Quarterly Progress Report for
USEPA Grant S-82874601-1

Evaluate Pilot and Full-Scale Treatment Processes
to Remove TBT from Industrial Wastewater

Submitted to:

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Summary of Third-Quarter Study Efforts

Research studies directed toward identifying a viable treatment process to remove tributyltin (TBT) from shipyard water have continued during the third quarter under the current research grant. Efforts during this period were primarily directed toward the operation of granular activated carbon (GAC) pilot contactor columns that were installed and operated on the barge, operation (sparingly after May 4) of the full-scale treatment plant, and performance assessment of a proprietary membrane filter developed for TBT removal by the 3M company. The GAC pilot columns and 3M system were operated under various operational schemes to determine the ability of each system to lower TBT concentrations to less than 50 ng/L. Results for the period through the end of July are reported in this report. Statistical analysis of data collected from the pilot GAC columns and reported in the previous progress report[1], are also included in this report.

Treatment Operations

The third quarter study effort continued work from the previous quarter with treatment using the full-scale, barge-based treatment plant, the pilot GAC contactors, and the 3M TBT-selective membrane. During this period, no ships with TBT paint were in drydock at any of the Virginia shipyards. However, this occurrence was anticipated and more than 150,000 gallons from work done on the commercial vessel Sealand Oregon (from early May) were saved and added to approximately 50,000 gallons previously collected from other ships. Of this water, 80,000 gallons were stored in the barge mounted storage tanks while the remainder was added to "TBT water" collected from previous ship washing/hydroblasting efforts and held in the Newport News Shipbuilding tank barge, Nancy Bean.

The pilot GAC and 3M TBT systems were operated under various treatment configurations during this period but primarily disconnected from the full-scale plant process train. This operation differed considerably from the earlier efforts where the pilot GAC columns and 3M system were used to treat water after it first passed through the full-scale plant's DAF and sand filter. Two circumstances were primarily responsible for the decision to operate in this mode. One was premature fouling of the TBT-selective membrane that appeared to be the result of organic polymer carry through (and possibly iron from the ferric sulfate coagulant). Full-scale plant changes were made to minimize the use of the inorganic coagulant and the coagulant aid (organic polymer). However, these efforts were not successful and the decision was made to not operate the 3M system following the sand filter. The second circumstance that dictated treating water with the pilot systems separate from the full-scale treatment plant was the lack of water to sustain operation of the full-scale treatment plant. The full-scale plant when operated under typical conditions treats 21,000 gallons/day an amount that would have consume the stored water in nine days.

[1] Quarterly Report to the USEPA for the Project "Evaluate Pilot and Full-Scale Treatment Processes to Remove TBT from Industrial Wastewater," May 15, 2001.

Treatment conditions for the pilot GAC columns, and the 3M system are provided in Figures 1-4 (NOT AVAILABLE IN PDF FORMAT) and summarized in Tables 1 and 2. Conditions from earlier in the year are also included to illustrate the progression of operational conditions since pilot studies began in March. During the 9 March to 13 April period, the pilot GAC columns were operated primarily to assess the influence of flow rate on GAC removal of TBT, to examine TBT removal occurring over four GAC columns (GAC1–GAC4) operated in series, and to assess whether the pilot columns could provide treatment similar to the full-scale process train. During the remainder of the study period, GAC3 and GAC4 were not operated due to intermittent operation of the full-scale plant and the use of all pilot columns (GAC5-GAC8) for evaluation of four GAC contactor columns in series (31 May – 29 June). In July, another pilot GAC column was taken off line to allow simulation of a three-GAC contactor configuration, a treatment configuration that was under consideration for the full-scale plant and has since been implemented.

Table 1.
Operational Conditions for the Pilot GAC Contactor Columns.

	Pilot Activated Carbon Column Operational Conditions					
Dates	**GAC3**	**GAC4**	**GAC5**	**GAC6**	**GAC7**	**GAC8**
3/9 - 4/13	Operated in series following GAC 2		Operated in series following sand filter		Operated in series following sand filter	
5/31 – 6/29	Not operated		GAC5 – GAC8 operated in series. Feed water is effluent from 1 μm filter.			
7/5 - 7/24	Not operated		GAC5-GAC7 operated in series. Feed water is effluent from 50μm filter.			Not operated

Table 2.
Operational Conditions and Filter Cartridges and Membranes in the 3M Filter System.

