

**BENCH STUDY OF CHLORDANE AND DIELDRIN ADSORPTION**

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**Project Report  
for**

**“Granular Activated Carbon Adsorption of Chlordane and Dieldrin”**

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Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the Water Resources Research Center.

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## 1.0 INTRODUCTION

### 1.1 History of Chlordane and Dieldrin in Hawaii

Chlordane and dieldrin were introduced to Hawaii as pesticides used mainly for termite control, crop cultivation, and landscaping. Chlordane and dieldrin are chlorinated hydrocarbons. They do not break down easily, and as a result their toxicity remains for a long period of time. When released to soil, they are very persistent. They can reach the air by volatilization, or adsorption onto dust particles. Soil run-off transports chlordane and dieldrin into water systems. When released to water, chlordane and dieldrin do not undergo hydrolysis or biodegradation. Both have the tendency to adsorb to sediments present in water (Spectrum Laboratories, Inc., 1998).

The EPA banned all uses of chlordane in April 1988 due to increasing environmental and health concerns (Brown & Caldwell, 1998). In 1992, the EPA set the maximum contaminant level at 2 ppb with a MCL goal of zero ppb. Chlordane is a suspected carcinogen. It may enter the human body by ingestion, inhalation, skin absorption, and possibly other routes. Chlordane affects the nervous system, digestive system, and the liver. Symptoms of exposure of lower concentrations include nausea, headaches, abdominal pain, and vomiting. At higher concentrations, symptoms include convulsions, unconsciousness, or even death. Long term exposure may cause cancer, reproductive, liver, and kidney damage, and acne-like rash (Brown & Caldwell, 1998). Technical chlordane consists of several isomers and related compounds including primarily *cis*-chlordane, *trans*-chlordane, *cis*-nonachlor, *trans*-nonachlor, heptachlor, and octachlordane (Dearth and Hites, 1991).

In October 1974, the EPA banned dieldrin from all agricultural use. In 1989, it was banned for termite control (Brown & Caldwell, 1998). Currently, there is no federal MCL for drinking water. However, EPA has proposed a long-term health advisory level of 0.5 ppb. The solubility of dieldrin is about 190 ppb (Pirbazari and Weber, 1984). Like chlordane, dieldrin may enter the human body by ingestion, inhalation, skin contact, and other possible routes. Laboratory test results show that dieldrin may be carcinogenic and teratogenic. Acute effects include headaches, dizziness, irritability, loss of appetite, nausea, muscle twitching, convulsions, loss of consciousness, and even death at higher doses. Long term exposure may lead to headaches, dizziness, vomiting, irritability and muscle spasms (Brown & Caldwell, 1998).

### 1.2 Chlordane and Dieldrin in Board of Water Supply Wells

The Honolulu Board of Water Supply (BWS) has detected chlordane and dieldrin in several wells in the Honolulu area. Dieldrin was detected at Wilder Ave., Kaimuki, Kalihi, and Jonathan Springs. Both chlordane and dieldrin were detected in Jonathan Springs. The Jonathan Springs well is not currently in operation. The Kaimuki and Kalihi wells operate intermittently and contain very low concentrations of dieldrin, making them poor candidates for obtaining samples for use in adsorption experiments. The Wilder Avenue wells (except the one well in which dieldrin was detected) are in service pumping a mean of 6.99 mgd of water to the vicinity.

One of the Wilder Ave. wells contains approximately 0.01 ppb of dieldrin. Uncontaminated water from Wilder Avenue was utilized in this research.

### ***1.3 Removal of Chlordane and Dieldrin with Granular Activated Carbon Using Small Scale Columns***

Because granular activated carbon (GAC) has a large surface area, the force of attraction the GAC has on the pesticides is greater than the force which keeps the pesticides suspended in the water. These pesticides have high molecular weights, therefore they are less soluble in water and readily adsorbed onto the carbon.

The objective of this research is to facilitate the design of full-scale GAC columns. Because full-scale and even pilot-scale GAC adsorption experiments are very time-consuming and expensive, this research explores the efficiency of GAC in bench-scale columns. Rapid small-scale column tests (RSSCTs) are commonly used to aid in the design of full-scale GAC treatment units. Procedures for design of such tests are well documented in the technical literature (Crittenden et al., 1987 and 1991). These bench-scale tests are more advantageous than pilot-scale studies because the operation time is decreased, extensive isotherm or kinetic studies are not required, and the volume of water required is minimal (Ewald, 1998). However, it is recommended that pilot studies follow the RSSCTs prior to full-scale design.

The use of GAC for removal of chlordane and dieldrin in Hawaii's BWS wells is non-existent. Currently, there are five BWS pumping stations that have successfully used GAC for the removal of other pesticides (primarily EDB, TCP and DBCP) since 1986. These pumping stations include Mililani I and II, Kunia II, and Waipahu I and II. Because of the similar nature of DBCP to chlordane and dieldrin, it is anticipated that GAC will also be successful for removal of these chemicals (Brown & Caldwell, 1998).

## 2.0 METHODS

### 2.1 Small-Scale Column Calculations

Small-scale columns were used in this research to simulate the performance of a full-scale column. The literature contains a set of design calculations for properly sizing the small-scale columns (and the powdered carbon that goes in them) for RSSCTs based upon the full-scale column size and treatment capacity. The calculations are quite detailed and are presented in Appendix I. It was decided to size mini-columns to mimic a surface loading rate of 6 gallons per minute per square foot (gpm/sf) at three different empty-bed contact times (EBCTs). This mimics the existing BWS contactors (diameter 12 feet) which operate at 6 gpm/sf. A range of EBCTs was chosen to possibly reduce the depth of the contactors. As a result, three small-scale columns with different EBCT and bed volumes were designed. The characteristics of these mini-columns are given in Table 1.

