3665	536	253	293	150	<DL
1.5 /10	3612	404	103	<DL	56	<DL
Mean	**3443,5**	**472,8**	**154**	**183,6667**	**43,9**	
Standard Deviation	**299,9601**	**71,2161**	**62,45532**	**127,2412**	**46,41946**	
Minimum	**2904**	**334**	**43**	**44**	**10**	
Maximum	**3918**	**576**	**253**	**293**	**150**	
Standard Deviation (%)	8,71%	15,06%	40,56%	69,28%	105,74%	

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Task 3550 Treatment of sediment
Chapter 2: Lagooning of the sediment
Final report october 2004

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CHAPTER 2: LAGOONING OF THE SEDIMENT.

Table of contents

List of figures

List of tables

CHAPTER 2: Lagooning experiments.

2.1. Introduction.

The main objective of the treated sediments is their beneficial reuse as engineering materials, e.g. for backfill purposes. That is why in any case, prior to, during, or after any treatment technique, the sediments require dewatering. Having typical initial (i.e. in-situ) dry matter content of 40 %, and ready-for-use dry matter contents of around 80 % in mind, the sediments should be dewatered to more than half of their initial weight. In other words, this means that about 80 % of the initial water content has to be removed. Most of the water leaves the sediment through evaporation.
Dewatering of the sediments is hence an inevitable step in the treatment process. Prior to the treatment methods bioremediation or phytoremediation, in order to get the sediment in an aerobic condition, the sediment's structure has to be improved via natural dewatering, in other words lagooning.

2.2. Lagooning.

Lagooning is the process in which sediments are dried by evaporation of their pore water in the open air. In general, lagooning is carried out in large lagooning fields, where the sediments are tilled by hydraulic excavators in order to expose the sediments surface to the air and in order to improve the structure of the sediments. Lagooning of sediments takes about 4 to 5 months in a typical Belgian climate. Lagooning consists primarily of two phases: first the sediments will further settle and drain by consolidation, then, from the moment the sediments can be piled, mainly evaporation takes place (figure 2.1).

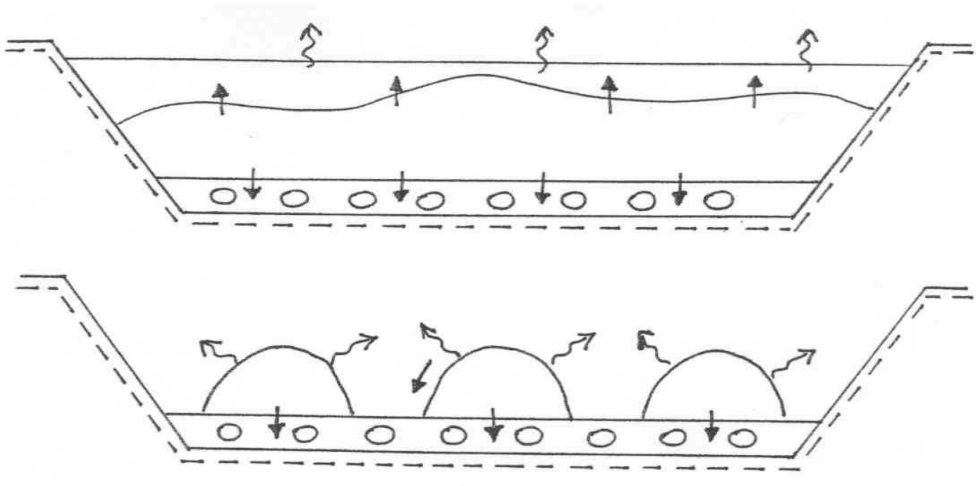

Figure 2.1: two phases in lagooning: up: sedimentation+drainage; down: evaporation.

A typical view on the sediments during various stages of the evaporation phase during lagooning can be seen in figures 2.2 to 2.4.

Figure 2.2: early stage of evaporation phase.

Figure 2.3: intermediate stage of evaporation phase.

Figure 2.4: Final stage of evaporation phase.

Next to loss of water, lagooning causes many other phenomena to happen within the sediments: oxidation of the minerals and organic fractions (e.g. turning the sediment from black to grey-brown due to oxidation of iron sulfides), improvement of structure (sticky sediment to soil like structure),… Mainly the oxidation process is important: as sulfides are getting oxidized to sulphate, an increase in leachability of metals occurs, pH decreases, redox increases, etc. In addition, anaerobic fauna is being replaced slowly by aerobic species. All these physico-chemical and biological changes that happen during the lagooning can and will of course affect the behaviour of pollutants in the sediments. Finally, during lagooning the sediments are exposed to sunlight, giving a chance of photolytic destruction.

With respect to organotin compounds the following phenomena could occur due to lagooning:

- Changes in adsorption behaviour of organotins to organic matter and clay minerals in the sediment. In analogy with heavy metals during the initial stages of lagooning a desorption will occur (due to breakdown of organic matter), while later on resorption can occur (due to adsorption on iron-(hydr)oxides formed during lagooning).
- Reduction of the water solubility of e.g. TBT due to acidification of the pore water due to sulphide oxidation.
- Aerobic biodegradation of organotins, a process which is much faster than anaerobic biodegradation.
- Photolytic destruction of organotin compounds.

- Photolytic destruction of phases to which organotins are associated, such as paint flakes, organic matter,…

It is obvious that the behaviour of organotins can be seriously interacted by the lagooning process. Therefore a pilot research study was undertaken.

2.3. Objectives of the pilot lagooning tests.

The main objectives of the pilot lagooning tests were the following:

- Simulation of a real scale lagoonation.
- Evaluation of the effect of biodegradation of organotins during lagooning.
- Evaluation of the effect of photolysis of organotins during lagooning.
- Evaluate the leachability of organotins during the lagooning phase.

2.4. Materials and methods.

DEC decided to carry out the pilot lagooning tests in specially constructed lagooning fields. The fields were completely lined and welded with a thin HDPE liner in order to prevent possible contamination to the subsoil and in order to be able to collect any drainagewater coming from the sediments.
The installation of the lagooning fields can be seen in figures 2.5 and 2.6.
The dimensions of the entire field inside the dykes were 18 m long by 8 m wide by 1 m deep.

The lagooning field was divided into four compartments of each about 25 m^3 of sediment. For each of the two batches of sediment from the first dredging campaign two compartments were provided: one blank and one lagooned. Blank means that the sediment has been left untouched in the compartment during the whole duration of the tests, only being subject to surface drying or rainfall. Lagooned means that the sediments were weekly tilled by an hydraulic excavator to simulate a full scale lagooning process. The configuration of the four compartments is shown in figure 2.7.

Figure 2.5: installation of the lagooning fields: view on welded liner and drainage collection pipes.

Figure 2.6: installation of the lagooning fields: drainage layers and separation dykes.

Side of building

BATCH 1.5 (low TBT) Lagooned	BATCH 2.1 (high TBT) Lagooned
BATCH 1.5 (low TBT) Blank	BATCH 2.1 (high TBT) Blank

Figure 2.7: Configuration of compartments in the small lagoon.

2.5. Sampling strategy.

Distinction was made between blank and lagooned for each batch of sediment in order to isolate the effect of photolysis on organotins and in order to evaluate differences between optimal aerobic (= lagooned) and anaerobic or less aerobic (= blank) sediments.

It was expected that, if photolysis would occur, the (aerated) surface of the blank compartment would show a higher organotin degradation than the (aerated) sediment from the lagooned compartment.

On the other hand, the deeper layers of the blank compartment, which were only slightly aerated by diffusion, would have to show a much lower degradation of organotins than the deeper layers of the lagooned compartment.

In order to see whether this hypotheses is confirmed, sampling was done as well on the surface (0 to 10 cm) as in depth (50 to 70 cm). Each sample was a composite sample consisting of 10 individual samples from each compartment and depth. The time interval of each sampling was one month. The total duration of the lagooning experiment was four months.

2.6. Lagooning procedure.

A few days after the first dredging campaign the lagooning fields were filled. First of all, a one month sedimentation and drainage period was foreseen. After one month, the sediments had sufficient consistency to excavate and pile up, as can be seen on figures 2.8 and 2.9. During this period, excess surface water (during rainfall) was evacuated via the separation dykes between the compartments, as these were constructed of drainage sand without liner.

From that moment the second phase of the lagooning took place: the evaporation phase. Just like in a full scale lagooning, the sediments were weekly tilled (not the blanks!). In total, this second phase was continued for 3 months. The lagooning took place during the summer of 2003, which was hot (average temperature 20 °C) and of course was beneficial for lagooning, biological activity, and UV radiation.

Figure 2.8: Lagooning fields after 1 month of sedimentation+drainage.

Figure 2.9: Lagooning fields during tilling with the excavator.

2.7. Follow up of the lagooning.

As mentioned, the four compartments were sampled at regular intervals and the samples were analysed by ERC for organotins. The results are outlined in figures 2.10 to 2.15.

2.7.1. Lagooning of batch 1.5 low TBT.

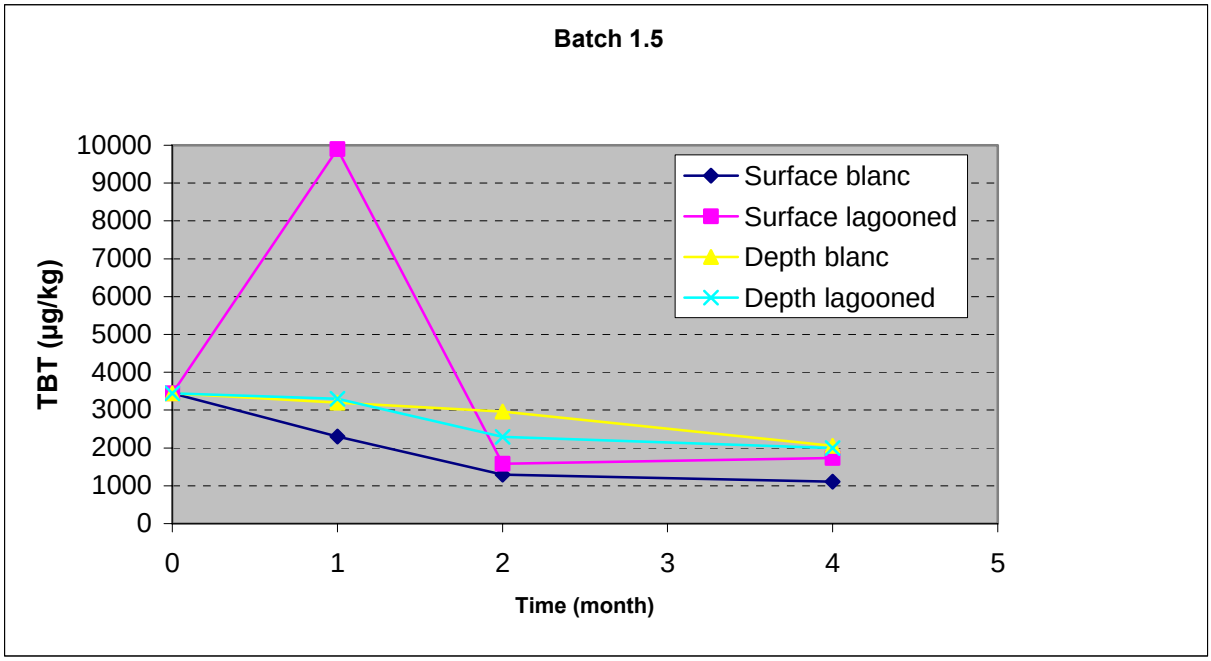

Figure 2.10. TBT evolution during lagooning of batch 1.5.

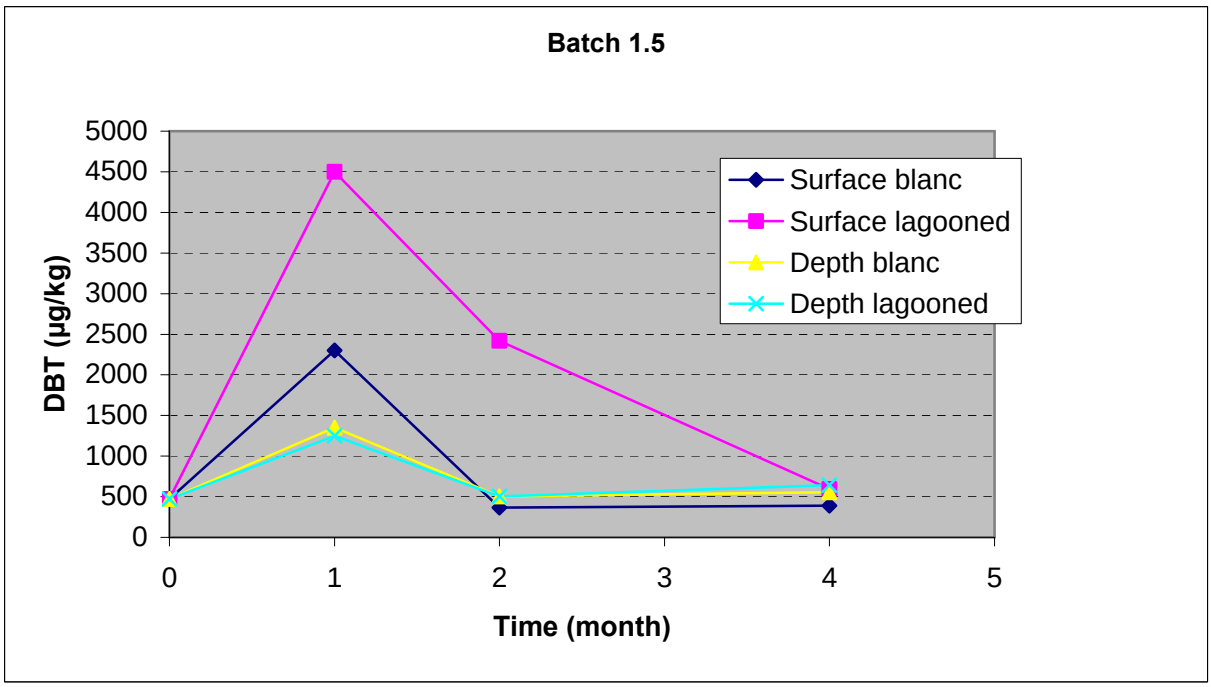

Figure 2.11. DBT evolution during lagooning of batch 1.5.

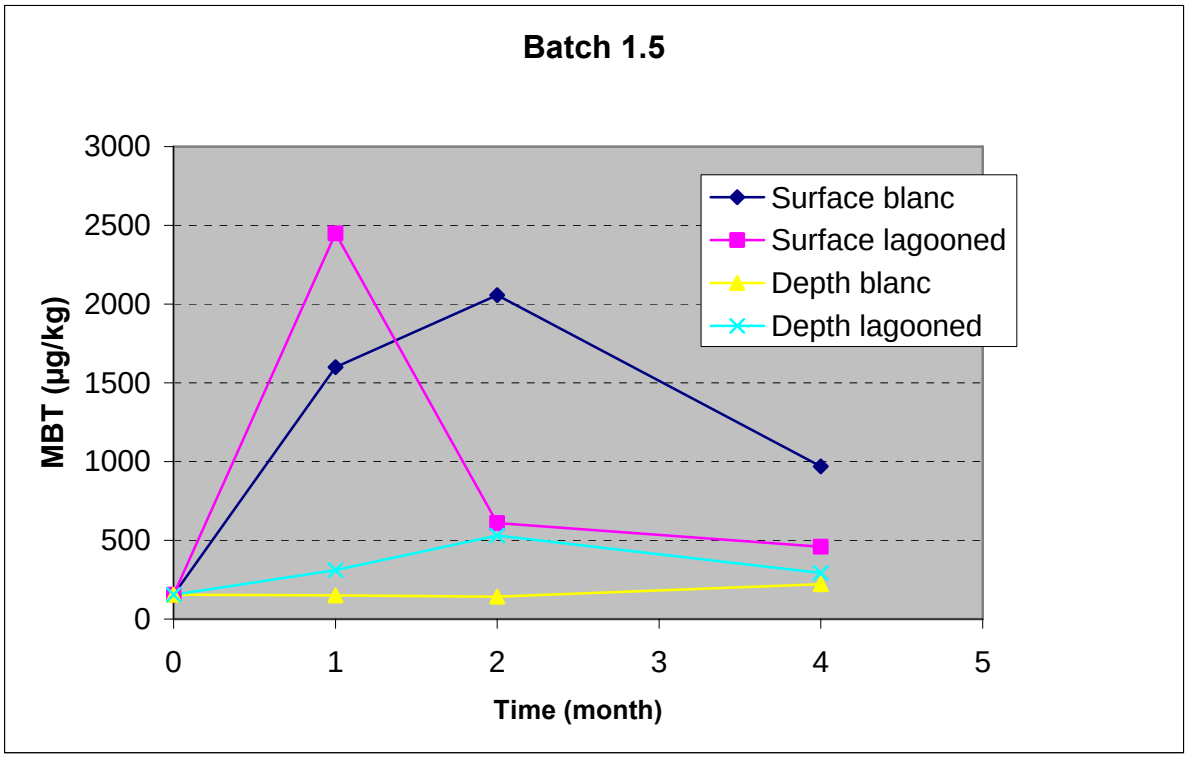

Figure 2.12. MBT Evolution during lagooning of batch 1.5.

2.7.2. Lagooning of batch 2.1 high TBT.

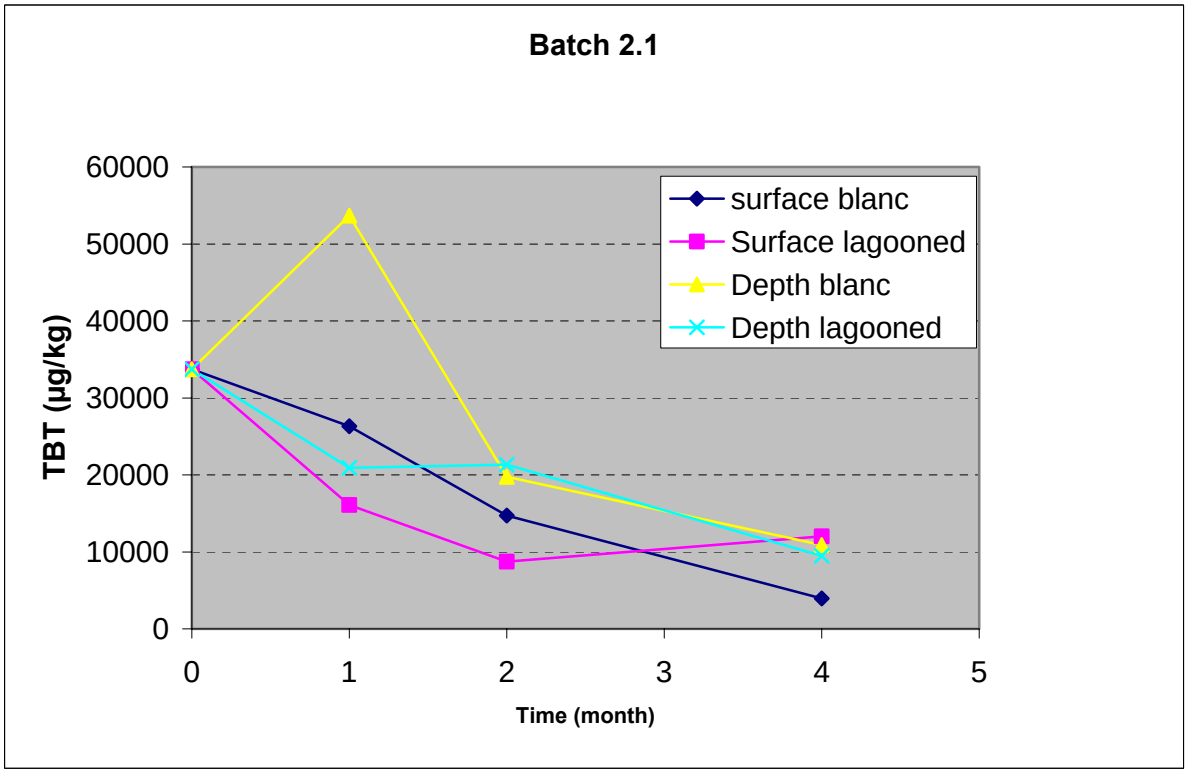

Figure 2.13. TBT evolution during lagooning of batch 2.1.

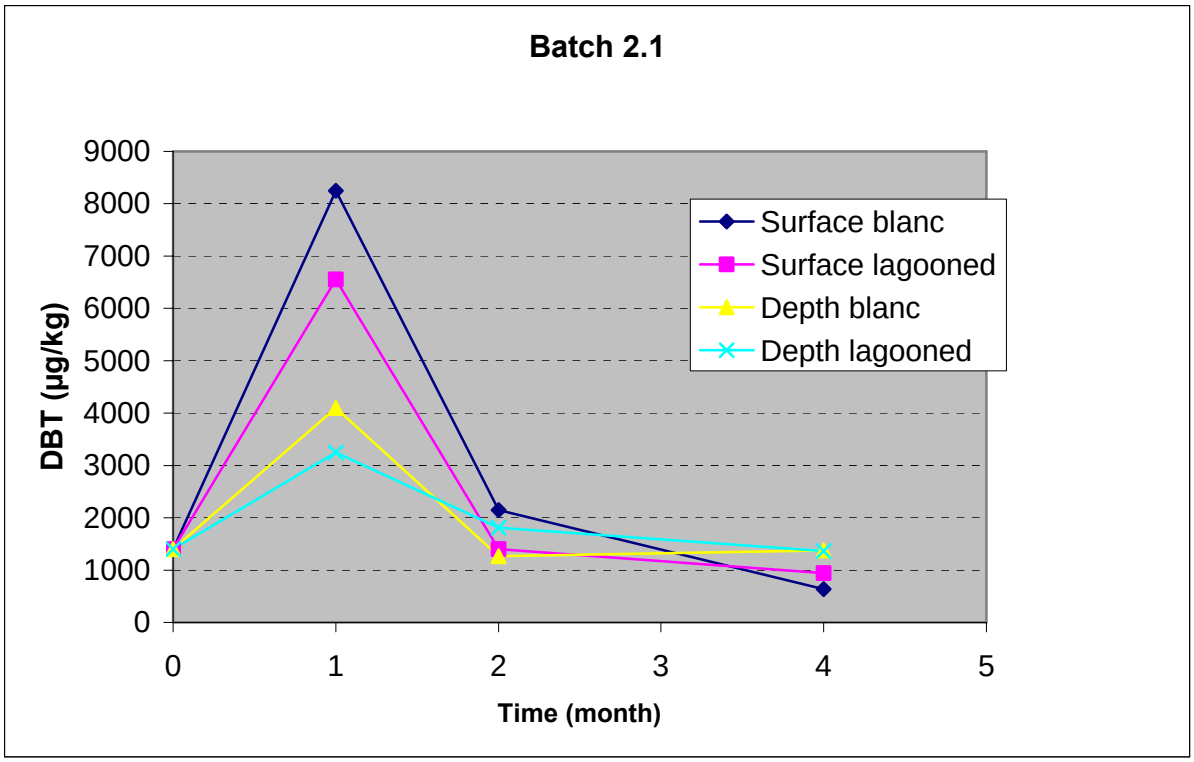

Figure 2.14. DBT evolution during lagooning of batch 2.1.

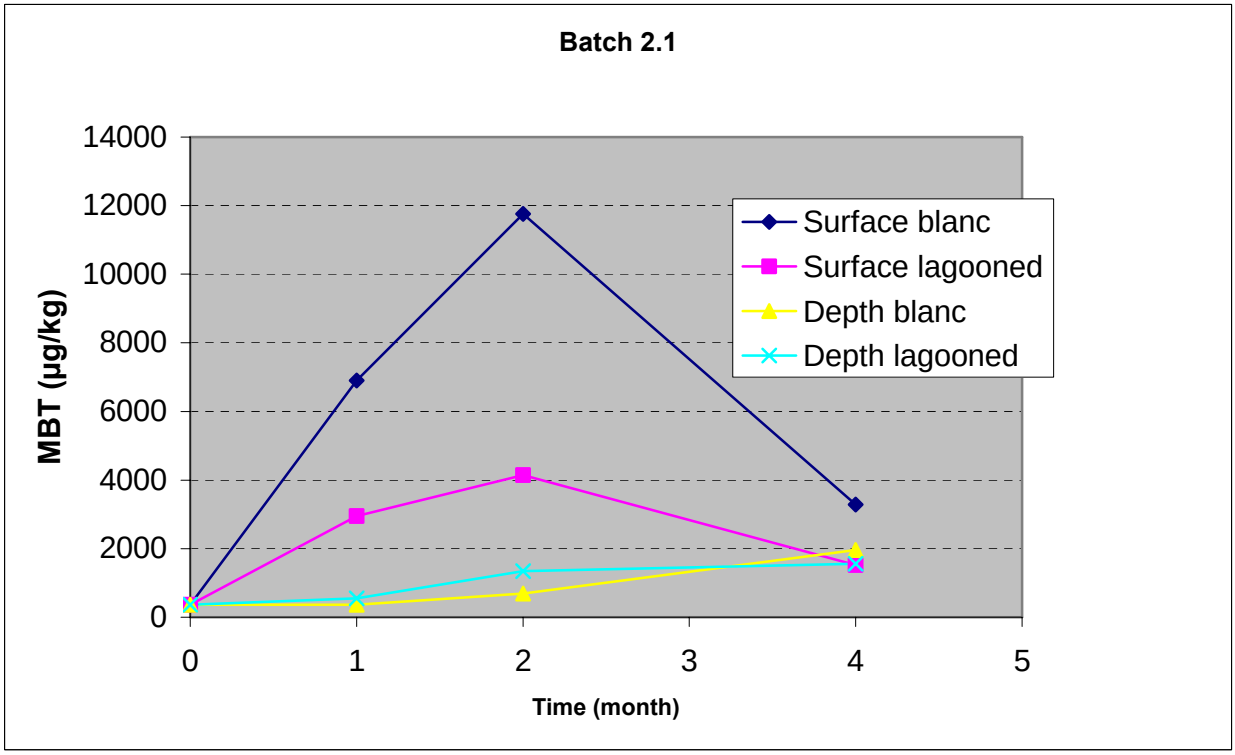

Figure 2.15. MBT evolution during lagooning of batch 2.1.

2.8. Discussion of the lagooning experiments.

2.8.1. Batch 1.5 low TBT.

When comparing the evolution of TBT versus DBT and MBT as its metabolites (figures 2.10 to 2.12), it is obvious that degradation is taking place. While TBT is generally decreasing with time, DBT is initially formed, and then broken down itself to MBT. This is the case for all situations (blank or lagooned, surface or at depth).

In case of the situation where degradation conditions are most optimal (surface blank) the degradation indeed is happening at the highest rate. TBT concentrations are decreasing steadily and its metabolites are formed. However the degradation seems to slow down from 3 months on, which might be due to drying out of the sediment which inhibits the biological activity, a reasonable reduction of about 68 % was observed.

Although a sudden organotin overshoot happens at 1 month, again a tendency for organotin degradation is seen in the lagooned samples. Probably the overshoot is due to the heterogeneity in the sediments, as confirmed by the high value for all organotins at this point in time.

It can also be observed that the deep samples from the unlagooned compartment show TBT degradation, however much slower. Still a TBT reduction of 40 % was observed.
This is in line with the expectations as at that depth less oxygen (hence less aerobic biological activity) is present and no UV degradation can occur. It is known that oxygen diffuses in soils to about a depth of 0.6 to 1 m , which explains that the deeper layer (at 0.5 m) is still slightly aerobic. Analyses of the buffer containers in which the same sediments were kept anoxic, however showed no significant TBT degradation at all.

It is not clear from the experiments within the timeframe, if further reduction of TBT in time would occur. Nevertheless these experiments confirm the possibility of natural aerobic enhanced breakdown of organotins.

If an exponential decrease in TBT is assumed, the half-life time can be roughly estimated as 1.5 (optimal) to 2 months (general).

2.8.2. Batch 2.1 high TBT.

Again when comparing the evolution of TBT versus DBT and MBT as its metabolites (figures 2.13 to 2.15), degradation occurs. The same phenomena occur as with batch 1.5:

slowest degradation in deeper samples, highest degradation when the sediment is exposed to constant aeration and sunlight.

Within the potential dispersion in sampling and analyses a clear trend is observed, with reductions in TBT of up to 88 % in the most optimal condition within four months. Although the TBT reduction seemed to stagnate in batch 1.5 after 4 months, a trend for further decrease can be noticed in batch 2.1. Again the potential for large scale degradation of organotins is confirmed, and again a half-life time of about 2 months is observed, which corresponds to a 90 % reduction over about 5 to 6 months in optimal conditions.

Table 2.1 gives an overview of the obtained TBT reductions during lagooning for all compartments at all sampling depths.

Table 2.1. TBT reductions after 4 month lagooning tests.

	Batch 1.5 low TBT	Batch 2.1 high TBT
Blank – bottom	40.39 %	67.74 %
Blank – surface	67.86 %	88.29 %
Lagooned – bottom	41.93 %	71.92 %
Lagooned – surface	49.54 %	64.42 %

2.9. Conclusions of the lagooning experiments.

When sediments are aerated during lagooning, breakdown of organotins was observed. As degradation is not observed in the anoxic stored sediments, the degradation is probably caused by bioremediation. This will be further confirmed in the chapter 3 ‘Bioremediation of the sediments’. The degradation rate is quite fast if aeration is constant (e.g. by means of regular tilling of the sediments) and shows a half-life time of about 2 months. The experiments were carried out during the very hot summer of 2003 which probably encouraged all physicochemical and biological processes in the sediments.

In addition, it was proved that sunlight increased the breakdown rate of organotins, probably due to two facts: first of all the oxidation and UV enhanced destruction of paint flakes and organic matter to which TBT is associated, secondly the UV destruction of organotin molecules themselves, as stated in literature. The first process, i.e. destruction of paint flakes, must occur as it was observed that in most sediments tested about 20 % of the TBT present was associated to the coarser fractions (probably paint flakes). The second process was confirmed by the experiments done in Task 3551 ‘Water treatment’.

A simple dewatering process as lagooning hence causes an important reduction of organotin concentrations without any further additions of nutrients. It should be carried out however if possible during summer months as higher temperatures and radiation indexes can be expected.

This lagooning study formed the basis for the bioremediation study in which the conditions for biological breakdown were studied and improved in order to increase the degradation rate.

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Thesis - Faculteit Landbouwkundige en Toegepaste Biologische Wetenschappen RUG (1994)

VERMEULEN J., GROTENHUIS T., JOZIASSE J., RULKENS W.
Ripening of clayey dredged sediments during temporary upland disposal
Sub-departement of environmental Technology, Wageningen (2003)

VERVAET Y.
Technieken ter behandeling van baggerslib
Thesis - Faculteit Toegepaste Wetenschappen RUG (1995)

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

Task 3550 Treatment of sediment
Chapter 3: Bioremediation of the sediment
Final report march 2005

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CHAPTER 3: BIOREMEDIATION OF ORGANOTIN COMPOUNDS.

Table of contents

List of figures

List of tables

Executive summary

TBT biodegradation in dredged sediments was investigated both on lab scale and full scale. In the lab scale study five combinations were compared with each other to determine which factors could influence TBT breakdown :

- Anaerobic conditions
- Aerobic conditions
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5)
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5) + *Trametes Versicolor*
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5) + surfactant

In the full scale trial an aerated blank control was compared with sediments which received respectively a treatment with nutrients and a treatment with nutrients and selected inocula.

Both lab scale and full scale degradation tests have shown that a residual fraction of organotins is likely to remain in the sediments. A strong correlation between TBT breakdown and CO2 production was noted in the lab scale tests. This proposes the hypothesis of cometabolism of TBT while degrading easily biodegradable organic components. Organotin degradation might have stopped because of an exhaust in easily degradable organic compounds at the end of the treatment. Another explanation for the residual fraction is the fact that some of the organotins are not bio-available due to their association to e.g. paint flakes.

At the time of this report, i.e. after 4 months, the removal efficiency is only up to 50%, which is less than could be expected from the lagooning tests where no nutrients or micro-organisms were added. This might be due to the larger scale of the tests and the lower average temperature the tests were carried out in.

TBT is converted to less toxic DBT and MBT but some inhibitions seem to prevent the complete breakdown to Sn. The addition of nutrients seems to be beneficial and can play a role in lifting these inhibitions. On lab scale the addition of inocula helped to achieve final levels at an earlier stage but this is not confirmed during these full scale tests. Outdoor conditions are probably too harsh for the survival of the added inocula. In the next months it will be verified whether the addition of an easily available carbon source can increase the degradation efficiency.

CHAPTER 3: BIOREMEDIATION OF ORGANOTIN COMPOUNDS

3.1. Introduction

TBT biodegradation in dredged sediments was investigated both on lab scale and full scale. In the lab scale study five combinations were compared with each other to determine which factors could influence TBT breakdown :

- Anaerobic conditions
- Aerobic conditions
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5)
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- Aerobic conditions + nutrients (C:N:P = 250 :10 :5) + surfactant

In the full scale trial an aerated blank control was compared with sediments which received respectively a treatment with nutrients and a treatment with nutrients and selected inocula.

This report describes the results from the lab scale tests and the results of the full scale trial after 4 months of treatment (trial is still ongoing).

3.2. Set-up of lab scale tests

The aim of the tests on lab scale was to assess the influence of several parameters on TBT degradation : presence or absence of oxygen, addition of nutrients (ammonium nitrate and sodium-tri-poly-phosphate), surfactant (Tween 80) and TBT degrading microorganisms (*Trametes Versicolor*). Trametes Versicolor was chosen after a literature review on TBT biodegradation. Five combinations were compared with each other, each sample consisted of approximately 1 kg :

- Anaerobic conditions
- Aerobic conditions
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5)
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5) + *Trametes Versicolor*
- Aerobic conditions + nutrients (C:N:P = 250 :10 :5) + surfactant

The characteristics of the initial sample are shown in table 3.1.

Performance of the anaerobic test took place according to the guidelines which are formulated and validated in the Dutch Nobis project « Selection and validation of a practical protocol for anaerobic dechlorination ». Non biological losses of TBT, e.g. due to volatilisation, were kept minimal since closed glass bottles with solvent impermeable septa were used. The samples were incubated for 6 months in closed fermentation flasks at 20°C, no replicas were used. In all cases the dry matter content in the bottles was about 10%. At this

dry matter content the sediment samples can be mixed thoroughly and aeration is kept optimal. Aeration occured by regular flushing of the headspace above the slurry samples. All experiments were performed in daylight.

Table 3.1. Characterististics from the initial sediment used during treatment tests.

Parameter	Value
dry matter content	51,3%
organic matter content	9,8%
pH	7,3
nitrate as N	< 4,5 mg/kg dm
total phosphate as P	1,6 mg/kg dm
ammonium as N :	120 mg/kg dm
total aerobic bacteria (MPN method)	7. 10^6 /g dm
TBT	6430 µg/kg dm
DBT	530 µg/kg dm
MBT	150 µg/kg dm

During six months every month a sediment sample was taken and analysed for TBT, DBT and MBT. All the organotin analyses were conducted by ERC. Furthermore the mineralisation activity (expressed as mg CO2-C/kg dm) and total amount of aerobic bacteria (by MPN analysis) was followed up.