		Filters/Membranes Present in the 3M System (Cartridge Filter Pore Size in Microns)				
Dates	**Influent Description**	**P1**	**P2**	**C1**	**C2**	**C3**
3/9 - 3/22	Full-scale plant sand filter effluent used as influent	10	0.5	TBT	TBT	TBT
4/2 – 4/13	Full-scale plant sand filter effluent used as influent	10	0.5	0.1	TBT	TBT
5/4 – 6/15	Untreated influent	10	1	0.5	0.2	TBT
6/26-6-29	Untreated influent	empty	empty	1	0.2	TBT
7/5 - 7/24	P2 effluent was routed through three pilot GAC columns before returning to C1	10	empty	1	0.2	TBT

The 3M-filtration system consists of a modular array of five cartridge filter holders that can accept spiral wound, dead-end cartridge filters that are readily available in the marketplace or the proprietary TBT-selective membrane produced by 3M. They are designated P1, P2, C1, C2, and C3 and water being treated passes through them in the sequence presented. Since the study with the TBT-selective membrane began, the filtration system has been operated with from one to three TBT-selective membranes following cartridge filters of various sizes (Table 2). The system has been operated in a number of configurations including pretreatment prior to the whole filter array or treatment in an intermediate position of the filter array. Descriptions (Table 2) and illustrations (Figures 1-4) depict the variable conditions tested to date.

Statistical Analysis Comparing Pilot Columns and the Full-Scale Treatment Plant

In the previous quarterly progress report (May 15, 2001) results were presented comparing pilot- and full-scale GAC contactors operated under similar conditions and comparing identical pilot GAC contactors operated under different flow conditions. A statistical analysis[2] of these data was conducted during the recent quarter and the observations made in the previous report were validated statistically. These conclusions are:

- Treatment performance was not statistically different between the full-scale GAC columns and the pilot-scale columns operated at a flow rate of 2.6 gpm/ft^2.
- Treatment performance was not statistically different between the pilot columns operated at a flow rate of 2.6 gpm/ft^2 and a flow rate of 1.6 gpm/ft^2.

Pilot GAC Contactor Column Treatment Efforts

Pilot-scale and combined full-scale and pilot scale treatment of TBT-containing waters illustrated the benefit of increased amount of GAC in the treatment system. Results for GAC2 and GAC4 during the 9 March to 27 April 2001 period illustrate that TBT concentrations in the GAC2 effluent are elevated and substantially exceed the established regulatory limit in Virginia (50 ng/L). GAC4 effluent samples where generally low (all concentrations < 100 ng/L) as would be expected for water exiting the fourth GAC column. Summary statistics were calculated for the TBT concentrations in the effluent of these two GAC columns and the results illustrate the frequency distribution of TBT values. For GAC2 samples, the median value exceeded 50 ng/L indicating that more than 50% of the samples would exceed the discharge limit. GAC 4 TBT concentrations were well below the limit and even at the 3rd quartile (75%) the concentration (20 ng/L) was well within the limit.

[2] See detailed report in the Appendix

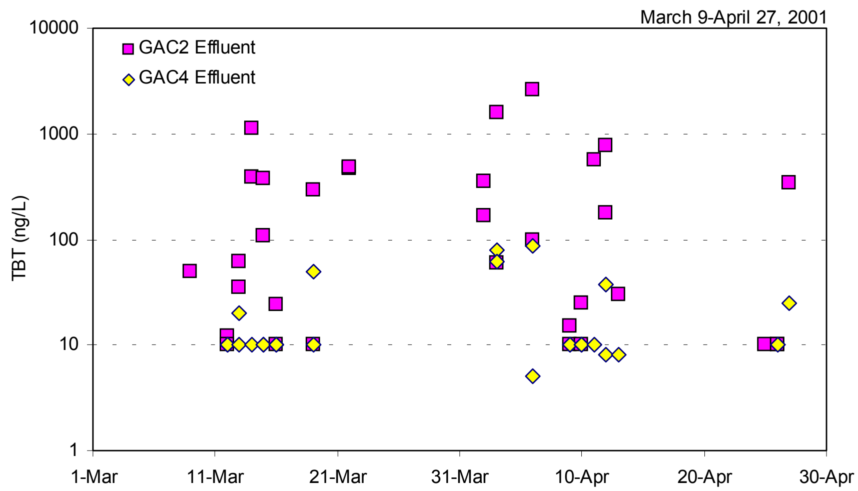


Figure 5. TBT concentrations in the effluent of GAC2 and GAC4 while operated in series during the 9 March to 27 April 2001 period.

Table 3.
Summary Statistics for GAC2 and GAC4 Effluent TBT Concentrations During Sequential Treatment (GAC1 to GAC4) from 9 March to 27 April 2001.

Statistical Parameter	GAC2 TBT (n=33)	GAC2 TBT∝ (n=25)	GAC 4 TBT (n=25)
Minimum	bd*	bd	bd
1st Quartile	12	12	bd
Median	62	60	bd
3rd Quartile	381	340	20
Maximum	2,600	2,600	87

∝ GAC2 TBT concentrations not paired with GAC4 TBT concentrations were eliminated from the data set and statistical analysis

* bd = TBT concentration below the detection limit; detection limit was approximately 10 ng/L

TBT concentrations in the GAC2 effluent during the spring-summer 2001 period were not significantly different than observed previously. Comparison of the frequency distributions for GAC2 effluent TBT concentrations from 9 March through 24 July 2001 with frequency distributions previously observed (Figure 6) illustrates a striking similarity with the December 1999 through September 2000 period. The relatively consistent trend between these two periods reflects a similarity of influent concentrations for both periods (not shown). The higher effluent TBT concentration distribution for the October to December 2000 (Figure 6a) period reflects a period of much higher influent concentrations, dissimilar to the most recent period of study.