**Table 1 – RSSCT mini-column characteristics.**

EBCT <sub>LC</sub>	EBCT <sub>SC</sub>	H <sub>SC</sub>	PAC <sub>MASS,SC</sub>	Bedvolume
7.5 min. = 450 sec.	87.4 sec.	8.79 cm	0.8735 g	1.46 mL
10.0 min. = 600 sec.	116.5 sec.	11.7 cm	1.1647 g	1.94 mL
15.0 min. = 900 sec.	174.7 sec.	17.5 cm	1.7471 g	2.91 mL

Where: LC = large column, SC = small column, PAC = powdered activated carbon, H<sub>SC</sub> = depth of carbon in the small column

### 2.2 Analytical Methods

Practical extraction and quantification methods were developed for both chlordane and dieldrin. Extractions were performed using a micro liquid-liquid extraction procedure (see Table 2). A gas chromatographic (GC) method was developed using a Hewlett Packard GC (Model 5890) and Integrator (Model 1396). Pure chemical standards of chlordane and dieldrin were purchased (Ultra Scientific) and analyzed to create standard curves for quantification of concentrations. As mentioned above, technical chlordane consists of several different compounds which happen to be detectable as separate peaks (see example chromatogram in appendix). At the spike concentrations utilized here, there were seven primary peaks which were summed together to create a standard curve. Dieldrin chromatographed as a single peak distinct from the chlordane peaks. Using the analytical methods developed, the practical detection limits for chlordane and dieldrin in water samples were 2 ppb and 0.1 ppb, respectively. The GC conditions are summarized in Table 2. Standard curves for both chlordane and dieldrin are given in the appendix.

**Table 2 – Extraction and gas chromatographic method protocols**

Liquid-liquid microextraction conditions:	Gas Chromatographic Operating Conditions:
Sample size = 35 mL Hexane amount = 2 mL Stopper+shake time = 2 min. Let separate > 10 min. Pipet hexane layer to 5-mL vial Add NaSO <sub>3</sub> to remove water GC sample with 10 µL syringe	GC Column: DB5 30m x 0.53 mm Detector: ECD 300 °C, Ar/CH <sub>4</sub> make-up Injector: splitless, 300 °C, helium carrier Initial Temp: T <sub>0</sub> = 230 °C, 1 min. hold Ramp: 10 °C/min. Final Temp: T <sub>f</sub> = 300 °C, 3 min. hold Sample size: 2 µL

### 2.3 Carbon Preparation

Virgin GAC (12 x 40 mesh) was obtained from BWS. The carbon was pulverized in a blender (Waring Del Model 702B) for 5 min. Sieves No. 80, No. 100, and a pan were arranged from top to bottom, and the pulverized carbon was poured into the top. The sieves were hand shaken vigorously for 2 minutes to allow the carbon to pass through the No. 80 sieve and be retained on the No. 100 sieve. Any carbon retained on the No. 80 sieve was returned to the blender to be pulverized further. This was repeated until a sufficient amount of carbon was retained on the No. 100 sieve. Deionized water was used to allow the fines to pass through the sieve onto the pan.

The remaining carbon on the No. 100 sieve was transferred into a 500 mL beaker and deionized water was poured up to the 500 mL mark. After stirring and 15 to 20 minutes of settling, a supernatant layer was formed and discarded carefully so that carbon would not be lost. Deionized water was again poured to the 500 mL mark, and stirring and settling of the carbon was completed. This was repeated until the supernatant layer was fairly clear.

The beaker was covered with foil and holes were pricked into the foil. The beaker was placed into a 180 C oven for 18 hours, then into a dessicator until cooled to the touch. Deionized water was poured into the beaker to the 500 mL mark and stirring and settling of the carbon was again completed. This was repeated until the supernatant layer was fairly clear. The beaker was covered with foil and holes were pricked into the foil. The beaker was placed into a 180 C oven for 6 hours and placed in a dessicator until cooled. The carbon was placed into a 50 mL opaque bottle, labeled, and placed into the dessicator until the small-scale columns were ready to be packed.

### 2.4 Column Setup

Three columns were obtained and rinsed with deionized water and acetone. The columns were placed in a 180 C oven for 18 hours then cooled in a dessicator. The columns were packed starting from the effluent end. Using a steel rod, an inch of glass wool was first packed in, followed by half an inch of glass beads (No. 11), then half an inch of glass wool. The column was put on a scale and tared. This was to ensure the exact weight of carbon was placed into the column. The carbon was added slowly, tapping the column gently so that the particles would not

adhere to the sides, until the exact desired weight of carbon was poured into the column. The depth was measured. More carbon was added until the calculated depth was desired. The column was weighed and recorded. A final layer of glass wool (one inch) was packed into the column.

### **2.5 Pump Set up and Operation**

The columns were each connected to a pressure gage and a high pressure HPLC pump (Dionex or Accuflo). Flows of approximately 1 mL/min were pumped continuously by the pumps (see photos in the Appendix). This resulted in pressures in the range of 1500 - 2500 psi. To ensure adequate flow rate, all air bubbles were removed from the influent and effluent lines. Initially, deionized water was pumped through the columns to wet the carbon and to check if the setup was correct. Deionized water was pumped continuously until water samples were obtained.