3.3. Degradation results lab scale tests.

3.3.1. TBT degradation

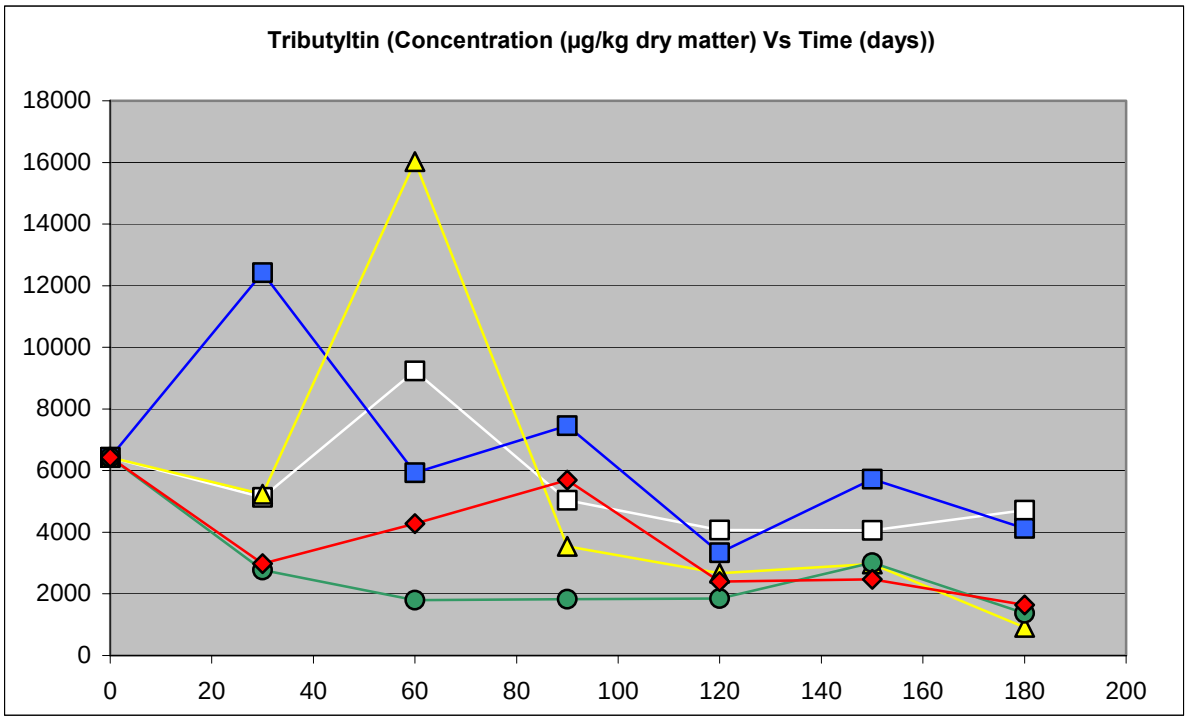

Figure 3.1: Degradation of Tributyltin. Conditions: (■)Aerobic blank; (□)Anaerobic blank; (◆)Aerobic with nutrients and surfactants; (●)Aerobic with nutrients and *Trametes Versicolor*; (▲)Aerobic with nutrients.

Figure 3.1 shows the evolution of the TBT concentration. One can observe that this concentration decreases for all samples considered. Despite the obvious high heterogeneity of the samples (see for example the second and the third point of respectively the blue and the yellow curves), the trend towards a diminution of [TBT] appears clearly.

It can be seen that all combinations with additives scored better than the blank controls. A possible explanation for the degradation in the anaerobic control can be sunlight. Adsorption of TBT to the vessel walls was minimised as glass bottles were used. The breakdown in the sample with inoculum initially occurred faster but reached a lag phase after 2 months. The quick breakdown in the sample with the inoculum offers perspectives for the full-scale application and needs to be checked. In the other samples degradation slowed down after 4 months. This could be expected as in the beginning the easily degradable organic material (from the sediments and contaminants) is broken down and what remains is a difficult to degrade fraction of organic material with tightly bound contaminants. If one looks at the CO2 production (discussed later) one can see that the CO2 production slows down after 3-4 months, which means that less organic material is broken down. It is possible that only the easily available fraction is broken down and what remains is the non-bioavailable fraction.

The same kind of graphical representation can be drawn for the products resulting from the degradation of TBT. This process is a stepwise debutylation so the concentration of dibutyltin (DBT) and monobutyltin (MBT) were also followed during the experiment. Results are presented in the following paragraphs.

3.3.2. DBT and MBT degradation

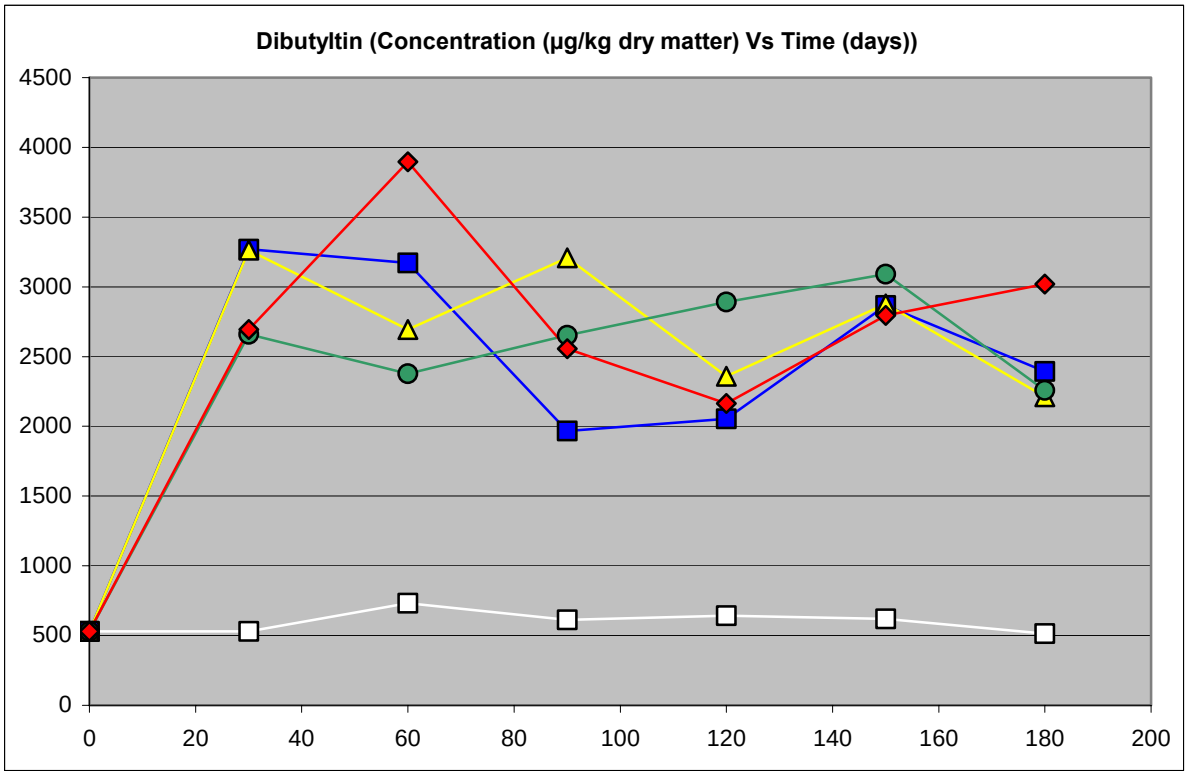

Figure 3.2: [Dibutyltin] in function of reaction time. Conditions: (■)Aerobic blank; (□)Anaerobic blank; (◆)Aerobic with nutrients and surfactants; (●)Aerobic with nutrients and *Trametes Versicolor*; (▲)Aerobic with nutrients

Although TBT concentration decreases with time in the anaerobic control, this is not compensated with an increase in DBT or MBT as is the case for all other combinations including the aerobic control. This might indicate that the removal of TBT in the anaerobic test cannot be attributed to biological action. It looks like TBT is initially broken down to DBT and MBT, but the subsequent breakdown of DBT to MBT is inhibited in some way after 3-4 months. The loss of DBT is also not compensated by an increase in MBT. A possible explanation for the inhibition could be a nutrient limitation for the TBT degrading organisms. With the addition of easily available nitrogen and phosphorus the degradation might be stimulated again. This is only an assumption and no hard fact, but it is a point of interest for the full scale test and needs to be checked. It is also remarkable that the DBT and MBT production in the aerobic blank is as high as in the other aerobic samples (although the decrease in TBT was not so high compared to the other samples).

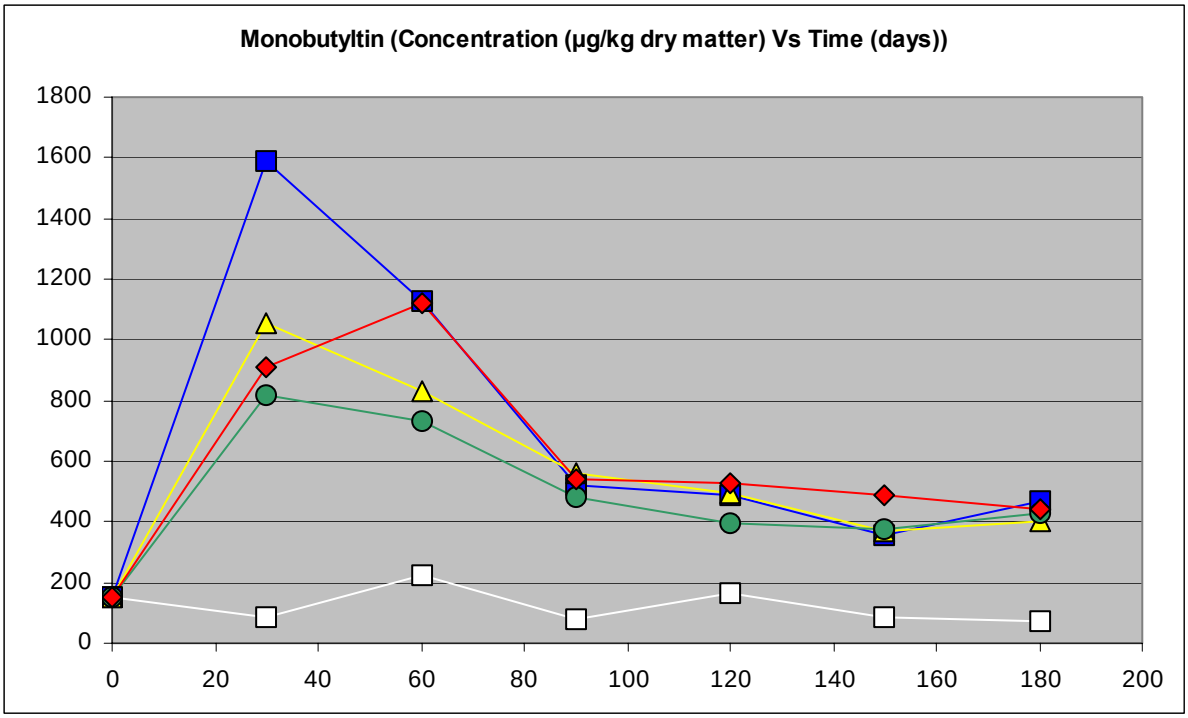

Figure 3.3: [Monobutyltin] in function of reaction time. Conditions: (■)Aerobic blank; (□)Anaerobic blank; (◆)Aerobic with nutrients and surfactants; (●)Aerobic with nutrients and *Trametes Versicolor*; (▲)Aerobic with nutrients

3.3.3 Overall removal of organotins

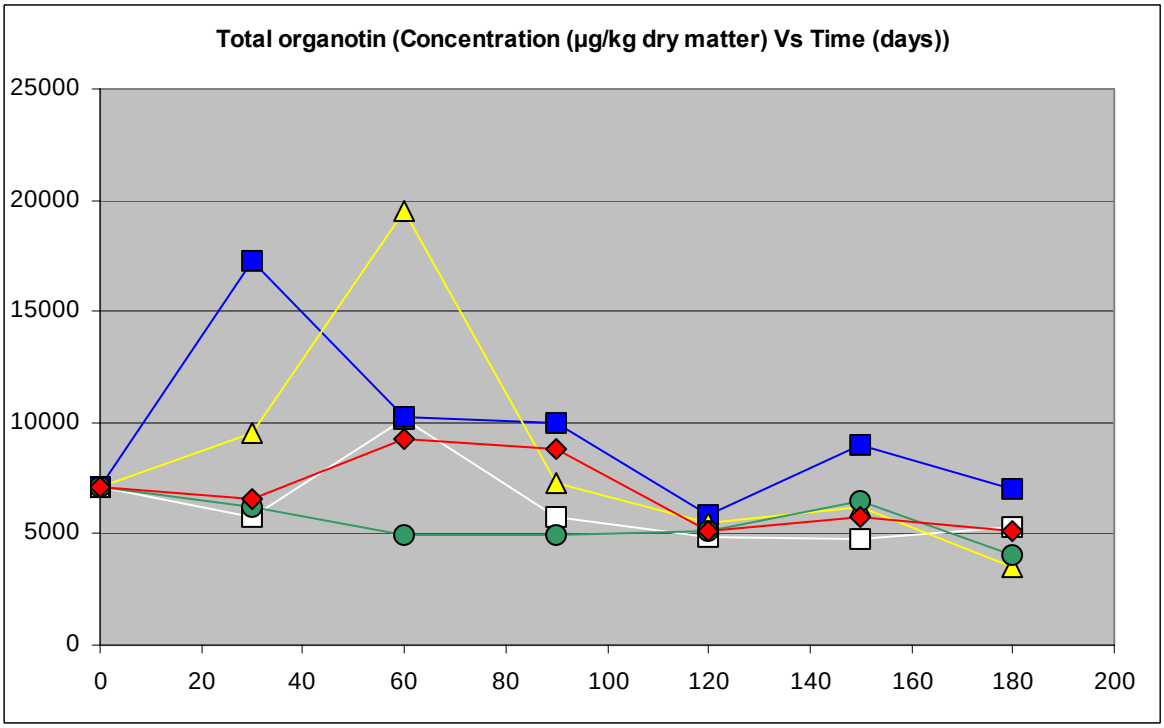

Figure 3.4: [Total organotin] in function of reaction time. Conditions: (■)Aerobic blank; (□)Anaerobic blank; (◆)Aerobic with nutrients and surfactants; (●)Aerobic with nutrients and *Trametes Versicolor*; (▲)Aerobic with nutrients

Figure 3.4 shows the evolution of the total organo tin content of the samples with time. A 50% reduction is reached for the sample containing nutrients and exposed to oxygen.

Figure 3.5 shows that the relative importance of the TBT fraction in the total organotin content decreases with time during the test. The organotins in the initial sample consisted for 90% of TBT while in the treated sample this is decreased to 30%.
As TBT is considered as the most toxic compound of the organotins it is likely that toxicity of the sample has decreased significantly with time.

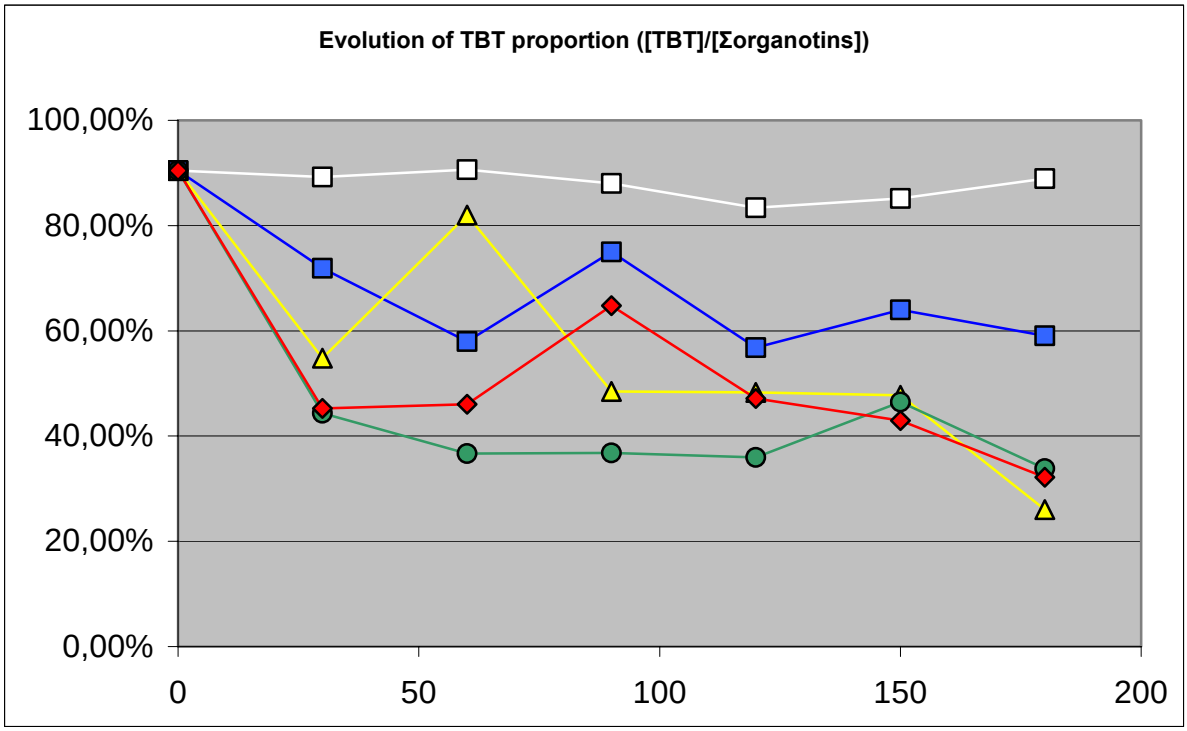

Figure 3.5 : Evolution TBT proportion with reaction time. Conditions: (■)Aerobic blank; (□)Anaerobic blank; (◆)Aerobic with nutrients and surfactants; (●)Aerobic with nutrients and *Trametes Versicolor*; (▲)Aerobic with nutrients

3.4. Bacterial activity

The bacterial activity was screened during the experiment by measuring the production of carbon dioxide - produced by the consumption of oxygen and organic matter – and by counting the number of bacteria in the samples (MPN method). The following graphs show the results of these measurements.

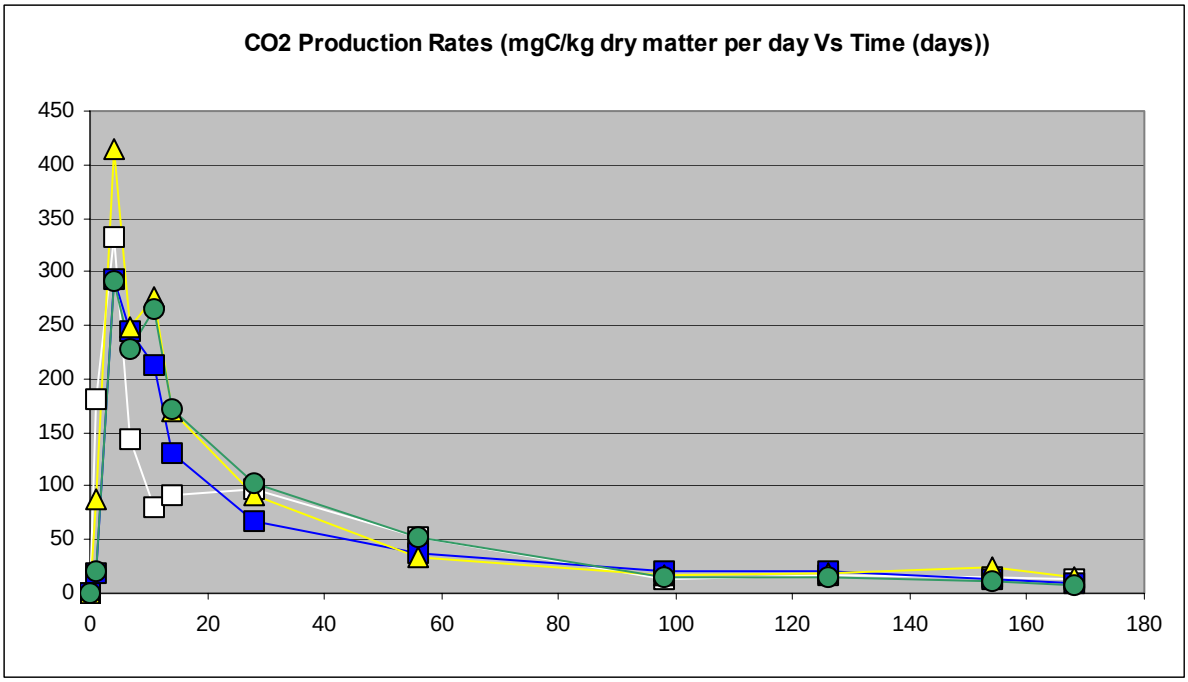

Figure 3.6: CO2 production rate in function of reaction time. Conditions: (■)Aerobic with nutrients; (□)Aerobic blank; (●)Aerobic with nutrients and surfactants; (▲)Aerobic with nutrients and *Trametes Versicolor*

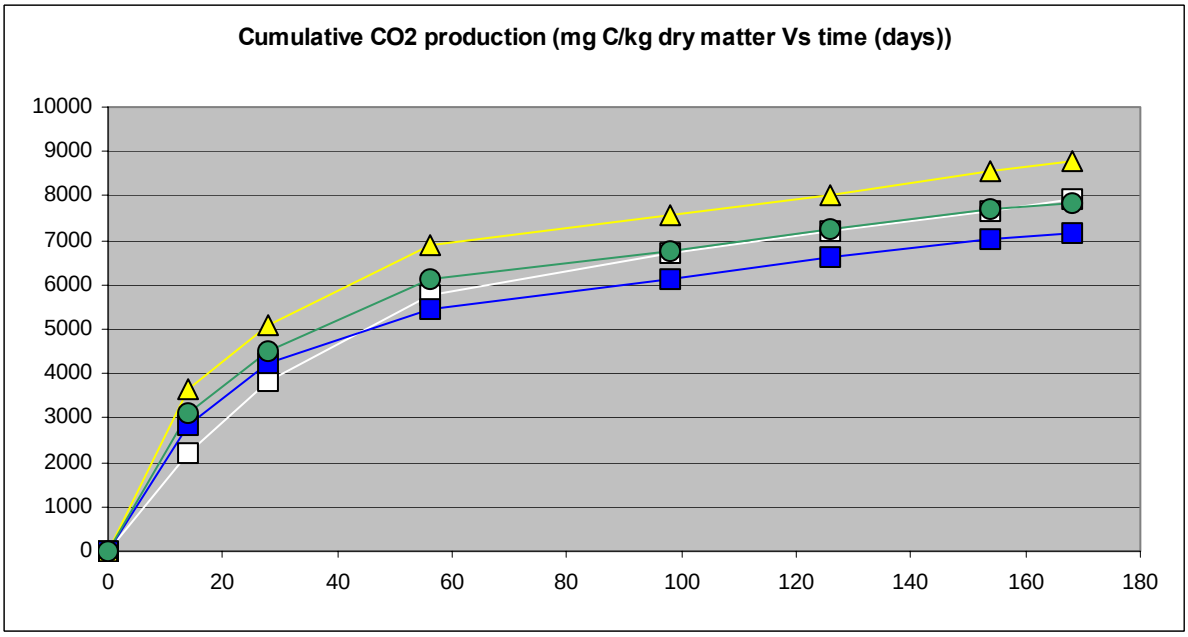

Figure 3.7: Cumulative CO2 production in function of reaction time. Conditions: (■)Aerobic with nutrients; (□)Aerobic blank; (●)Aerobic with nutrients and surfactants; (▲)Aerobic with nutrients and *Trametes Versicolor*

The CO2 measurements show that the dosing of nutrients, surfactants and inocula have no effect on the biological activity. Apparently there is no direct lack of nutrients in the sediments. The cumulative CO2 production is approximately 8000 mg CO2-C/kg dm. This

CO2 production means that approximately 16 g/kg dm organic matter is biodegraded to CO2-C. This CO2 production is much higher than the amount of CO2-C that can be produced if TBT is completely biodegraded. This amount (3,5 mg CO2-C/ kg dm) is only 0,02% of the total amount produced in the tests.

As discussed in paragraph 2 a correlation was noted between CO2 production and TBT breakdown. This might indicate that perhaps TBT is debutylized in a co-metabolic reaction while degrading easily biodegradable organic compounds. No indication for this was found in literature but this hypothesis should be investigated further during the full scale tests.

Figure 3.8 shows the evolution of the amount of bacteria during the test.

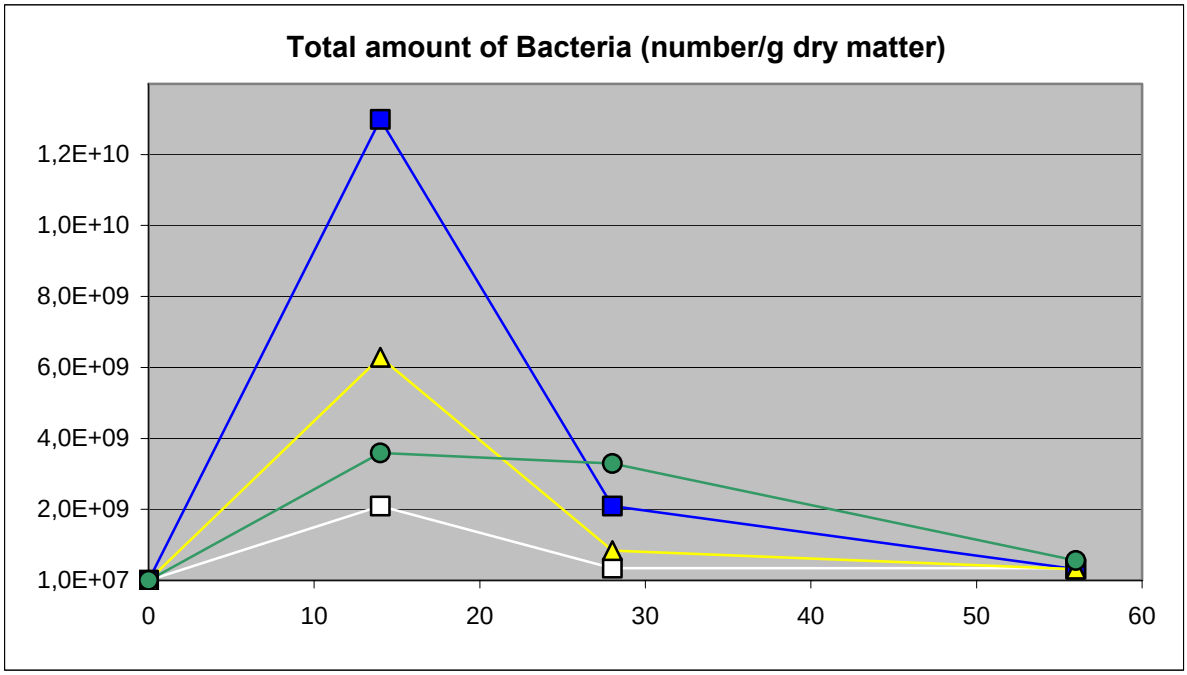

Figure 3.8 : Evolution bacterial population with incubation time. Conditions: (■)Aerobic with nutrients; (□)Aerobic blank; (●)Aerobic with nutrients and surfactants; (▲)Aerobic with nutrients and *Trametes Versicolor*

The number of aerobic bacteria increased (factor 1000) from 10^6 to 10^9 bacteria/gdm in all the tests during the first two weeks of incubation. This increase is due to the optimised aerobic condition. After two months the amount of bacteria decreased to 10^8 bacteria/gdm in all tests. This decreasing number of bacteria, accompanied by a decreasing mineralisation activity, is also indicating extensive mineralisation of the easily biodegradable fraction in the organic matter. The bacteria seem to be able to survive when all easily degradable organic matter is already removed. Additions of nutrients, surfactant or TBT degrading organisms seem to have no significant effect on the development of the total number of aerobic bacteria present.

3.5. Set-up full scale tests

Based on the results of the lab scale tests it was decided to test following conditions:

- blank aerated control
- addition of nutrients
- addition of nutrients and selected inocula

These conditions were tested on two types of dredged sediments, one heavily contaminated with TBT and the other one moderately contaminated. Each condition was tested on 20 m3 of dredged material. The sediments were dredged from the port of Antwerp on 21/1 and their characteristics are summarised in table 3.2.

Table 3.2. Sediment composition.

sample		1	2	3	4	5	average
name		location 1.5	location 1.5	location 1.5	location 1.5	location 1.5	location 1.5
dry weight	%	57,3	57,3	57,1	57,4	57,1	57,2
TBT	µg/kg dw	1724	1800	1941	1996	1914	1875
DBT	µg/kg dw	233	253	285	289	311	274,2
MBT	µg/kg dw	32	34	58	55	59	47,6
som (TBTt/m MBT)	µmol/kg dw	7,1	7,5	8,2	8,4	8,2	7,9
fraction TBT		84	83	81	82	80	81,9
fraction DBT		14,0	14,4	14,8	14,6	16,1	14,8
fraction MBT		2,5	2,6	4,0	3,7	4,0	3,3

sample		6	7	8	9	10	average
name		location 2.1	location 2.1	location 2.1	location 2.1	location 2.1	location 2.1
dry weight	%	49,5	49,4	50	49,7	49,6	49,6
TBT	µg/kg dw	56965	72701	61076	70334	93474	70910
DBT	µg/kg dw	2317	2908	2032	1933	2606	2359,2
MBT	µg/kg dw	406	552	427	407	509	460,2
som (TBTt/m MBT)	µmol/kg dw	208,1	265,6	221,1	252,5	335,5	256,6
fraction TBT		94	94	95	96	96	95,0
fraction DBT		4,7	4,7	3,9	3,3	3,3	4,0
fraction MBT		1,1	1,2	1,1	0,9	0,8	1,0

If we compare table 3.1 and table 1.3 the same order of magnitude of organotin concentrations can be observed within the same dredge locations. However here the location 1.5 batch from this second dredging campaign has about half of the organotin content compared to the first dredging campaign, while for location 2.1 the opposite shows. Unfortunately, this will render comparison of the bioremediation trials and the lagooning trials more difficult.

Again, it can be seen that the dispersion is much larger for the location 2.1 batch compared to location 1.5. This shows that very high fluctuations of organotin concentrations can be expected within the dredging areas.

After dredging the sediments were transported by barge to the Sediment Recycling Centre in Ruisbroek . Here the sediments were placed in a lagoonation field and left to dry. After more than two months (end of march) the consistency of the sediments made it possible to create piles. In april the piles were tilled twice and at the beginning of may the sediments were sufficiently aerobic to start the bioremediation and mix in the additives.

The amount of nutrients, nitrogen and phosphorus, dosed to the landfarm was calculated based on the amount of CO2 produced in the bench scale feasibility tests. Of all biodegraded carbon it was assumed that 50% is produced as CO2 and the rest is used for the growth of biomass. For aerobic degradation processes the amount of nutrients is calculated by using the ratio between organic carbon, nitrogen en phosphorus being C : N : P = 250 : 10 : 5.

A mixture of 30% ammonium nitrate and 8,9% sodium hexa meta phosphate was chosen as nutrient solution.

The inocula consisted of Trametes Versicolor (fungi) and Pseudomonas Fluorescens (bacteria). It was decided to add Pseudomonas as well since bacteria have a bigger change to survive in outdoor conditions compared to fungi. Both cultures are known to be active in biological degradation processes of TBT. The cultures were cultivated in the laboratory of Bioclear. The two piles selected for addition of inocula and nutrients received both 75 liters of Trametes Versicolor suspension and 75 liters of Pseudomonas Fluorescens suspension.

Both nutrients and inocula were dosed by spraying the solution on the pile using a pump and a hose with spraying nozzle. After dosing the piles were immediately turned over using an excavator to achieve a good mixing. A picture of the different piles while adding nutrients and inocula is given hereunder in figure 3.9.

The piles are being monitored for a period of one year. From the beginning of April the piles were tilled twice a month and at the beginning of every month a composite sample was taken of each pile for analysis of TBT and its degradation products and nutrients.

For sampling from each pile six sediments samples are taken. The samples are mixed and these mixed samples are used for analysis. All samples are taken in the middle of depth of the pile. Sampling at several depths was not done since the sediments were turned over twice a month.

Figure 3.9. Large scale bioremediation piles: addition of nutrients.

3.6. Degradation results of full scale tests - results and discussion

The full scale tests were conducted for a period of about 6 months.

3.6.1. Moderately contaminated sediments – batch 1.5

A first thing that needs to be remarked is that a considerable decrease in TBT concentration was noticed in the period between dredging and start of the bioremediation. As mentioned in table 3.1 the average TBT concentration of the dredged sediment was 1875 µg/kg TBT. The average concentration at the start of the bioremediation (beginning of May) was 1170 µg/kg or a decrease of 37% i.e. during the lagooning phase. This loss is probably partially attributed to aerobic biodegradation, partially to UV-radiation, similar as in the lagooning experiments.

3.6.1.1 TBT degradation

Figure 3.10 shows the TBT degradation after 6 months. The TBT concentrations in the blank pile seem not to have significantly decreased since the beginning of May. For the nutrients amended pile and pile amended with nutrients and inocula the decrease is significant, i.e. respectively 58% and 24% compared to the starting point of bioremediation, or 66% and 39% compared to the initial fresh sediment. This confirms our findings from the lab scale trial that the addition of nutrients is important for this type of sediments. The addition of inocula on the other hand does not seem to give a significant additional effect.

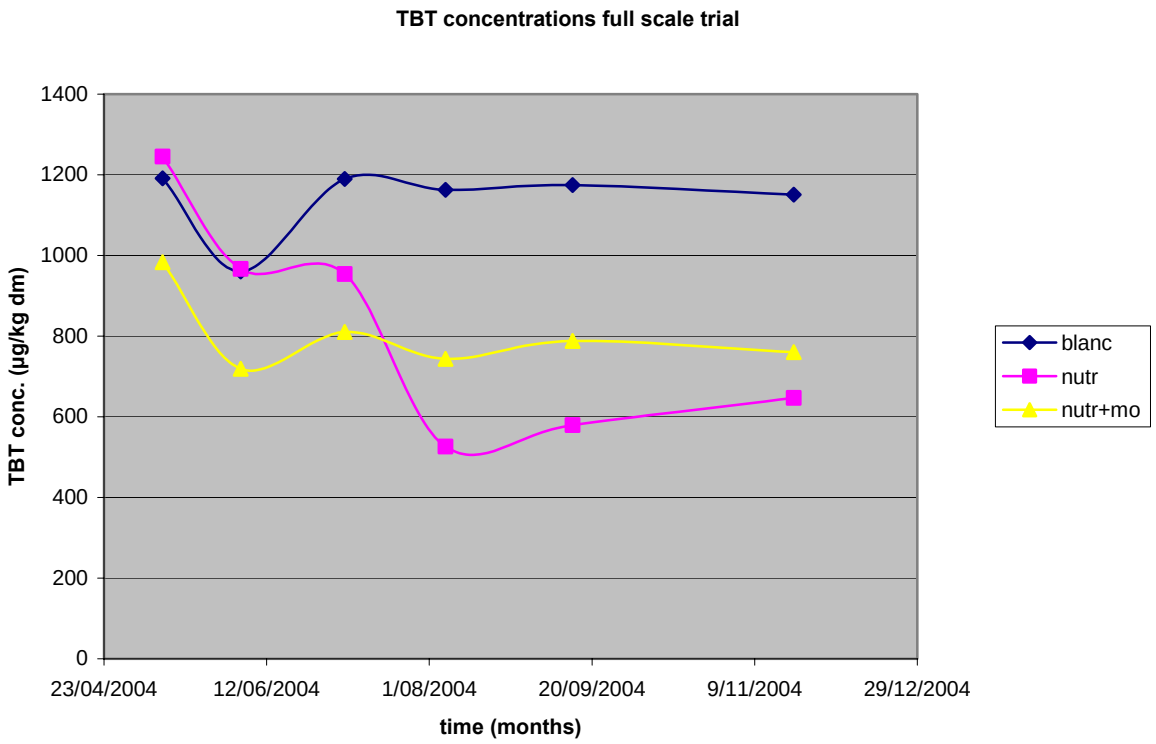

Figure 3.10. TBT evolution during the bioremediation of batch 1.5.

3.6.1.2 DBT and MBT degradation

Figures 3.11 and 3.12 show the DBT and MBT concentrations in the piles. In all three piles an increasing trend of DBT and MBT is observed. This confirms the fact that bioremediation is indeed taking place. It is unclear however why the increase in DBT and MBT, in particular in the blank, does not correspond to a proportional TBT decrease of about 500 µg/kg. Perhaps this is again due to dispersion in sampling and analyses.

