



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 3551
Treatment of the water phase

Kris Pynaert and Inge Van Cauteren



ERC

Environmental • Research • Center

Hekkestraat 51, Hofstade-Aalst

B-9308, Belgium

TABLE OF CONTENTS

List of figures.....	2
List of tables.....	2
Executive summary.....	3
1. Introduction.....	4
2. Principle of chemical and photo-oxidation.....	5
2.1. Chemical oxidation with ozone and permanganate	5
2.2. Photo-oxidation using UV-radiation.....	6
3. Lab-scale experimental results of chemical oxidation and UV-treatment.....	7
3.1. Chemical oxidation with ozone	7
3.2. Photo-oxidation and combined photo- and chemical oxidation	9
4. Lab-scale results of stripping experiments	12
5. Overall conclusions.....	14

LIST OF FIGURES

Figure 1. Schematic representation (left) and photograph of the ozone system (right) used to enrich water with ozone. (1) Ozone generator; (2) Reactor inlet; (3) Reactor vessel (4 L); (4) Reactor outlet, discharge; (5) Recirculating pump; (6) Kynar injection valve; (7) Pressure gauges; (8) Ozone destruction unit; (9) Off gas vent.

Figure 2. Schematic representation (left) and photograph of the UV-system (right). (1) UV lamp; (2) Stainless steel outer tube; (3) Reactor vessel; (4) Recirculating pump; (5) Flow meter; (6) Reactor discharge; (7) Reactor inlet; (8) Control panel.

Figure 3. Results of the organotin degradation during UV-experiments.

Figure 4. Results of a UV test run during which TBT-contaminated water was exposed to UV light (no extra chemical oxidant added)

Figure 5. Photographs of the lab-scale stripping set-up for TBT-removal

Figure 6. Results of temperature variation on stripping of organotin compounds

Figure 7. Results of pH variation on stripping of organotin compounds

LIST OF TABLES

Table 1. Relevant characteristics of ozone as a chemical oxidizing agent

Table 2. Experimental results of two ozone experiments (expressed in ng organotin/L)

Table 3. Results of the chemical oxidation and combined photo- and chemical oxidation (organotin compounds in ng/L, COD in mg/L).

EXECUTIVE SUMMARY

Mechanical dewatering of contaminated sediment as a pre-treatment step for e.g. thermal treatment is frequently used in practice. To improve dewaterability, lime or poly-electrolyte (PE) can be added. One of the side effects of lime addition is a significant pH increase of the filtrate water. Due to this pH increase, TBT is desorbed and enriched in the water phase. Also addition of PE causes TBT-release, however to a lesser extent, so in both cases the filtrate water needs treatment before discharging it. In this report, water treatment with ozone and permanganate as a means of chemical oxidation, ultraviolet light as photo-oxidation, a combination of UV and permanganate and finally stripping were tested. Ozone performed very well, with complete TBT-removal after 15 minutes of ozone treatment. A combination of UV and a limited amount of permanganate also showed good removal efficiencies, however fine-tuning is necessary to meet the required effluent concentrations. Stripping was also successful for TBT-removal, but not for DBT. The latter technique however only shifts the TBT-problem to the gas phase, which needs further treatment.

This report only gives an indication of the feasibility of the different water treatment techniques on lab-scale, for practical implementation supplementary full-scale tests need to be carried out. A detailed cost-benefit analysis of such full-scale systems should be carried out before deciding on the type of treatment, however this is not included because the energy consumption and sizing of the full-scale installations are too vague to make a useful estimation of costs.

1. INTRODUCTION

Remediation of TBT-contaminated dredged sediment can be achieved through different treatments. These techniques include thermal treatment, bio- and phytoremediation, direct (electro)chemical treatment, ..., techniques which have been tested during the course of the TBT-project (see reports of Task 3550: Treatment of the solid phase). Sediment dewatering is included in several of these proposed treatment schemes, and is an important step for both the success of the remediation as for the related treatment cost (see cost-benefit analysis made for the TBT-project). Sediment dewatering can be achieved through lagooning, or mechanically by using e.g. a filter press, after pre-treatment with for example lime or polymers.

A successful mechanical dewatering step results in two streams: a relatively dry filter 'cake' (dry weight around 60-70%) and a water stream low in suspended solids. Depending on the sediment characteristics (pH, clay content, organic matter, ...) and the type of dewatering agent used (lime or polymer), the water phase will also contain different kinds of contaminants like COD, NH_4^+ , P, ... In case of TBT-contaminated sediment, the TBT which is present in the pore water or is chemically or mechanically released from the sediment particles during dewatering, will also be present in the water phase. As a consequence, this water stream also needs a treatment step before discharging it.