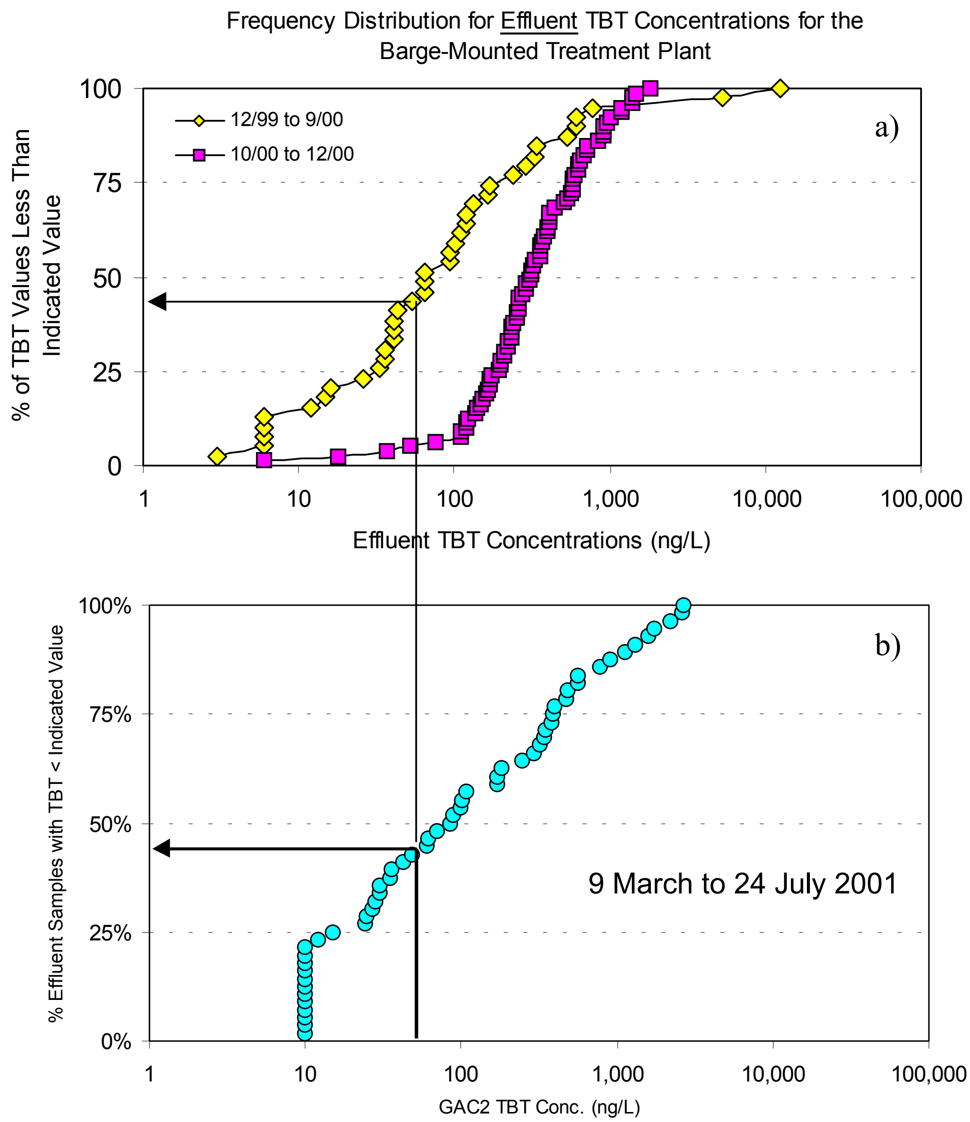


Figure 6. Frequency distribution for effluent (GAC2) concentrations for the full-scale treatment plant for the indicated periods.

GAC Removal of TBT: Full-scale Treatment

Removal of dissolved TBT in the full-scale plant has previously been shown to occur primarily in the GAC contactors with the bulk of removal (100x greater) occurring in the first GAC contactor[3]. During the spring 2001 period (March 9 - May 4, 2001), removal was observed to strongly correlate with influent concentration (Figure 7) in a relationship that was strongly linear (GAC1 TBT removal = 0.993(GAC1) – 1297, r^2 = 0.9986; GAC2 TBT removal = 0.909(GAC2) – 284, r^2 = 0.9548). Over this period no deterioration in removal was detected over time (not shown) indicating that "saturation" of the activated carbon in GAC1 and GAC2 was not causing TBT removal to decrease over time.