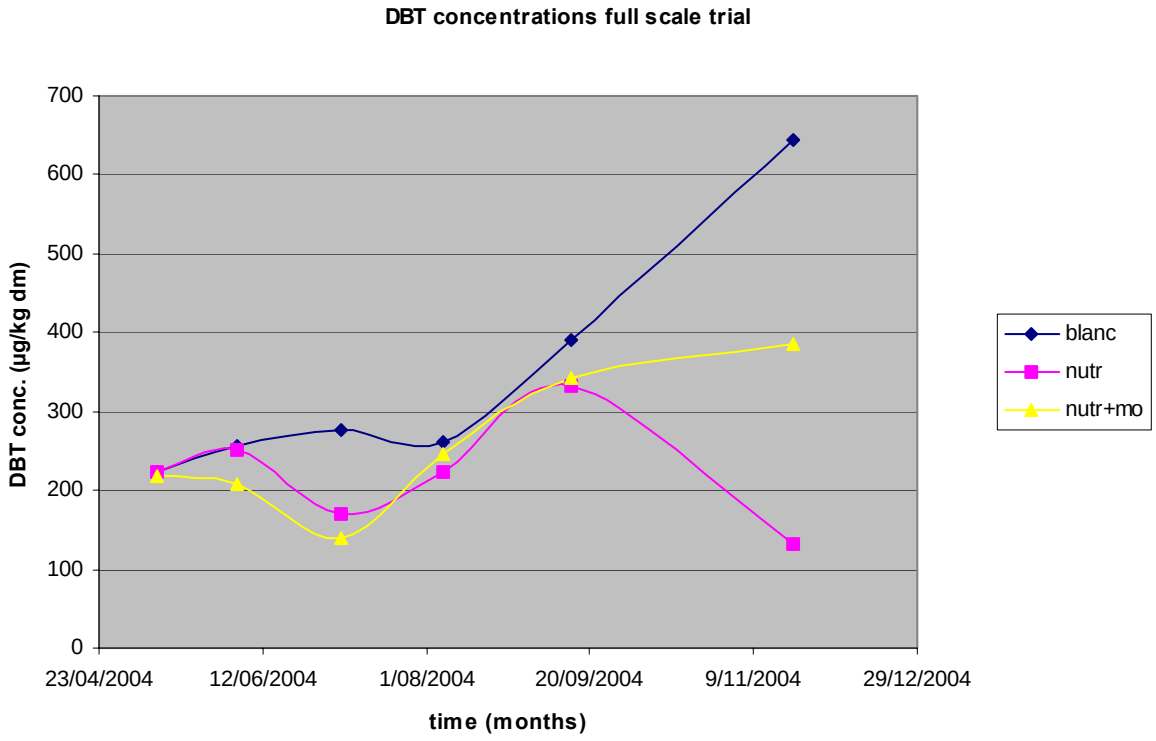

Figure 3.11. DBT evolution during bioremediation of batch 1.5.

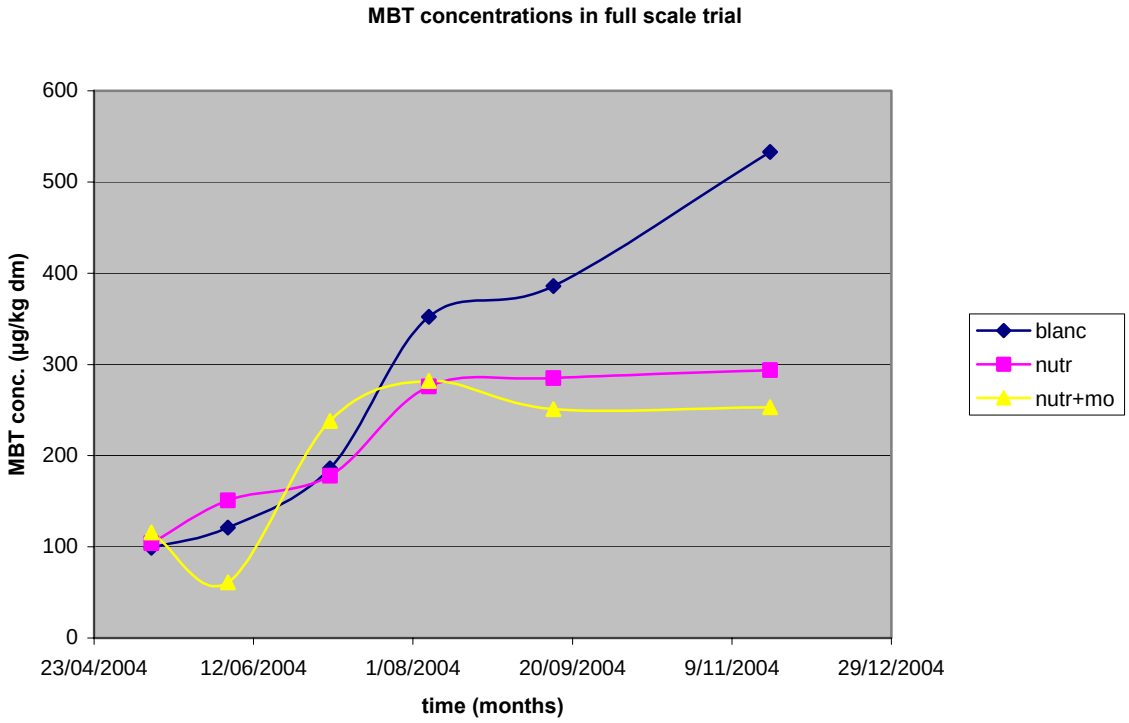

Figure 3.12. MBT evolution during bioremediation of batch 1.5.

3.6.1.3 Nutrients

Figures 3.13, 3.14 and 3.15 show respectively the concentrations of NH4-N; NO3-N and PO4-P in the different piles.

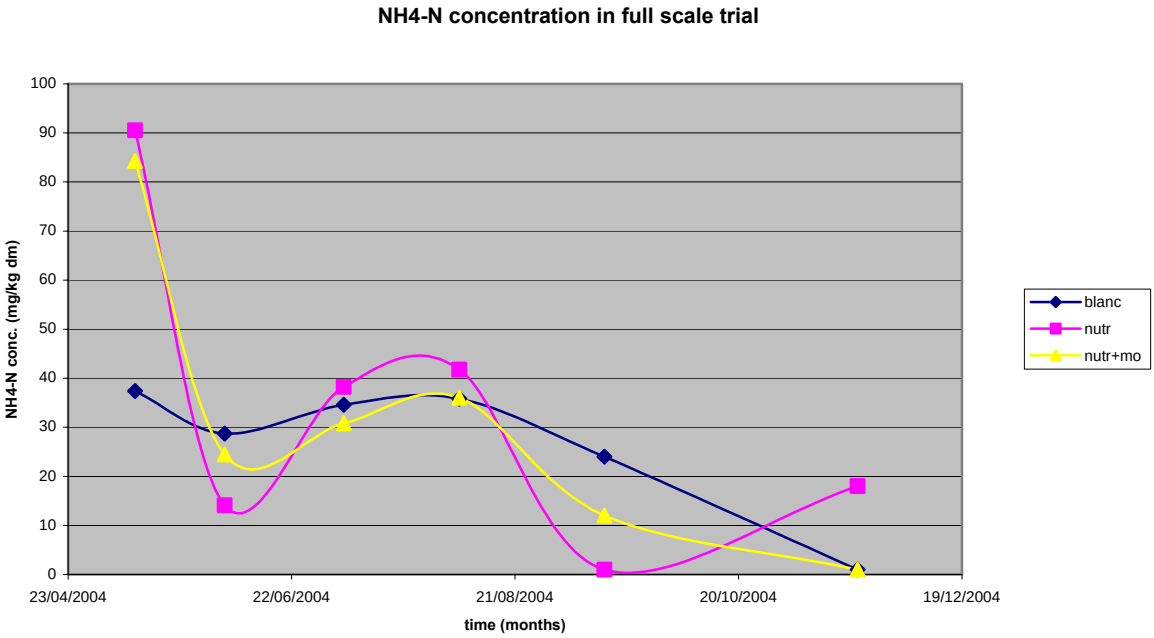

Figure 3.13. Evolution of ammonium concentration during bioremediation of batch 1.5.

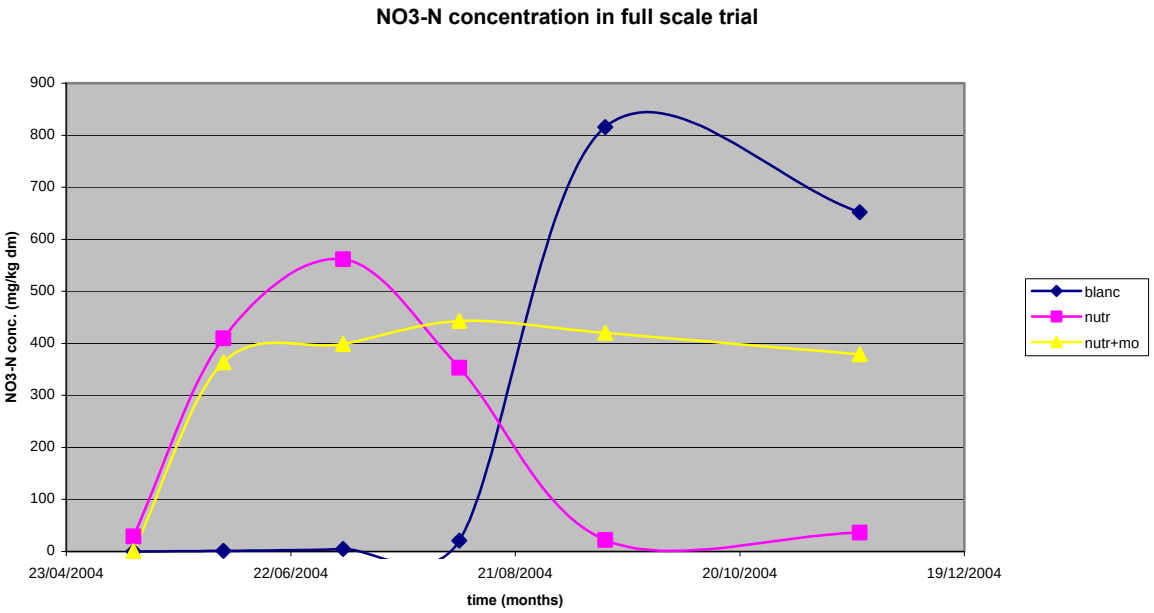

Figure 3.14. Evolution of nitrate concentration during bioremediation of batch 1.5.

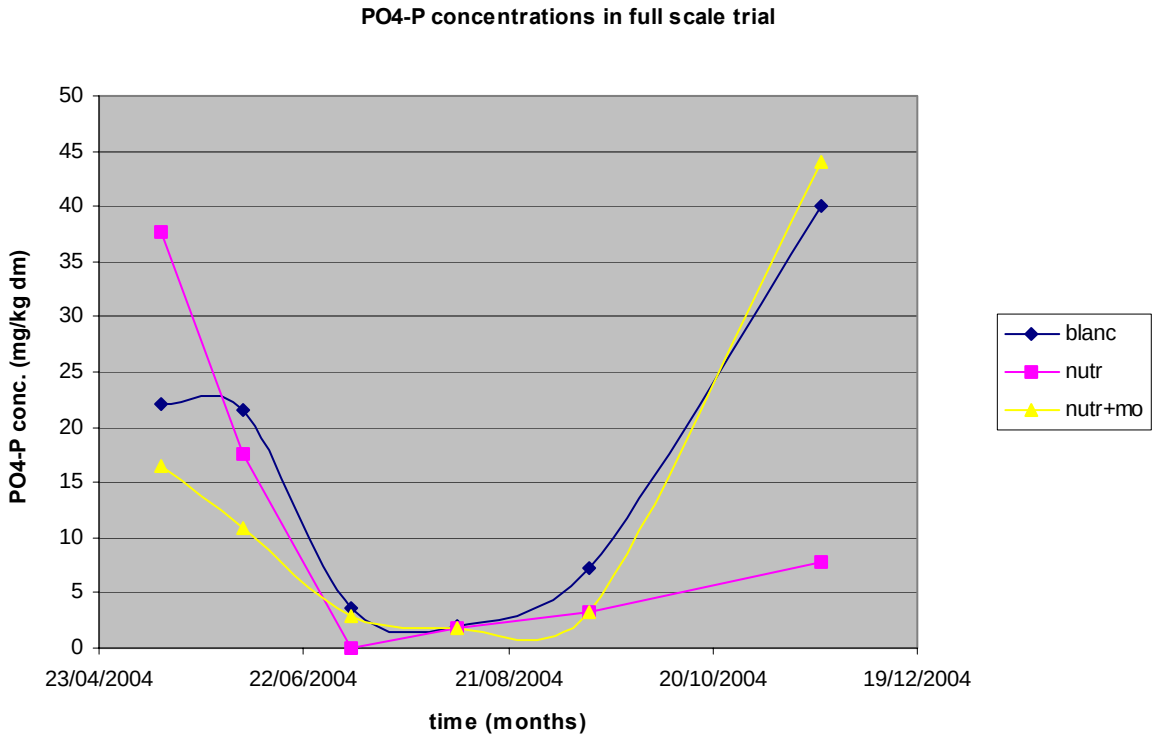

Figure 3.15. Evolution of phosphate concentration during bioremediation of batch 1.5.

Although the fact that a solution of ammonium nitrate was used only a significant increase in nitrates can be observed in the nutrient amended piles. The ammonium concentrations are immediately reduced to the low levels which are also present in the blank controls. It is unclear why the ammonia levels are so low compared to the nitrate levels. Volatilisation is unlikely, perhaps nitrification does occur.

Only NH4-N is readily available for the micro-organisms, NO3-N first needs to be converted to NH4-N before it comes available to the micro-organisms which is energy consuming. Based on nitrate concentrations there is a sufficient amount of nitrogen present in the nutrient amended soils. In the blank control on the other hand a nutrient deficit could explain why TBT is not being degraded in this pile.

Also a steady decrease in PO4-P concentrations is noted in all piles. The effect of the phosphate addition can only be seen when performing a total phosphorus analysis. Phosphate is very reactive and precipitates after addition. Phosphate is then slowly released from this precipitation and presumably only this fraction is measured as phosphate.

Although there is probably no nutrient deficit in the piles it was decided to add extra nutrients after 4 months to increase the concentrations of easily available ammonia and phosphorus. On both piles an extra 50l of ammonium nitrate solution 51% and an extra 6kg of natrium

hexa meta phosphate pellets were mixed with the sediments. In this way also the water content in the piles was optimised again as the piles were partially drying out. However this addition was not reflected by the analyses.

3.6.2. Heavily contaminated samples – batch 2.1

Here also already a decrease in TBT concentration was noted between the dredged sediments (end January 70910 µg/kg dm) and the start of the bioremediation (beginning of May, average of 44254 µg/kg dm). Again this is in accordance with the observations during the lagooning experiments. As mentioned before again a high degree of heterogeneity was found in TBT concentrations which makes interpretation of the results difficult.

3.6.2.1 TBT concentrations

Figure 3.16 shows the TBT concentrations in the different piles.

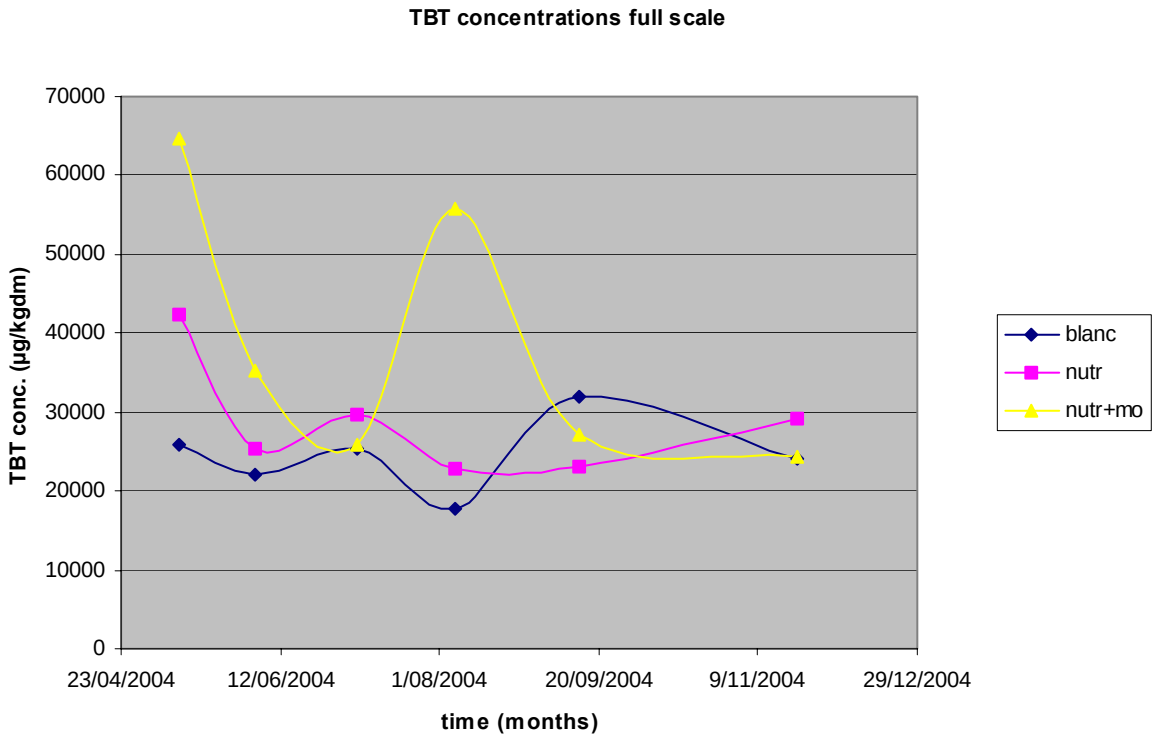

Figure 3.16. Evolution of TBT during bioremediation of batch 2.1.

It can be seen that the piles with nutrient and nutrient + inocula amendment show a decreasing TBT concentration while the TBT concentration in the blank pile remains relatively constant. This confirms again the important role of the nutrients.

In comparison with the lagooning experiments, the decrease of TBT is less, and the TBT concentration seems to stagnate at around 20 to 30 ppm. This can have various reasons: or biodegradation stopped due to the fact that all readily bio-available TBT is exhausted, or again the heterogeneity (dispersion) gives false information. Most probably bioremediation is still ongoing, as DBT and MBT are still generated (see figures 3.17 and 3.18).

3.6.2.2 DBT and MBT concentrations

Figures 3.17 and 3.18 show the DBT and MBT concentrations in the different piles.

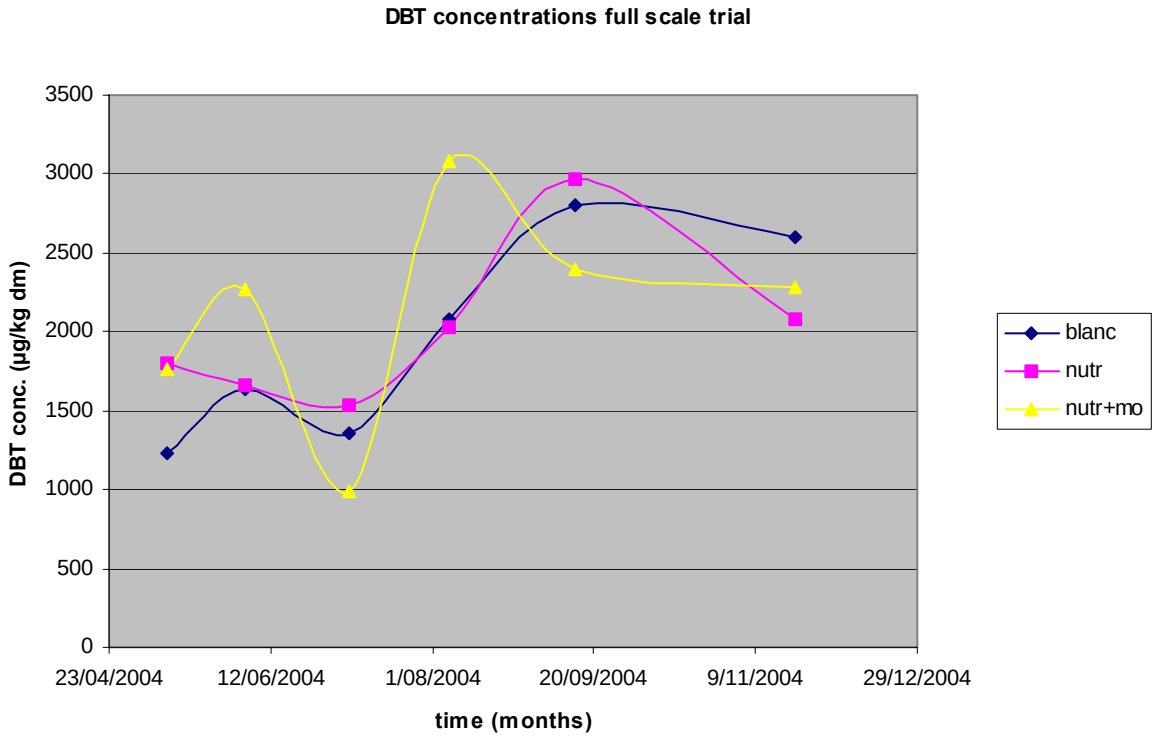

Figure 3.17. Evolution of DBT during bioremediation of batch 2.1.

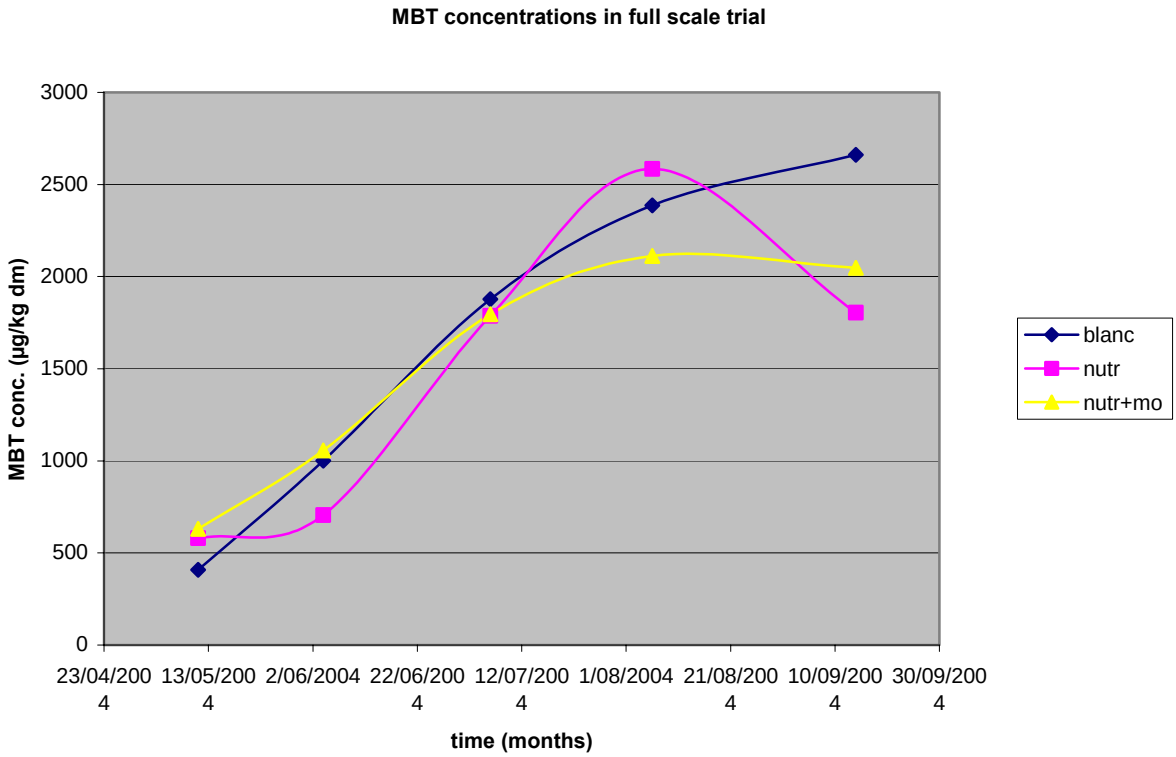

Figure 3.18. Evolution of MBT during bioremediation of batch 2.1.

It can be seen that DBT and MBT concentrations show an increasing trend in all samples. Again this is the best indication that TBT breakdown is actually occurring.

3.6.2.3 Nutrients

The same effects as discussed for the moderately contaminated sediments were also noted for the heavily contaminated samples. For the same reasons extra nutrients were added after 4 months.

3.7. Effects on other pollutants.

Other pollutants than the butyltins and mineral oil were not followed during the trials, as their presence was too low or no effects were expected (e.g. heavy metals). In case of mineral oil no significant decrease was observed. This is due to the fact that this parameter, as measured by GC-FID, is strongly influence by the organic matter in the sediments, and does not really represent mineral oil as a biodegradable pollutant.

3.8. Full scale application.

Full scale application of bioremediation requires a lot of space and time. Lagooning prior to bioremediation is necessary to enhance sufficient oxygen diffusion, but is no lost time in terms of TBT degradation, as TBT already breaks down during lagooning.

A full scale flowsheet is shown in figure 3.19.

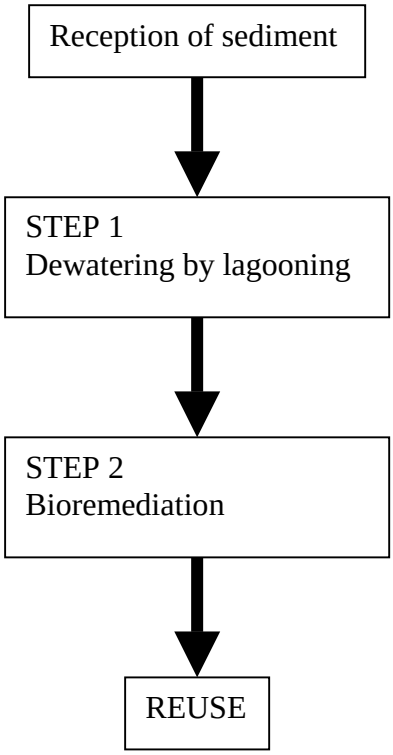

Figure 3.19. Full scale flowsheet for bioremediation.

3.9. Conclusions

Both lab scale and full scale degradation tests have shown promising results, although these are biased by dispersion in organotin concentrations due to sampling and analysis. A strong correlation between TBT breakdown and CO2 production was noted in the lab scale tests. This proposes the hypothesis of cometabolism of TBT while degrading easily biodegradable organic components. Organotin degradation might have slowed down because of an exhaust in easily degradable organic compounds after four months, however this is in contradiction with the ongoing generation of DBT and MBT at this point of time. The bias in the TBT concentrations can be the reason that interpretation is difficult

At this moment a removal efficiency for TBT of 70% seems to be possible for moderately contaminated sediments. A treatment period of about 6 months is needed. The relative proportion of the toxic TBT fraction in the total organotin fraction is decreased with 2/3 rd after treatment. TBT is converted to less toxic DBT and MBT but some inhibitions seem to prevent the complete breakdown to Sn. The addition of nutrients seems to be beneficial and can play a role in lifting these inhibitions. On lab scale the addition of inocula helped to achieve final levels at an earlier stage but this was not confirmed completely during the full scale tests. Outdoor conditions are probably too harsh for the survival of the added inocula.

3.10. References.

Blunden, S. J., and A. H. Chapman. 1982. The Environmental Degradation of Organotin Compounds - a Review. *Environmental Technology Letters* **3**:267-272.

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

Task 3550 Treatment of sediment
Chapter 4: Phytoremediation of the sediment
Final report October 2004

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CHAPTER 4: PHYTOREMEDIATION OF THE SEDIMENTS

Table of contents

List of figures

List of tables

Executive summary

This sub-project of the TBT CLEAN project investigated the feasibility of growing plants on dredged harbour sediments and the influence of vegetation on TBT degradation. The toxicity of TBT to vascular plants was determined with the willow tree transpiration test. Compared to other species, the toxicity of TBT to willows was very low. In a field study from 2003, however, willows did not survive in fresh harbour sediment. A plausible reason is the salt content of the substrate: willows have a low salt tolerance. Besides, the structure of the soil resulting from the sediment was not supporting plant growth. It was therefore decided to lagoon the sediments before bringing plants out.

In a laboratory growth test, seeds of several plants were sown into fresh sediments, lagooned sediments, garden soil and in garden soil irrigated with salt water. Barley (*Hordeum vulgare*) performed best in these studies.

The sediment was characterized as clay loam/sandy clay loam with a high content of nutrients and neutral pH. Fresh sediments were highly saline, with electrical conductivities up to 14 mS/cm, but upon lagooning, the salinity dropped to moderate levels of 3.7 mS/cm.
In the outdoor growth test, fresh and lagooned sediment with high (around 33 mg/kg) and low TBT (about 3 mg/kg) content were used, respectively the batches 2.1 and 1.5 from the first dredging campaign which have been lagooned during the lagooning pilot tests. Several plant species were growing excellently in this substrate, in particular barley (9 to 10 tons/ha dry weight) and sorghum (10 to 13 tons/ha dry weight). The TBT content had no negative influence on the growth of plants. Many species even grew better on the highly contaminated sediment.

Samples were taken below vegetation and below unvegetated blanks in a depth of 5 – 15 cm and 50 cm and analyzed for TBT and its degradation products. Below barley, the degradation was significantly enhanced. No measurable uptake of TBT and metabolites was found for barley (corn), whereas TBT, DBT and MBT were taken up in the other two investigated crops, reed and clover/grass.

It was concluded that the dredged sediment is – after lagooning – a good substrate for plant growth. Although plants support the degradation of TBT, phytoremediation is a slow process which will take several years. The transfer of TBT into crops does not allow an agricultural use of the substrate. Non-food production, such as rape-seed for biodiesel or barley for alcohol, might be an alternative.

CHAPTER 4: PHYTOREMEDIATION OF THE SEDIMENTS

4.1. Introduction

This report was written as a part of the TBT CLEAN project, aimed at finding an integrated approach for the removal of tributyltin from waterways and ports. In the scope of choosing an appropriate treatment option for the large amounts of sediment, which are dredged each year from large ports (in this case port of Antwerp, one of the biggest harbours of the world), phytoremediation needed to be assessed as an alternative/addition to land dumping, thermal treatment, bioremediation and other techniques. For that purpose, laboratory experiments were performed at DTU, Denmark, and field experiments at DEC site in Ruisbroek, Belgium.

4.2. General TBT problem

Tributyltin was used since the late 1960s as an antifoulant for ships. Effects on aquatic species were detected soon after. In the Arcachon bay, for example, imposex among marine species associated with tributyltin (Alzieu et al. 1986) was first observed in 1970, followed by a complete collapse of the oyster population. In addition, Bryan et al. (1986) found evidence that wide-spread imposex among dogwhelk populations in southwest England was also caused by tributyltin. In the 1980s, governments took action by reducing the maximum permissible content of organotins in paint and prohibiting the use of this paint for small ships (< 25 m length). At the International Convention on the Control of Harmful Anti-fouling Systems held in 2001, the agreement on controlling the use of TBT was finalized. World-wide prohibition of the new application of organotin antifoulants has been enforced from 2003 with the view that the existing organotin coatings should be replaced by the year 2008 (Santillo et al. 2001). However, TBT is still present in ship paints, seawater, and in harbour sediment. The maximum concentration of TBT in dry sediment of 470 mg/kg was found in the German Baltic Sea (Helcom EC 1999). The OSPAR convention (OSPAR 2002), which has been in force in the European Union and other countries since March 1998, therefore protects the North-East Atlantic, setting the limits for the dumping of dredged material into the sea to 7 μg TBT / kg. Brandsch et al. (2001, 2002) discussed several treatment methods including the possibility of land-based dumping.

4.3. Chemistry of TBT

Organotin chemicals are compounds containing at least one bond between tin and carbon. The central tin atom (Sn^{4+}) can bind to one (mono-), two (di-), three (tri-) or four (tetrasubstituted) carbon groups. The group of organotin chemicals is therefore quite large and diverse. "Tributyltin" is the common name for a number of substances characterized by a tin atom in the center of the molecule, with three butyl groups covalently bound to it. Without substituent, TBT is a monovalent cation, named TBT^+, which deprotonates to TBTOH at pKa 6.25 (Hunziker et al. 2001). Tributyltin chloride (TBTCl) is the chloride salt of this cation. The tributyltin cation can also form complexes with other anions, e.g. nitrate. Speciation and water solubility of TBT salts depend on pH and ion composition of the solution.

4.4. Pre-studies

Bremerhaven. Brandsch et al. (2001, 2002) reported that some wild and domestic plant species were growing successfully already the first year on the land-disposed sediment from Bremerhaven (port on the North Sea coast of Germany). The study also measured the uptake in plants growing outside on dumped sediments with TBT contamination ranging from 170 to 590 μg/kg (mean 490 μg/kg). The maximal uptake into the above-ground parts of plants was 15 μg/kg.

Uptake of TBT into willows. The uptake of TBT into willow trees was investigated by Ciucani et al. (2004) in a laboratory study. Chemicals investigated were the weak base tributyltin chloride (TBTCl) and the neutral tributyltin hydride (TBTH). Organotins were extracted from solution and plant material with toluene, and analyzed as tin by AAS with graphite oven. The pH in solution varied from pH 4 to pH 7. The sorption to living and dead roots, stems and leaves was measured in shaking experiments. The uptake into intact trees was measured at nominal levels of 1 and 10 mg TBT/l for TBTH and TBTCl at low and high pH. The sorption to roots and leaves dropped for dead tissue but did not vary much with pH. The sorption to stems increased for dead stems and with pH. The solubility of TBTCl in water was below 10 mg/l and lowest at pH 4. Concentrations of TBTCl and TBTH in solutions with trees dropped rapidly to low values. Highest TBT contents in trees were found in roots and lower stems. The concentrations followed the concentrations in solution. The pH had only a small effect on the plant uptake of TBTCl, and no effect on the uptake of TBTH. No effective translocation to higher stems or leaves was found. An ion trap mechanism that accumulates the weak base TBTCl in the xylem sap of plants and leads to upward translocation could not be detected. Neither TBTCl at low or high pH, nor the neutral lipophilic chemical TBTH, were translocated effectively to leaves. The TBT^+ cation sorbed strongly to plant tissue. The exact mechanism for the strong sorption of the cation is

unknown, but similar effects have been observed for algae, liposomes and isolated biomembranes. No ion trap occurred, and it was concluded that phytoextraction of TBT was not feasible.

Toxicity of TBT to willows. In a parallel study, the toxicity of TBT to the willow trees was quantified (Trapp et al. 2004). The phytotoxicity of tributyltin chloride (TBTCl) and tributyltin hydride (TBTH) was measured at pH 4 and at pH 7 using the willow tree transpiration test. Different pH levels of the nutrient solutions were achieved by adding ammonium salt (low pH) or nitrate (high pH) as nitrogen source. At low pH (pH 4), all trees showed symptoms of poor health. Transpiration decreased at concentrations above or equal to 0.1 mg TBTCl/l and 1 mg TBTH/L. The TBT toxicity was more pronounced at pH 7. The trees survived even the highest dose of 10 mg/l TBTCl or TBTH, although their growth and transpiration was strongly reduced. In contrast to other organisms, TBTCl and TBTH were less toxic to higher plants. The study showed that the toxicity of TBT would not be a hindrance for establishing vegetation on TBT-contaminated sediment. The authors came to the conclusion that phytoremediation and cash crop production could be possible with suitable plants.

Field trial with willows in dredged harbor sediments. Because willows were resistant to the TBT in the laboratory study, a field trial was made with TBT-contaminated harbour sediment in the year 2003 by DEC in Belgium. Willow cuttings were planted into fresh sediment in April 2003. None of the willows started to grow. The exact reason is not known, but it may be speculated that it was either the unusually dry and hot weather in 2003, or the structure of the soil, or the salt content.

Figure 4.1. Field trial with willows in fresh harbour sediment 2003.

Salt tolerance of willow trees. In a master thesis at DTU by Boeck (2004), the sensitivity of willows towards salinity of hydroponic solution was determined. Willow trees were exposed to standard solution with different NaCl concentrations: 0, 0.1, 1, 3, 6 g/l, whose corresponding electrical conductivity measured was 0.6 (controls), 1, 2.3, 6.7 and 10.7 respectively. The toxicity was measured by tracking the transpiration of the trees ("healthy trees transpire more", Trapp et al. 2000) In Figure 4.2 is seen that there is a high correlation between normalized relative transpiration NRT and NaCl concentrations, having a coefficient of correlation 0.97 for 24 and 72 hours of exposition and 0.94 for 48 hours. This means that the willows cannot stand elevated salt concentrations in soil solution.