One possible option for water treatment was already discussed in another part of the report of Task 3551, namely activated carbon. The results were satisfactory, and activated carbon proved to be a good adsorbent for organotin compounds as well as other organic contaminants. A drawback of this method is that the organotin compounds are not destroyed in the process; they are only relocated from the water to a solid phase. The latter has to be treated as well (e.g. by thermal treatment) to destroy the organotins.

An alternative for activated carbon adsorption and post-thermal treatment could be chemical oxidation or photo-oxidation. Chemical oxidation with reagents like ozone (O_3) or potassium permanganate (KMnO_4) is known to be very efficient for removal of organic pollutants like e.g. trichloroethylene (TCE), and could also be effective for organotin removal. As for what photo-oxidation is concerned, it is well-described in literature that the ultraviolet (UV) component in natural sunlight is responsible for the stepwise debutylation breakdown of TBT in water, causing TBT to have a much lower half-life in water compared to when it is adsorbed onto sediment particles. Another advantage of these techniques is that the organotins are destroyed in one treatment step, without the need for post-treatment steps. In this report, results of experiments with ozone, KMnO_4 and UV-radiation are described in more detail.

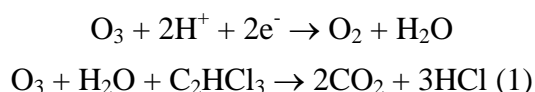
A last technique that was tested was stripping. However, the experiments were very limited and only the possibility to remove organotins from the water (and not from the air they are

released in) by stripping was examined. Thus, no complete destruction/removal experiments were done.

2. PRINCIPLE OF CHEMICAL AND PHOTO-OXIDATION

2.1. Chemical oxidation with ozone and permanganate

Chemical oxidation with e.g. ozone and KMnO_4 is based on direct oxidation or via the production of radicals that react with organic pollutants. The latter are oxidized to CO_2 and H_2O (complete oxidation) or intermediate products that are in most cases less refractory and more easily biodegradable in a post-treatment step. An example of the reaction of ozone with TCE is shown in equation 1.



In the case of ozone, the reaction precedes best under acid conditions. It is also known that ozone is a very reactive and unstable chemical, with a relatively short half-life in water. In Table 1, an overview is given of the most relevant characteristics of ozone.

Table 1. Relevant characteristics of ozone as a chemical oxidizing agent

Property	Value
Half-life gaseous @ 20°C	3 days
Half-life in water @ 20°C, pH 7	20 minutes
Oxidizing potential	2.07 V
Solubility @ 20°C ⁽¹⁾	12.86 mg/L
pH effect	Lowers
Density	2.144 g/L

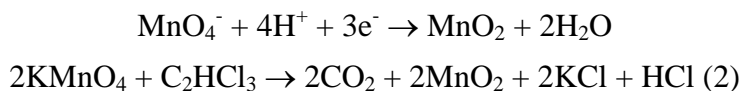
⁽¹⁾ For an ozone concentration in the gas phase of 3%

The main advantages given by ozone suppliers are:

- The most powerful oxidant available
- Quickly decomposes organic waste by oxidation
- Environmentally friendly, breaks down to oxygen and leaves no residual

Permanganate is another well-known chemical oxidizer, however less strong than ozone (oxidizing potential of 1.67 V). It has a very complex reaction stoichiometry in natural systems and has slower reaction kinetics. An advantage compared to ozone is that it works in

a broad pH interval (3-12). Depending on the pH, the reaction can proceed through direct electron transfer or via hydroxyl-radical formation. An example of the reaction of TCE with permanganate is shown in equation 2.



It has been demonstrated that these oxidizers can also be effective in breaking the Sn-carbon bonds in organotin compounds. The exact mechanism has not been demonstrated yet, however stepwise debutylation of TBT seems most likely.

2.2. Photo-oxidation using UV-radiation

Several reports on TBT half-lives in water mention a breakdown pathway of organotin compounds under influence of sunlight. This is due to the direct splitting of the Sn-C bond by the UV-component in sunlight, or indirect oxidation by hydroxyl radicals produced by UV-light. The latter is low-wavelength, high-energy light and is frequently used in post-treatment of water streams as a disinfectant (e.g. in drinking water production). Advantages are:

- No addition of chemicals needed
- Does not influence taste, odour, colour and pH of water
- No production of poisonous by-products
- UV-systems are compact, simple to install and nearly care-free

It is known that irradiation with UV-light of a water stream in which a chemical oxidizer like permanganate is added increases the efficiency of the oxidation process compared to a non-irradiated stream. This is caused by a supplementary production of radicals.