Water samples were collected from Wilder Avenue BWS wells in 4-L amber bottles then stored at 4°C until use. Before running samples through the columns, the water samples were spiked with 2 ppb of dieldrin or 20 ppb of chlordane.

### **2.6 Extraction and GC Analysis**

Extractions of influent and effluent samples were completed daily. First, the volume of the effluent was measured and recorded. Next, 35-mL of the effluent was placed in a 50 mL tube containing 7 grams of sodium chloride. With a micro-pipette, 2-mL of hexane was placed into the tube. The tube was capped and shook for 2 minutes. After the 2 minutes, two distinct layers of hexane and water was formed. The top layer of hexane was removed with a pipette and placed into a 15-mL centrifuge tube. The centrifuge tube was placed on a Maxi Mixer I (Type 16700) for 15 seconds. A 10- $\mu$ L syringe was used to obtain 2  $\mu$ L of extract from the centrifuge tube. This was injected into the GC and the peak area was recorded to calculate pesticide concentration.

### **2.7 Experimental Runs**

Ideally, RSSCTs should be run with actual contaminated water. This is important since both the water matrix components (particularly dissolved natural organic matter, NOM) and target compound concentrations greatly affect the adsorption process. NOM is known to effectively compete with synthetic pesticides for adsorption sites in general and this has been shown in Hawaii as well for EDB, DBCP, and TCP (Ewald, 1998). Matrix effects cannot be ignored or duplicated in the laboratory. Similarly, the concentration of the target compound affects the run time of a GAC column and it is difficult to accurately extrapolate field-scale performance from bench-scale tests with spiked water. However, the constraints of this project were such that there was no available supply of actual water significantly contaminated with chlordane or dieldrin.

The next best case was to use actual water (from an adjacent operating uncontaminated well) spiked with known quantities of purchased pesticide chemicals. In this way, at least the



matrix effects would be considered. The next step was to decide what concentrations to utilize for the spikes. This was decided based upon the practical detection limits for dieldrin (0.1 ppb) and chlordane (2 ppb), the existing MCL/health advisories (0.5 ppb and 2 ppb, respectively), and GAC adsorption process characteristics. The practical detection limits are very similar to the MCL/health advisories which might imply that spikes of these magnitudes would be useful. However, target compound concentrations at or near the analytical detection limit pose a problem for adsorption studies.

In general for GC methods, the highest uncertainty for quantification of pesticide concentration occurs when working at or near the detection limit. It would not be practical to utilize a spike concentration equal to the practical detection limit, because there would always be doubt regarding the concentration or even presence of the pesticides due to very tiny random analytical errors and tiny potential errors in the spiking procedure. This point can be illustrated as follows. If one were to look at the long-term monitoring data for the pesticides in BWS's Central Oahu wells, they would find that there is a certain degree of variability both in the short term and in the long term. The long-term variations are usually called trends (increasing or decreasing). The short-term variations (i.e. between adjacent wells or between sampling dates for a single well) are more difficult to interpret, but are generally assumed to be related to random errors due to sampling, handling, extraction, and analysis (rather than due to actual differences in the concentrations in the water). Looking at the short-term variations, one would find that their magnitude was similar to or even greater than the detection limit. This means that if a water source contains a pesticide at a concentration near the detection limit, it will sometimes be detected and sometimes will not be detected.

In addition, if a spike concentration equal to the practical detection limit were utilized, it would not be possible to generate a breakthrough curve. In adsorption studies, one looks for a breakthrough curve to characterize the adsorption process. A time series plot of the effluent pesticide concentration in an adsorption test generally consists of a period of non-detectable concentrations followed by a rising saturation-type curve which eventually increases to the point where the effluent concentration equals the influent concentration (breakthrough curve). In order to generate such a curve, the pesticide must be detectable at a concentration of 1/5 to 1/10 the influent concentration (so that the initiation of breakthrough can be observed in spite of any tiny random analytical errors). If the influent pesticide concentration is equal to the detection limit, then the first point at which it would be detected in the effluent would be after complete carbon saturation. The time for complete carbon saturation may be 20% (or more) longer than the time to initial breakthrough.

Based upon these considerations, it was decided to utilize spike concentrations of approximately 10 times the practical detection limits (i.e. 2 ppb and 20 ppb for dieldrin and chlordane, respectively). A set of six experimental runs (RSSCTs) were selected (see Table 3).

**Table 3 – Experimental run characteristics**

Run	Compound(s)	EBCT (min)	Water type
1	Dieldrin	7.5	Spiked well water
2	Dieldrin	10	Spiked well water
3	Chlordane	7.5	Spiked well water
4	Chlordane + Dieldrin	7.5	Spiked well water
5	Chlordane + Dieldrin	7.5	Spiked well water
6	Chlordane + Dieldrin	7.5	Spiked distilled water