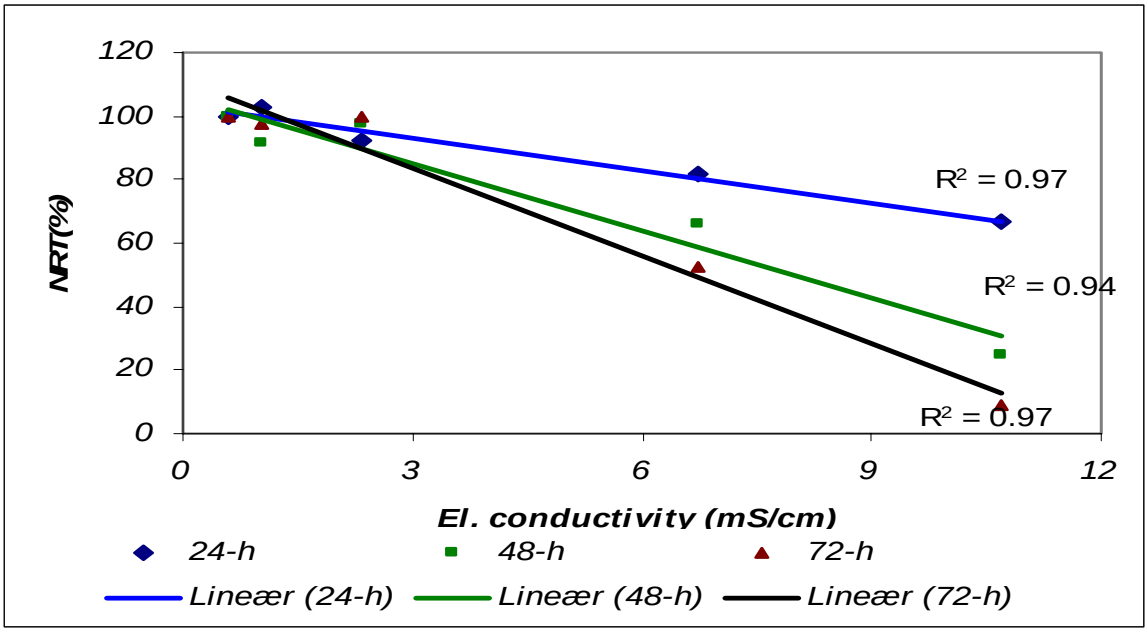

Figure 4.2. Normalized relative transpiration; trees exposed to different NaCl concentrations.

4.5. Objectives of the TBT Clean project.

The implementation of Directive 1999/51/EC supports the global prohibition of the application of organostannic compounds in antifouling systems on ships by 1 January 2003. However, in order to prevent reintroduction of TBT into the marine environment due to desorption from sediments, effective removal and treatment methods for TBT contaminated sediments needed to be implemented simultaneously. Therefore, the TBT CLEAN research project was originated by the Antwerp Port Authority and funded by the European Commission within the LIFE-Environment program. Main objective is the development of an integrated approach for the removal of tributyltin from waterways and ports.

The first goal of this study was to find plants that can grow on dredged harbour sediments. Therefore, plants that have a certain salt tolerance were selected and grown in a laboratory experiment. In this experiment, 4 different plots were compared: a commercial garden soil, a commercial garden soil irrigated with salt water, fresh sediment and lagooned sediment. Plants, grown successfully on sediment in this study, were then sown out in a large field trial in May 2004 and grown until August 2004. Then, the produced fresh and dry mass of the plants in the field trial was determined. Samples were taken from top soil, deep soil and vegetation, and analysed for organotin compounds. The results were compared to blanks (unvegetated samples) in order to determine the influence of vegetation on the degradation of TBT.
The two major aspects of the study can be summarized as:

1) The usability of dredged harbour sediments as a growth substrate for plants
2) The impact of vegetation on the fate of tributyltin.

4.6. Materials and Methods

4.6.1. Origin of the sediments

The Port of Antwerp, where the dredging of the investigated sediments took place, is situated in the upper estuary of the Scheldt river (Figure 4.3), which is partly influenced by saline water from the North Sea.

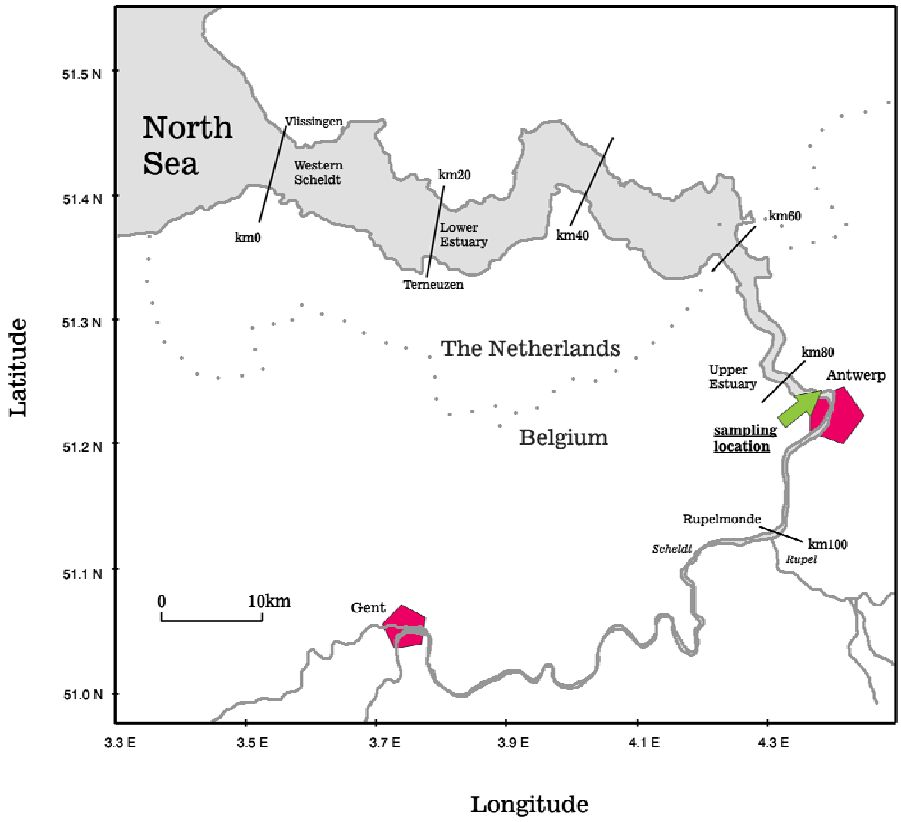

Figure 4.3. Map of the Scheldt Estuary. Lower estuary (km 0–km 60) and upper estuary (km 60–km 100).

The sediment was categorized as either highly (batch 2.1) or lowly polluted (batch 1.5) depending on one of the two sample sites from which it was taken. Each of the two samples was further divided into so-called “lagooned” sediment and “fresh” sediment. “Lagooned” sediment was obtained by disposing the dredged sediments in lagoonation fields. The sediment was turned around regularly. This procedure dewatered and aerated the polluted soil. The “fresh” sediment on the other hand was kept in sealed containers before being analysed. This guaranteed that the sediment kept its high water content and was not exposed to the influences of air and light.

Analysis was performed on sample 2.1 – with the highest TBT concentration measured in the Port of Antwerp sediment in the scope of the TBT CLEAN project – and sample 1.5, which is moderately polluted. This numbering system is adopted from Pynaert et al. (2003), but in this report sample 2.1 and sample 1.5 are mainly referred to as “high” and “low” polluted sediment respectively. On the map below the two sampling locations are presented. Figure 4.4 shows the dredging location on a larger scale map.

Sampling time. As mentioned before, part of the sediment was kept in closed containers near the test field, the other part was spread out over lagoonation fields. Twice samples were taken and sent to Denmark for analysis: first in November 2003 and for the second time in May 2004.

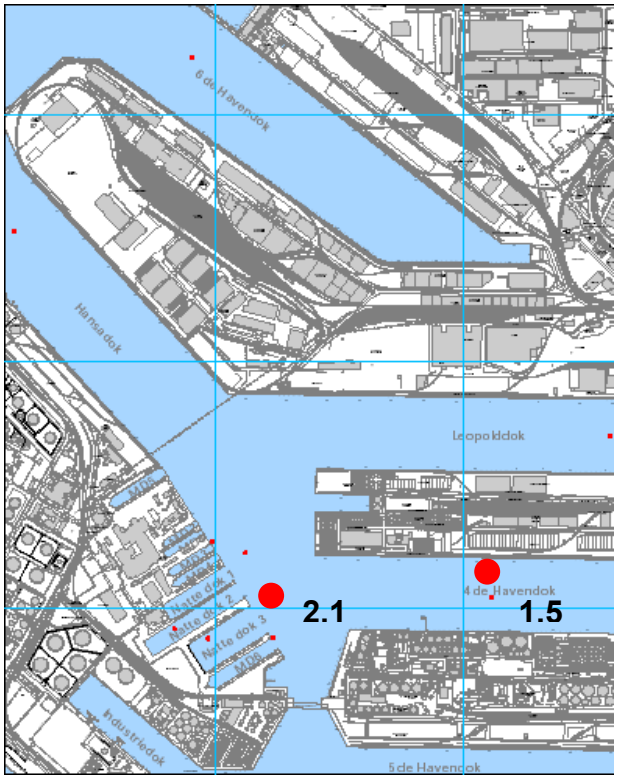

Figure 4.4; Map of the harbour with indication of the two sample locations that have been used for phytoremediation purposes (Pynaert et al. 2003, GIS-map Gemeentelijk Havenbedrijf Antwerpen)

4.6.2. Sediment characterization.

Laboratory analysis was done both in ERC Laboratories (and at Environment & Resources DTU.

Measurement of salinity. The electrical conductivity (EC) of the soil as measure of salinity was determined with an electrode in a solution extracted from the soil sample. The saturation paste extract method was used. The special advantage of the saturation-extract method for

measuring salinity lies in the fact that the saturation percentage is directly related to the field-moisture range. The saturation extract has a soluble-salt concentration of about one-half of the concentration of the soil solution at the upper end of the field-moisture range (field capacity) and about one-fourth the concentration that the soil solution would have at the lower, dry end of the of the field-moisture range (field capacity). The salt-dilution effect occurring in fine-textured soils because of their higher moisture retention is thus automatically taken into account. For this reason, EC obtained with this measuring method can be used directly for appraising the effect of soil salinity on plant growth (Richards 1969). The EC was corrected for temperatures different from 25°C (Rhoades 1996).

Procedure (saturated paste extract). Oven- or air-dry sediment or soil sample is grinded to pass through a 4 mm screen. Sediment is weighed into a bottle and deionized water is added until the saturation point is achieved (the soil paste glistens, flows slightly when the container is tipped, and slides cleanly from a spatula). Weights of both sediment and water are recorded. The paste is left standing overnight to fully dissolve the salts and checked if the saturation criteria are still met. If not, more sediment or water is added. Water is then extracted from the paste by using a Buchner funnel and applying vacuum. EC is measured with an electrode.

Measurement of the cations sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}). The elements were extracted from 1 g of homogenized oven-dry sample with 20 mL of 7N HNO_3 in an autoclave at 120°C. Extracts and standards were diluted using a lanthanum nitrate, cesium chloride and nitric acid solution and elements concentrations measured with Perkin-Elmer AAnalyst 200 Atomic Absorption Spectrophotometer. Calcium (422.67 nm wavelenght) and magnesium (285.21 nm wavelenght) were measured using flame atomic absorption, and for measurement of sodium (589.00 nm wavelenght) and potassium (766.49 nm wavelenght) both flame atomic absorption and flame emission were used.

pH. The pH was measured according to the ISO standard procedure ISO/DIS 10390. A suspension of air-dry soil was made up in five times its volume of deionized water and shaken for 5 minutes. pH meter was calibrated using the standard buffers and pH was measured after approx. 20 hours in the settling suspension. The pH was also measured in the saturated paste extract used for the determination of electroconductivity (procedure described above).

Nutrients. Nitrate and ammonium were extracted from the sample by adding deionized water and shaking for an hour. The extract was then filtered and analyzed photometrically within the next 24 hours with a Technicon Autoanalyzer.

Grain size distribution. The analysis to determine the grain size distribution was done in Belgium by ERC. Samples were examined using laser diffraction (type Malvern mastersizer). No sample pretreatment was carried out (Pynaert et al. 2003).

Bulk density. Bulk density was determined by the ratio of the mass of oven-dried soils to the volume of the bulk soil and calculated by the equation:

$$D_b = \frac{m_s}{V_o},$$

where m_s is mass of oven-dried sample and V_o is the original volume of the sample before drying. Bulk density was measured for non-grinded and grinded samples.

Water content. Water content was measured and calculated according to the equations:

- mass water content: $wc_m = \frac{m_w}{m_s}$,
- volumetric water content: $wc_v = \frac{V_w}{V_o}$,

where m_w is mass of water in the sample, m_s is mass of oven-dried sample, V_w is volume of water in the sample and V_o is the original volume of the sample (before drying).
Water content was measured for original samples as received from Belgium (moist, non-grinded) and air-dried non-grinded and grinded samples.

Laboratory growth experiments

Laboratory growth experiments were performed under controlled laboratory conditions with artificial light in a climatized growth chamber (25 °C).
Four large balcony pots were filled with:

- garden soil, irrigated with tap water
- garden soil, irrigated with 2% saltwater solution
- fresh harbour sediment, irrigated tab water
- lagooned harbour sediment, irrigated tab water

Artifical salt water was mixed with salt provided from an aquarium shop to obtain a 2% salinity. 12 selected types of seeds were sown into each pot. Table 4.1 shows the seeds list.

Table 4.1: Seeds, used in the laboratory growth test.

Common name	**Latin name**	**Seeds per pot**	**Provider**
Salt tolerant grasses ”turfline”	50% Festuca rubra communa *40% Festuca rubra*	40	Prodana, DK

	trichophylla *5% Agrostis stolonifera* *5% Agrostis capillaris*		
Barley ”Ami”	*Hordeum vulgare*	10	Dreschflügel, D
Pea	*Pisum sativum*	10	Dreschflügel, D
(Sugar) Maize	*Zea Mays*	10	Dreschflügel, D
Barley ”California coast”	*Hordeum vulgare*	10	Dreschflügel, D
Hemp	*Cannnabis sp.*	10	Garden shop, DK
Alfalfa (Lucerne)	*Medicago sativa*	10	Garden shop, DK
Barley ”Cluj”	*Hordeum vulgare*	10	Dreschflügel, D
Wheat	*Triticum aestivum*	10	DK

4.6.3. Field growth experiments

A lagoon of approximately 6 x 12 m size was made by using a waterproof plastic membrane. It was split into 4 parts and the plots were separated by sand (Figure 4.5). Drainage tubes were installed in the bottom. Sediment, dredged in May 2003 from the locations mentioned above, was put in the lagoons - one half of the field was filled with highly polluted and the other half with lowly polluted sediment. Before the start of the field growth experiment, the sediment was lagooned in the field. One half of the sediment was turned around 4 times, and the other half was turned around only once, just before sowing. Samples were taken from the sediment turned 4 times. Field growth tests started in May 2004 with sowing and planting 27 different plant species and 2 grass mixes (Table 4.2).

High polluted turned	**High polluted** not turned
Low polluted turned	**Low polluted** not turned

Figure 4.5. Scheme of the lagoonation field

4.6.4. Analysis of organotins.

Laboratory analysis was done both in ERC Laboratories and at Environment & Resources DTU according to a similar protocol.
After derivatization, TBT (tributyltin), DBT (dibutyltin) and MBT (monobutyltin) were analyzed gaschromatographically.

Table 4.2. Species, used for the field growth experiment

Common name	**Latin name**	**Provider**
Quackgrass	*Agropyron repens*	H.Ch. Schobbers, NL
Common marshmallow	*Althaea officinalis*	Medigran, NL
Visnaga	*Ammi visnaga*	Medigran, NL
Scarlet pimpernel	*Anagallis arvensis*	Medigran, NL
Thrift	*Armeria maritima*	Medigran, NL
False Oatgrass	*Arrhenaterum elatium*	H.Ch. Schobbers, NL
Orach	*Atriplex hortensis*	Garden shop, DK
Sugarbeet	*Beta vulgaris*	Philip Seeds, B
Rapeseed, canola	*Brassica napus*	Philip Seeds, B
Pampas grass	*Cortaderia selloana*	Garden shop, B
Sea Kale	*Crambe maritima*	Garden shop, DK
Barley	*Hordeum vulgare*	Philip Seeds, B
Barley ”Cluj”	*Hordeum vulgare Cluj*	Dreschflügel, D
Barley ”Ethiopia”	*Hordeum vulgare Ethiopia*	Dreschflügel, D
Garden cress	*Lepidum sativum*	Aveve, B
Scentless Chamomile	*Matricaria maritima*	Medigran, NL
Alfalfa	*Medicago sativa*	Garden shop, DK
Common reed	*Phragmites australis*	Garden shop, B
Pea	*Pisum sativum*	Aveve, B
Knotgrass	*Polygonum aviculare*	Medigran, NL
Purslane	*Portulaca oleracea ssp. sativa*	Medigran, NL
Curly Dock	*Rumex crispus*	Medigran, NL
Rye	*Secale cereale*	Philip Seeds, B
Sorghum	*Sorghum bicolor*	KVL, DK
Strawberry clover	*Trifolium fragiferum*	H.Ch. Schobbers, NL
Persian clover	*Trifolium resupinatum*	Medigran, NL
Triticale	*Triticosecale Wittmack*	Philip Seeds, B
Salt tolerant grasses	*Lolium perenne* Amadeus 10% *Poa pratensis* Geronimo 10% *Festuca rubra* Dawson 33% *Agrostis capillaris* Highland Bent 10% *Festuca ovina Duriuscula* Crystal 30% *Trifolium repens* Retor 3% *Trifolium pratensis* Merviot 4%	Prof. Vangronsveld, B
Salt tolerant grasses ”turfline”	*Festuca rubra communa* 50% *Festuca rubra trichophylla* 40% *Agrostis stolonifera* 5% *Agrostis capillaries* 5%	Prodana, DK

4.7. Sediment Characterization - results and discussion

The results are given for the laboratory tests and the field trials. First, physical properties of the dredged sediments are presented and discussed, then the chemical properties.

4.7.1. Physical properties of the dredged sediments

The physical properties of the sediments, as grain size distribution, bulk density, water content and saturation percentage, have a large influence on the quality of the sediments for plant growth.

Grain size distribution. The chemical, biological and physical properties of the soil largely depend on the sizes of mineral particles. Table 4.3 shows the measured grain size distribution of the dredged sediments (% of dry weight).

Table 4.3. Grain size distribution of the dredged sediments (% of dry weight).

Sample	High polluted	Low polluted
Fraction < 2 µm	33.1	21.9
Fraction <63 µm	59.9	44.3
Fraction 63-125 µm	12.6	10.9
Fraction 125-250 µm	24.8	33.8
Fraction > 250 µm	2.65	11.0

Using the German classification, which defines clay as a fraction with a diameter < 2 µm, silt with 2 µm to 63 µm and sand with 63 µm to 2 mm (here: > 63 µm), we get the soil texture in Table 4.4.

Table 4.4. Soil texture of the dredged sediments; German classification.

Sample	High polluted	Low polluted
Clay	33.1	21.9
Silt	26.8	22.4
Sand	40.0	55.7
Classification	Clay loam	Sandy clay loam

According to the usual triangular diagram and the determined particle size distribution, our samples can be assigned to the textural classes clay loam and sandy clay loam. Clay loam and

sandy clay loam have both a relatively high clay content and thus possess high cohesive properties (such as stickiness and plasticity) when moistened, but tend to become hard when dry.

Bulk density. Table 4.5 shows the measured bulk densities of the samples. The bulk densities were very low for the garden soil (peat), and still low for the sediment samples.

Table 4.5. Bulk density of the samples.

Parameter	**Bulk density (non-grinded) [kg/m^3]**	**Bulk density (grinded) [kg/m^3]**
Method	ISO/DIS 11272	
Garden soil	140	300
Garden soil + saltwater	/	230
Fresh low polluted sediment (Nov. '03)	700	860
Fresh low polluted sediment (May '04)	/	900
Lagooned low polluted sediment (Nov. '03)	620	840
Lagooned low polluted sediment (May '04)	720	770
Lagooned highly polluted sediment (May '04)	/	990

Water content. Table 4.7 shows the mass water content (method: ISO 11465:1993) and the volumetric water content (ISO/DIS 11461) of the samples. Obvious is the large difference for garden soil, due to the low density. Besides, these data are of course highly variable, changing from very high water contents after dredging to lower contents during lagooning.

Table 4.6. Mass water content (method: ISO 11465:1993) and volumetric water content (ISO/DIS 11461) of the samples.

Parameter	**Mass water content (field moist)**	**Volumetric water content (field moist)**
Garden soil	1,0	0,1
Garden soil + saltwater	/	/
Fresh low polluted sediment (Nov. '03)	0,9	0,6

Fresh low polluted sediment (May '04)	/	/
Lagooned low polluted sediment (Nov. '03)	0,3	0,2
Lagooned low polluted sediment (May '04)	/	/
Lagooned highly polluted sediment (May '04)	/	/

Therefore, the saturation percentage (Table 4.8) was also determined by using the data from the saturation extract method:

$$SP[\%] = \frac{(amountofwater(g), added) \times 100}{(massofairdrysoil(g)) \times ((100 - P_w)/100)}$$

The SP-values derived for dredged sediments are rather typical for clay loams, between 52 and 64 percent.

Table 4.7. Saturation percentages of sediment and soil samples

Parameter	**Weight of sediment/soil [g]**	**Weight of added water [g]**	**Saturation percentage [%]**
Fresh low polluted sediment (Nov. '04)	200	125	64
Fresh low polluted sediment (May '04)	200	123	63
Lagooned low polluted sediment (Nov. '04)	206,5	119	59
Lagooned low polluted sediment (May '04)	205,5	117	58
Lagooned highly polluted sediment	205,5	120	51,5
Garden soil	150	384	280
Garden soil + salt water	100	226	247

4.7.2. Chemical parameters of the dredged sediments

pH. The pH in the sediments was slightly alkaline (Table 4.9), whereas it was acidic in the garden soil, probably due to the high content of humic acids.

Table 4.8. pH of the samples

Parameter	**pH**	
Method	ISO/DIS 10390; air dried, 1:5 volume ratio	saturated paste extract
Garden soil	4,7	4,5
Garden soil + salt water	4,5	4,3
Fresh low polluted sediment (Nov. '03)	7,4	8,0
Fresh low polluted sediment (May '04)	7,7	7,4
Lagooned low polluted sediment (Nov. '03)	7,2	7,2
Lagooned low polluted sediment (May '04)	7,0	7,6
Lagooned highly polluted sediment (May '04)	7,3	7,6

Soil pH is the single most informative measurement that can be made to determine soil characteristics and at a single glance, and it tells more about a soil than merely indicating whether it is acidic or basic. For example, availability of essential nutrients and toxicity of other elements can be estimated because of their known relationship with pH (Thomas 1996). The main impact of soil pH on plant growth is that it influences the solubility of nutrients. It also affects the activity of micro-organisms responsible for breaking down organic matter and most chemical transformations in the soil (USDA 1998).
Plants grow best at a pH of 6 to 7, below 5.5 calcium, magnesium and phosphorus are less available. At low pH, the solubility of aluminium, iron and boron is high; and low for molybdenum. pH above 7.8 accounts for good calcium and magnesium availability, but may

present a risk of low availability for iron, manganese, copper, zinc, and especially of phosphorus and boron.
Also, the behaviour of TBT - which is a cation - may be influenced by pH. Without substituent, TBT is a monovalent cation, named TBT^+, which deprotonates to TBTOH at pKa 6.25 (Hunziker et al. 2001). The K_d (sorption to soil) of the cation is, however, similar to that of the neutral compound.

Nutrients. The values in Table 4.10 were determined in the contract laboratory ERC (pers. comm., Pynaert). What is obvious is an extremely good supply with phosphorus and total nitrogen. However, also chloride and sulphur have elevated levels. This may be explained by the marine influence (chloride), and eventually by sulfide precipitation due to anoxic conditions.
After arriving at DTU, the supply with nitrate was much lower (Table 4.11). This might be explained with denitrification processes during transport. Since these samples were used later for growth studies, this might have had a (negative) influence.

Table 4.9. Concentrations of macronutrients in fresh samples analyzed shortly after dredging.

Sample	**Fresh low polluted sediment**	**Fresh highly polluted sediment**
Nitrate-N [mg NO_3^-/kg DW]	70	95
Ammonium-N [mg NH_4^+/kg WW]	95	65
Chloride [mg/kg DW]	1900	1550
Phosphorous [mg P/kg DW]	2000	2550
Nitrogen total [mg N/kg DW]	1500	2100
Sulphur [mg S/kg DW]	9050	8550
TOC [%C]	1,7	2,7

Table 4.10. Nutrients concentrations in air-dry samples used at DTU.

Element	**NO^{3-} [mg/kg DW]**	**NH^{4+} [mg/kg DW]**
Method	extraction with H_2O and KCl, Technicon Autoanalyser	extraction with H_2O, Technicon Autoanalyser
Garden soil	1000-3000	55
Fresh low polluted sediment (Nov. '03)	< 0,06	20
Lagooned low polluted sediment (Nov. '03)	0,23	0,7

Salinity. Table 4.12 shows the measured electrical conductivity (EC) of the fresh and the lagooned harbour sediments. The EC of fresh sediment is about 14 mS/cm. During lagooning, the values dropped to 7.3 and 3.7 mS/cm.

Table 4.13 shows the EC of the control garden soil used in the lab experiments. EC values for this soil (4.2 mS/cm) are comparable to the values after lagooning the sediments. When this soil was irrigated with salt water (2% salt), the resulting EC-values were about 50 mS/cm.

Table 4.11. EC_s [mS/cm] of different sediment types

Parameter	Method	**Fresh moderately polluted sediment**	**Lagooned moderately polluted sediment**	**Lagooned highly polluted sediment**
EC_s of the sediment, sampled in November 2003 [mS/cm]	saturation paste extract	14.4	7.3	/
EC_s of the sediment, sampled in May 2004 [mS/cm]	saturation paste extract	13.7	3.7	3.7

Table 4.12. EC_s [mS/cm] of the control garden soils (lab test).

Parameter	**Method**	**Garden soil**	**Garden soil + salt water**
EC_s of the soil, sampled after 1 month irrigation with salt water [mS/cm]	saturation paste extract	4.2	~50

The electrical conductivity is a measure for the total ion content of soil solution. The salinity of the soil depends, however, on the composition of these ions. Table 4.14 shows the measured content of the cations sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}). As can be seen from Table 4.14, the level of sodium in the lagooned sediment is generally higher than in the garden soil, unless this is irrigated with salt water.

Table 4.13. Measurement of the cations sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}).

Element	**Na^+ [mg/kg DW]**	**Ca^{2+} [mg/kg DW]**	**K^+ [mg/kg DW]**	**Mg^{2+} [mg/kg DW]**
Method	extraction with HNO_3, AA, FE	extraction with HNO_3, AA	extraction with HNO_3, AA, FE	extraction with HNO_3, AA
Garden soil	320	10500	2650	2800
Garden soil + salt water 14 days	25200	10700	2100	4900
Garden soil + salt water 1 month	34730	10700	2200	5450
Fresh low polluted sediment (Nov. '03)	2330	42800	8050	5500
Fresh low polluted sediment (May '04)	1650	48600	6400	5130
Lagooned low polluted sediment (Nov. '03)	1120	39500	6650	4810
Lagooned low polluted sediment (May '04)	970	43000	6230	4640

Lagooned highly polluted sediment (May '04)	420	41000	5640	4180

Comparing the sodium concentration, relative to the other cation concentrations, provides a measure for the so-called sodicity. The sodicity defining parameter known as the sodium absorption ratio (SAR), is calculated by the following equation:

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{[Mg^{+2}]+[Ca^{+2}]}{2}}}$$

Concentrations of ions in the equation are expressed in milli-equivalents per liter (meq/L). To convert ppm or mg/L Na^{+} to meq/L, divide by 23, for Ca^{2+} divide by 20, for Mg^{2+} divide by 12,2 and for K^{+} divide by 39,1. The sodium absorption ratio SAR is given in Table 4.15. The SAR of fresh sediment is far higher than for garden soil, but much lower than for garden soil irrigated with salt water. During lagooning, the values drop, but are still elevated. Low TBT polluted soil has the higher value, compared to high TBT polluted soil.

Table 4.14. The sodium absorption ratio (SAR) for different samples

Parameter	**Na^{+} [meq/L]**	**Mg^{2+} [meq/L]**	**Ca^{2+} [meq/L]**	**SAR**
Garden soil	13.9	229.5	525	**0.7**
Garden soil + salt water 14 days	1095.7	401.6	535	**50.6**
Garden soil + salt water 1 month	1510.0	446.7	535	**68.2**
Fresh low polluted sediment (Nov. '03)	101.3	450.8	2140	**2.8**
Fresh low polluted sediment (May '04)	71.7	420.5	2430	**1.9**
Lagooned low polluted sediment (Nov. '03)	48.7	394.3	1975	**1.4**
Lagooned low polluted sediment (May '04)	42.2	380.3	2150	**1.2**

Lagooned highly polluted sediment (May '04)	18.3	342.6	2050	**0.5**

Influence of salinity on the growth of plants

Saline soil by definition contains soluble salts with electrical conductivity of the saturation paste extract being higher than 4 dS/m, while pH of the saline soils is 8,5 or less (Richards 1969). Essential ions in saline soils are Na^+, Mg^+, Ca^{2+}, K^+, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^2. The most common are chlorides or sulfates, and less than half of the cations are sodium (Brady 1996). Salinity has a negative effect on growth of most crop plants. Usually growth is gradually reduced as salinity increases above a threshold value which varies for different species. Many of the most salt-tolerant higher plants (halophytes) can survive salinities which at times exceed that of seawater (about 55 dS/m), and at the other extreme, growth of the most salt-sensitive glycophytes (non-halophytes) is severely limited at concentrations as low as 4 dS/m (Table 4.16).

Table 4.15. Crop responses to soil salinity measured in the saturated paste extract (Plaster 2003).

Class	**Salinity (dS/m)**	**Crop response**
Non-saline	0-2	Salinity effects unimportant
Slightly saline	2-4	Yields of sensitive crops lowered
Moderately saline	4-8	Yields of many crops lowered
Strongly saline	8-16	Only tolerant crops yield well
Very strongly saline	More than 16	Only most tolerant crops yield well

The classical accounts of the effect of salinity on plants emphasize four main ways in which salinity can affect plant growth:

a) water deficit due to the osmotic problem

It arises because of the high osmotic pressure (low water potential) of the soil, which narrows the gap between the external and the internal water potential and tends to withdraw water from the plant, which in the case of salt-sensitive plants results in rapid and irrecoverable wilting (Rozema 1996, Bustan et al. 2003).

b) ion toxicity which disrupts the metabolic activity of the cell

Unless the influx of salts (especially sodium and chloride) is limited it will rapidly reach toxic concentrations within the plant (Bajji et al. 1998).

c) nutrient imbalance

Salt may interfere with the ability of plants to acquire or assimilate other nutrients (Grattan et al. 1992).

d) restriction of CO_2 uptake

Salinity decreases net CO_2 assimilation through effects on stomatal opening and the efficiency of the photosynthetic machinery (Ungar 1991).

Since our sediment had a salinity of approximately 14 dS/m upon dredging, it can be considered strongly saline and therefore only tolerant crops are expected to perform well on it. With lagoonation over a time period of several months, the salinity dropped only to approx. 3.7 dS/m, which is still a hindrance to good establishment of salt-sensitive crops. Therefore the plant species, used for phytoremediation of TBT-polluted sediment from the port of Antwerp, had to be chosen on the basis of their salt tolerance.

Sodicity. Sodic soils are low in the kinds of salts found in saline soils but high in sodium (Plaster 2003). Soil sodicity is usually measured with one of two indices; one is the sodium absorption ratio (SAR) which gives information on the comparative concentrations of Na^+, Ca^{2+} and Mg^{2+} in a soil solution and the second one is the exchangable sodium percentage (ESP), which measures the degree to which the exchange complex is saturated with sodium. The critical values for considering a soil sodic are a SAR above 13 and an ESP value of minimum 15 (Brady 1996).

In contrary to saline soils, the pH of sodic soils is higher than 8,5 (Plaster 2003). This is due to the hydrolysis of sodium carbonate:

$2Na^+ + CO3^{2+} + H_2O \leftrightarrow 2Na^+ + HCO^{3-} + OH^-$

The sodium complex also undergoes hydrolysis:

$Na^+ + H_2O \leftrightarrow H^+ + Na^+ + OH^-$

In soils containing clay particles this exchange of sodium ions for calcium ions can result in swelling and dispersion of those particles. Subsequently waterlogged conditions, poor aeration and impenetrable soil structure may occur (Figure 4.6).

Figure 4.6. A typical example of sodic soil. Due to dispersion of soil aggregates, the structure is destroyed, leading to cracks and sparse vegetation.

Fine textured soils (i.e. clays, clay loams, silts, silt loams, etc.) may experience dispersion and crusting already for SAR levels above 5 to 6 (Silvertooth 2001). This is far above the SAR determined for the dredged sediments, even after lagooning. Nonetheless, the sediments used in the field trial showed signs of sodic soils, probably due to the high clay content and a salt enrichment in the top cm due to water evaporation. The cracked cement-like structure of the sediment from the port of Antwerp after disposition in lagoonation fields and subsequent drying up is visible. In soil with such structure plants cannot grow well.
Besides reduced permeability, poor aeration and waterlogging, which are consequences of soil sodicity, direct toxic effects of sodium to plants as well have to be taken in account. Crops vary in their tolerance to sodium. For the most sensitive crops, like citrus fruits, the toxic effects of sodium are more important than its effects on structure. For sodium-tolerant crops, poor growth results mainly from soil conditions. Table 4.17 shows the sodium tolerance of some selected crops (Plaster 2003).

Table 4.16. Sodium tolerance of plants; bold: used in tests.

Sensitive Sodium Percentage (ESP = 2-20)	**Moderately Tolerant (ESP = 20-40)**	**Tolerant (ESP = 40-60)**	**Most Tolerant (ESP Above 60)**
Deciduous fruit	**Clover**	**Wheat**	Crested wheatgrass
Nuts	Oats	Cotton	Tall wheatgrass
Citrus fruit	Tall fescue	**Alfalfa**	Rhodesgrass
Avocado	Rice	**Barley**	
Bean	Dallisgrass	Tomato	
		Beets	

Pollutants in the dredged sediments

Analysis of the dredged sediments on other pollutants than organotins was done by ERC. Analysis was performed on heavy metals, polycyclic aromatic hydrocarbons, PCB (Table 4.18), and several other pollutants, among them monocyclic aromatic hydrocarbons (all <0.2 mg/kg), chlorobenzenes (all below detection limits, ranging from 0.1 to 0.005 mg/kg), chloroorganic solvents, including TCE, vinylchloride and tetrachloroethene (all below 0.1 mg/kg), mineral oil (about 700 mg/kg), organochloropesticides such as DDT, lindane, aldrin etc (all < 0.005 mg/kg), but ppDDE was found (0.018 mg/kg), chloroanilines (all < 0.1 mg/kg) and organophosphorpesticides (all < 0.02 mg/kg).

Most values for heavy metals lie between the "quality standard" and the "intervention value" (Dutch list). PAH and PCB are relatively low.

Table 4.17: Environmental pollutants measured in the dredged harbour sediment. Source: ERC

Chemical	**Unit**	**Sample "low" (location 1.5)**	**Sample "high" (location 2.1)**	**Average of 16 different locations**
Arsenic	mg/kg DS	31	38	44.8
Cadmium	mg/kg DS	3.4	5.2	8.9
Chromium	mg/kg DS	97	120	135.4
Copper	mg/kg DS	63	280	106.3
Mercury	mg/kg DS	0.64	1.5	1.3
Lead	mg/kg DS	111	180	230.6
Nickel	mg/kg DS	15	30	31
Zink	mg/kg DS	342	780	839.9
Naphthalene	mg/kg DS	0.23	0.25	0.29
Acenaphthylene	mg/kg DS	0.02	0.12	0.07
Acenaphthene	mg/kg DS	0.07	0.05	0.10
Fluorene	mg/kg DS	0.09	0.23	0.15
Phenanthrene	mg/kg DS	0.31	0.56	0.44
Anthracene	mg/kg DS	0.11	0.2	0.15
Fluoroanthene	mg/kg DS	0.51	0.62	0.84
Pyrene	mg/kg DS	0.51	0.6	0.82
Benzo(a)anthracene	mg/kg DS	0.26	0.31	0.43
Chrysene	mg/kg DS	0.38	0.49	0.58
Benzo(b)fluoranthene	mg/kg DS	0.65	0.59	0.96
Benzo(k)fluoranthene	mg/kg DS	0.2	0.26	0.30

Benzo(a)pyrene	mg/kg DS	0.36	0.33	0.53
Dibenzo(a,h)anthracene	mg/kg DS	0.07	0.08	0.10
Benzo(g,h,i)perylene	mg/kg DS	0.23	0.24	0.28
Indeno(1,2,3,c,d)pyrene	mg/kg DS	0.29	0.2	0.36
Sum		4.29	5.1	6.13
PCB 28	mg/kg DS	0.010	not determined	n.d.
PCB 52	mg/kg DS	0.025	n.d.	n.d.
PCB 101	mg/kg DS	0.018	n.d.	n.d.
PCB 118	mg/kg DS	0.011	n.d.	n.d.
PCB 138	mg/kg DS	0.039	n.d.	n.d.
PCB 153	mg/kg DS	0.034	n.d.	n.d.
PCB 180	mg/kg DS	0.019	n.d.	n.d.