For the purpose of treating a TBT-contaminated water stream, 4 treatment strategies were compared:

1. Chemical oxidation with ozone
2. Chemical oxidation with permanganate
3. UV-irradiation
4. Permanganate oxidation combined with UV-irradiation

These experiments are described in the following sections.

3. LAB-SCALE EXPERIMENTAL RESULTS OF CHEMICAL OXIDATION AND UV-TREATMENT

3.1. Chemical oxidation with ozone

A lab-scale ozone set-up was purchased from an international ozone system supplier (Ozone Solutions Inc, USA). A schematic representation is shown in Fig. 1, a photograph of the set-up is also included. Ozone is generated by corona discharge in an oxygen flow, through which oxygen atoms (O) are produced that react with molecular oxygen (O₂) to form ozone (O₃). The ozone-enriched gas stream is then injected into a water stream through a specially designed valve that produces very small bubbles with high gas-water contact surface. Depending on the percentage of ozone in the gas stream, high amounts of dissolved ozone can be obtained within minutes. Off gasses, containing ozone that could not be dissolved into the water, are passed through an ozone destructor containing a catalyst to reduce ozone to oxygen. Water is continuously recirculated in the system, in order to obtain high dissolved ozone concentrations.

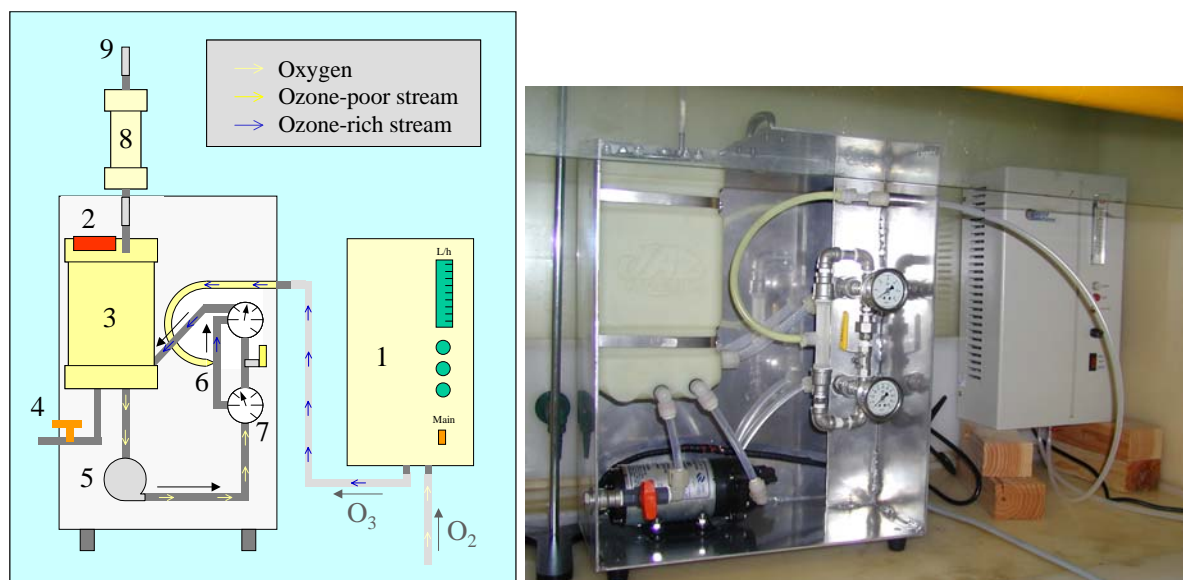


Figure 1. Schematic representation (left) and photograph of the ozone system (right) used to enrich water with ozone. (1) Ozone generator; (2) Reactor inlet; (3) Reactor vessel (4 L); (4) Reactor outlet, discharge; (5) Recirculating pump; (6) Kynar injection valve; (7) Pressure gauges; (8) Ozone destruction unit; (9) Off gas vent.

The filtrate water that was used in the experiments was supplied by Envisan NV, and originated from the full-scale dewatering of highly TBT-contaminated sediment after lime addition. The lime caused the water pH to rise to around 10, a pH that favours desorption of TBT to the water phase (see report Task 3545 Release of TBT). As a consequence, high

organotin concentrations were measured in the water, ranging from 1 to nearly 10 $\mu\text{g/L}$ for the different compounds in some experiments.

The ozone experiments were conducted as follows:

- Water volume: 4 L
- Oxygen flow to the generator without ozone production: 5 L/min
- Oxygen flow leaving the generator when ozone is produced: 3 L/min
- Samples were taken after 5, 10 and 15 minutes treatment with ozone
- Samples were measured after all ozone had disappeared

Experiments were always carried out at room temperature (around 20°C).