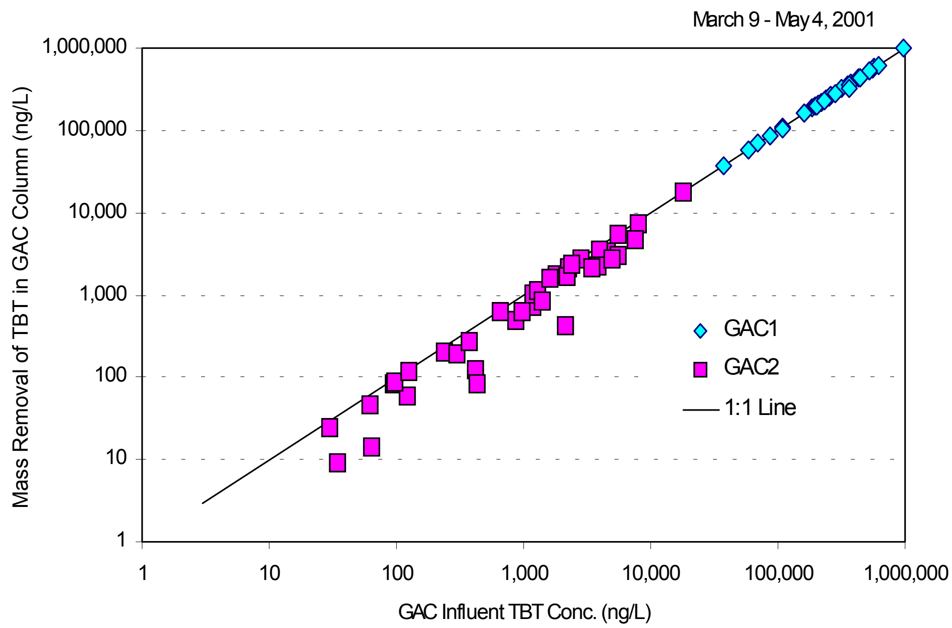


Figure 7. Relationship between TBT removed (per liter) as a function of TBT influent concentration to GAC1 and GAC2.

Both of the linear regression analyses for TBT removal in GAC1 and GAC2 for the March – May period have negative intercepts indicating that TBT removal decreases with decreasing influent concentration. This relationship is not as apparent in evaluating mass removal (Figure 7) but is seen when the percent removal analyses are examined.

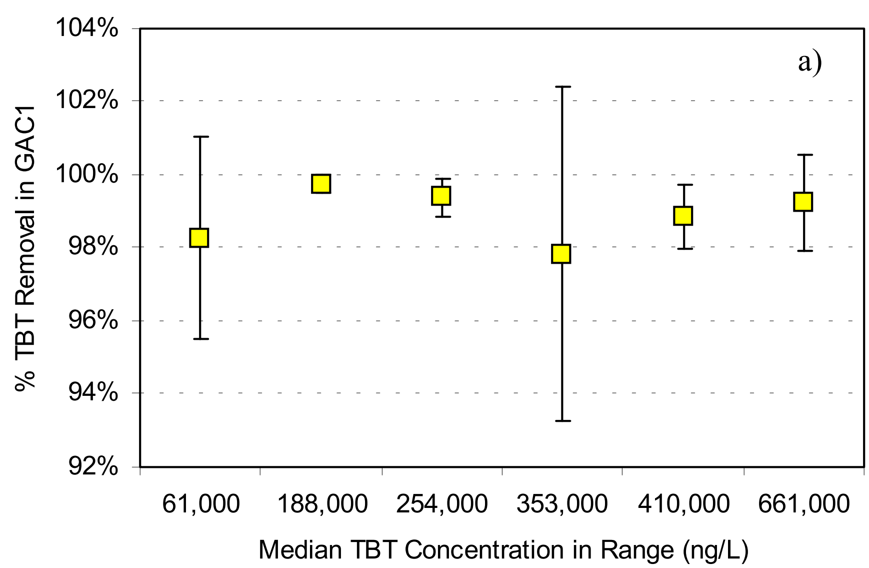
[3] Schafran et. al., 2001. "Removal of tributyltin (TBT) from shipyard waters: laboratory evaluations and one year of full-scale, shipyard-based treatment. Paper presented in the specialty session on Pollution Prevention at Shipyards at the Oceanology 2001 Conference, Miami, FL April 3-5, 2001

Examination of percentage removal for each column indicates the higher removal in GAC1 and the high variability that existed in removal occurring across GAC2 (Table 4).

Table 4.
Statistical Characterization of TBT Removal Occurring in Each Full-Scale GAC Contactor Column: March 9 – May 4, 2001.