4.8. Growth tests - results and discussion

4.8.1. Laboratory growth tests

Seed germination test. The germination of seeds was tracked over several weeks. Figure 4.7 shows the germination after 8 days, Figure 4.8 after 15 days.
Some seeds did very badly in all soils. To mention first hemp (*Cannabis*). The seeds had been heated to avoid misuse by drug-abusers, as we found out later. And less than 40% of wheat seeds germinated. This may be due to the age of the seeds (2 years), or bad storage.
In lagooned harbour sediments, seed germination was generally good, usually as good as in garden soil. In fresh harbour sediments, germination was generally bad. Best germination showed salt tolerant turfline, pea and some barley races.
Only the three barley races did well in garden soil irrigated with salt water. This remarkable result differs from the germination in fresh sediment and shows that salt in the harbour sediments is not a big problem for the seeds. This is in agreement with the chemical measurements of the electrical conductivity.
Another criterion measured is the time needed until germination. An early germination is a positive sign, whereas delayed germination shows an inhibition by the substrate. Figure 4.9 shows the time course of germination for the barley race ”Ami”. As can be seen, this barley germinated quickly in garden soil, both with tap and salt water irrigation; germination in lagooned sediment was delayed; germination in fresh sediment was slowest, and with the lowest number.

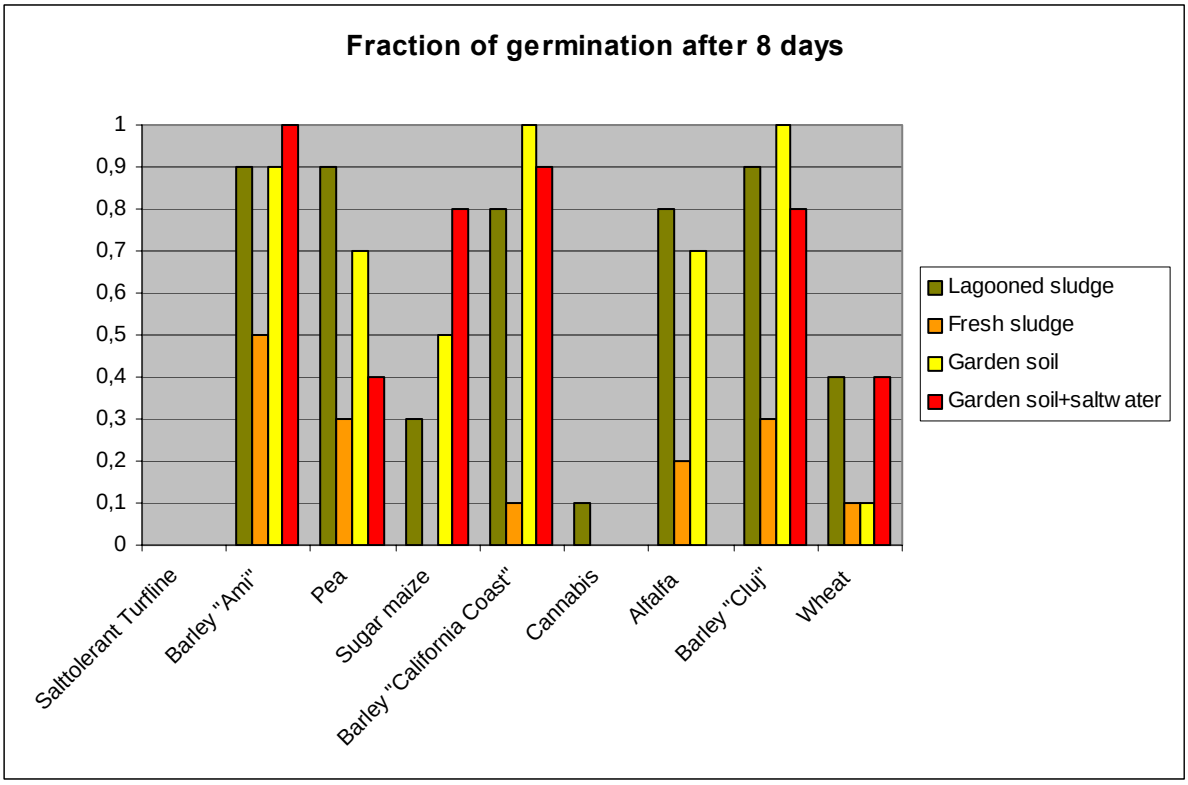

Figure 4.7: Germination of seeds after 8 days.

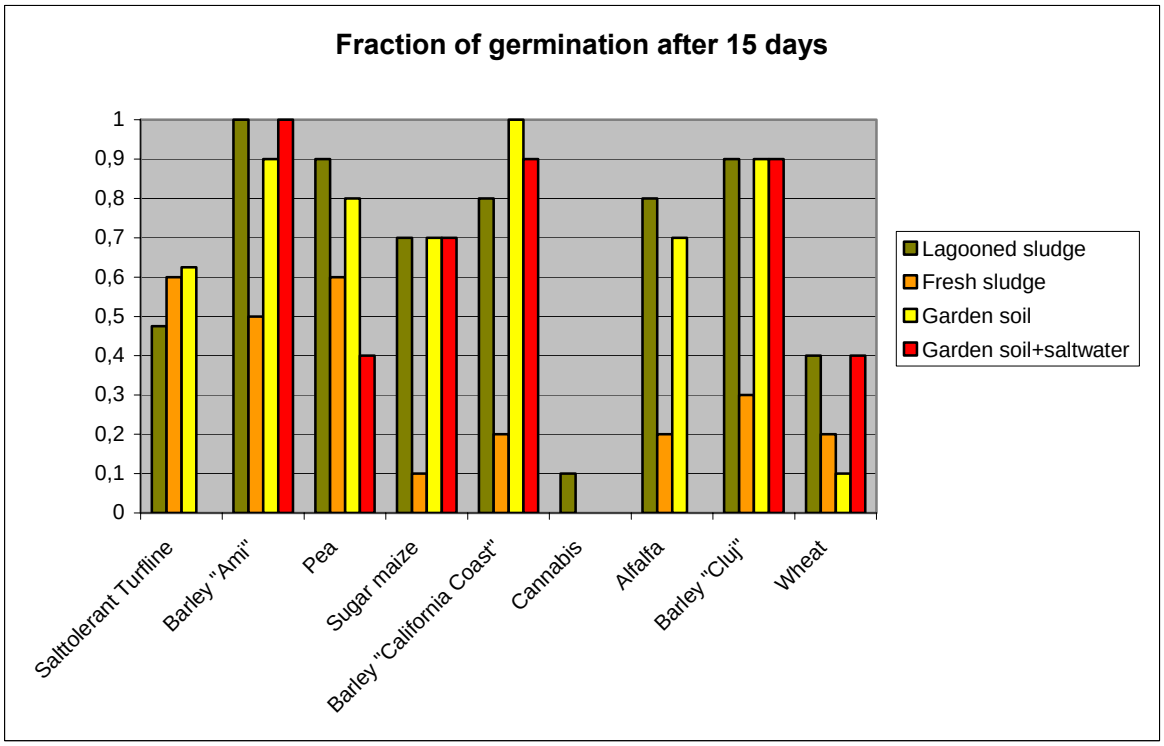

Figure 4.8: Germination of seeds after 15 days.

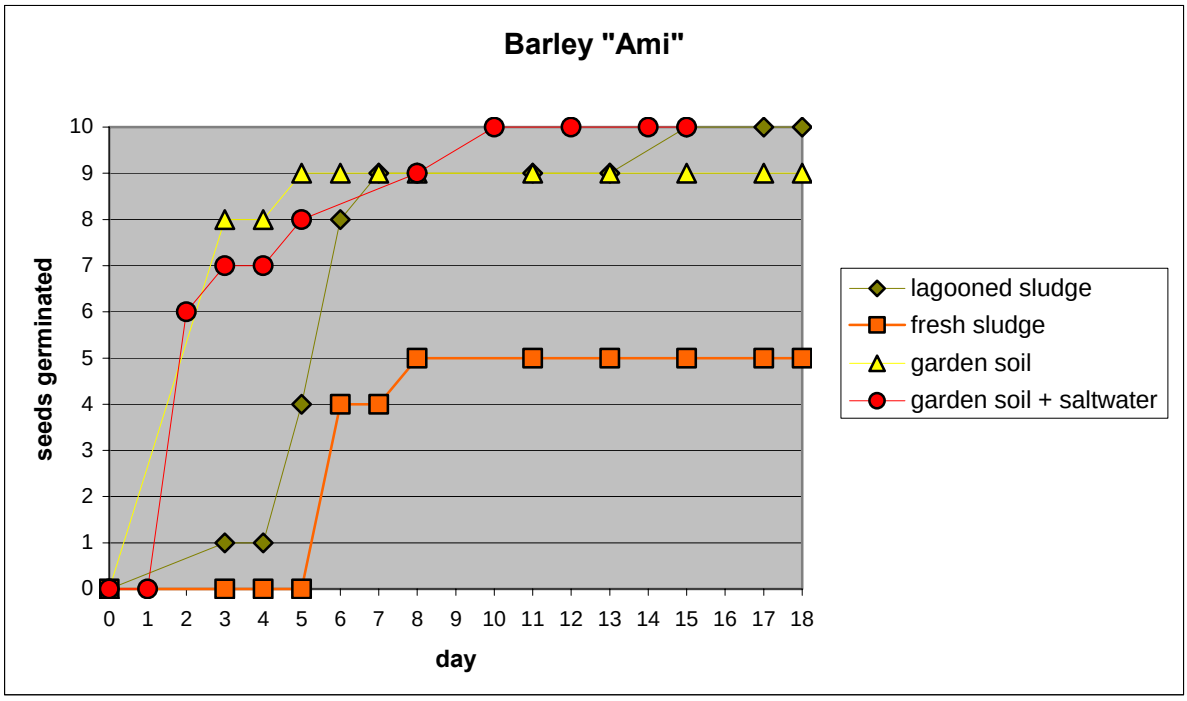

Figure 4.9. Time needed for germination, Barley ”Ami”.

Growth of plants. There were big differences in the growth of the plants on the four different substrates. The ”salt tolerant grasses” grew well in garden soil and lagooned sediment (Figure 4.10). Growth in fresh sediment was 50% reduced. Growth in garden soil watered with salt water was none. This makes us doubt about the salt tolerance of the selected species. *Festuca rubra* is mentioned in the halophytes database (Lieth and Mochtchenko 2003); it tolerates 1.6% salt (2% was used). *Agrostis stolonifera* tolerates 3.6% salt (sea water).

Pea grew well in garden soil, and – with some reduction – in lagooned sediment. It had serious problems in fresh sediment and salt garden soil (Figure 4.11). Sugar maize grew in all plots the same velocity, except in fresh sediment (Figure 4.12). Alfalfa had problems in fresh sediment, and failed when irrigated with salt water (Figure 4.13). Once germinated, wheat grew fine in all soils. Wheat is known to be salt tolerant to a certain limit (Figure 4.14). Barley was the only species which generally grew better in fresh sediment than in lagooned sediment. Also, salt water irrigation provided no problems (Figures 4.15-4.17).

For some of the plants it could be seen that after initially fast growth in lagooned sediment, leaves turned yellow, and growth slowed down. This might be due to a lack of nutrients in lagooned sediment, possibly inorganic nitrogen, which had been lost due to denitrification.

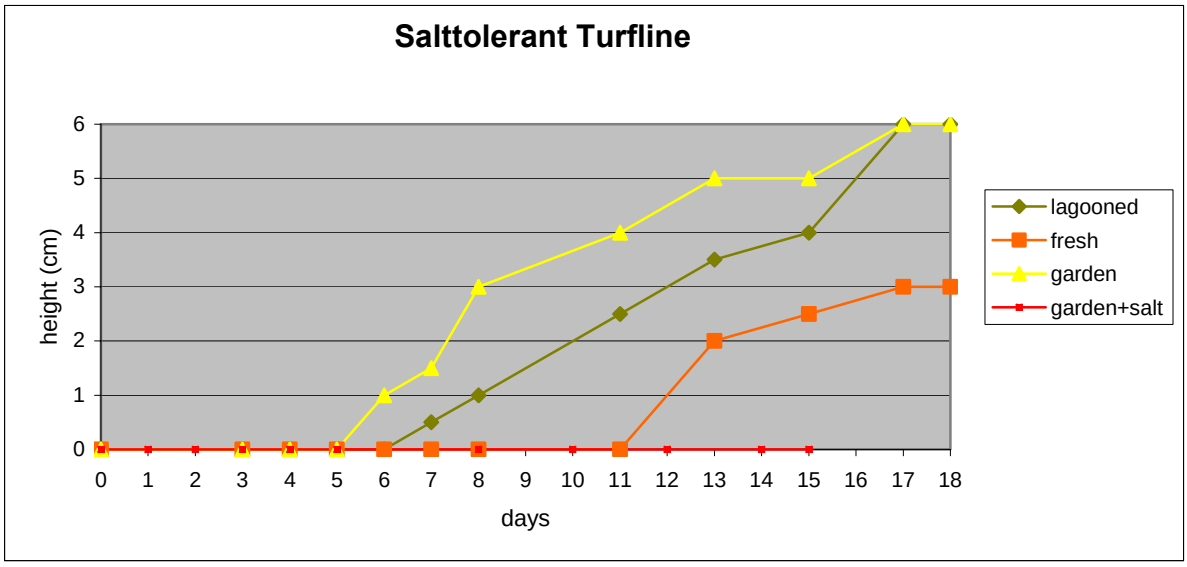

Figure 4.10. Growth of salt tolerant turfline.

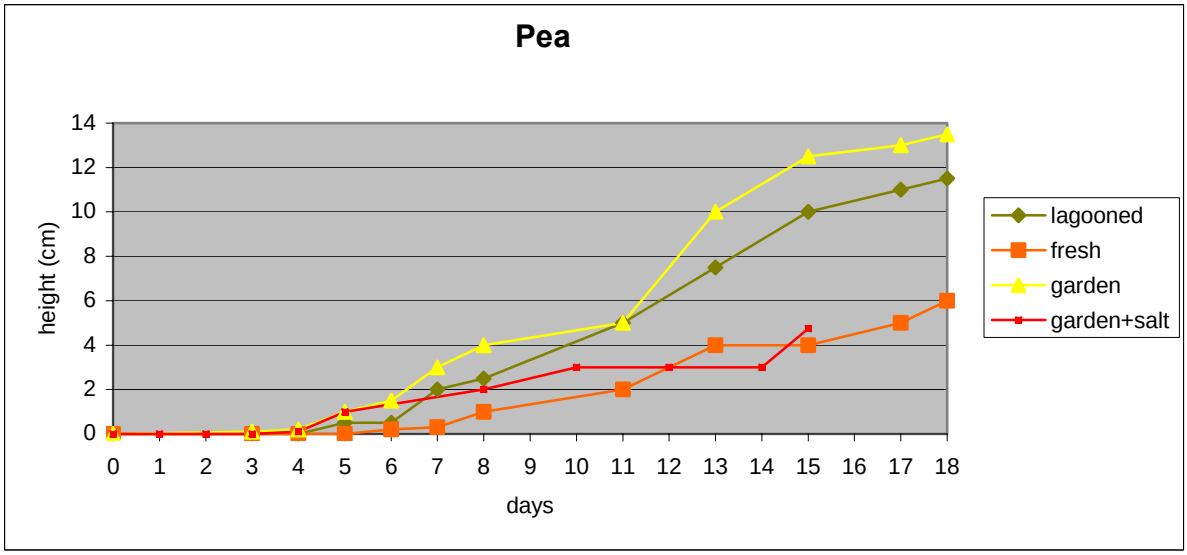

Figure 4.11. Growth of pea.

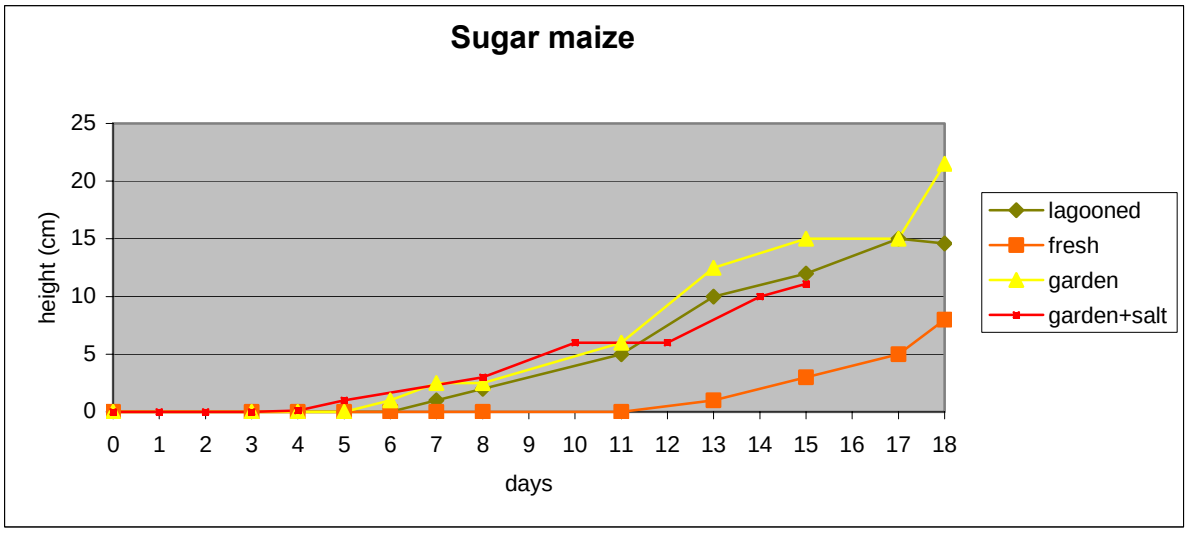

Figure 4.12. Growth of maize.

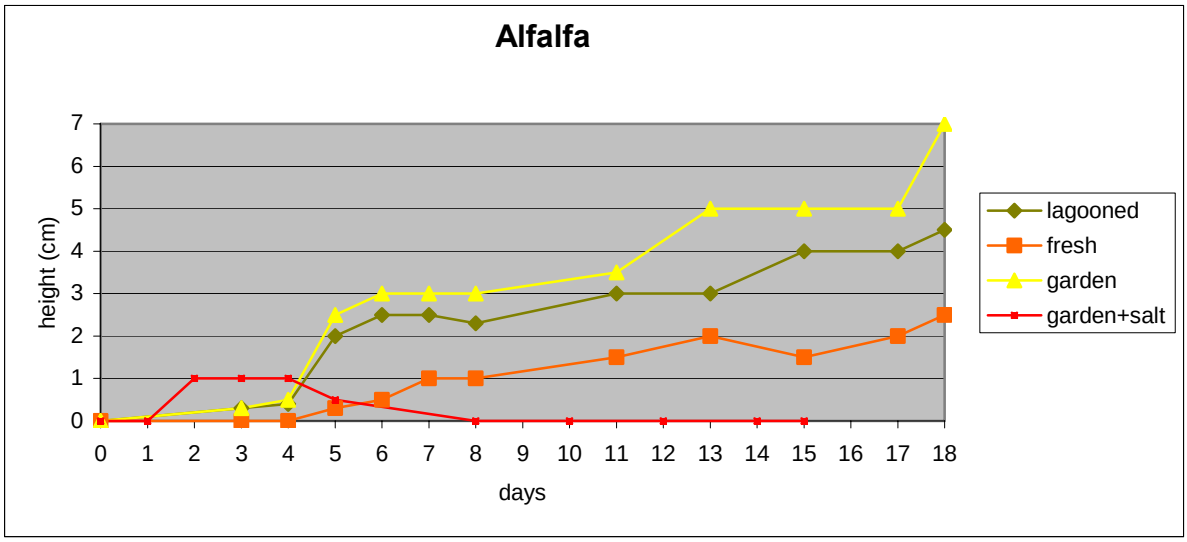

Figure 4.13. Growth of alfalfa.

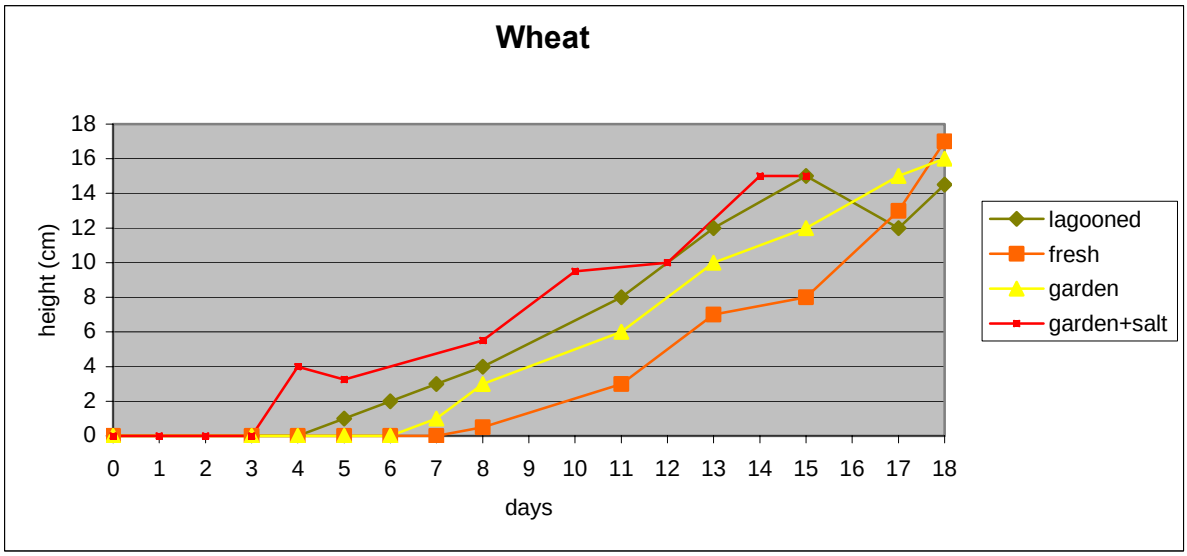

Figure 4.14. Growth of wheat.

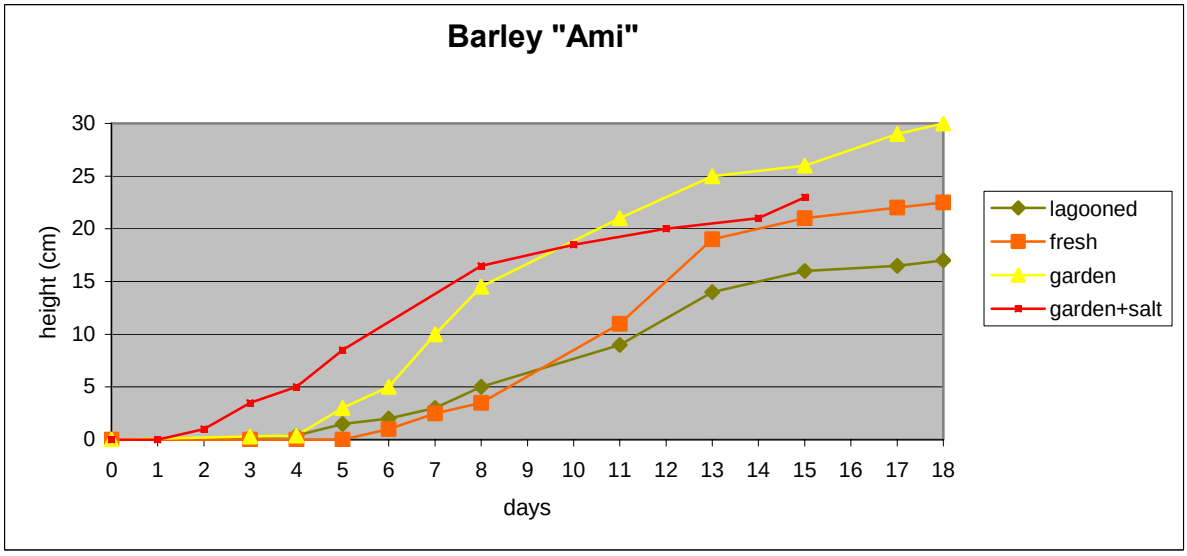

Figure 4.15. Growth of barley ”Ami”.

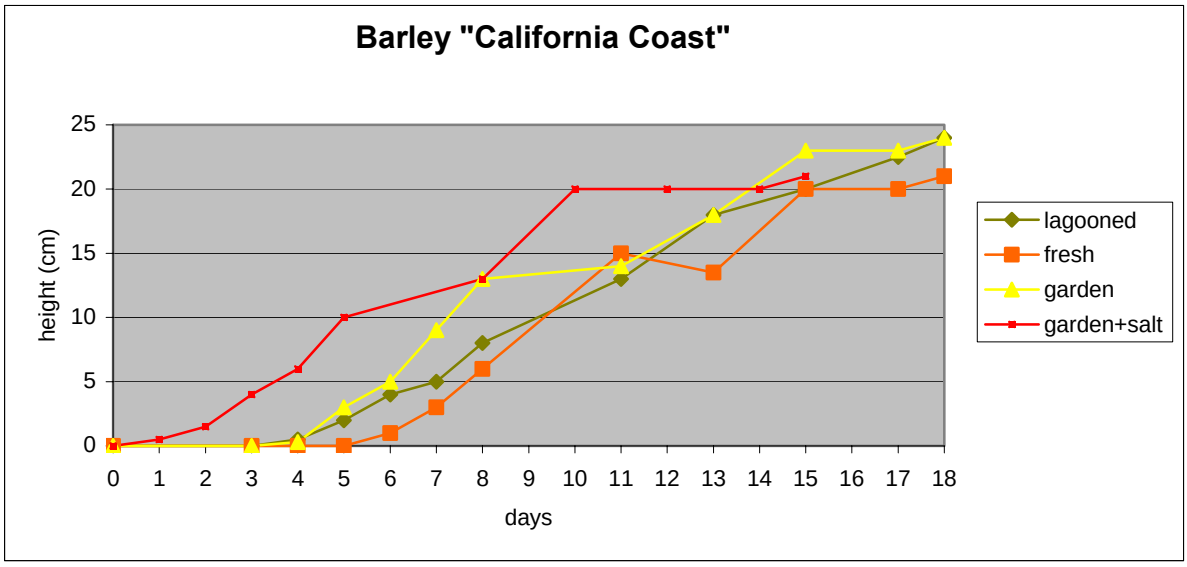

Figure 4.16. Growth of barley ”California coast”.

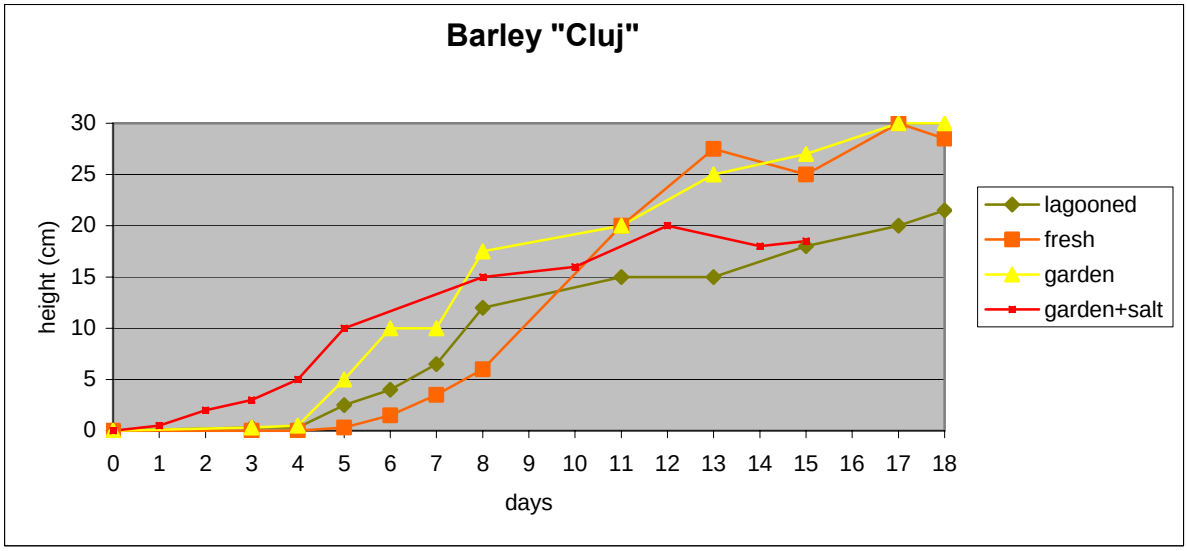

Figure 4.17. Growth of barley ”Cluj”.

The results first show that salt toxicity is not the only problem of plants on harbour sediments: Plants that are not very resistant to salt, such as the so-called ”salt tolerant grasses” and the pea, could grow on fresh or lagooned sediment. This is supported by the chemical analysis which showed elevated, but not exceptionally high electrical conductivity in harbour sediment.

To select the best plants for growth in harbour sediment, the seed germination and the growth of seedlings have to be combined. Sufficient germination in fresh sediment (> 30%): salt-tolerant grasses, 2 barleys, pea. Sufficient germination in lagooned sediment (> 30%): all plants, except cannabis. Sufficient growth in fresh sediment (> 50% of controls): All barley species, wheat. Good growth in fresh sediment (similar to controls): 2 barley species, wheat.

Sufficient growth in lagooned sediment (> 50% of controls): all species. Good growth in lagooned sediment (similar to controls): salt-tolerant grasses, 1 barley species, wheat.
Taking these results together, only one plant species, that is barley, can be recommended for sowing on fresh harbour sediment: In both germination and growth test, barley made the best. This can also easily be seen by a visual inspection (photo in appendix 1). However, there were differences between the races. On lagooned sediment, most species have a fair chance to establish, with barley again performing best in the experiments.
Barley has been selected for testing due to the fact that in the old days, barley was grown in the marsh land along the North Sea coasts. In principle, marsh land, which is land freshly won from the sea, has many similarities to fresh harbour sediment. Barley is as well one of the major agricultural plants and therefore easily available in several races and varieties. Barley can be sown in April (summer barley) or in autumn (winter barley). There are no special agricultural practices needed, and the harvest product might have an economic value (e.g., for seed production).

Figure 4.18. A photo from the laboratory system; from left to right: lagooned sediment, fresh sediment, garden soil and garden soil irrigated with salt water.

4.8.2. Field growth test

Both sediments (batch 1.5 and 2.1) were planted according to the scheme in figure 4.19.

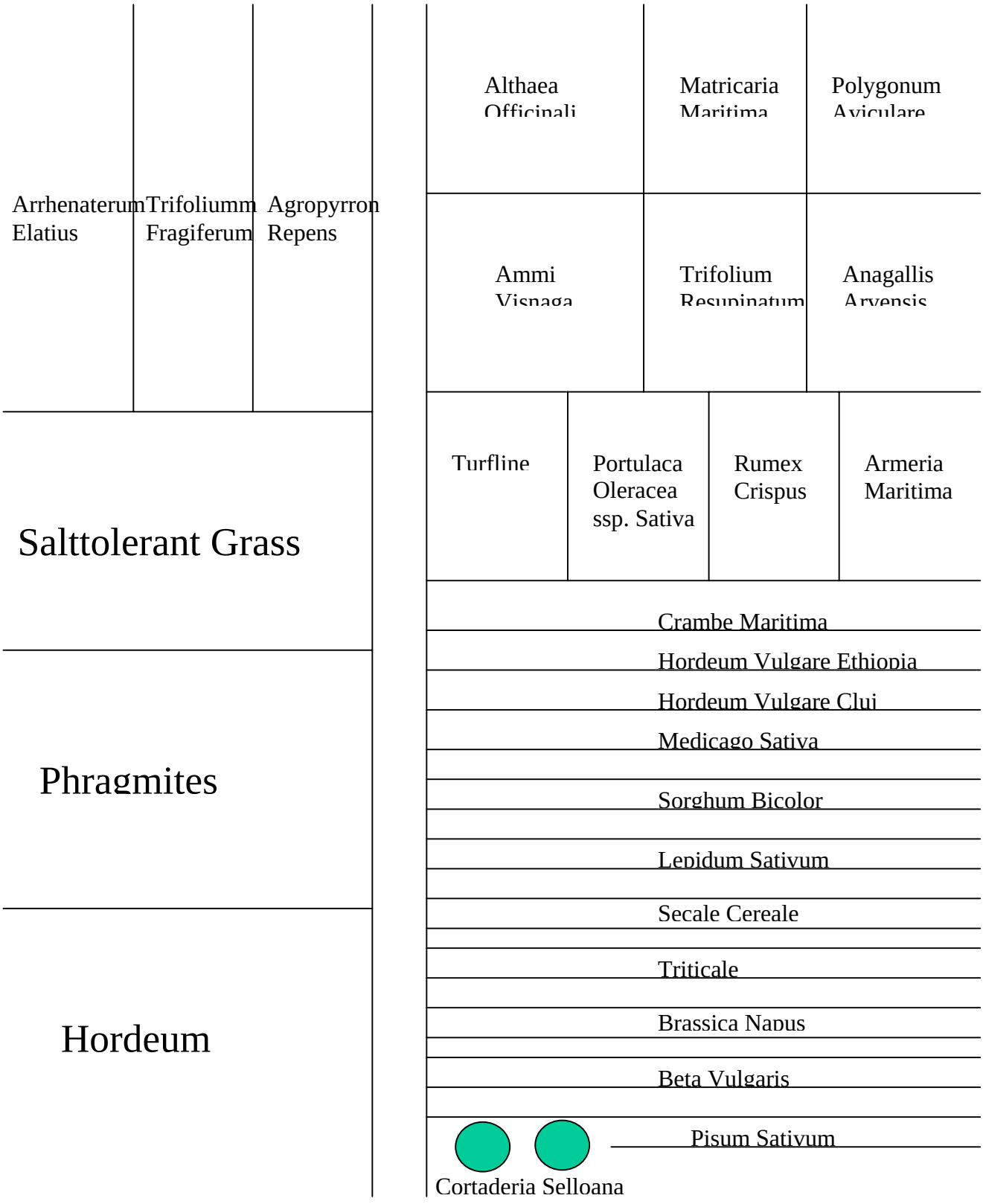

Figure 4.19. Planting scheme for the phytoremediation fields.

The field growth test gave as result the very good growth of *some* of the selected species. This is illustrated in figures 4.20 to 4.26.

Figure 4.20. End of May 2004, shortly after sowing.

Figure 4.21. August 2004, barley ripe for harvest.

Figure 4.22. Sorghum (millet).

Figure 4.23. A rape-seed plant held by Jana Novak.

Figure 4.24. Panoramic overview of the phytoremediation fields (End of June 2004)

Figure 4.25. View on the medicago sativa, sorghum, lepidum sativum, secale cereale.

Figure 4.26. View on the triticale, brassica napus, beta vulgaris.

Figure 4.27. Some of the grass and herb mixes (see top right planting scheme figure 4.19).

As becomes obvious from the photos, the growth of several plant species was as good as in agricultural fields. It must be mentioned that the responsible gardeners are non-professionals, and neither pesticides nor fertilizer were used.
Table 4.19 gives the results from the dry weight production measurements on the field sites. For convenience, the results were recalculated from fresh weight / 0.25 m^2 to dry weight in tons per hectare. Results represent the complete dry mass production above surface, not specifying for the harvest product.

The highest dry mass was produced by Sorghum, a close related of maize and like that a C4-plant. The yield was higher on the "high" TBT contaminated plot, reaching 13 tons/ha, although the plant was not yet ripe. For barley (*Hordeum vulgare*), 10 tons/ha were yielded on the "low" plot, and 9 tons/ha on the "high" plot. The salt-tolerant clover/grass mix yielded 6.24 and 8.7 t/ha on the "high" and "low" plot, respectively. Rapeseed (*Brassica napus*) yielded 7 and 2 tons on the "high" and "low" plot, respectively.

So there were differences between the "low" and "high" TBT-contaminated plots. However, the differences in growth cannot be contributed to eventual differences in salinity. The salt-tolerant barley had on both plots high yields, the less salt-tolerant *Brassica* had a far higher yield at the "high" TBT plot, and *Atriplex*, a salt-tolerant vegetable, had a factor 10 lower harvest yield at the "low" contaminated plot. Generally, the growth on the high-TBT contaminated plots was similar or better than on the "low" plot.
This might be due to the different texture of both soils: the "high" plot consisted of clay loam, whereas the "low" plot had more sand and was therefore classified as sandy clay loam. Generally, loam is supplying plants better with water and nutrients than sand and is therefore a better substrate for most plants.
It might, however, also be speculated that TBT is toxic to most enemies of the plants, such as snails, insects, nematodes, other soil invertebrates and fungi, whereas plants are not hit by the effect of this chemical. This might replace pesticides, which would be used in normal agriculture.