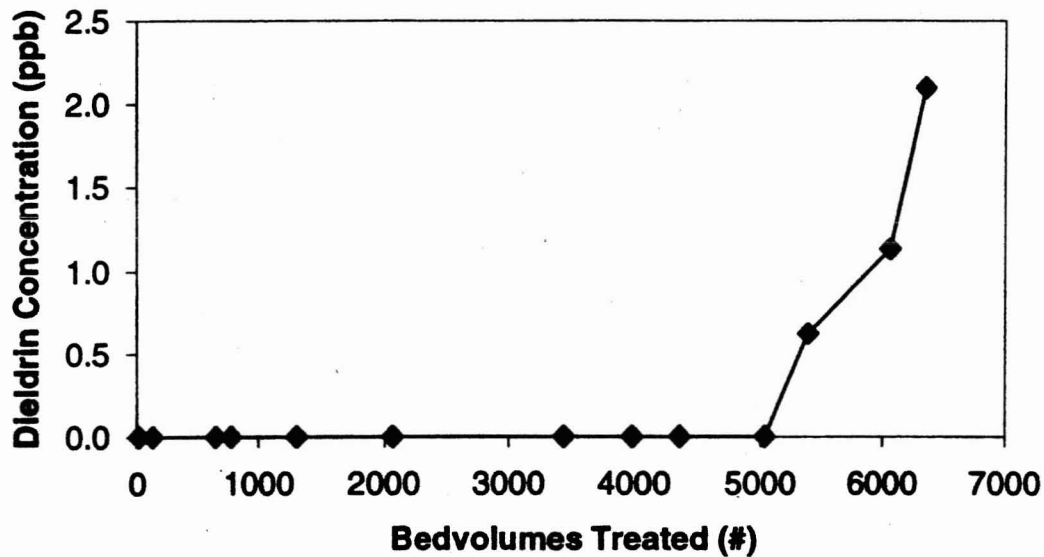
The first two RSSCTs were designed to compare the effects of EBCT on dieldrin adsorption capacity. The fourth and fifth RSSCTs are duplicates to check reproducibility. The sixth run was designed to investigate the degree of competition with NOM. Initially, an EBCT of 15 minutes was tested (Preliminary Run B), however, the increased carbon mass created high backpressures which were hard on the pump system components causing frequent leaks and breakdowns. Thus, further runs with EBCTs of 15 minutes were abandoned.

It should be noted that the detection limit problems associated with the bench-scale RSSCTs which necessitated the use of large spike would not be a problem in pilot-scale tests. The sample size (volume for analysis) utilized during the RSSCTs was 35 mL which represents approximately 20 bedvolumes. For pilot scale columns, larger samples (approximately 1,000 mL) would be feasible and would reduce the detection limits to approximately 0.005 ppb and 0.05 dieldrin and chlordane, respectively. This would allow actual contaminated water to be utilized. For the RSSCTs, if we were to utilize 1000 mL samples, this would represent approximately 600 bedvolumes which would make it impossible to observe a breakthrough curve.

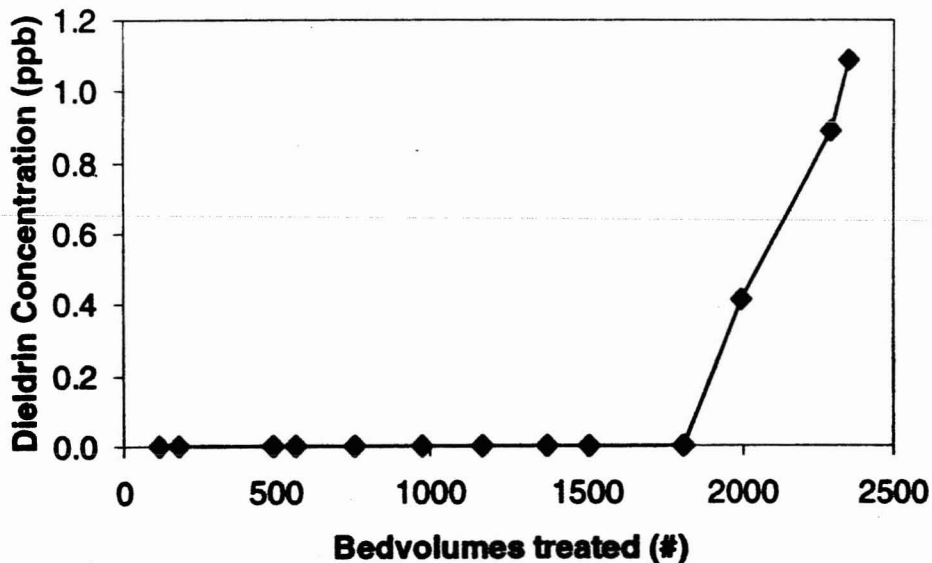
### 3.0 RESULTS

Preliminary RSSCTs were completed in the summer of 1999. Preliminary Run A was set up using well water spiked with dieldrin and an EBCT of 7.5 min (same set up as Experimental Run 1). Preliminary Run B was set up using well water spiked with dieldrin and an EBCT of 15 min. The data collected is shown below (Figures 1 and 2). The reason why this data is called preliminary is discussed below.

**Figure 1 – Dieldrin breakthrough curve – Preliminary Run A (EBCT 7.5 min)**



**Figure 2 - Dieldrin breakthrough curve – Preliminary Run B (EBCT 15 min)**



Figures 1 and 2 show effluent dieldrin concentration versus bedvolumes of spiked well water treated. These curves indicate that the dieldrin breaks through after treating only 2,000 to 5,000 bedvolumes. It is not necessary to operate the RSSCTs until complete breakthrough is achieved. Unexpectedly, the RSSCT with the longer EBCT broke through first which is counter-intuitive. We are unsure how to interpret this finding which must be assumed to be an artifact. A possibility is that the 15-min EBCT column experienced a failure such that a preferential flow path was created allowing influent dieldrin to pass through the column without being adsorbed causing early (apparent) breakthrough. Such a phenomena has not been observed in numerous previous RSSCTs in our laboratory which accurately mimic full-scale BWS contactors. However, in the previous RSSCTs, less GAC was used and consequently lower backpressures were observed. The adsorbed mass of dieldrin was about 16  $\mu\text{g/g}$  of GAC for Preliminary Run A and about 5.5  $\mu\text{g/g}$  of GAC for Preliminary Run B. These results (Runs A and B) were difficult to explain, so they were considered preliminary and new runs were started. In the late summer, we had some personnel turnover and problems with high-pressure pump seal supply. We were unable to receive shipment of spare parts that were backordered for approximately 2 months, during which the pump seals leaked so badly that the volume of water treated per day became very low.