Statistical Parameter	% TBT Removal in GAC1	% TBT Removal in GAC2
Minimum	88.50	19.35
1st Quartile	98.88	58.23
Median	99.55	74.83
3rd Quartile	99.90	89.91
Maximum	99.99	99.82

The generally lower removal in GAC2 is likely a result of the lower TBT concentration water entering GAC2. To examine and illustrate the relationship between influent concentration and percent removal, data were sorted in increasing concentration for each contactor and the mean and standard deviation for each grouping (generally n=6 per grouping) were calculated and graphed (Figure 8a, b). Influent concentration to GAC1 did not appear to influence the %TBT removal in GAC1 (Figure 8a) but it is clearly higher than the percent removals occurring across GAC2 (Figure 8b). A weak, positive relationship between percentage TBT removal and influent TBT concentration can be seen (Figure 8b) for GAC2 but the high variability of removal within each range makes the relationship not statistically significant. However, TBT removal is clearly higher on a percentage basis in GAC1 than GAC2.



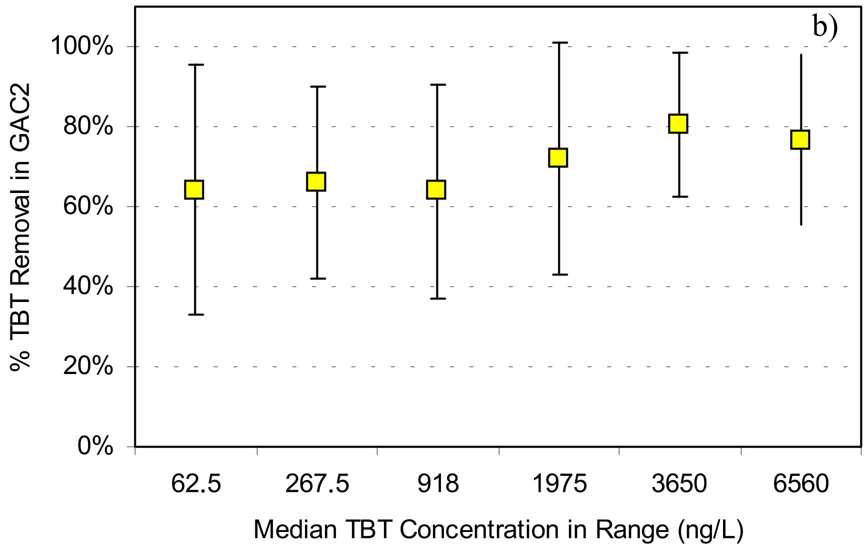


Figure 8. Percentage removal of TBT for (a) GAC1 and (b) GAC2 activated carbon columns for equivalent sized (n=6) ranges of data for the period March 9, 2001 – May 4, 2001. Error bars indicate standard deviation for each range.

GAC Removal of TBT: Pilot-Scale Treatment

Pilot-scale treatment with the GAC columns was conducted under a number of treatment scenarios (as noted under the Treatment Operations section) and comparison between columns operated at different flow rates and in sequence with the full-scale contactors was previously shown (May 2001 progress report). Follow-on treatment that specifically evaluated performance of a three-column-in-series GAC system is presented and discussed in this section. The three-column pilot study was conducted to determine if superior removal of TBT could be achieved with three GAC columns compared to the two GAC contactor systems that had been examined at pilot and full-scale.

During the July 5 – July 24, 2001 period, TBT wash water was treated by passage at a flow rate of 0.5 gpm through a 10-µm cartridge filter and then sequentially through the GAC5, GAC6, and GAC7 pilot columns. Samples were collected to the influent of GAC5 and following GAC7 to assess performance. Treatment beginning on 5 July followed a period of 20 days in which the pilot GAC columns were not operated. During this inactive period the columns remained immersed in water, a condition similar to between-treatment storage conditions of the full-scale system.

Treatment with the three-GAC-columns-in-series was observed to vary temporally with the highest effluent TBT concentration occurring on the first day of treatment and decreasing on subsequent days (Figure 9). The temporal trend in effluent TBT concentrations was not correlated to influent concentrations which averaged 140,000 ng/L over the study period. Fractionation of TBT (into particulate and dissolved TBT) was not conducted during this effort and it is not known whether changes in the TBT fractions in the influent or mobilization from the GAC columns contributed to this trend.