Wild species.
Besides the plants cultured on the plots, several wild species could be found. Determined were:

- *Atriplex litoralis, A. hastata* or other *Atriplex sp.*
- *Matricaria maritima* (which had also been used in the growth experiments)
- *Polygonum lepathifolium*
- *Artemisia vulgaris*
- *Lactuca serriola*

Generally, the growth of these wild species was good.

Table 4.18: Dry weight of the plants on the field.

plant species	**sowing spacing (cm)**	**fresh weight g/0,25m^2**	**% dry matter**	**dry weight g/m^2**	**Dry weight t/ha**
Hordeum vulgare (barley) low	15	355	0.72	1024	10.2
Hordeum vulgare (barley) high		295	0.77	908	9.1
Grass/clover mix low	0	850	0.26	867	8.7
Grass/clover mix high		676	0.23	624	6.24
Brassica napus (rapeseed) high	30-40	1430	0.12	700	7.0
Brassica napus (rapeseed) low		475	0.11	209	2.1
Phragmites australis (reed) low	30-40	295	0.28	326	3.3
Phragmites australis (reed) high		375	0.27	411	4.1
Medicago sativa (alfalfa) low	15-20	620	0.17	417	4.2
Medicago sativa (alfalfa) high		750	0.24	719	7.2
Triticale low	15	290	0.47	548	5.5
Triticale high		335	0.36	487	4.9
Sorghum bicolor low	50	945	0.27	1033	1.0
Sorghum bicolor high		1250	0.26	1299	1.3
Matricaria maritima low	0	277	0.23	258	2.6
Matricaria maritima high		643	0.26	681	6.8
Atriplex hortensis low	50	57	0.15	34	0.34
Atriplex hortensis high		464	0.18	342	3.4
Portulaca oleracea low	0	2350	0.10	931	9.3
Portulaca oleracea high		1340	0.08	453	4.5
Salttolerant grass mix “Turfline” low	0	70	0.37	103	1.0
Salttolerant grass mix “Turfline” high		165	0.30	195	2.0
Rumex crispus low	0	51	0.12	25	0.25
Rumex crispus high		114	0.16	72	0.72

4.8.3. TBT balance - results and discussion

This paragraph describes the effect of the vegetation on the TBT degradation in the field trial. It will start, however, with the effect of lagooning.

4.8.3.1. Effect of lagooning on the fate of TBT

Lagooning (in this report the word “lagooning” is used for periodically turning the sediment around) experiments were performed on the field in Ruisbroek by DEC before the start of the phytoremediation trial.
As described before, the growth of plants in the fresh sediment was quite limited, whereas lagooned sediment was a good substrate. Lagooning not only dewaters the sediments and improves significantly the structure of the resulting soil, it also has a positive effect on TBT degradation.
Figure 4.28 and 4.29 show the measured concentrations of TBT in fresh and lagooned sediment in the low and high contaminated sediment before the start of the experiment (Nov. 2003). The columns named "blank" are the results from the unvegetated soil from the field plot at the end of the field trial in August 2004, taken at a depth of 5 - 15 cm and at 50 cm (blank deep).
For the low contaminated site ("low"), there is a reduction of the TBT content of about 40% due to repeated lagooning. The results in August 2004 from the field trial (blank) are close to the measured values after lagooning from November 2003, but higher both at the upper and lower depth. This means that there was not much reduction in unvegetated soil, compared to the initial values. That the values are higher in 2004 than in 2003 may be explained by the relatively small sample size.

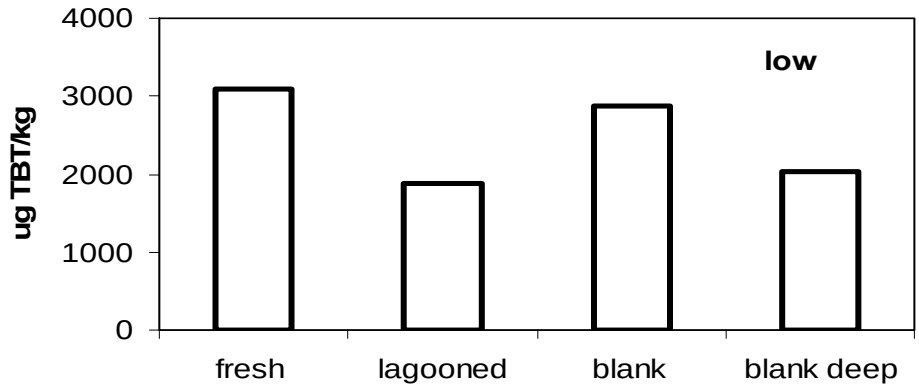

Figure 4.28. Measured TBT concentrations in the fresh sediment (n = 3), the lagooned sediment (n = 3), in the blanks of field trial at 5 - 15 cm depth (n = 5) and 50 cm depth (n = 2); low contaminated site.

For the high contaminated site ("high"), there is a reduction of the TBT content of about > 70% due to repeated lagooning. However, the results from the field trial are almost twice at high as the values after lagooning, showing that the effect of lagooning is maybe overestimated due to "lucky" sampling (only 1 and 2 samples have been taken, whereas the blanks together consist of 7 composite samples).
Nonetheless, the lagooning technique is a necessary step for vegetating the sediment, and it obviously reduces the TBT content.

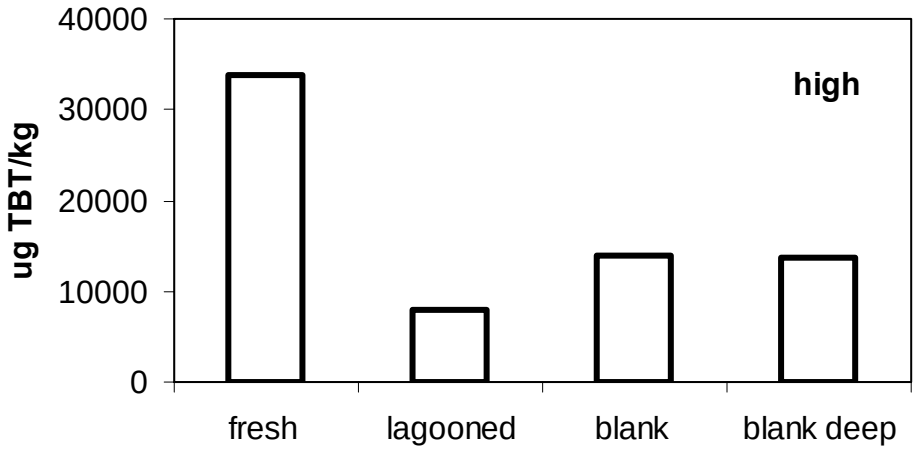

Figure 4.29. Measured TBT concentrations in the fresh sediment (n = 1), the lagooned sediment (n = 2), in the blanks of field trial at 5 - 15 cm depth (n = 5) and 50 cm depth (n = 2); high contaminated site.

4.8.3.2. Influence of vegetation on the TBT degradation

Figure 4.30 shows the measured concentrations of TBT, DBT and MBT in the top layer of the soil (5 - 15 cm) from the field trials in unvegetated soil (blank), below barley, reed (phrag) and below a clover/grass mix (clover) for the low contaminated sediments. As can be seen, the mean TBT concentration in samples from all vegetated plots is lower than in the unvegetated blanks. On the opposite, the mean of MBT is similar or even higher. This indicates a more rapid degradation of TBT in the vegetated plots. Also, the sum of TBT, DBT and MBT is generally lower below the vegetated plots. However, this difference is not statistically significant in a one-tailed t-test at $\alpha = 5\%$ level.

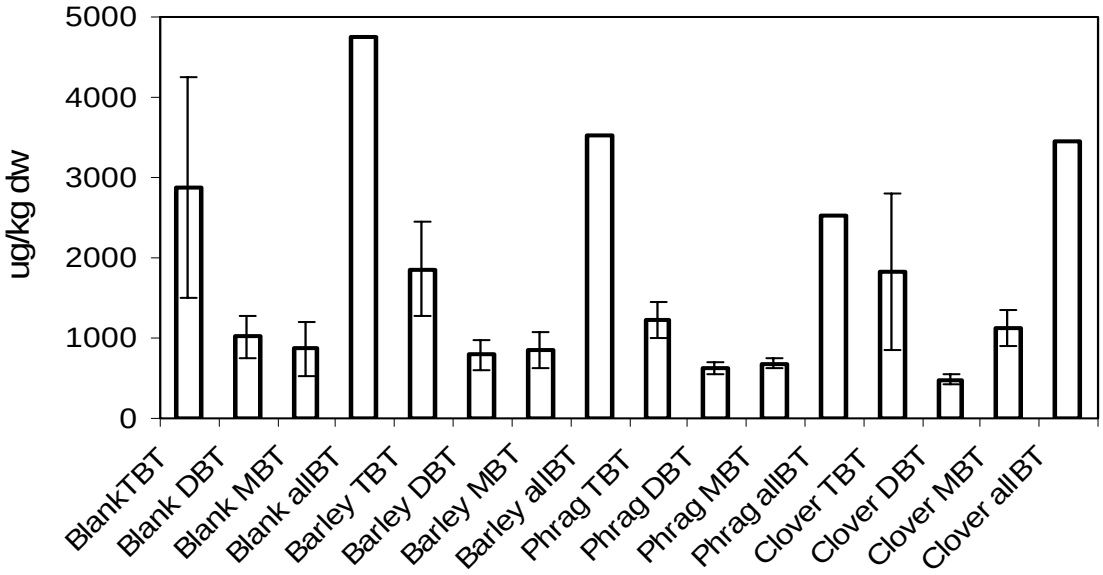

Figure 4.30. Organotin compounds TBT, DBT and MBT in the top layer of the soil (5 - 15 cm) from the field trials in unvegetated soil (blank), below barley, reed (phrag) and a clover/grass mix (clover). Error bars indicate 95% confidence interval (CI); 5 replicates each; low contaminated sediments.

Figure 4.31 shows the measured concentrations of TBT, DBT and MBT in the deep layer of the soil (50 cm) for the low contaminated sediments. Two replicates were measured, and both are given in the figure. The TBT concentration in samples below barley and reed is lower than in the blanks, whereas there does not seem to be much difference for the clover/grass mix.

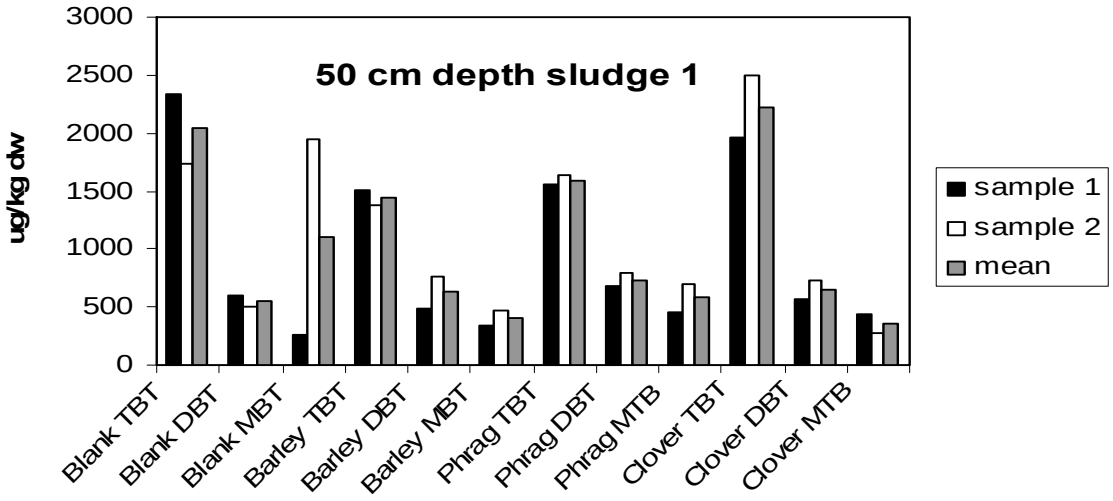

Figure 4.31. Organotin compounds TBT, DBT and MBT in the deep layer of the soil (50 cm) from the field trials in unvegetated soil (blank), below barley, reed (phrag) and a clover/grass mix (clover). Two replicates are given; low contaminated sediments. August 2004.

For the sediments with high initial TBT content, the results are more obvious. Figure 4.32 shows the measured concentrations of TBT, DBT and MBT in in the top layer of the soil (5 - 15 cm depth) for the high contaminated sediments. Again, the TBT concentrations of the samples from vegetated plots are lower than in the unvegetated blanks. There is a significant reduction (at α = 5%) of TBT of > 40% in the samples below barley compared to the blanks. DBT is also significantly lower below barley, but not MBT. In samples taken below barley and clover is MBT > DBT, indicating rapid ongoing degradation. The concentration of TBT is > 20% lower in samples taken below reed, compared to the blanks, but this result is not significant. For samples taken below clover/grass, the reduction of TBT is quite small.

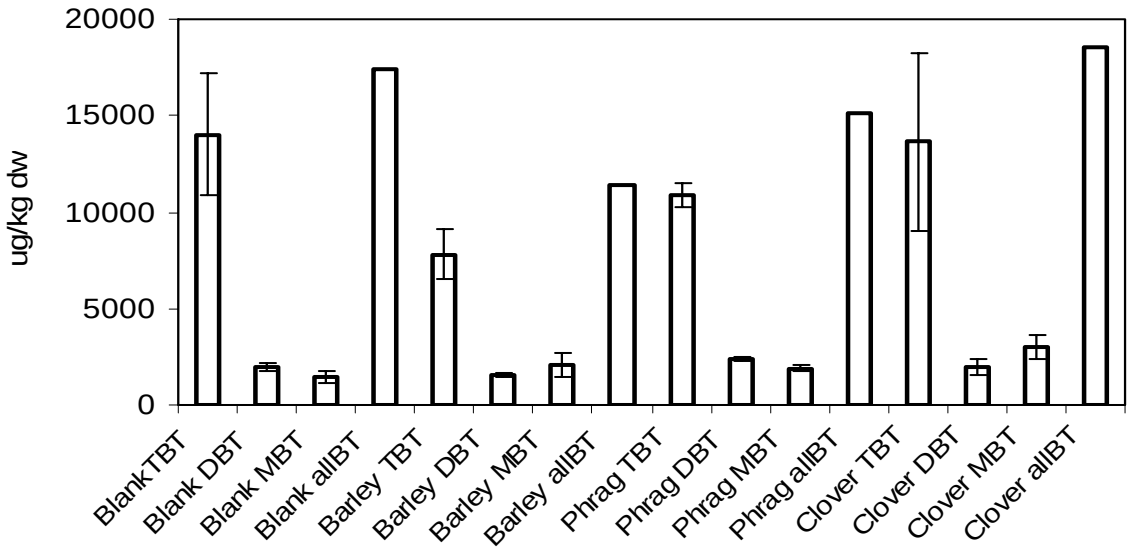

Figure 4.32. Organotin compounds TBT, DBT and MBT in the top layer of the soil (5 - 15 cm) from the field trials in unvegetated soil (blank), below barley, reed (phrag) and a clover/grass mix (clover). Error bars indicate 95% confidence interval (CI); 5 replicates each; high contaminated sediments. August 2004.

The results for the deeper layer of the sediments with high initial TBT content consistent with the results for the top layer (Figure 4.33), although we cannot give a statistical verification of the results, due to the small sample size (n = 2). TBT is obviously reduced below the barley, whereas the effect of reed and clover/grass on the TBT degradation is less pronounced. However, one sample taken below reed shows a very low TBT content.
MBT is again elevated both below barley and clover/grass.

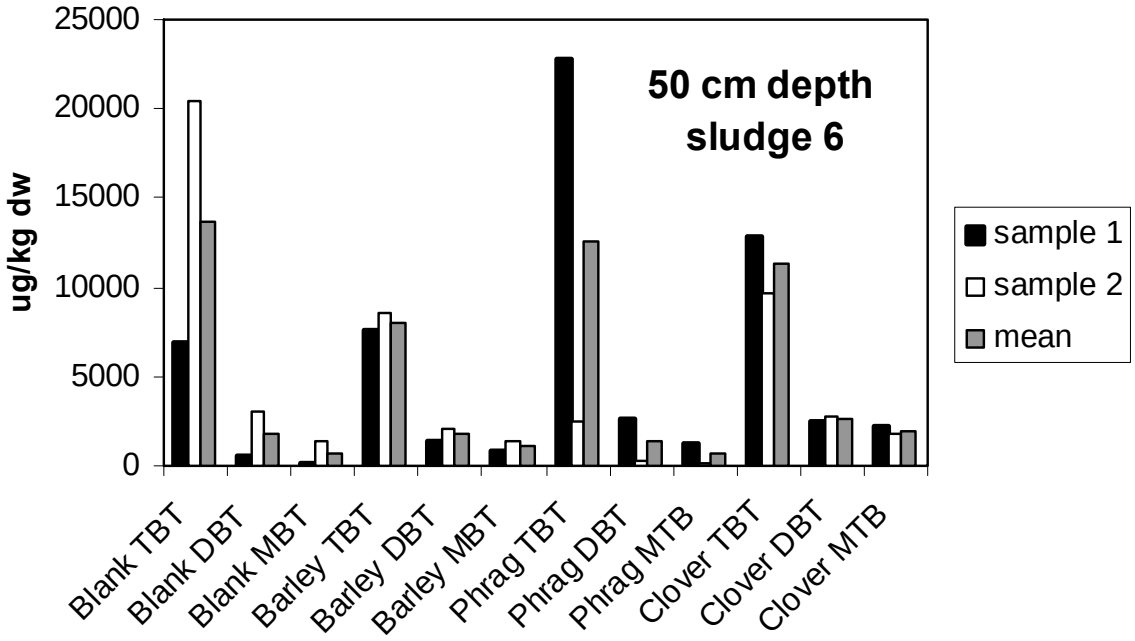

Figure 4.33. Organotin compounds TBT, DBT and MBT in the deep layer of the soil (50 cm) from the field trials in unvegetated soil (blank), below barley, reed (phrag) and a clover/grass mix (clover). Two replicates are given; high contaminated sediments. August 2004.

4.8.3.3. Uptake of TBT into vegetation

Tables 4.20 to 4.25 presents the results of the measurement of uptake of TBT, DBT and MBT into barley (corn), reed (whole plant) and the meadow (clover/grass mix). Additionally, the bioconcentration factor BCF is given, which is the ratio of the concentration in plants divided by the average concentration in soil (5 - 15 cm depth, dry weight based). No uptake was found into corns of barley (detection limit 5 µg/kg), neither for the plot with high TBT contamination, nor for the plot with low contamination. For reed and the clover/grass mix, uptake was found. Surprisingly, uptake was higher on the low contaminated plots. The highest BCF was generally found for MBT.

4.8.3.4. Effect on other pollutants.

Effects on other pollutants, such as hydrocarbons and heavy metals were not followed during these experiments, as no effect was expected based on literature. After all, the concentrations of the other pollutants in the sediments were negligible.

Table 4.19: Uptake of TBT into corns of barley, low TBT contaminated sediment.

Barley low	TBT	DBT	MBT
Soil mean	1861.4	791	860.6
Barley low	< 5	< 5	< 5
BCF	0	0	0

Table 4.20: Uptake of TBT into corns of barley, high TBT contaminated sediment.

Barley high	TBT	DBT	MBT
Soil mean	7802.6	1567.4	2068.6
Barley high	0	0	0
BCF	0	0	0

Table 4.21: Uptake of TBT into reed plants (*Phragmites communis*), low TBT contaminated sediment.

Phrag. low	TBT	DBT	MBT
Soil mean	1221.8	625.8	684.2
Phrag low	105	43	259
BCF	0.086	0.069	0.38

Table 4.22: Uptake of TBT into reed plants (*Phragmites communis*), high TBT contaminated sediment.

Phrag. high	TBT	DBT	MBT
Soil mean	10875.8	2368.2	1908.4
Phrag high	0	0	16
BCF	0	0	0.0084

Table 4.23: Uptake of TBT into clover/grass mix, low TBT contaminated sediment.

Clover low	TBT	DBT	MBT
Soil mean	1828.6	485.8	1124.2
clover low	50	14	47
BCF	0.027	0.029	0.042

Table 4.24: Uptake of TBT into clover/grass mix, high TBT contaminated sediment.

Clover high	TBT	DBT	MBT
Soil mean	13668.6	1939.8	2984.4
clover high	0	0	5
BCF	0	0	0.00168

4.9. Full scale application of phytoremediation.

Phytoremediation requires a lot of space and time, since the impact in depth is limited, and the plant roots, together with natural diffusion, are the only pathways to insert oxygen into the sediment. A typical full scale flowsheet is shown below in figure 4.34.

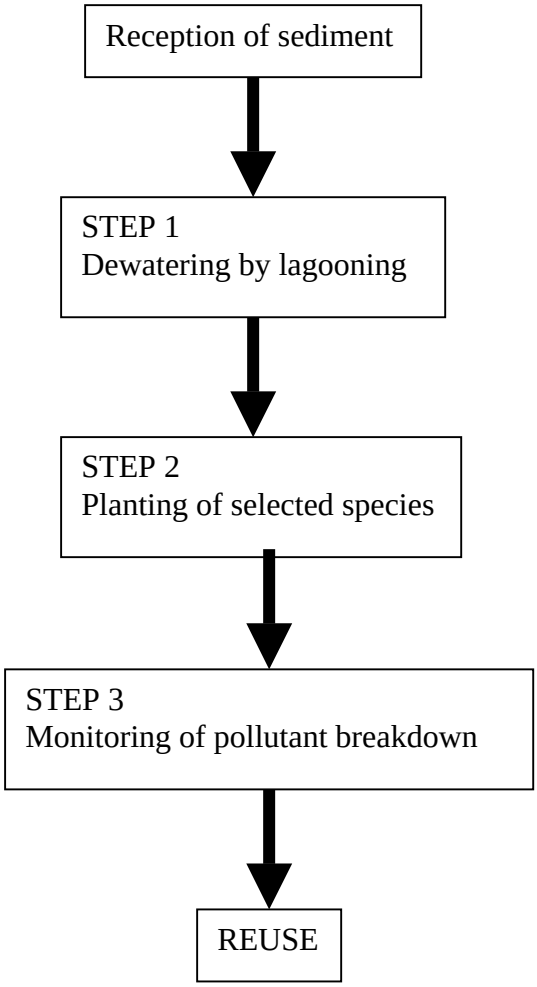

Figure 4.34. Full scale flowsheet of phytoremediation.

4.10. Conclusions.

The conclusions from this study can be summarized in 11 thesis.

- The dredged sediments are rich in nutrients, salt and TBT.
- Lagooning reduces the salinity of the sediments, improves the soil structure and enhances TBT-removal.
- Fresh sediments are a bad substrate for plant growth.
- Many plants grew very fine on dredged harbour sediments after lagoonation.
- TBT contents have either no influence or a positive influence on growth of plants.
- TBT is faster degraded below vegetation.
- Fytoremediation only serves as an enhancement of the ongoing bioremediation and cannot be used as such for TBT removal.
- TBT, DBT and MBT were taken up into plants, but not into the corn of barley.
- The usage of the dredged sediments in agriculture for food production can therefore not be recommended.
- Agriculture of non-food products, such as biodiesel, is possible; other uses could be for noise-reduction walls, dikes etc.
- Thermotreatment of the sediment will probably rob the positive properties for plant growth and destroy this valuable and fertile soil.

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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

Task 3550 Treatment of sediment
Chapter 5: Chemical oxidation of the sediment
Final report October 2004

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CHAPTER 5: CHEMICAL OXIDATION OF THE SEDIMENTS

Table of contents

List of figures

List of tables

CHAPTER 5: CHEMICAL OXIDATION OF THE SEDIMENTS

5.1. Introduction.

Chemical oxidation techniques have been introduced in the remediation of contaminated soils and groundwater the past few years, mostly for the destruction of organic pollutants. Next to the knowledge of the oxidants and their reactions with the pollutants to be destroyed, also field experience exists on side reactions (e.g. with organic matter), stability of the oxidants, and of course efficiency of destruction.

Based on this soil remediation experience the TBT Clean team had the idea to apply similar techniques on the chemical oxidation of TBT in sediments.

Chemical oxidation techniques are characterized by the use of added oxidants (high redox potential), whereby transfer of electrons can occur between the matter which have to be oxidized (the pollutant) and the oxidant. The general objective of this method for the treatment of sediment is the transformation of the problematic pollution to less inconvenient or even harmless matter. In the ideal course complete transformation of the organic pollutant into CO_2 and H_2O (and possibly halogen acids) takes place. Due to this process the sediment can be reused, if necessary after an extra treatment.
This oxidation technique is particularly useful for the removal of pollutants of organic nature, but also has the ability to decompose an amount of anorganic compounds.

The chemical oxidation of organometals, and specifically of organotin compounds, will cause a destruction of the molecule. Based on this theory lab and pilot experiments are started up, in which the decrease in concentration of the organotins is followed up.

The intention of this report is to become a realistic view on the feasibility of this treatment technique. To achieve this objective following parameters which have control over the process have been investigated:

- The properties of the oxidant
- The dosage of the oxidant
- The physical effects after adding the oxidant (temperature, gas generation, foam generation, …)
- The stability of TBT and TPHT compared to other organic compounds
- The mixing technique (adding the oxidant pure or as a solution?)

5.2. Chemical oxidants.

Chemical oxidation, when used for clean-up operations, mostly is characterized by the use of one of next oxidants:

- Sodium permanganate and potassium permanganate ($NaMnO_4$ / $KMnO_4$)
- Hydrogen peroxide (H_2O_2)
- Sodium persulfate ($Na_2S_2O_8$)
- Ozone (O_3)

The oxidant, typified by a high redox potential, functions as electron acceptor in the chemical (redox) reaction. This means that after adding the oxidant, electron transfer will take place between the contaminant and the oxidant; so the valention level of the contaminant will increase.
A redox can occur in two ways: by a direct reaction or by a radicalair process. In a direct reaction the oxidant attacks the chemical bounding of the pollutant. This creates an instable situation by which the pollutant is decomposed and non-noxious products such as CO_2, H_2O en H^+ are produced. In a radicalair proces the reaction runs by intervention of free radicals. Those radicals have one electron or two unpaired electrons in their upper shell, so they are extremely reactive and unstable.

Two oxidants have been selected for the research on the chemical oxidation of TBT-polluted sediment: $KMnO_4$ and H_2O_2. The motivation for picking out those two and a description of the most important properties are described in a summary of the most used oxidants available at present.

5.2.1. Potassium permanganate / Sodium permanganate

There are two common forms of permanganate, potassium permanganate ($KMnO_4$) and sodium permanganate ($NaMnO_4$). Both forms have similar chemical reactivity. Sodium permanganate is typically sold as a liquid, at concentrations up to 40%, while potassium permanganate is typically sold as a solid.

Both forms of permanganate are strong oxidants with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups or hydroxyl groups. Under normal subsurface pH and temperature conditions, the carbon-carbon double bond of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion.

Permanganate (E = 1,68V) is made out of two elements: manganese and oxygen. Both occurs frequently in the ground, as well as the reaction product after reduction (MnO_2).

Reactions:

half-reaction

$$MnO_4^- + 4\,H^+ + 3e^- \leftrightarrow MnO_2 + 2\,H_2O \qquad E = 1,68V$$

self-decomposition (0,1 à 1% / day)

$$4\,KmnO_4 + 4H^+ \leftrightarrow 3\,O_2 + 4\,MnO_2 + 2\,H_20 + 4\,K^+$$

Reaction products:

The redox reaction produces MnO_2, CO_2 and decomposed organic components.

Characterisations:

Oxidation by permanganate runs non-selective; not only the aimed polution will be attacked, but also a lot of other compounds, like metals and natural organic matter, will be oxidized. Despite the fact that permanganate is a moderate oxidant compared to Fenton's reagent, this oxidant is much better applicable for chemical oxidation of sediment. Permanganate has a longer half-life through which it has a more stable character than hydrogen peroxide. As a result of his longer stay in the sediment, permangante will undergo a better diffusion, so a wider zone can be treated. So it's evident that permanganate is very usefull for applications characterized by a low permeability, such as (harbour) sediment.

5.2.2. Hydrogen peroxide, Fenton's reagent.

Although hydrogen peroxide alone is an oxidant, at low concentrations it is not strong enough to degrade many hazardous organic pollutants. However, the addition of a ferrous salt (Iron II) dramatically increases the oxidative strength. This increase is attributed to the production of hydroxyl radicals (OH ▪). Radicals are molecular

fragments that have an unpaired electron, which causes them to be highly reactive and short lived. In addition, a chain reaction can be initiated causing the formation of new radicals. Because it was first discovered by Fenton, the reaction of iron catalyzed peroxide oxidation is called a Fenton's Reaction and the iron/peroxide mixture is known as Fenton's Reagent.

Hydrogen peroxide (E = 1,78) can be bought as a clear solution (30-70%). The half-life of H_2O_2 is short, so it soaks less into the sediment before it decomposes.
The reaction with hydrogen peroxide or hydroxyl radicals runs very fast and exotherm. Oxygen is generated because of the appearing self-decomposition reaction and because of the contact with the water in the sediment. The combination of this quickness of reaction and oxygen production can in some situations cause fire and explosions.
The quickness of reaction can be controlled by using low hydrogen peroxide concentrations (< 10%).

Reactions:

direct oxidation half-reaction

$$H_2O_2 + 2\,H^+ + 2e^- \leftrightarrow 2\,H_2O \qquad E = 1{,}78V$$

$$H_2O_2 + 2e^- \leftrightarrow 2\,OH^- \qquad E = 1{,}78V$$

radicalair reaction

$$H_2O_2 + e^- \xleftrightarrow{Fe} OH^- + OH^\bullet$$
$$OH^\bullet + H^+ + e^- \leftrightarrow H_2O \qquad E = 2{,}80V$$

$$H_2O_2 + H^+ + e\text{-} \xleftrightarrow{Fe} H_2O + OH^\bullet$$
$$OH^\bullet + e^- \leftrightarrow OH^- \qquad E = 2{,}80V$$

self -decomposition

$$2\,H_2O_2 \leftrightarrow 2\,H_2O + O_2 + \Delta G$$
$$4\,OH^\bullet \leftrightarrow 2\,H_2O + O_2 + \Delta G$$

Reaction products.

The reaction with hydrogen peroxide produces H_2O and CO_2; both are innocent and can be found in every natural bottom. The oxygen generated during the decomposition reaction promotes the biological destruction of organic pollutions.

5.2.3. Other oxidants.

There exists a lot of other oxidants, but they haven't been selected for this research because of various reasons.

Sodium persulfate

Compared to potassium permanganate, persulfate has a higher molecular weight, so a larger mass of oxidant has to be applied to destruct an amount of polluent. Furthermore the selectivity of persulfate differs from the selectivity of permangane: persulfate will react less with organic matter, so it is not the obvious means to oxidize organotin.
The slow way of reacting (4 weeks or longer) can be speeded up by adding a catalyst to the sodium persulfate solution, for instance iron or heat. The catalyst will promote the formation of sulfate radicals ($SO_4^{-\bullet}$) which are similar to the hydroxyl radicals. The addition of this catalyst will decrease the reaction time (2 days).
An important side effect after adding sodium persulfate is the increase of sulphate and the decrease of the pH, which can cause a release of metals in the bottom.

Ozone

Ozone is an extremely powerfull oxidant and is able to oxidize most organic pollutions. The oxidation can run on two ways: by direct oxidation or by the formation of radicals. The importants restrictions of ozone are the high cost price, the limited availability and the high toxicity. The oxidation by ozone will not cause an increase of the pH, but there will be an increase of the ionic strength of the sediment, by which metals can be released.

5.3. Lab experiments.

The lab experiments are done to get a first view on the oxidation of TBT in the sediment. Two variants of harbour sediment (high TBT-polluted sediment: batch 2.1; mild TBT-polluted sediment: batch 1.5) are treated with an amount of oxidans ($KMnO_4/H_2O_2$). This applied quantity of oxidans is calculated with the intentention to oxidize the total amount of organic carbon (TOC) .

5.3.1. Calculation of the amount of oxidant equivalent to the amount of organic carbon

The oxidation of organic carbon is combined to the transfer of four elektrons.

$KMnO_4$

REDOX REACTION

$$(\ MnO_4^- + 4\ H^+ + 3e^- \rightarrow MnO_2 + 2\ H_2O \ ) \quad X\ 4$$

$$(\ C + 2H_2O - 4e^- \rightarrow CO_2 + 4\ H^+ \ ) \quad X\ 3$$

$$3\ C + 4\ MnO_4^- + 4\ H^+ \rightarrow 4\ MnO_2 + 3\ CO_2 + 2\ H_2O$$

H_2O_2

REDOX REACTION

$$(\ H_2O_2 + 2\ H^+ + 2e^- \rightarrow 2\ H_2O \ ) \quad X\ 2$$

$$(\ C + 2H_2O - 4e^- \rightarrow CO_2 + 4\ H^+ \ )$$

$$C + 2\ H_2O_2 \rightarrow CO_2 + 2H_2O$$

The calculation of the quantity of oxidant is based on the total total organic carbon existing in the sediment. There is hypothesized that all existing organic carbon can be oxidized. The inorganic components which can be oxidized are not taken into consideration.

Batch 2.1.

TOC = 2,07 % (% on DW)

- Oxidant = $KMnO_4$

  1 kg DW → 20,7 g organic carbon = 1,725 mol organic carbon

  X 4/3

  → 2,300 mol $KMnO_4$

  = 363,4 g $KMnO_4$

- Oxidant = H_2O_2 (30%; 1,1 kg/l)

  1 kg DW → 20,7 g organic carbon = 1,725 mol organic carbon

  X 2

  → 3,450 mol H_2O_2

  = 355 ml H_2O_2

Batch 1.5

TOC = 3,17 % op DS !!

- Oxidant = $KMnO_4$

  1 kg DM → 31,7 g organic carbon = 2,642 mol organic carbon

  X 4/3

→ 3,522 mol $KMnO_4$

= 556,5 g $KMnO_4$

- Oxidant = H_2O_2 (30%; 1,1 kg/l)

1 kg DM → 31,7 g organic carbon = 2,642 mol organic carbon

X 2

→ 5,284 mol H_2O_2

= 544,4 ml H_2O_2

It can be seen that the amounts to be dosed are enormous.

5.3.2. Lab experiments.

1 kg dry sediment is treated with a quantity of oxidant that is equivalent to the total existing quantity of organic carbon. The experiments are done in small buckets. Because mixing solid potassium permanganate into the sediment is a very laborious and energy requiring process, the potassium permanganate is added as a 10% solution[1]. The hydrogen peroxide is added as a 10% solution[2] to decrease the self-decomposition reaction. The observed reaction time was about 1 hour, however further reaction could take place later on (time between the tests and the analysis in the laboratory).

Table 5.1: MBT, DBT, TBT, MPHT, DPHT and TPHT reduction after adding an equivalent quantity of oxidant – batch 2.1.

	Not treated	H_2O_2	Reduction	$KMnO_4$	Reduction
MBT	286	240	16,08%	911	-218,53%
DBT	1012	870	14,03%	338	66,60%
TBT	27955	8855	68,32%	5677	79,69%
MPHT	94	54	42,55%	42	55,32%
DPHT	229	53	76,86%	< 5	> 97,82%
TPHT	329	69	79,03%	< 5	> 98,48%

[1] Mass per cent
[2] Volume per cent

Table 5.2: MBT, DBT, TBT, MPHT, DPHT and TPHT reduction after adding an equivalent quantity of oxidant – batch 1.5.

	Not treated	H_2O_2	Reduction	$KMnO_4$	Reduction
MBT	123	142	-15,45%	236	-91,87%
DBT	366	571	-56,01%	23	93,72%
TBT	3942	2315	41,27%	61	98,45%
MPHT	53	25	52,83%	76	-43,40%
DPHT	< 5	13	-160,00%	< 5	---
TPHT	104	29	72,12%	< 5	> 95,19%

Both types of sediment have a similar course in TBT and TPHT reduction: $KMnO_4$ seems to be a better oxidizer compared to H_2O_2. The explanation for the difference in oxidizing-force is mainly attributed to the self-decomposition of H_2O_2.