Dissolved ozone concentration was measured using a colorimetric method provided by Ozone Solutions, up to concentrations of 10 mg/L. In all experiments, ozone dissolution proceeded very well during the first 5 minutes, reaching concentrations of about 4 mg/L. During the next minutes this concentration only slightly increased to about 5 mg/L, indicating that the gas stream from the generator probably contained about 1.5% ozone (derived from solubility values from literature and data provided by Ozone Solutions).

In Table 2, the results of two ozone experiments are shown. In both cases, organotin removal was efficient but not complete (some MBT remained in the water after 15 minutes of ozone enrichment). The tri-organotin compounds TBT and TPhT were both very susceptible to degradation with ozone. In the second experiment, COD removal was also measured, but this only amounted about 10%. The pH of the water slightly dropped during ozone treatment, from 9.68 to 8.79.

Table 2. Experimental results of two ozone experiments (expressed in ng organotin/L)

Experiment 1						
Time (min)	TBT	DBT	MBT	TPhT	DPhT	MPhT
0	3182	4051	1144	1789	91	390
5	<10	230	502	<10	46	452
10	<10	232	353	<10	27	310
15	<10	82	206	<10	0	154
Experiment 2						
Time (min)	TBT	DBT	MBT	TPhT	DPhT	MPhT
0	5696	3889	1000	2625	129	334
5	84	538	784	75	139	730
10	14	192	424	19	48	371
15	<10	107	268	<10	26	227

Based on the results obtained, we can conclude that ozone as a treatment method can work, however the treatment time still needs fine-tuning (also depending on the necessary removal efficiency and/or discharge limits).

In a third experiment, pH of the filtrate water was adjusted to 6 before the start of the experiment. Measurement of the organotins in the pH-adjusted water prior to ozone dosage no longer showed TBT. This is a clear indication that adsorption phenomena have a strong influence on the amount of TBT in the water when the latter is in contact with a surface (sediment particles, reactor wall, ...) and when the pH is changed. This observation is already used in a water treatment strategy, namely the adsorption to activated carbon. In the latter technique, the filtrate water needs pH adjustment prior to discharge (to meet the discharge limits imposed by law) and sulphuric acid is added. TBT molecules will rapidly adsorb to activated carbon under such conditions.

3.2. Photo-oxidation and combined photo- and chemical oxidation

3.2.1. Photo-oxidation

Exposure of water samples to UV-light is a known practice in drinking water production or water disinfection. In case of TBT, UV light is known to be a direct and indirect oxidizer, which makes it very interesting in the framework of our TBT-LIFE project.

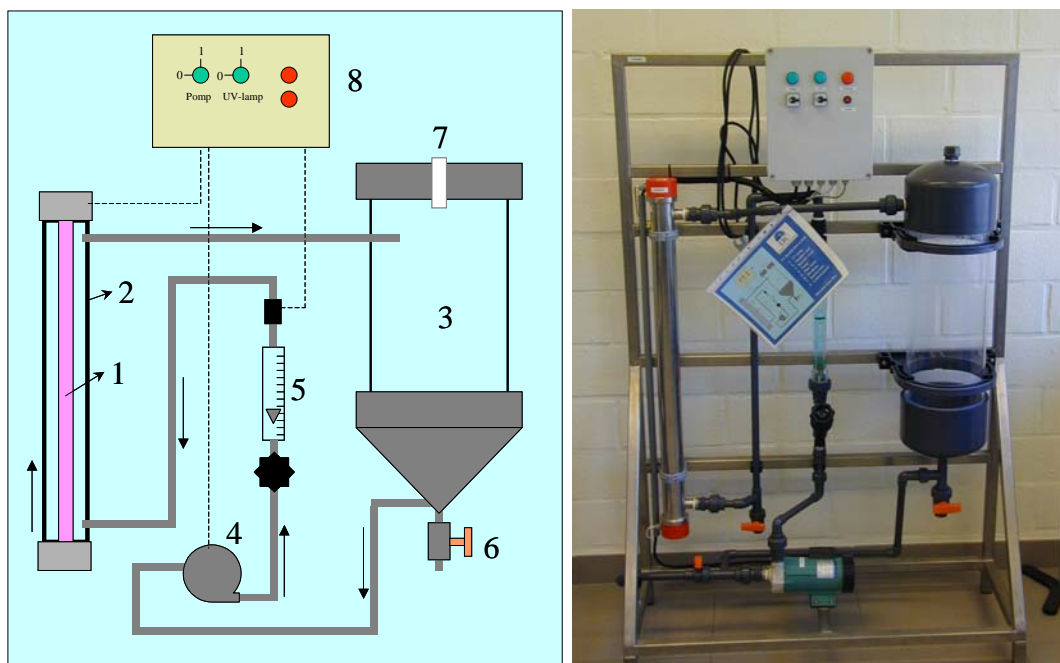


Figure 2. Schematic representation (left) and photograph of the UV-system (right). (1) UV lamp; (2) Stainless steel outer tube; (3) Reactor vessel; (4) Recirculating pump; (5) Flow meter; (6) Reactor discharge; (7) Reactor inlet; (8) Control panel.