Currently, RSSCTs described in Table 3 as Run 1, Run 2, and Run 3 are in progress (see Figures 3, 4, and 5). Figure 3 shows the Run 1 column (dieldrin, 7.5 min EBCT) which has not achieved breakthrough and has currently treated approximately 22,000 bedvolumes (dieldrin adsorbed = 39  $\mu\text{g/g}$  of GAC). Figure 4 shows the Run 2 column (dieldrin, 10 min EBCT) which has recently broken through after treating 9,000 bedvolumes (with an adsorbed mass of dieldrin of 21  $\mu\text{g/g}$  of GAC). Figure 5 shows the Run 3 column (chlordane, 7.5 min EBCT) which has not achieved breakthrough and has currently treated approximately 14,000 bedvolumes (chlordane adsorbed = 165  $\mu\text{g/g}$  of GAC). The same pattern observed in the preliminary runs is being repeated in these current runs. The shorter EBCT column (Run 1) seems to have a higher capacity for dieldrin than the longer EBCT column (Run 2). It is certainly possible that a column failure occurred for the Run 2 RSSCT (Figure 4) due again to excessive backpressures that were observed during the run which could have caused the development of preferential flow paths in the column. If we assume that full-scale GAC contactors are constructed for treatment of 1.0 mgd of flow, that the influent concentration of dieldrin is 0.2 ppb, and that same mass of dieldrin will be adsorbed to the GAC as observed in the RSSCTs, we can calculate how long the hypothetical full-scale contactors would operate prior to the onset of breakthrough. The existing data for dieldrin are summarized in Table 4.

**Table 4 – Existing data for dieldrin adsorption**

Run name	EBCT (min)	Dieldrin adsorbed ( $\mu\text{g/g}$ )	Full-scale Run time (days)
Prelim. Run A	7.5	16	118
Prelim. Run B	15	5.5	81
Run 2	10	21	206
Run 1	7.5	> 39	> 286

The existing data collected for dieldrin adsorption are not completely consistent with expectations. It is expected that longer EBCTs will result in greater dieldrin adsorption. It now seems likely that Preliminary Run A, Preliminary Run B, and Run 2 all represent column failures. Run 1 seems to be the only column which is operating correctly. In any case, the table above seems to indicate that GAC should not be ruled out for dieldrin removal. Additional evidence to this effect is as follows. Other researchers (Pirbazari and Weber, 1984) have previously found that GAC has a very high capacity for dieldrin (about 2,000  $\mu\text{g/g}$  of GAC) in pilot columns treating laboratory water spiked with NOM and dieldrin (this was calculated from their data). The current results do not agree with Pirbazari and Weber's results. However, Pirbazari and Weber noted the biodegradation of adsorbed dieldrin which is a complicating factor leading to greater apparent adsorption capacity.

The next step will be to complete Run 1 and determine the final dieldrin adsorption capacity based upon that data. At the same time, Runs 4, 5, and 6 will be completed to determine the adsorption capacities for mixtures of chlordane and dieldrin and the effects of NOM competition. These runs should be completed in mid-2000. In general, we are confident that our experimental methods are sound even though there have been several column failures. We hope to make sense of these data following completion of all six runs. We feel that it would be premature to eliminate GAC as a treatment method for dieldrin and chlordane. In fact, it is recommended that pilot testing be conducted to confirm which of the RSSCT data are most correct.

**Figure 3 - Dieldrin breakthrough curve - Run 1 (EBCT 7.5 min)**

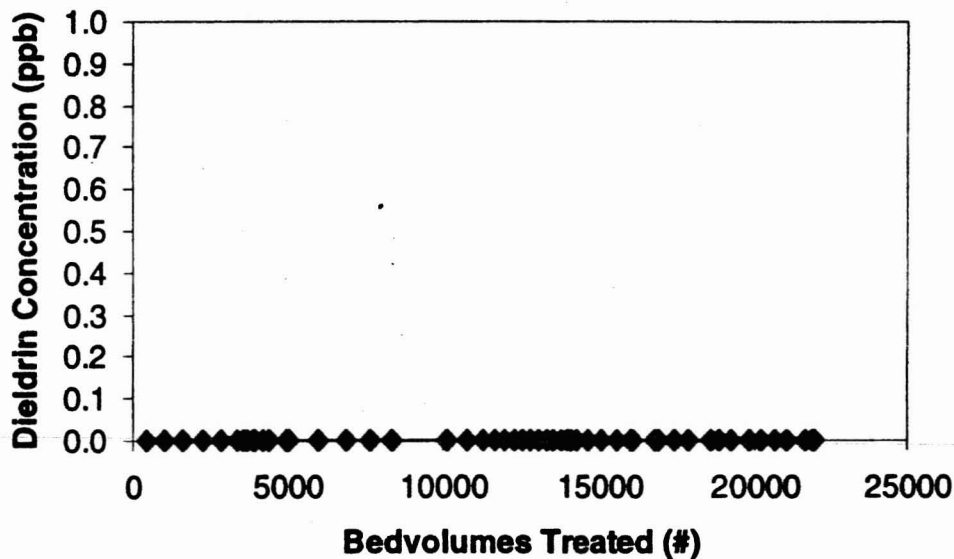


Figure 4 - Dieldrin breakthrough curve - Run 2 (EBCT 10 min)