The increase of MBT, DBT, MPHT and DPHT is ascribed to the step by step degradation of TBT and DPHT:

$$TBT \rightarrow DBT \rightarrow MBT$$
$$TPHT \rightarrow DPHT \rightarrow MPHT$$

Physical observations during the execution of the experiments are summarized in table 5.3.

Table 5.3: Physical observations during and after adding oxidant to the sediments.

	$KMnO_4$	H_2O_2
Temperature	Exothermic reaction: Temp ↑ to 60°C	Exothermic reaction: Temp ↑ to 70°C
Gas generation	Gas generation (CO_2, H_2O, O_2)	Gas generation (CO_2, H_2O, O_2) Intense (uncontrolled) effervescence because of the O_2 generation
Colour	Colour sediment: black → brown Purple colour as long as $KMnO_4$ is existing	Colour sediment: black → brown

A few important comments have to added to this observations:

- The oxidation with $KMnO_4$ goes initially (= shortly after adding the oxidant) laboriously, but after a temperature of roughly 60°C is reached, the reaction will run easily. The required temperature for an easy course of the oxidation of organic carbon is generated by the reaction itself (autocatalytic).

- The oxidation with H_2O_2 is coupled with an extremely intense effervescence (O_2 generation attributed to the self-decomposition of H_2O_2). There can be expected that the oxidation of sediment with this oxidizer will contain a considerable safety risk.

Figure 5.1. Intense effervescence after adding H_2O_2

Figure 5.2. Situation after adding $KMnO_4$

Figure 5.3. Reaction of $KMnO_4$ with the sediment

5.4. Pilot experiments

5.4.1. The pilot reactor.

For this project a pilot reactor of 1.5 m^3 was constructed by DEC. The reactor consists of an HDPE vessel. The vessel is foreseen with a stainless steel mixing device with controllable speed in order to homogenize the sediment slurry and mix the oxidants into the sediment. At the bottom a discharge valve is foreseen to empty the vessel.

Figure 5.4. Pilot reactor used for the experiments.

5.4.2. Objective of the pilot scale tests.

During this pilot experiments following aspects have been investigated:

- Minimal quantity of oxidant to achieve removal of the organotin compounds.
- Optimal mixing conditions (density of the sludge).
- Side reactions such as generation of gases such as H_2S, NH_3,…

Based on the observations during the lab scale tests, such as the effervescence and exothermic reaction, and the lower removal efficiency, it was decided that working with peroxide is not safe nor feasible. Therefore the pilot scale test was only carried out with permanganate.

5.4.3. Methods.

Based on the observations made during lab scale testing, $KMnO_4$ was added to the sediment as a 10 w/w % solution. If necessary water was added to keep the dry matter content of the mixture in the reactor below 30 %, as this is about the maximal density at which the mixture is still feasible to get homogenized in the reactor.

Various increasing amounts of permanganate were added. The reaction and consumption of the permanganate was followed visually. Once the purple colour had disappeared, all permanganate has been reacted. At this point of time samples were taken for analyses.

For the detection of gases Gastec detection tubes were used, with detection limits of 0.1 ppm for H_2S and ammonia. Also organoleptic observations were made.

Extreme safety precautions have been taken, as strong oxidizers are dangerous. Both pilot reactor operators wore Tyvec clothing, rubber gloves, full face masks with ABEK filters.

5.4.4. Results of the pilot scale tests.

5.4.4.1. Batch 2.1.

The results of the pilot tests on sediment of batch 2.1 are summarized in tables 5.4 and 5.5.

Table 5.4: Residual concentrations in the treated sediment for increasing additions of permanganate (batch 2.1)

$KMnO_4$ (kg $KMnO_4$/ kg DS)	MBT (µg/kg)	DBT (µg/kg)	TBT (µg/kg)
0,00%	265	1415	34126
6,51%	4222	1162	14644
15,38%	690	440	3138
24,24%	221	305	2711
54,27%	116	170	1233

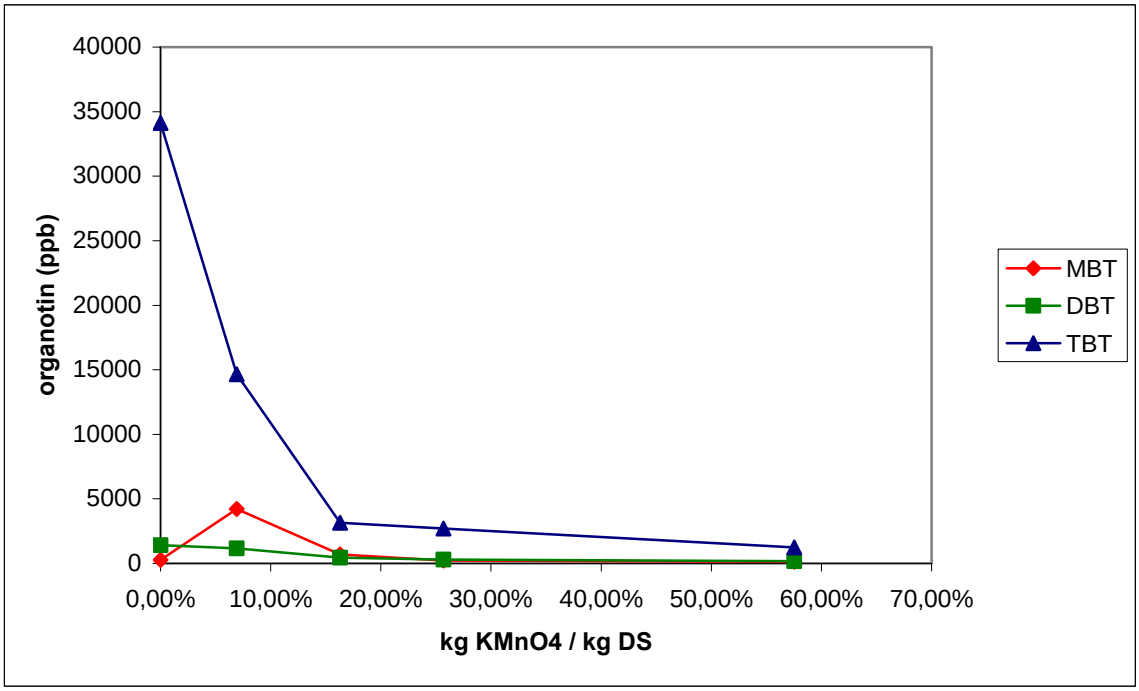

Figure 5.5. MBT, DBT and TBT versus the quantity of added oxidant ($KMnO_4$) batch 2.1.

Table 5.5: Residual concentrations of TBT and removal efficiencies in the treated sediment for increasing additions of permanganate (batch 2.1)

$KMn0_4$ (g KMnO4/ g DS)	TBT (µg/kg)	Reduction
0,00%	34126	0,00%
6,51%	14644	57,09%
15,38%	3138	90,80%
24,24%	2711	92,06%
54,27%	1233	96,39%

Next to all the butyltin compounds (MBT, DBT and TBT) the sediment also contains other organotin compounds. The phenyltins (monophrenyltin, diphenyltin and triphenyltin) are, after the butyltin compounds, the importants organotin polluents in the sediment.
The decomposition of MPHT, DPHT and TPHT in function of the quantity of added oxidant ($KMnO_4$) was followed and is reported in table 5.6 and figure 5.6.

Table 5.6: Residual concentrations in the treated sediment for increasing additions of permanganate (batch 2.1)

$KMnO_4$ (kg $KMnO_4$/ kg DS)	MPHT (µg/kg)	DPHT (µg/kg)	TPHT (µg/kg)
0,00%	236	67	49
6,51%	154	53	40
15,38%	140	265	18
24,24%	5	5	10
54,27%	5	5	5

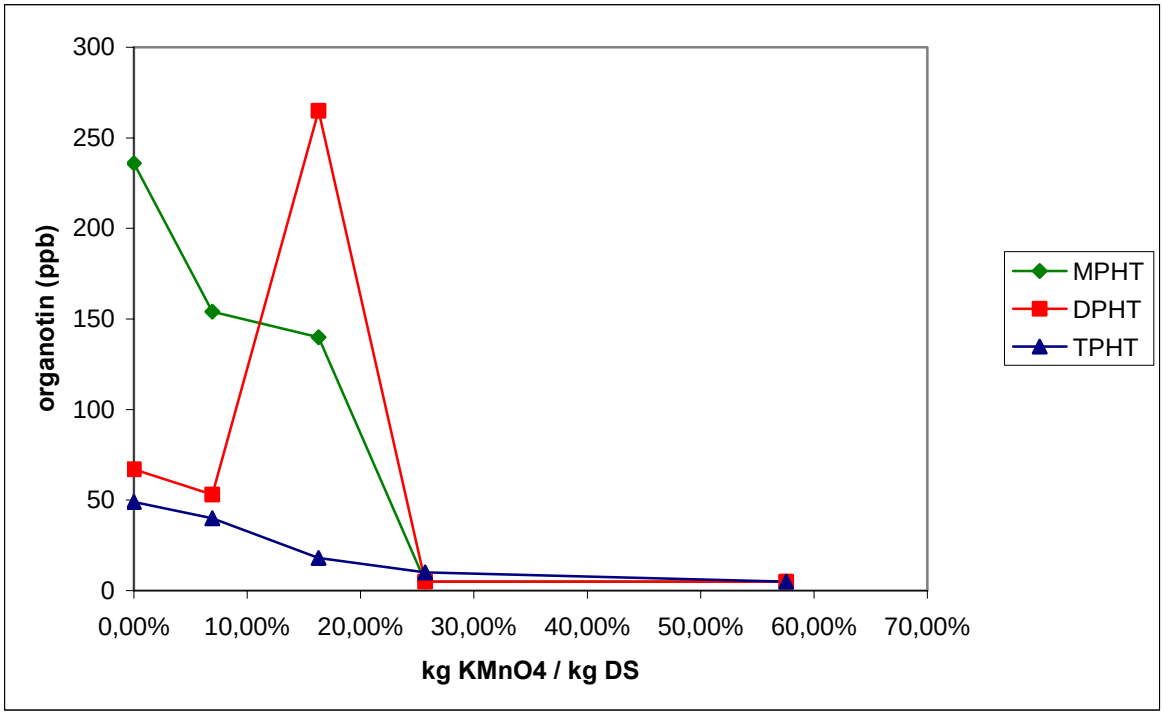

Figure 5.6. MPhT, DPhT and TPhT versus the quantity of added oxidant ($KMnO_4$) batch 2.1.

The chemical oxidation of the phenyltin variants mainly has the same mechanism as the chemical oxidation of the bytyltin compounds, i.e. a stepwise debutylation.

The oxidation of TPHT only runs quit fast after adding more than 5% $KMnO_4$ (also visible in the increase of the DPHT-concentration). So there can be concluded that the phenyltins are less reactive (= more stable) compared to the butyltins.

Until further notice it is not known how reactive the organotin compounds are compared to the other organic compounds (which are available for oxidation) in the sediment. To get an idea about the relative reactivity of the organotin molecules, the decrease of their concentration, the decrease of the TOC and the decrease of the COD is followed up.

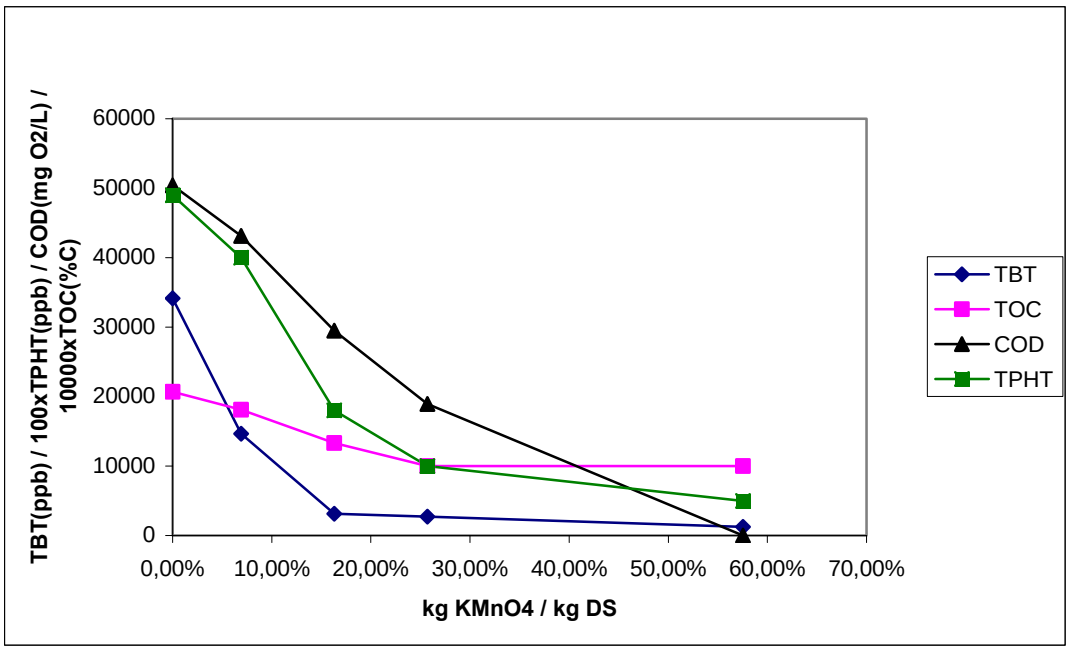

Figure 5.7. TBT, TPHT, TOC and COD versus the quantity of added oxidant ($KMnO_4$) batch 2.1

From the results in figure 5.7 it can be concluded that, compared to the other chemically oxidisable fractions in the sediment (expressed as COD), TBT is oxidized very quickly and more selectively. It can also be seen that, when expressed as TOC, only half of the TOC fraction can be chemically oxidized by permanganate; these might be coarser organic particles such as fibres, paint flakes,…

5.4.4.2. Batch 1.5.

The results of the pilot tests on sediment of batch 1.5 are summarized in tables 5.7 and 5.8.

Table 5.7: Residual concentrations in the treated sediment for increasing additions of permanganate (batch 1.5)

$KMnO_4$ (kg KMnO4/ kg DS)	MBT (µg/kg)	DBT (µg/kg)	TBT (µg/kg)
0,00%	191	470	3474
11,51%	491	94	711
23,97%	46	26	218
36,44%	16	12	82

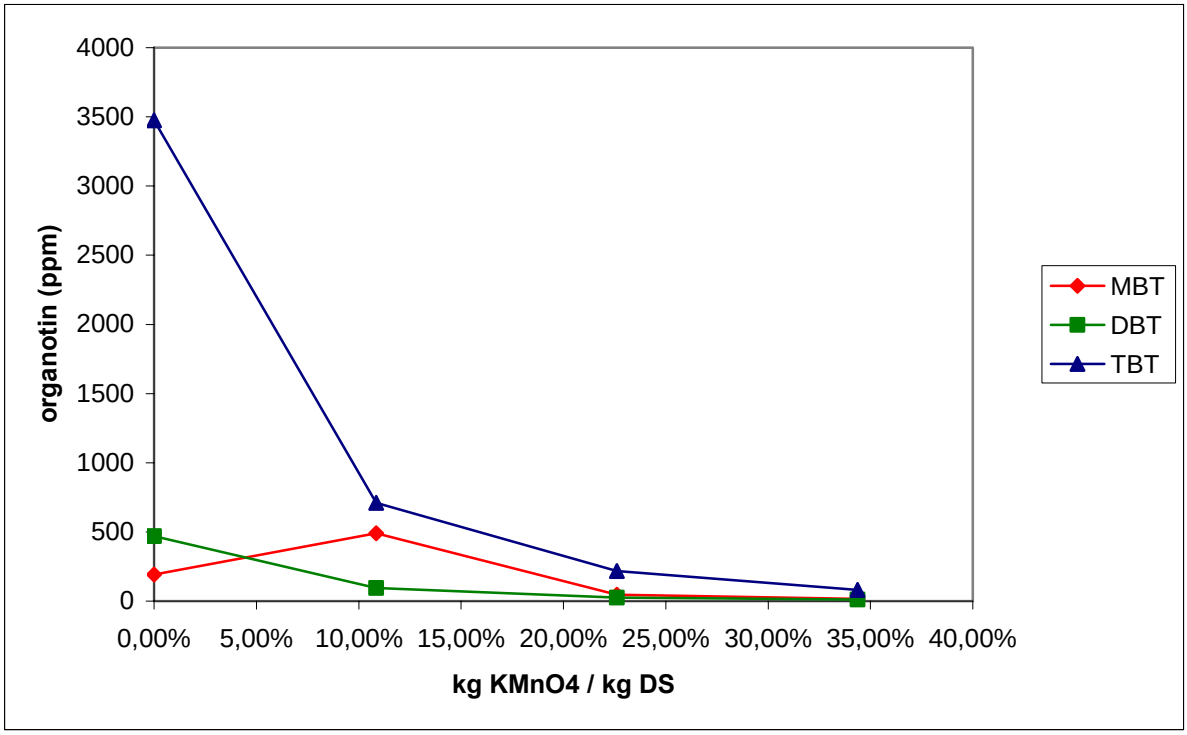

Figure 5.8. MBT, DBT and TBT versus the quantity of added oxidant ($KMnO_4$) batch 1.5

Table 5.8: Residual concentrations of TBT and removal efficiencies in the treated sediment for increasing additions of permanganate (batch 1.5)

KMn04 (g KMnO4/ g DS)	TBT (µg/kg)	Reductie
0,00%	3474	0,00%
11,51%	711	79,53%
23,97%	218	93,72%
36,44%	82	97,64%

Again, the phenyltin compounds were followed during the tests.

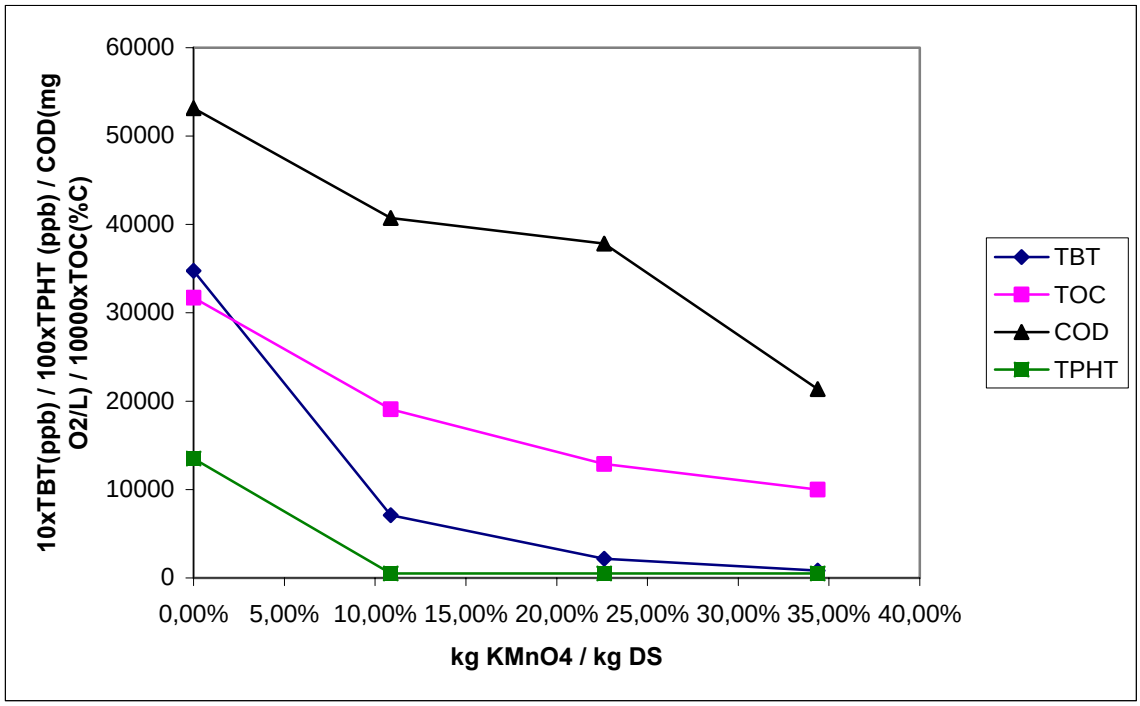

Figure 5.9. TBT, TPHT, TOC and COD versus the quantity of added oxidant ($KMnO_4$) batch 1.5.

Here it can be noticed that the TBT-concentration and TPHT-concentration decrease quite fast as the oxidant is added. Again the TBT-concentration and the TPHT-concentration reach much faster a high reduction compared to the reduction in TOC en COD. The TBT molecule and TPHT molecule seems to be a considerable reactive molecule compared to the other present organic molecules.

5.4.5. Emissions of toxic gases.

During addition of permanganate and during the mixing gas emission was measured in the headspace of the pilot reactor. However gas bubbles were observed (mainly CO_2 released during the oxidation of the organic matter), all measured gases (H_2S, SO_2, NH_3) were below detection limit of 0.1 ppm.

5.4.6. Effect on other pollutants.

The effect of chemical oxidation on heavy metals was not followed, as no effect can be expected. Other pollutants of interest, such as PAH, were not present. The influence on organic matter was followed via TOC and COD.

5.5. Full scale application.

Full scale application of chemical oxidation is not evident, due to all the boundary conditions attached. A preliminary flowsheet is shown in figure 5.10.

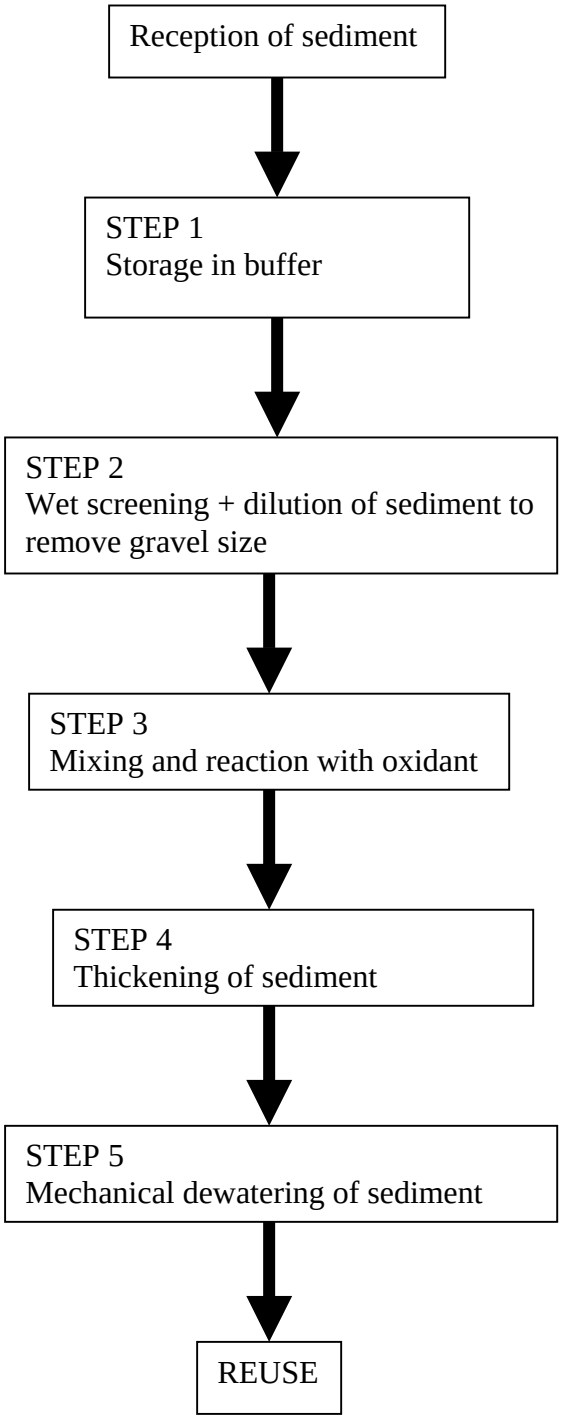

Figure 5.10. Full scale application flowsheet of chemical oxidation.

5.6. Conclusions.

The conclusions can be summarized as follows:

- For both sediments TBT can be removed with efficiencies of at least 96 %. This means that for the highly polluted sediment (batch 2.1) residual concentrations of around 1 ppm can be reached, and about 0.1 ppm for the medium polluted sediment (batch 1.5).
- The doses of oxidant in order to obtain these removal efficiencies are however very high (in the order of 0.5 kg permanganate per kg dry matter).
- The most cost-efficient result seems to be obtained at about 0.15 kg of permanganate per kg dry matter. At this doses about 90 % removal efficiency can be obtained.
- For higher doses, so in order to obtain higher removal efficiencies, the oxidation of organic matter is competing the TBT oxidation.
- The phenyltin compounds seem to be less prone to oxidation compared to the butyltins.
- After treatment, the sediments need dewatering as the process is carried out at a dry matter content lower than the in-situ dry matter content.
- Full scale application of this technique is not yet available, and will cope with serious safety issues.

5.7. References.

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Z. Van Eeckhoudt, Beschrijvende scheikunde, Course RUG

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

Task 3550 Treatment of sediment
Chapter 6: Electrochemical oxidation of the sediment
Final report October 2004

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CHAPTER 6: ELECTROCHEMICAL OXIDATION OF THE SEDIMENTS

Table of contents

List of figures

List of tables

CHAPTER 6: ELECTROCHEMICAL OXIDATION OF THE SEDIMENTS

6.1. Introduction

Chemical oxidation of organic pollutants within soils or sediments is a well-known process. In chapter 5 of this report, the potential and efficiencies of chemical oxidation of butyltin compounds in sediments have been studied and proved. However, it was also shown that, in order to get satisfying efficiencies, hugh amounts of chemical oxidants were required. This can be explained by the non-selectivity of the oxidants towards all oxidisable organic and anorganic compounds, of which the butyltin compounds are only a small fraction.

Electrochemically mediated oxidation is also a well known process, already applied in different applications. Probably the most commonly used process is the electrochemical desinfection of e.g. swimming pool water by means of the electrochemical oxidation of (sodium) chloride into hypochlorite. In this process hypochlorite is formed in the reactor at the anode out of sodium chloride which is added into the water.

In an electrochemical cell oxidation of species can take place in two ways: direct or indirect. In direct oxidation the reaction compounds are directly oxidized at the surface of the anode, i.e. electrons are directly transferred from the reaction compounds to the electrode according to:

$$X \rightarrow X^{n+} + n\,e^-$$

Direct oxidation is applied durino chlor-alcali-electrolysis where chlorine is formed at the anode out of chloride.

Indirect oxidation is based on the formation of an oxidant at the anode, which will further oxidize the compounds of interest in the solution. The electron transfer is via a ‘carrier’ compound, i.e. the oxidant. In fact, indirect oxidation is identical to chemical oxidation, only the oxidant is formed in the reactor itself and not added externally.

It is obvious that direct oxidation is only possible with molecules that are well soluble in water, and in high enough concentration in order to compete with the other oxidation reactions such as the oxidation of water into oxygen or the dissolution of the anode material. Direct oxidation is hence unlikely to happen to large molecules as butyltins, especially when these are associated with sediment particles.

On the other hand it is inevitable that indirect oxidation requires the presence of molecules that can be oxidized into (strong) oxidizers. Water itself will oxidize into oxygen gas, which is not a strong oxidizer, but also hydroxyl radicals will be formed which have a higher oxidation potential. Other potential oxidant forming compounds are e.g. chloride (chlorine and hypochlorite formation), ferro-salts (Fe^{3+}-formation),… It is obvious that the higher the concentration of these oxidant forming compounds, the more efficient the indirect oxidation will go on.

While direct oxidation can only occur on dissolved compounds, indirect oxidation can be applied on compounds that are associated with sediment particles. Hence e.g. sediment slurries can be electrochemically treated.

Stihnote et al. studied the indirect electrochemical oxidation of butyltins and some other organic pollutants in dredged sediments from Bremer Haven. Various contaminated sediments slurries were prepared and treated. His research shows that butyltins can be easily electrochemically oxidized, provided sufficient chloride is present in the sediment slurry. The amount of chloride already present in sea port sediments is not sufficient, and extra chloride (as NaCl) has to be added.

Stihnote works on 5 % dry matter content slurries, which means the sediment has to be diluted about 10 times in order to be compatible with the process. The sediment also requires sieving to below 1 mm to avoid sedimentation and clogging effects.
It was shown that over 99 % of TBT reduction can be obtained in case of highly contaminated sediments, similar to the sediment of batch 2.1 studied by TBT Clean group. As well, as can be expected, other organic compounds, such as PAH, were destroyed by the oxidation. However sufficient high concentrations of chloride has to be added, treatment times are relatively long (up to 24 hours), and the electrode current densities are very high (up to 800 A/m²).

The research work clearly shows the oxidation of butyltins is indirect, based on the formation of chlorine and hypochlorite at the anode, according to the reactions:

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$$

and

$$2\,OH^- + Cl_2 \rightarrow OCl^- + Cl^- + H_2O$$

Unfortunately the oxidation with hypochlorite has many side effects, such as formation of chlorinated organic compounds (EOX and AOX), which can remain in the sediment after

treatment and are very toxic. Ecotox tests showed an increase by a factor of 10 in toxicity caused by the treatment.

6.2. Objective of the experiments.

The basis principles of electrochemically mediated oxidation of organotins in sediments have be studied by Stihnote et al, mainly on laboratory scale. The TBT Clean project group however wanted to study the feasibility of applying this technology on a full scale, and evaluate the costs and operational conditions. Therefore a series of experiments have been set up.

As a first step, the sediments from the port of Antwerp were treated on a laboratory scale at TU Harburg by the team of Dr. Stihnote, in cooperation with DEC's R&D department. The objective of the laboratory tests were:

- Evaluate the feasibility of organotin destruction in the low and high polluted sediments.
- Find the process parameters, such as residence time, current density, potential difference, in order to obtain sufficient organotin destruction. These parameters will be used as the basis for pilot scale testing.
- Evaluate operational boundary conditions such as granulometry of the sediments, water content of the slurry, emissions of gases.

Secondly, a pilot scale test was organized at the SRC Ruisbroek site, one of DEC's sediment treatment centers. The objectives of the pilot tests were:

- Evaluate the feasibility of organotin destruction in the sediments.
- Optimise the process parameters, such as residence time, current density, potential difference, in order to obtain sufficient organotin destruction.
- Evaluate operational boundary conditions such as granulometry of the sediments, water content of the slurry, emissions of gases.
- Estimate the costs of full scale treatment.

6.3. Lab scale experiments.

6.3.1. Equipment set-up.

The laboratory scale set-up flowsheet is shown in figure 6.1. After being sieved on a 1 mm sieve, the sediment is diluted in a mixing tank to about 5 % dry matter content. The slurry is transferred into the reaction tank, from which the slurry is pumped continuously through a single electrochemical cell. In this cell, the oxidants (hypochlorite mainly) are being formed. The oxidants can continue reacting with the sediment particles in the reactor tank, where all particles are kept in suspension. Sampling of sediment and water can be carried out in the reactor tank at all times.
Emission of gases, mainly produced during electrolysis, are extracted and filtered in an activated carbon filter. In the laboratory, the whole set-up was operated in a fume cupboard, as illustrated in figure 6.2 to 6.4.

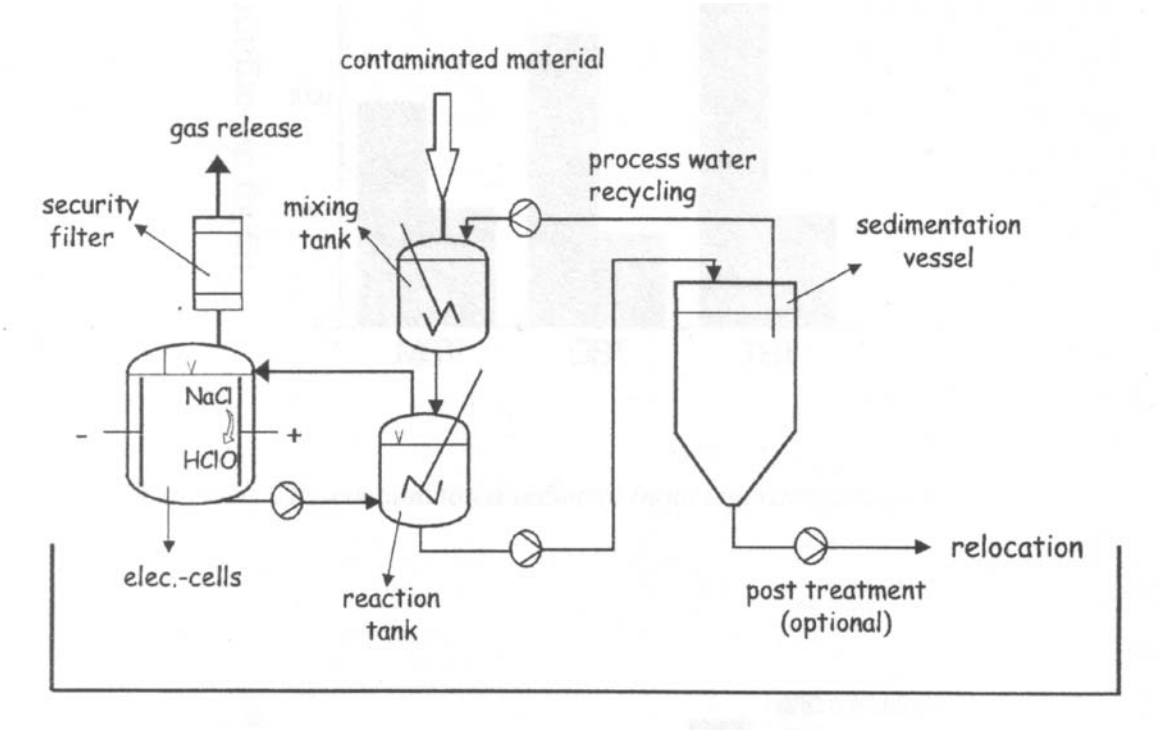

Figure 6.1. Typical set-up of laboratory and pilot scale equipment.

Figure 6.2. Overview of the lab scale set-up at TU Harburg: middle: electrolysis cell, right: current rectifier; left below: reaction tank.

Figure 6.3. Detail of the laboratory set-up: below: sediment buffer, right: electrolysis cell, top: pump.

Figure 6.4. View on the electrolysis cell. Gas formation at the electrodes is clear.

6.3.2. Execution of the tests.

From both types of sediment, batches 2.1 and 1.5, fresh samples have been taken. After screening on a 1 mm sieve, subsamples of 200 g dry matter (with 3.8 liters of tap water) were brought into the reaction tank. For each type of sediment a first orientating test has been carried out.
The current density applied was 600 A/m². For both sediments, in order to obtain this current density a voltage of 7.1 V was required. No extra salt was added as the conductivity of the sediments was sufficiently high.

Subsamples from the sediment slurry were taken at three points in time: at the start of the experiment (no current), after 1 hour, and after 3 hours. These samples were analysed by ERC on organotins, PAH and TPH in order to evaluate breakdown of these compounds. EOX (extractable halogenated organics) were also followed as a measure for the formation of ecotoxic chlorinated organic compounds.

6.3.3. Results of the first lab tests.

Figures 6.5 to 6.10 show the evolution of the various parameters with treatment time.