The UV set-up was constructed by LENNTECH (Delft, The Netherlands), and a MK-55 UV lamp of ATG Willand was incorporated in it (energy output 18 Watt in the UV-C spectrum, 254 nm wavelength). Figure 2 shows the UV lab-scale set-up.

The lamp (length 890 mm) is surrounded by a transparent quartz sleeve to protect it from the water (this sleeve adsorbs 10% of the lamp energy and has a diameter of 30 mm), and a stainless steel outer tube (inner diameter 47.5 mm) is installed to avoid the UV light to be omitted into the surrounding area. The water passes between the quartz and stainless steel tubes (inner volume of the lamp \pm 1 L), and is only exposed during the time interval of passage through the lamp. In most experiments, a water volume of 6 L and a recirculation flow of about 720 L/hour were applied, which means an actual irradiation time of the water of about 17% of the total duration of the experiment. This should be taken into account when scaling-up, because most systems in practice are designed for a single passage through the lamp, based on the needed irradiation time.

In a first set of experiments, a 2-hour residence time in the system was used. In one test run, a flow rate of 360 L/h was applied, in a second a flow rate of 720 L/h. The difference between the two experiments is rather small, only the time of actual irradiation in the lamp during one passage was half in the second experiment compared to the first. This was however compensated by the fact that the water passed twice as many times through the lamp in the same time interval in the second experiment compared to the first. The actual irradiation time (residence time of the water in the UV-lamp) was about 20 minutes. The results are presented in Figure 3.

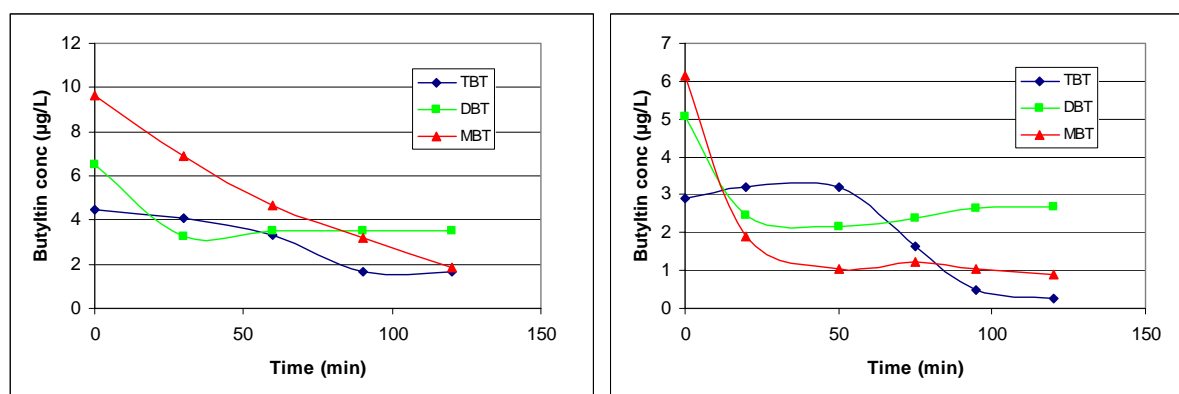


Figure 3. Results of the organotin degradation during UV-experiments.

During UV-treatment, the TBT and MBT-concentration drop considerably. The DBT-concentration however stays high after UV-treatment. This experiment showed that it could be feasible to use UV for water clean up. Longer irradiation times were however considered necessary.

In Figure 4, the results of a final UV test-run are shown. During 4 hours, water was exposed to UV-light (actual exposure time of about 41 minutes). All phenyltin compounds were

removed, but significant butyltin concentrations still remained in the water (TBT \approx 500 ng/L; DBT \approx 2000 ng/L; MBT \approx 800 ng/L). Removal efficiencies for TBT and MBT were calculated to be 90 and 93%, MBT was only removed to about 60%.