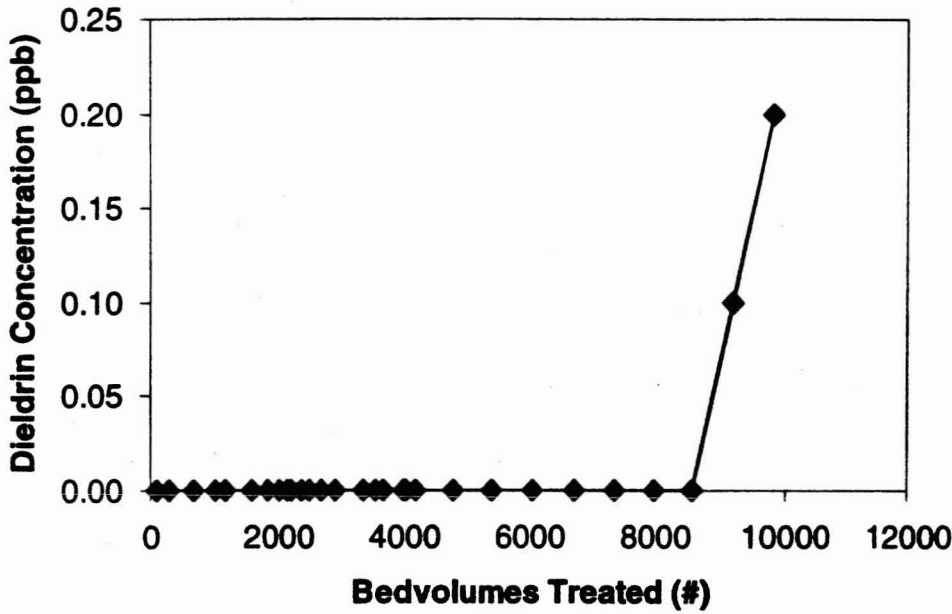
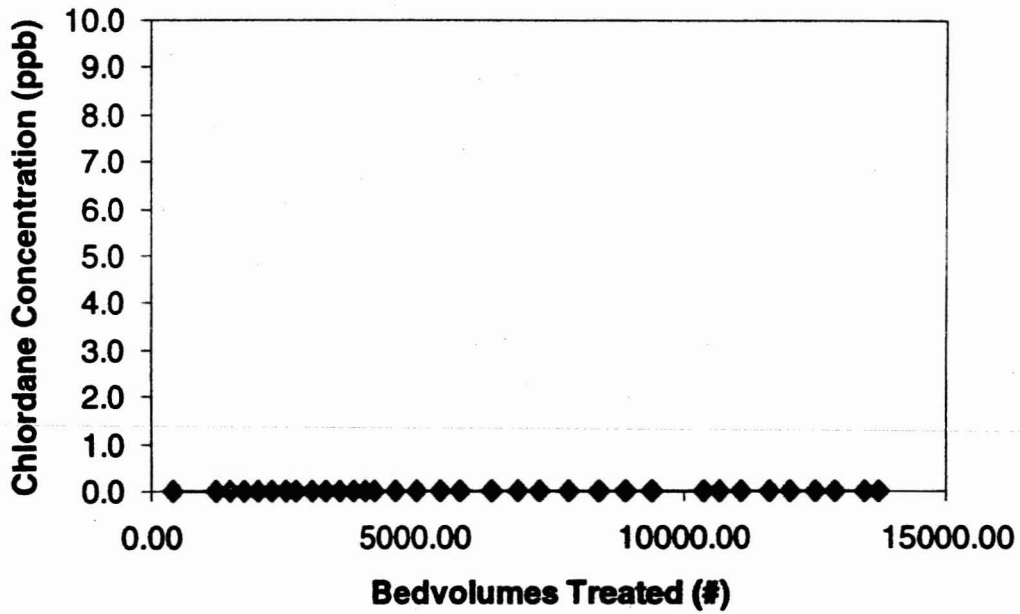


Figure 5 - Chlordane breakthrough curve - Run 3 (EBCT 7.5 min)



#### **4.0 PRELIMINARY CONCLUSIONS AND FUTURE WORK**

The preliminary results obtained and the ongoing runs allow the following preliminary conclusions:

- Chlordane and dieldrin are adsorbed onto BWS's GAC in RSSCTs
- Some of the RSSCTs conducted with dieldrin have not been consistent and probably are indicative of column failures due to excessive pressure build-up
- The GAC capacity for dieldrin is probably greater than 39  $\mu\text{g}$  pesticide/g GAC
- The GAC capacity for chlordane seems to be greater than 165  $\mu\text{g}$  pesticide/g GAC
- It would be premature to eliminate GAC as a treatment method for dieldrin and chlordane

As discussed above several RSSCTs are currently underway and several additional runs are planned. Even though the project period has expired, this additional work will be completed. A graduate student has committed to this work in his prospectus for the Master of Science degree. After completion of the experimental work, a supplemental report will be submitted (expected in mid-2000).