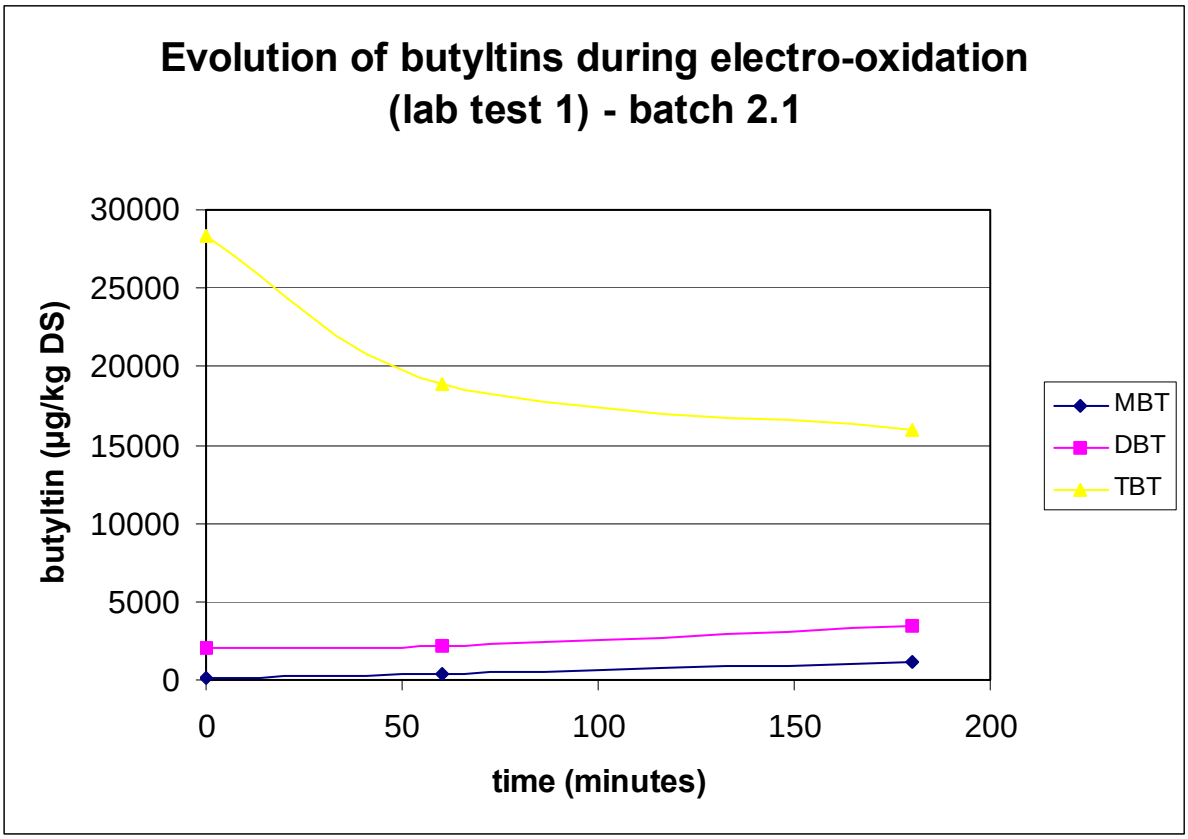

Figure 6.5. Evolution of butyltins during electrochemical treatment – batch 2.1.

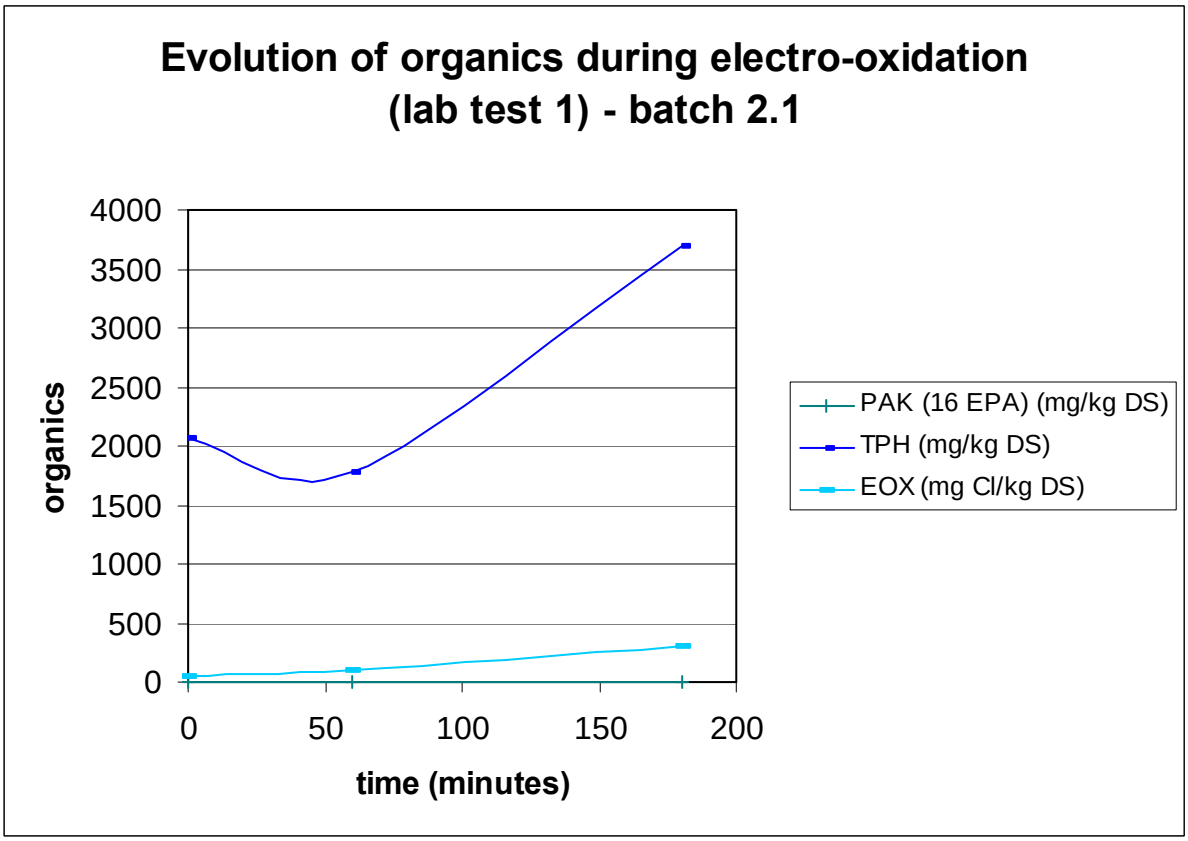

Figure 6.6. Evolution of organics during electrochemical treatment – batch 2.1.

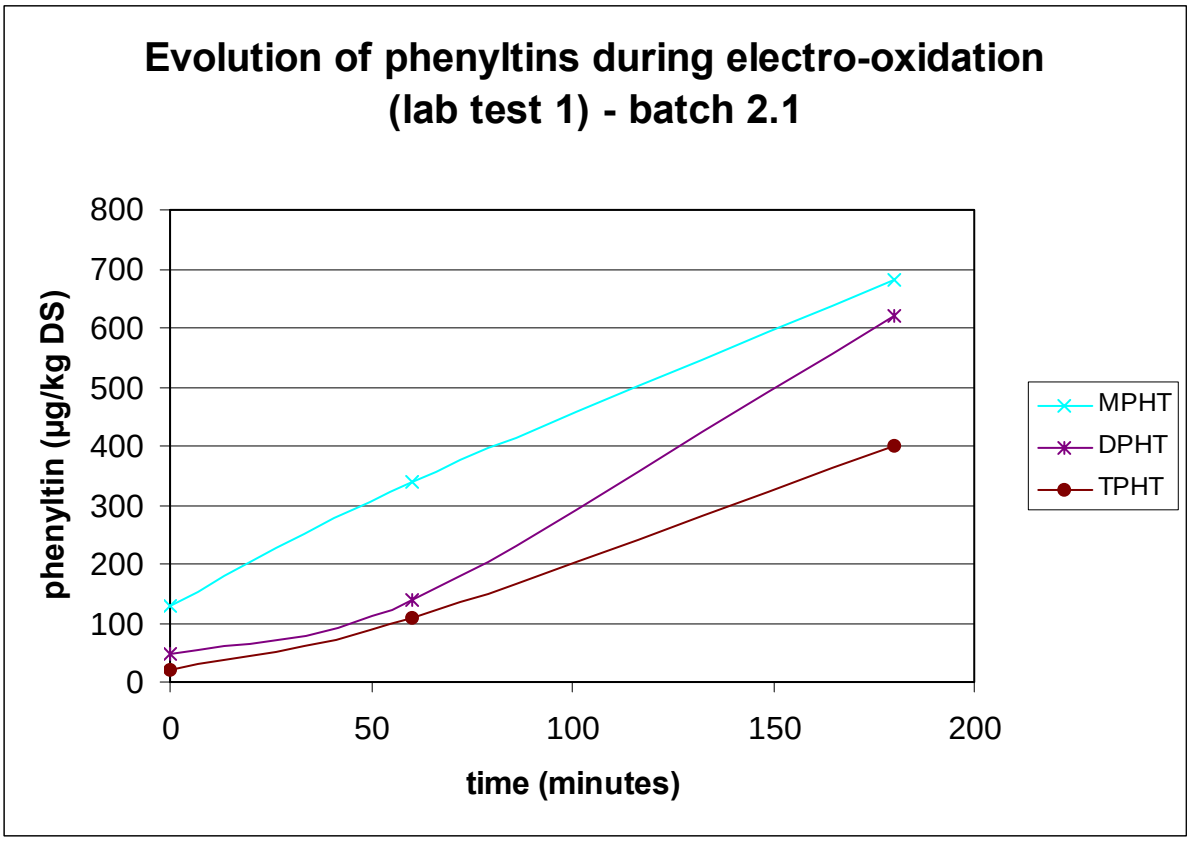

Figure 6.7. Evolution of phenyltins during electrochemical treatment – batch 2.1.

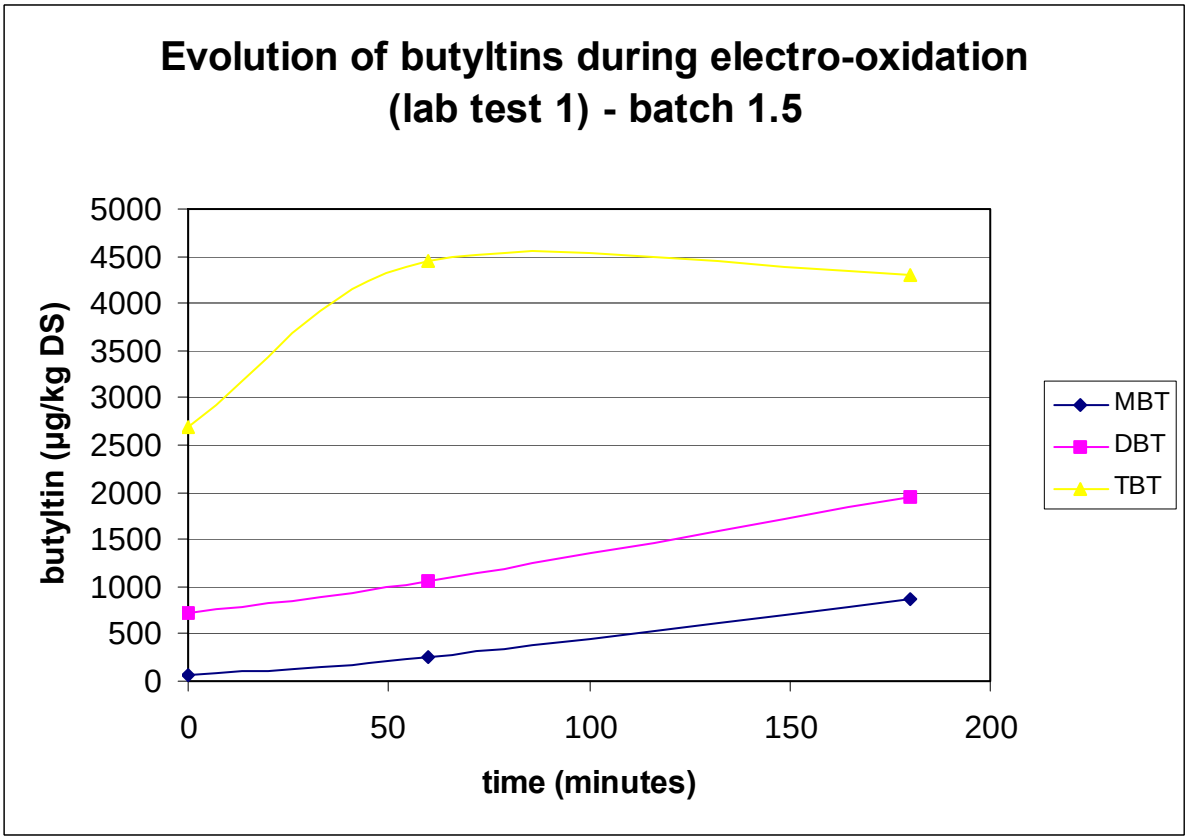

Figure 6.8. Evolution of butyltins during electrochemical treatment – batch 1.5.

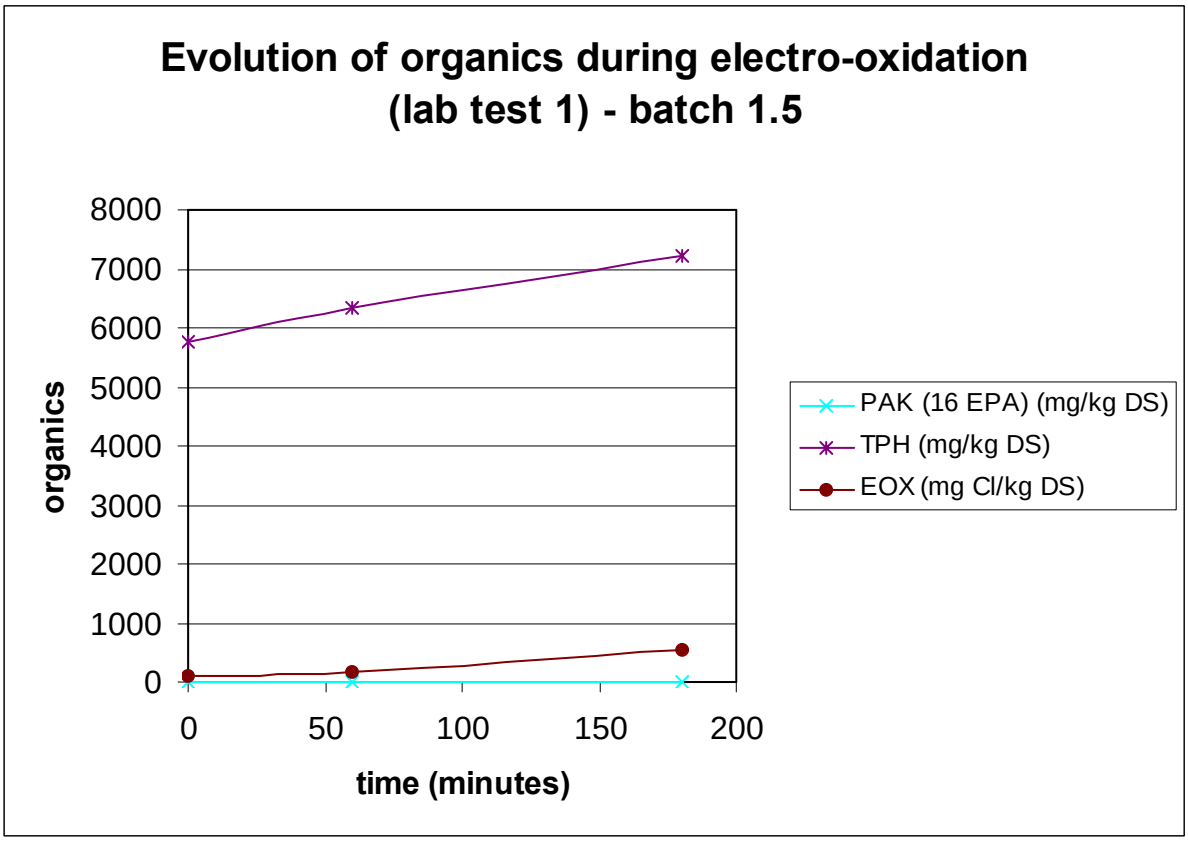

Figure 6.9. Evolution of organics during electrochemical treatment – batch 1.5.

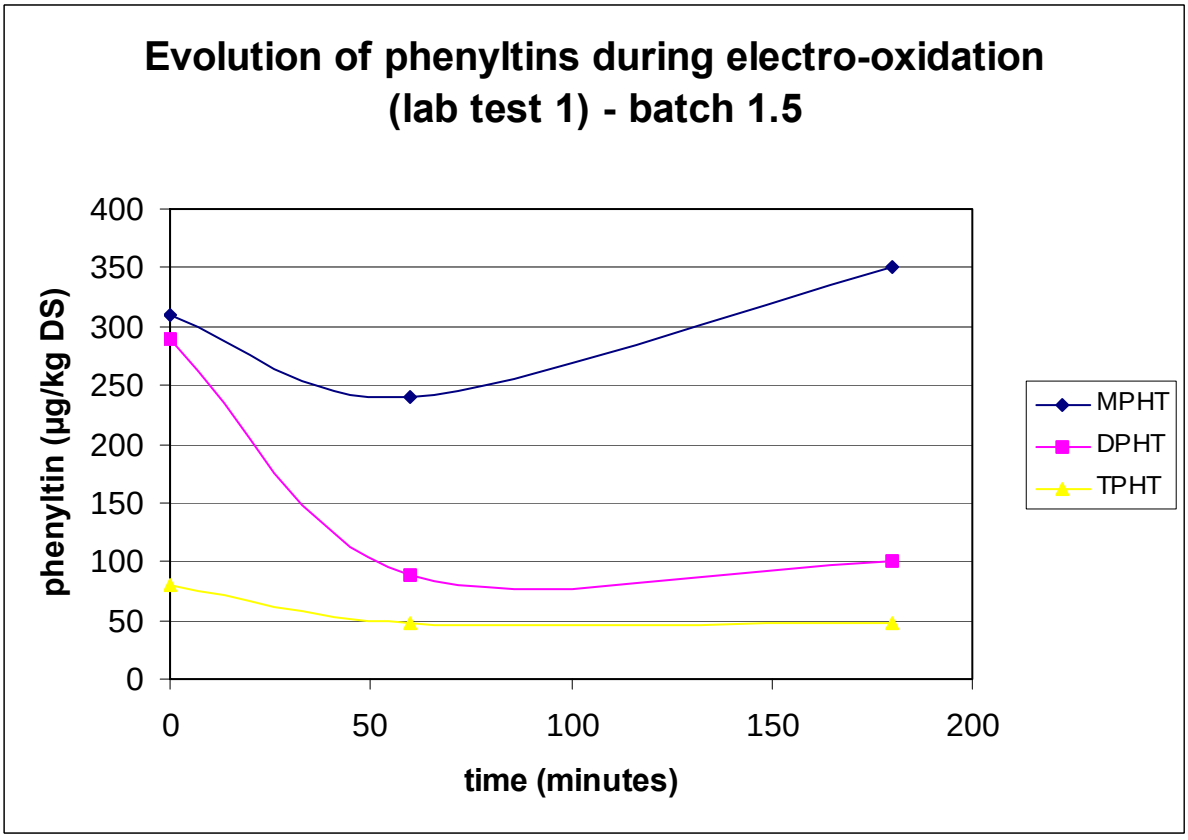

Figure 6.10. Evolution of phenyltins during electrochemical treatment – batch 1.5.

6.3.4. Discussion of the first lab tests.

6.3.4.1. Batch 2.1.

As expected and in analogy with the previous research of Stihnote, TBT concentration is decreasing with treatment time. Meanwhile, DBT and MBT show a slow increase. It is obvious that the treatment times applied during these first tests were too short and should be extended, e.g. to 24 h as in Stihnote's earlier experiments.
A remarkable trend is seen for the phenyltins and the TPH (mineral oil): all increase significantly in concentration. As for the mineral oil fractions (determined by GC-FID), this can be explained by the destruction of organic matter during the treatment, resulting in shorter chain molecules which are detected in the C10-C40 range of the gas chromatograph. However formed during the first stages of the treatment, further treatment will probably destroy these molecules as well. The increase of phenyltins is difficult to explain. It might be that butyltins are transferred into phenyltins - however very improbable – or that de novo synthesis is happening by combination of tin and phenylgroups that are formed during oxidation of the organic matter in the sediment. A third hypothesis is the release of strongly adsorbed phenyltins from the organic matter resulting in a better extraction recovery during analysis.
Also remarkable is the formation of (toxic) chlorinated hydrocarbons (EOX). A characterization of the various compounds is not carried out because of the analytical difficulty.

6.3.4.2. Batch 1.5.

In this case the all organotin concentrations increase with treatment time, which is of course unexpected, and can only be explained by the destruction of organic matter and the release of strongly adsorbed (or incorporated) organotins.
The other parameters follow a similar trend as for batch 2.1, except for triphenyltin, which is decreasing with treatment time.

6.3.5. Second series of lab scale tests.

Dr. Stihnote concluded from the first series of lab tests that oxidation is occurring, but slowly. Hence the treatment time should be prolonged in combination with the addition of salt. A second series of lab scale tests were carried out.
The only operational parameters that differed from the first series, was the dilution of the sediments with 0.1 M NaCl instead of tap water, and the treatment time extended to 24 hours. The voltage during this test, in order to maintain 600 A/m², was 4.2 V.

During these tests, only the organotin compounds were followed.

6.3.6. Results and discussion of the second lab scale test.

Figures 6.11 and 6.12 show the results on samples from batches 1.5 and 2.1 respectively.

These results are in analogy with the previous research of Stihnote, and show good results. TBT is degraded steadily, while DBT and MBT are formed during the first hours. After three hours a TBT degradation of 70 to 80 % is obtained, while the degradation is about 97 % after 24 hours of treatment. These tests prove that a sufficient amount of chloride should be added in combination with sufficient treatment time.

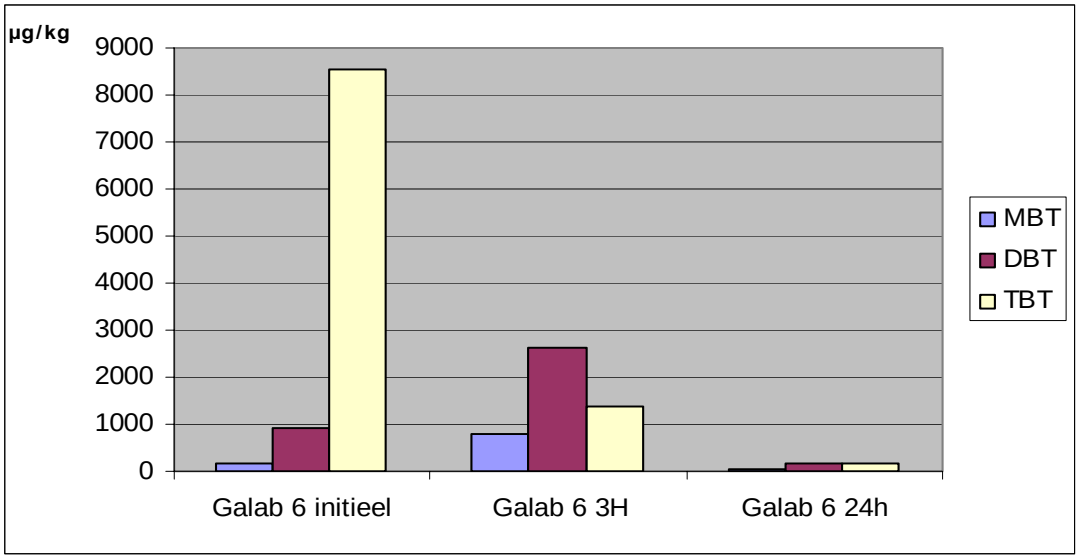

Figure 6.11. Evolution of the organotins during electrochemical treatment - batch 1.5.

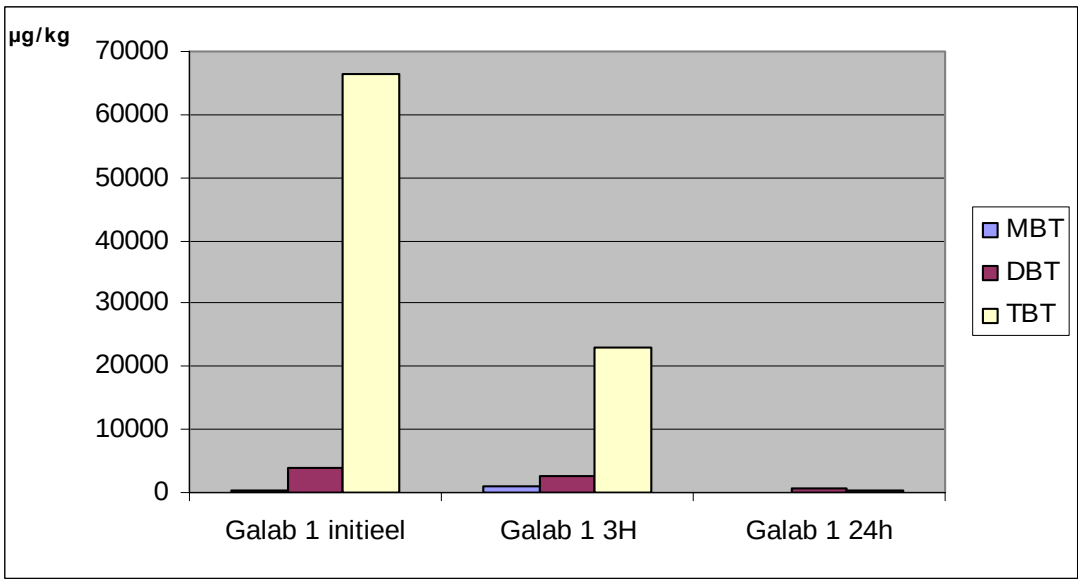

Figure 6.12. Evolution of the organotins during electrochemical treatment - batch 2.1.

6.4. Pilot tests.

6.4.1. Choice of the pilot plant.

For the pilot scale testing of the electrochemical oxidation two potential candidate plants were identified. The first plant was the pilot plant of TU Harburg used during preliminary testing by Dr. Stihnote, the second plant was a small demonstration plant of the German company Multiclair. The first plant is shown in figures 6.13 and 6.14, the second one in figure 6.15.

Both plants were evaluated based on the following criteria:

- Availability of the plant during the Spring of 2004.
- Technical condition of the plant: status of operation.
- Mobilisation and installation issues.
- Scientific expertise and back-up of the plant.
- Conflict with existing patents.
- Costs of the pilot tests.

Table 6.1: Evaluation of the pilot plants.

	Pilot plant TU Harburg	Pilot plant Multiclair
Availability	Available, but planning unsure.	Available
Operational status	Not operational, piping and electrical connections to be reinstalled; pumps to be replaced, electrodes to be purchased.	Operational
Mobilisation and installation	Large installation, complex mobilization and installation	Trailer based demonstration plant; set up in 1 hour.
Scientific back-up	A. Keller (former assistant of Dr. Stihnote). Dr Stihnote was not prepared to cooperate due to licencing issues.	Own R&D department.
Patents	TU Harburg patent Licencing discussions and disagreements were going on.	Patent pending.
Costs	3000 Euro rent of installation and operators.	> 30000 Euro.

After many technical and commercial discussions the pilot plant of Multiclair was chosen.

Multiclair is a contractor specialized in the treatment of waste waters by means of electrolysis based techniques, such as electroflotation. The waters treated have in general high COD loads, and vary from industrial waste water, domestic waste water, to contaminated sediments. They have a few mobile full scale plants for the treatment of waters and slurries.

Generally, Multiclair applies the technique of electroflotation to the wastewaters they treat. Electroflotation is based on the use of dissoluble anodes of steel (Fe) or aluminium. During the electrolysis process the iron and aluminium dissolves into iron (ferro/ferri) hydroxides and aluminiumhydroxides, which are known as very good anorganic flocculants. These hydroxides will adsorb and coprecipitate most of the COD in the water. In addition to this coprecipitation effect, indirect oxidation will occur, as many oxidants are formed at the anode (oxygen, ferric ions, chlorine and hypochlorite,…). Finally, the production and escape of gas bubbles at the electrodes (hydrogen at the cathode, oxygen and chlorine at the anode) will result in a flotation effect for the coagulated and flocculated compounds in the water.

The pilot plant has been demonstrated during the visit of the scientific advisory board end of May 2004.

Figure 6.13. Electrolysis cells of the TU Harburg plant.

Figure 6.14. Overview of the TU Harburg plant.

Figure 6.15. Multiclair plant.

6.4.2. Execution of the pilot test.

It was decided to restrict the pilot test to one type of sediment, i.e. batch 1.5, as the dispersion on the sampling and analyses of the other batch 2.1 is too high and can lead to false conclusions. Based on the lab scale tests, the following operational parameters were used:

- Dilution of the sediment to 5 % DMC with a 0.5 M NaCl solution.
- Current density: 600 A/m² at 3.2 V.
- Treatment time: 3 hours.
- Sampling at various points in time: 0', 25', 55', 180'.

The principle of the pilot scale reactor is basically similar to the lab scale reactor as shown in figure 6.1. For the pilot tests, 5 kg of dry matter is put into the system.

6.4.3. Results and discussion of the pilot test.

Figure 6.16 shows the results of the pilot test. Similar phenomena occur as observed during the lab scale trials: initially, the TBT concentration rises during the first half hour of treatment, and then decreases to about 100 µg/kg in 24 hours. DBT is also produced as an intermediate breakdown product, but is further destroyed during the process. MBT seems to stay low but rises slowly near the end of the process.

From an energetic point of view, the process is only promising in the lab scale, as illustrated in table 6.2. This is due to the addition of chloride, which enhances the formation of oxidant and the rate of reaction, as shown by Stihnote et al.

Table 6.2: Evaluation of power consumption of the electrolysis process.

	Lab scale test 1 *(Only partial removal !)*	Lab scale test 2	Pilot test
Ton dry matter treated	*0.0002*	0.0002	0.005
Potential difference	*7.1 V*	4.2 V	3.2 V
Current density	*600 A/m²*	600 A/m²	600 A/m²
Electrode surface	*0.02 m²*	0.02 m²	0.1 m²
Treatment time	*3 h*	24 h	3 h
kWh/ton DM	***1278***	**6048**	**115**
Energy cost per ton DM (at 0.1 €/kWh)	***128***	**605**	**11.5**

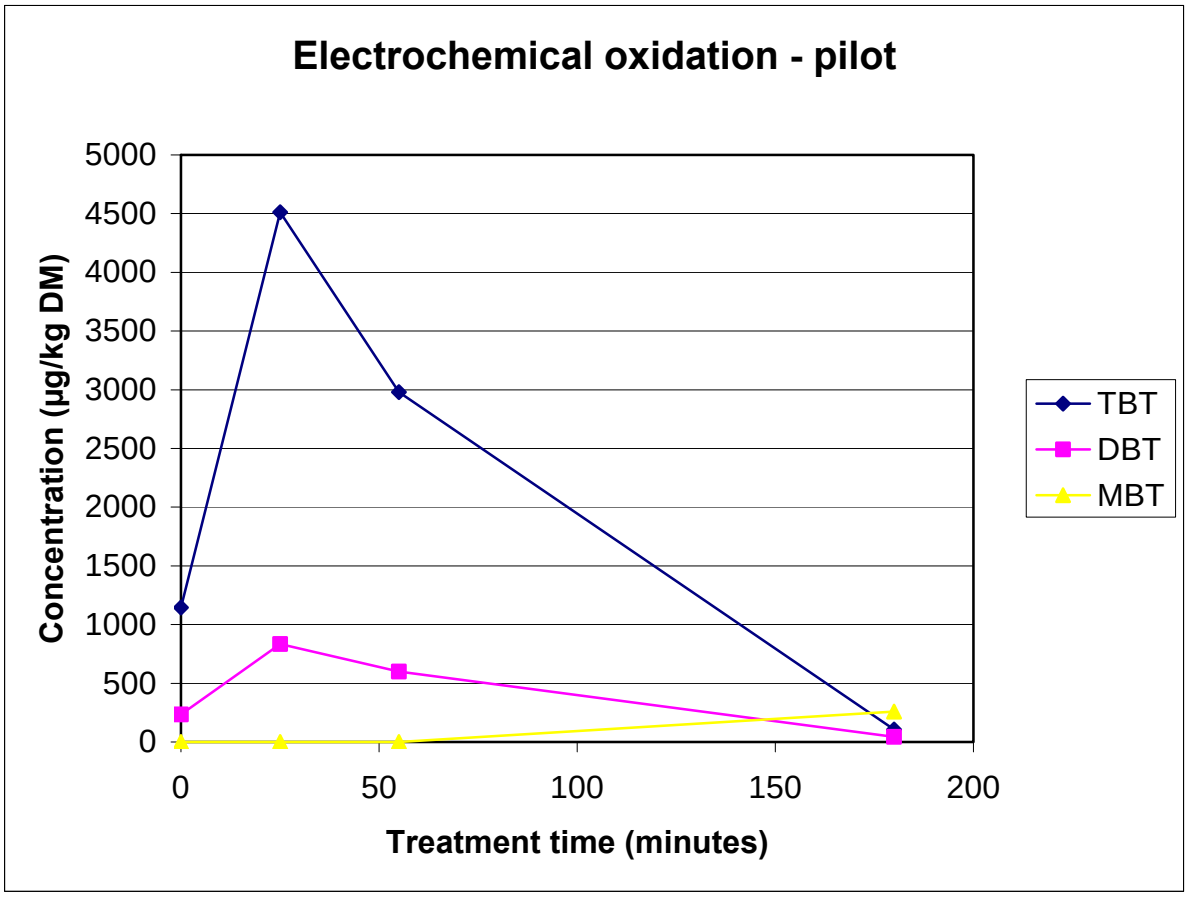

Figure 6.16. Evolution of organotins during pilot electrochemical oxidation.

6.4.4. Observations during the pilot scale testing.

Intrinsically to the process high amounts of gas were produced. At every point of the pilot plant a strong chlorine odour was perceived. After the treatment the sediment was well oxidized (brown colour) but had a typical chlorine smell. Again, high concentrations of chlorinated organic compounds, which are more bioavailable and oxic than TBT, can be expected.

Furthermore, no mechanical problems were observed in the plant such as clogging,… However, the sediments must always be sieved to about 1 mm, and diluted to a thin suspension. After treatment, the sediments will have to be dewatered again prior to reuse. Dewatering can again be natural (lagooning) or mechanical (filter press or sieve belt press). A point of attention is the use of flocculants during dewatering: probably organic flocculants (PE) will not work as they will be oxidized by residual oxidant in the sediment.

A full scale flowsheet is outlined in figure 6.17.

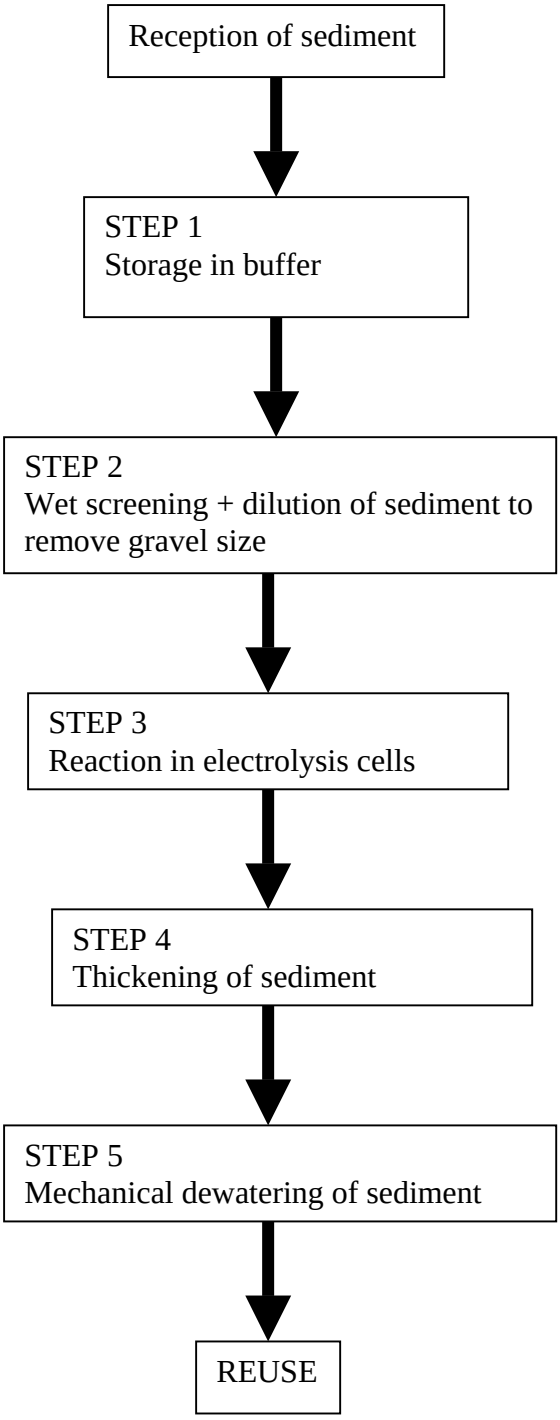

Figure 6.17. Typical flowsheet of a full scale electrochemical plant.

6.5. Conclusions.

- Electrochemical organotin destruction is feasible on full scale, however the sediments need to be conditioned before being compatible to the process.
- No experience exist on similar full scale applications. Upscaling will hence require a thorough risk and cost evaluation.
- Side effects such as formation of chlorinated compounds occurs (up to a few hundred mg/kg), making the sediment not suitable for reuse (standard in Flanders is 3 mg/kg). Also adverse effects were noticed on some pollutants such as the formation of mineral oil compounds probably due to the breakdown of organic matter in the sediment.
- The power consumption is moderate, provided sufficient chloride is added to the process. However, the more chloride added, the more EOX will be produced.

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