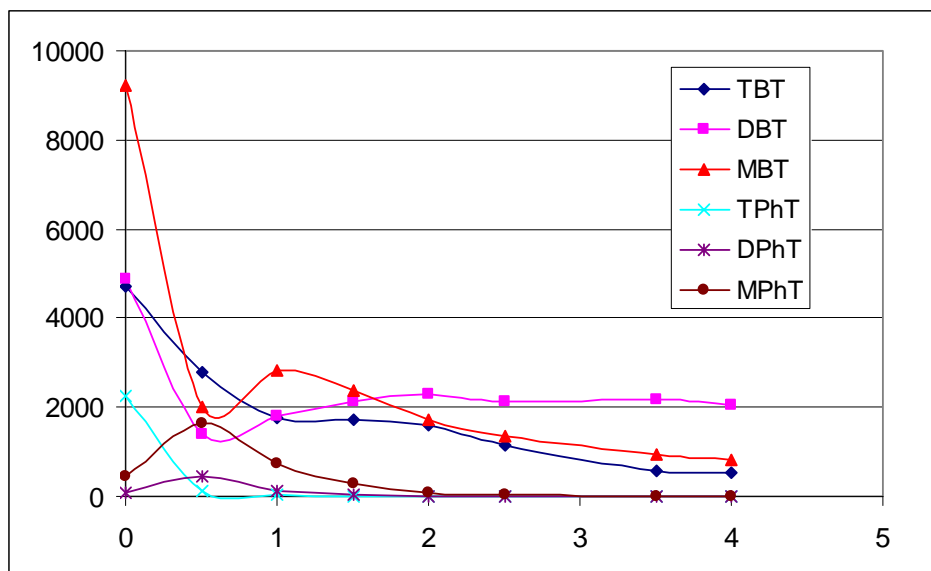


Figure 4. Results of a UV test run during which TBT-contaminated water was exposed to UV light (no extra chemical oxidant added)

To fully remove all organotins, longer treatment times would be necessary. This is practically not feasible, due to too high investment costs for the UV-lamps. Therefore, other options were examined.

3.2.2. Combined photo- and chemical oxidation

In a next phase, addition of a chemical oxidant (KMnO_4) and subsequent UV-treatment was compared to chemical oxidation with KMnO_4 only (Table 3).

Table 3. Results of the chemical oxidation and combined photo- and chemical oxidation (organotin compounds in ng/L, COD in mg/L).

Treatment	TBT	DBT	MBT	TPhT	DPhT	MPhT	COD
Blank (no treatment)	5966	3988	1280	2710	127	407	77
80 min 15 mg KMnO_4/L	58	3652	395	1299	138	75	81
240 min 30 mg KMnO_4/L	107	357	169	1313	171	37	75
25 min UV + 15 mg KMnO_4/L	560	3900	610	1136	485	117	79
50 min UV + 30 mg KMnO_4/L	25	1490	223	183,5	258,5	59	77
90 min UV + 60 mg KMnO_4/L	25	355	131	221	199	34	47

Addition of potassium permanganate causes a change in watercolour to pinkish-purple. As the permanganate is slowly reduced to MnO_2 , the water starts to show a more brownish colour. Once all permanganate is reduced, a filtered sample no longer shows colour. The duration of the tests was chosen according to this decolourisation of intermediate water samples. A first observation when looking at the results in Table 3 is that UV light significantly reduces the time necessary for complete permanganate reduction to MnO_2 . This confirms the theory that UV light produces an extra amount of hydroxyl radicals and as such accelerates the redox reactions in the water.

A second observation is that when the treatment time and or permanganate concentration are not sufficient, DBT often accumulates. This was shown for three out of five treatments. The best result was obtained for a treatment of 90 minutes in the UV set-up with 60 mg/L KMnO_4 mixed in the water. The actual UV-light exposure time is however only 17% of the test duration time, which corresponds to a continuous exposure of about 15 minutes. In case a system is designed where the length and/or the volume of the UV lamp is chosen according to the flow of water that needs to be treated, a hydraulic residence time of 15 minutes should thus give a similar efficiency (e.g. a UV lamp volume of 30 L if a water flow of 2 L/min needs to be treated). As for the ozone experiments, fine-tuning of these UV/chemox experiments is still required, depending on the needed (legislation) effluent quality.

4. LAB-SCALE RESULTS OF STRIPPING EXPERIMENTS

Due to their hydrophobicity, organotins have the tendency to sorb to non-polar surfaces like organic molecules, but also to air bubbles. The latter could thus be a way of water treatment.



Figure 5. Photographs of the lab-scale stripping set-up for TBT-removal

Several studies showed that TBT is removed from oceans due to volatilisation and adsorption to bubbles that explode at the surface of the water. In our experiments, TBT-rich water was aerated with an air pump (see Fig. 5) and samples were taken over time. No gas sampling was done, which means that this technique alone is not sufficient as a remediation technology and should be combined with a subsequent off gas cleaning (which was not tested).