## 5.0 REFERENCES

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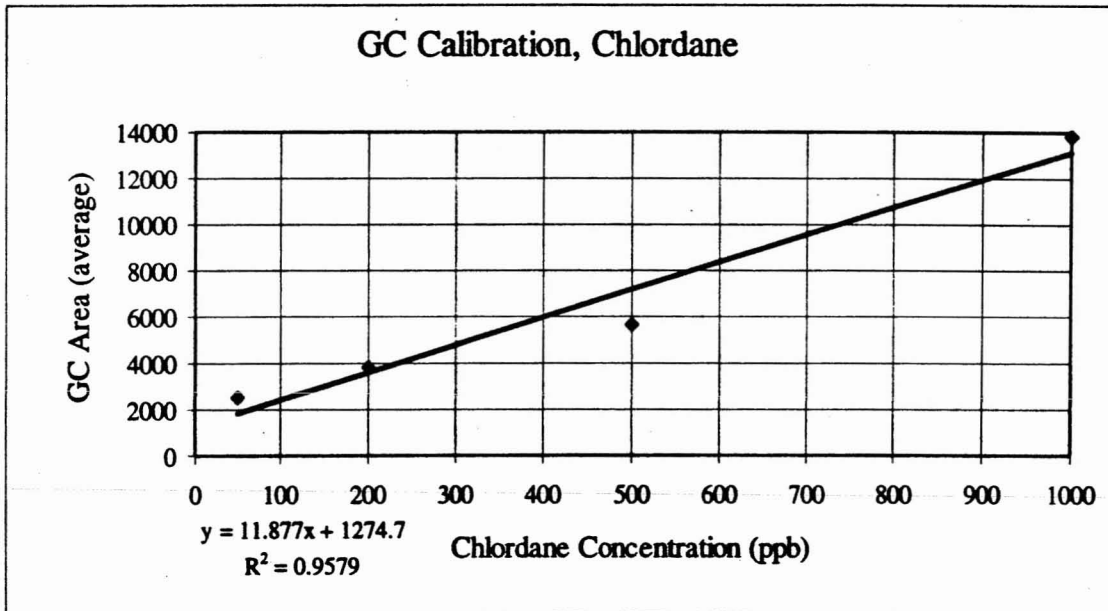
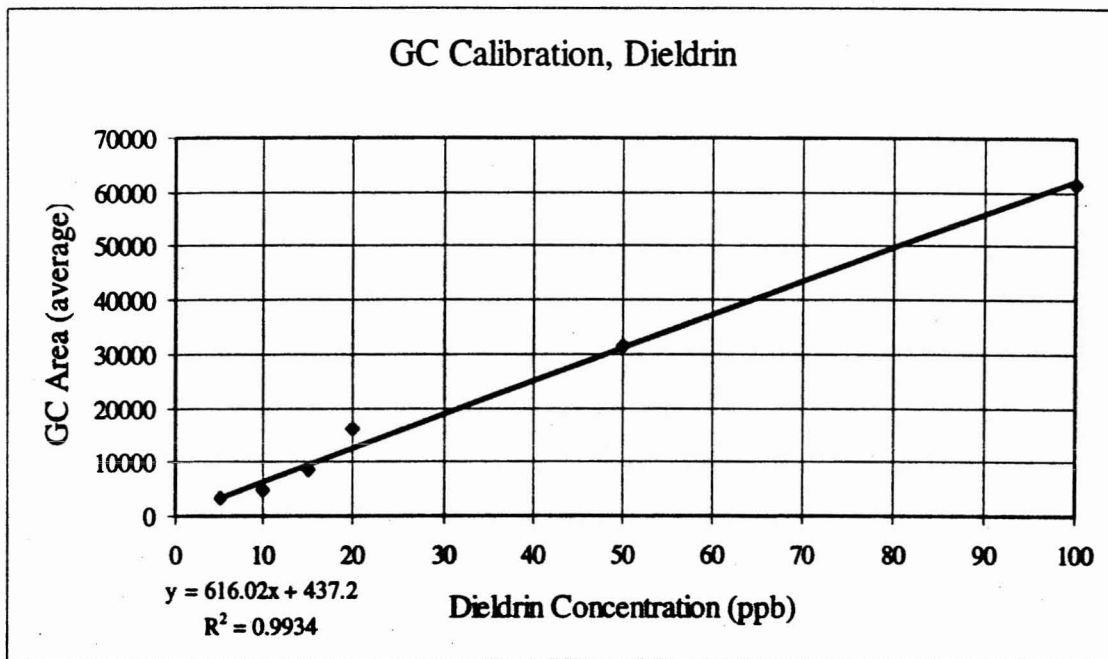
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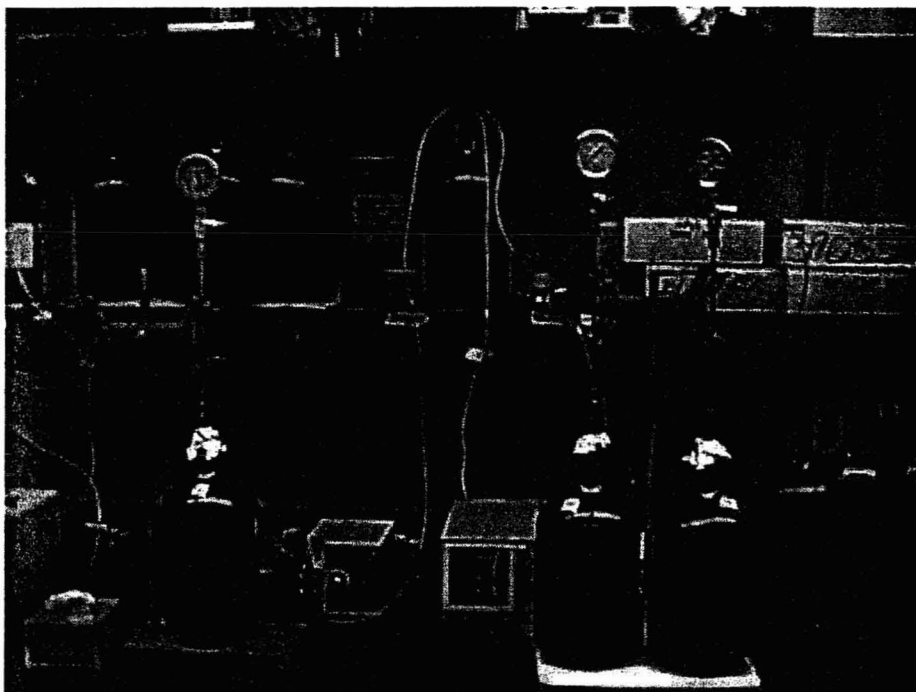