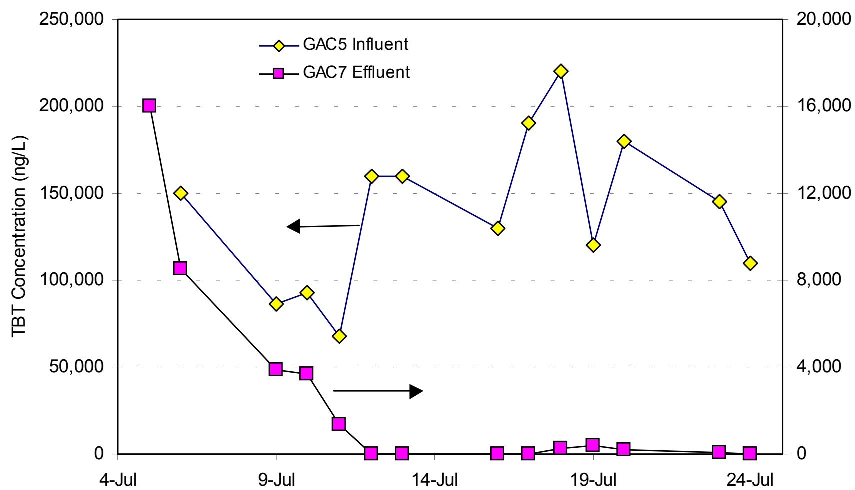


Figure 9. Influent and effluent TBT concentrations for the three-column pilot GAC system operated between July 5 and July 24, 2001.

Dissolved organic carbon concentrations for the influent and effluent of the three-column pilot GAC system were also evaluated to determine whether a trend similar to TBT occurred helping explain the variations in effluent TBT concentrations. Influent DOC concentrations decreased gradually for most of the period with a sharp decline on 23 July (Figure 10). In contrast, effluent concentrations increased for the majority of the period before decreasing on the last two dates. The effluent DOC concentrations contrast with the TBT trend and do not suggest that their removals were similarly influenced over this period (Figure 11). The trend observed for these two parameters is consistent with competitive adsorption where favorable removal of one organic compound occurs at the expense of other compounds. Previous efforts over longer periods of operation to discern a trend in removal between DOC and TBT have revealed no statistically significant relationship. However, over shorter periods of time, a negative correlation has been observed between DOC and TBT. Changes in the characteristics of organic material (e.g. increases in a poorly adsorbed fraction of DOC) in the influent due possibly to prolonged storage and elevated temperatures may have contributed to the relationship as the DOC in the TBT wash water.

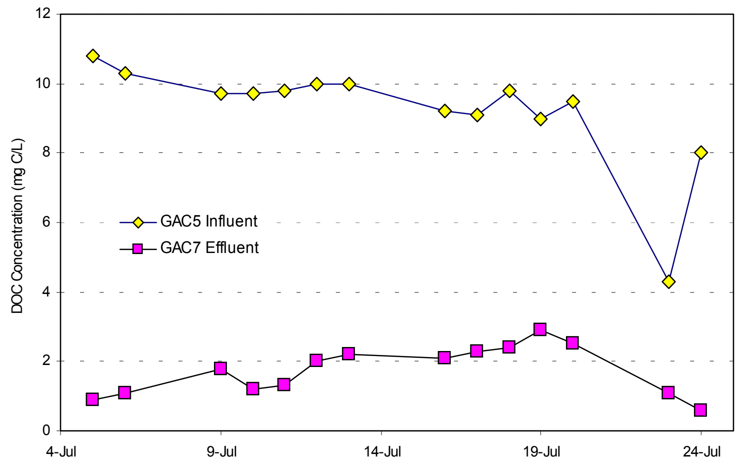


Figure 10. Influent and effluent DOC concentrations for the three-column pilot GAC system operated between July 5 and July 24, 2001.

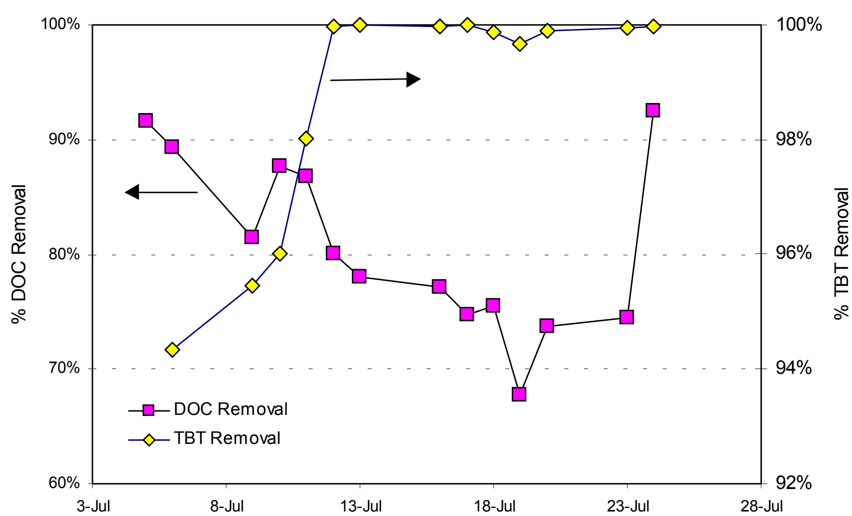


Figure 11. Percentage removal of TBT and DOC for the three-column pilot GAC system operated between July 5 and July 24, 2001. (Note different scales)