Two environmental parameters were changed during these experiments: temperature and pH. Four different values of both parameters were tested and results are shown in Fig. 6 and 7.

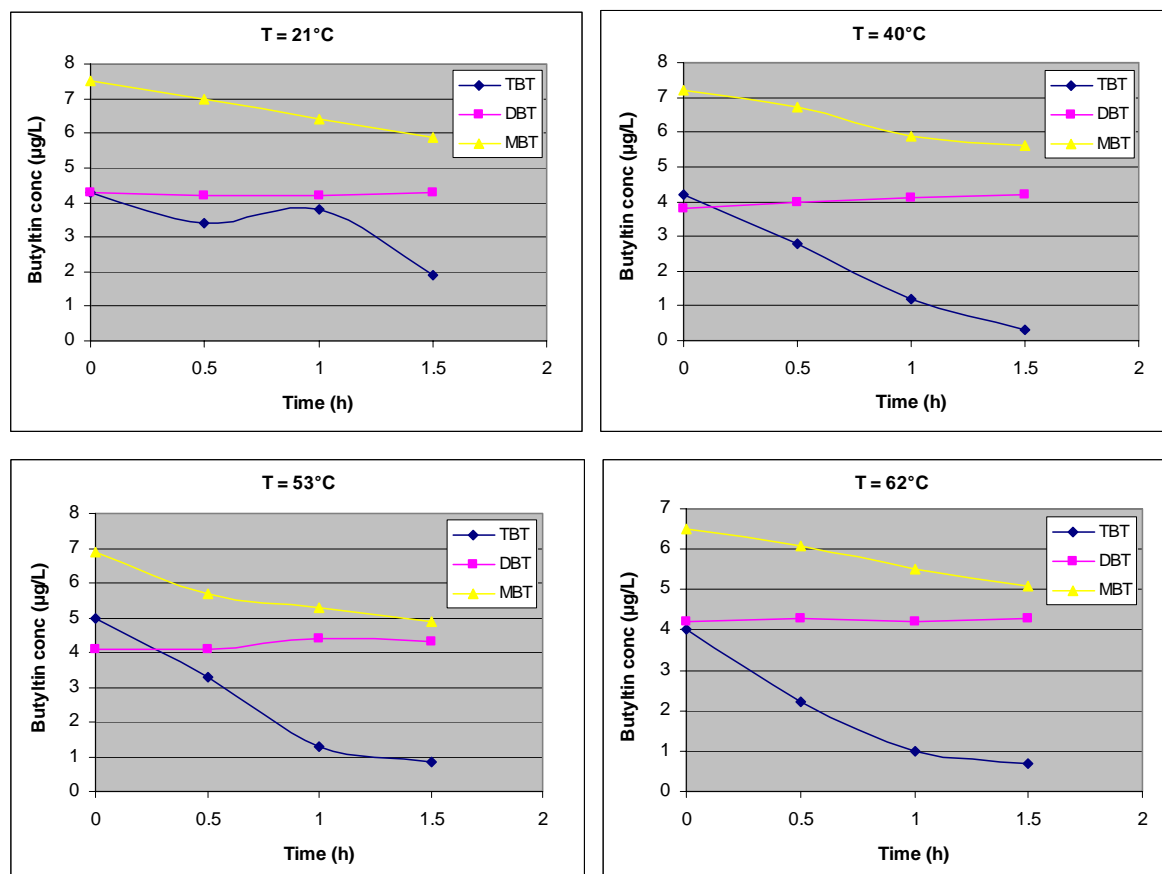


Figure 6. Results of temperature variation on stripping of organotin compounds

TBT-removal efficiencies of 80-90% were achieved after 1.5 hour stripping. Increasing temperature improves stripping, however not drastically in the tested interval. It is however considered not relevant to test higher temperatures, due to practical considerations of warming up significant quantities of water. TBT and MBT seem to be more susceptible to stripping than DBT, which remains in solution. Considering that breakdown of TBT to DBT and MBT is only expected to a very minor extent, the constant DBT concentration in all graphs cannot be explained by DBT formation out of TBT while DBT is stripped. Compared to activated carbon adsorption, stripping will not be advantageous, also due to the need for an activated carbon filter for off gas treatment.