Removal of TBT by the 3-M Selective Membrane

The 3M TBT-selective membrane was previously observed to be capable of lowering TBT concentrations to less than the Virginia discharge standard (50 ng/L) and continued evaluation during the most recent period was conducted to determine whether this incipient technology is a viable option for meeting the regulatory discharge limit. The 3M system in previous efforts was operated for an extended period (March and April) treating water first processed through the DAF and sand filter. In early May (May 4) the system was converted to treating influent water fed directly through a series of cartridge filters and then to the 3M membrane. Treatment of influent water by cartridge filters and then the 3M system was continued for much of the most recent study effort and is reported here. Treatment schematics for the various operating conditions for the system are shown in Figures 1-4 and descriptions of the cartridge filter utilization is found in Table 2.

TBT concentrations exiting the 3M system have varied considerably. During the March-April period, TBT concentrations were typically low and primarily below detection during this period of operation (Figure 12). After switching operations to treat the influent utilizing a series of cartridge filters and one TBT-selective membrane, TBT concentrations were low for the first day of operation under this scenario but then increased dramatically during treatment in late May and June. During this period of operation, cartridge filters and the TBT membrane were replaced when headloss (back pressure) became elevated. The TBT membrane was replaced on May 3, June 4, and June 26. Water flow rates varied over the study with flow rates of 1 gpm for March through early May, between 2 and 4 gpm between May 29 and June 7, 1 gpm June 8-July 3, and 0.5 gpm for July 5 onward. Since kinetics play an important role in most treatment processes including surface adsorption, the flow rate at which the system was operated may have influenced TBT removal. The effect of flow rate was specifically studied during the early June period and particularly on June 4.

The effects of flow rate and membrane "saturation" on TBT removal were examined on June 4 by operating the treatment system at various flow rates for a TBT-selective membrane that was installed on May 3 and a membrane that was installed during the middle of the evaluation. Pertinent data indicating test conditions are provided (Table 5). TBT concentrations were negatively correlated to flow which is evident particularly for the samples taken while evaluating the 1-month old membrane installed on May 3 (Figure 13). After change out of the membrane and operation of the system under the same flow conditions, TBT concentrations were much lower than observed when the 1-month old membrane was in place. Note, the relationship between flow and TBT concentration is not directly discernible for the 2.5 and 1 gpm efforts due to matrix interference and poor TBT spike recovery. The concentrations were estimated at 20 ng/L as noted in Figure 13. The lower concentrations observed after the installation of the new membrane suggest that the removal kinetics were slower for the 1-month old membrane possibly due to the loss of sites available for TBT removal.

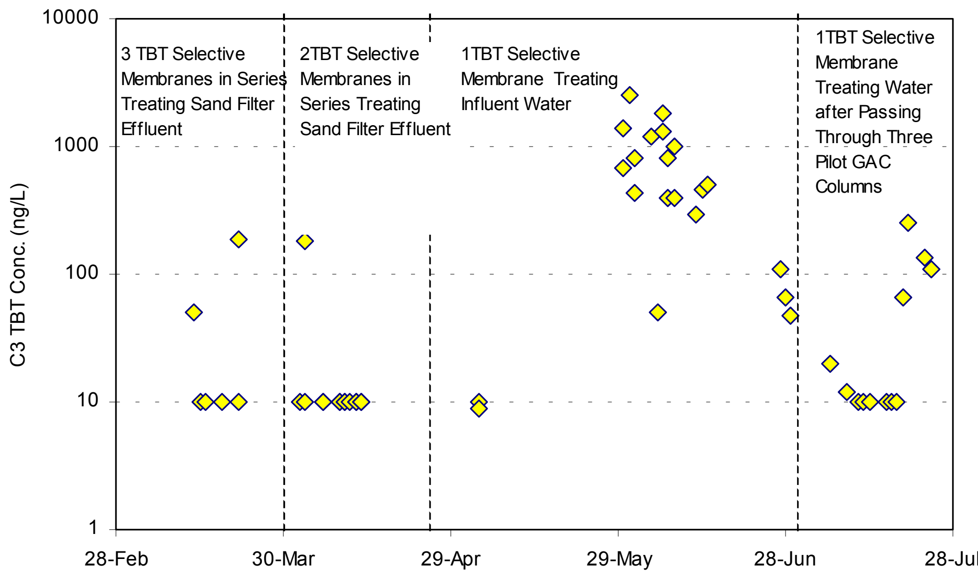


Figure 12. TBT concentrations in the final effluent (C3) of the 3M filtration system.