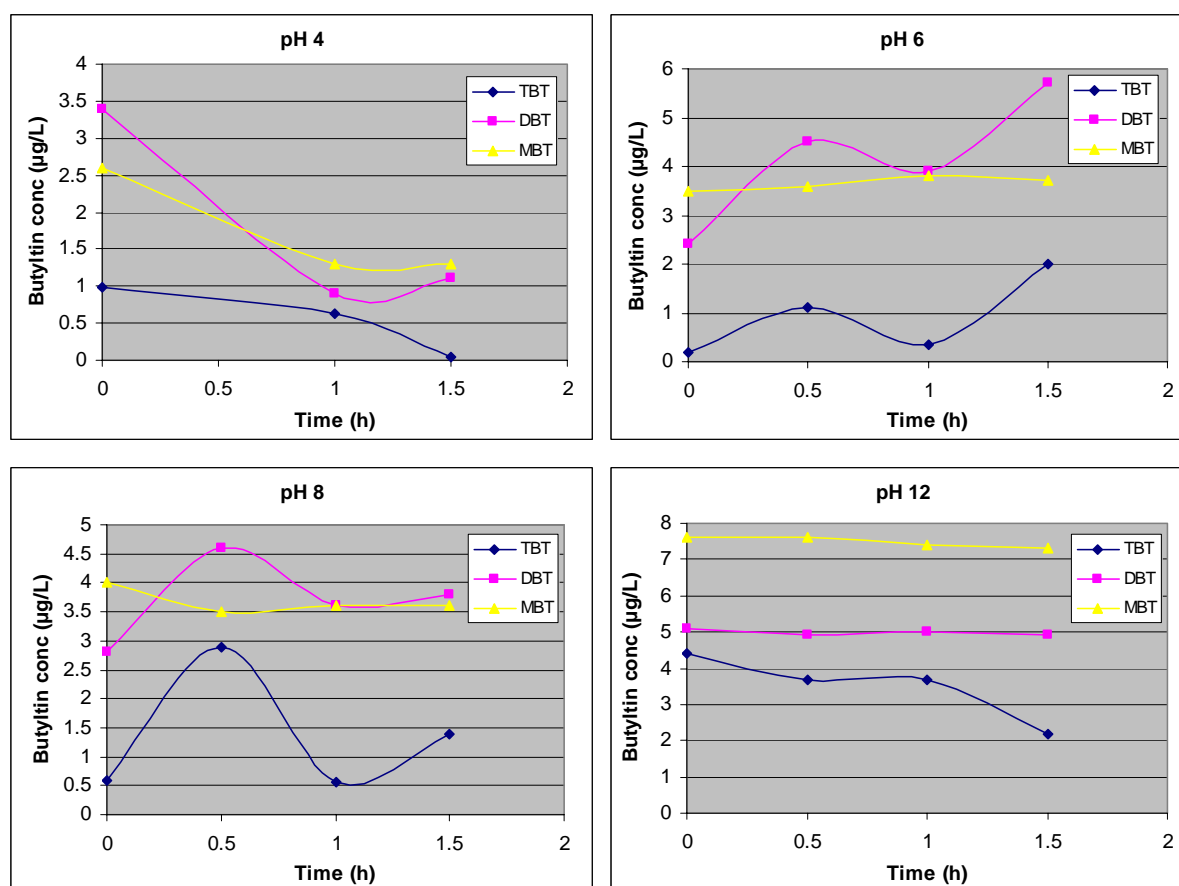


Figure 7. Results of pH variation on stripping of organotin compounds

Based on the graphs presented here, pH adjustment has a significant influence on the initial organotin concentrations of the water. Neutral pH was already shown in previous reports to improve adsorption, a phenomenon that is also observed in these experiments (and in the previous ozone experiments). Correction of pH from 10.5 (initial pH of the water) to e.g. 6 caused a massive decrease in initial organotin concentration, indicating that these compounds rapidly adsorb to suspended and dissolved organic matter and to the glass wall. Stripping itself was not really influenced by pH adjustments.

5. OVERALL CONCLUSIONS

The experiments conducted for this part of Task 3551 were carried out to check the feasibility of other water treatment methods, next to activated carbon filtration. Ozone and UV/chemox experiments gave good results, but however need fine-tuning in order to obtain the effluent quality standards required (which depend on legal and ecotoxicological issues). Depending on the exposure time to UV-light, TBT-removal efficiencies of 90% could be achieved. Treatment time and efficiency could be significantly improved by adding a small amount of chemical oxidant like KMnO_2 to the water. Ozone treatment resulted in complete TBT removal after 15 minutes of ozone enrichment. Stripping was shown to be effective for TBT-

removal, but not for DBT. An additional drawback is the needed after-treatment of the gas-phase. Overall, the decision on the type of water treatment should be based on several criteria: cost-benefit, safety issues, ease of operation, ... A full-scale cost-estimation based on lab-scale installations like in this report is however not appropriate, as costs for energy consumption and up-scaling of the equipment are very difficult to predict.