Table 5.
Test Conditions and Results for the Flow Influence on TBT Removal Study

Sample Location	Sample Collection Time	C3 Filter Installation Date	Flow Rate (gpm)	TBT (ng/L)	DOC (mg/L)
C2	1510	-	-	65,000	16.6
C3	1445	May 3, 2001	4	970	17.6
C3	1505	May 3, 2001	2.5	620	18.2
C3	1525	May 3, 2001	1	230	16.4
C3	1605	June 4, 2001	4	83	17.3
C3	1620	June 4, 2001	2.5	20	14.0
C3	1635	June 4, 2001	1	20	15.5
C2	1640	-	-	73,000	17.6

C2: Influent to C3 (TBT-selective) membrane

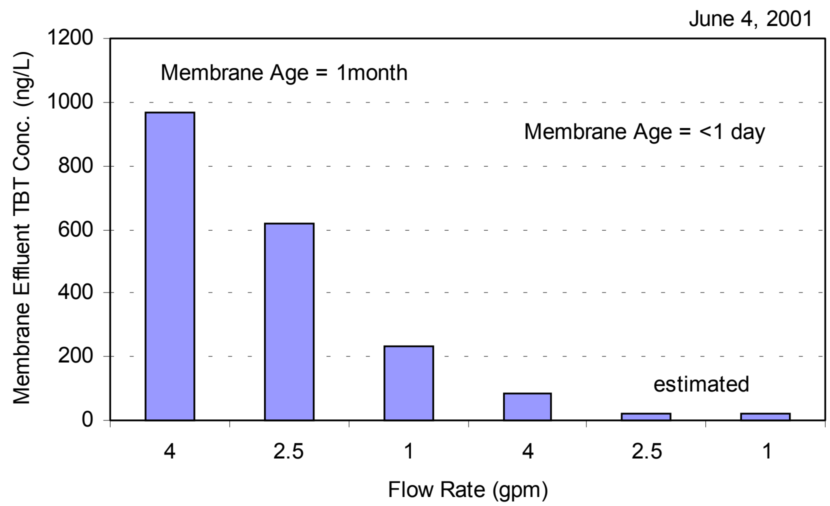


Figure 13. TBT concentrations in the final effluent of the 3M filtration system as a function of flow rate and membrane age.

Since effluent TBT concentrations were influenced by flow rate it is likely that the TBT loading rate to the membrane substantially influences TBT removal and effluent TBT concentrations. Effluent TBT concentrations from the 3M system were examined relative to the TBT loading rate (loading rate calculated as flow rate to the membrane multiplied by the membrane influent concentration) with an expectation that effluent TBT concentrations would be positively correlated to the loading rate. While there is scatter to the data the trend is consistent with increasing effluent TBT concentrations due to increasing loading rate (Figure 14).

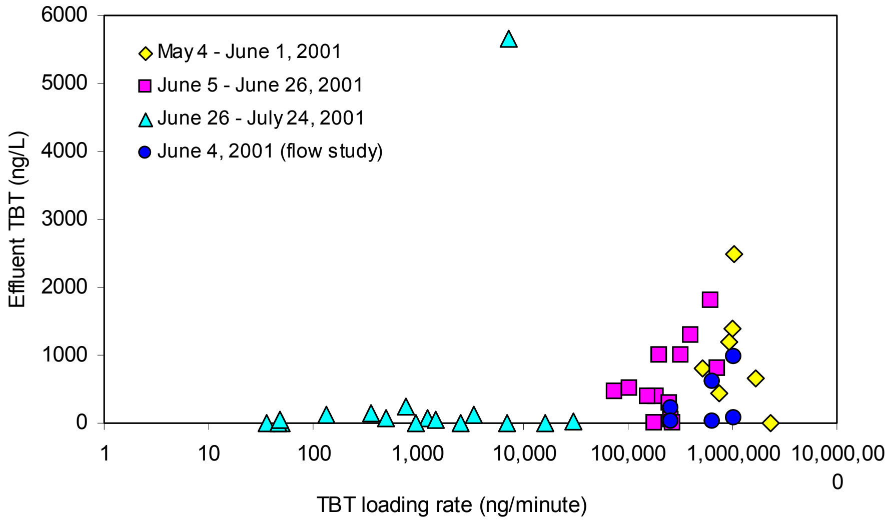


Figure 14. Effluent TBT concentrations in the 3M filtration system as a function of TBT loading rate to the TBT-selective membrane.

Continuing Studies

Research efforts are continuing specifically in three areas. A pilot-scale ozonation system is under construction and will be operated in the environmental engineering laboratory at Old Dominion University during the next quarter of this study. Water to be treated will be water collected from the four ships planned for docking and hull work during this quarter. Water will also be pretreated and then transported to Norfolk Naval Shipyard for a short-term study of the effects of UV irradiation on TBT removal. During this effort we will operate the system at 30 to 50 gpm both with and without peroxide addition to assess the effects on TBT in the water undergoing treatment. Additionally, the inter-method comparison study will be conducted utilizing samples with different matrices to assess the comparability of results from the TBT-hydride generation analytical method with the results from laboratories using the Grignard derivitization, solvent extraction and determination by GC with FPD analytical method.