APPENDICES

I. Standard Curves

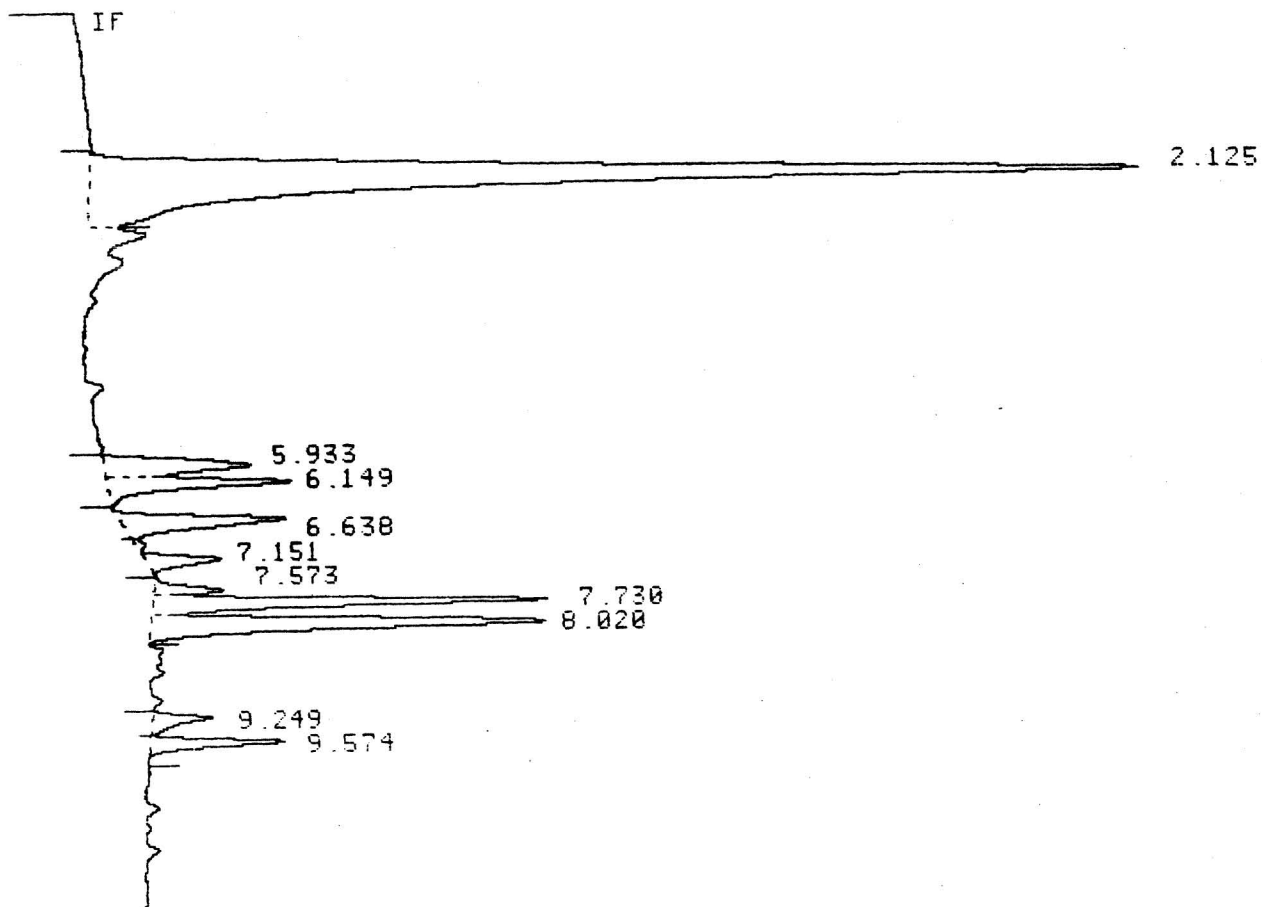


## II. Mini-Column Equipment Set-up



### III. Chlordane Chromatogram

RUN # 33 SEP 25, 1999 13:44:34



END OF SIGNAL

#### **IV. Mini-Column Scaling Calculations**

*Mini Column Scaling (SC)*

Q = volumetric flow rate = 1 mL/min

$d_{sc}$  = Column diameter = 4.6 mm

$A_{sc}$  = Column area = 16.62 mm<sup>2</sup>

GAC particle size = No. 80 x No. 100 mesh

$R_{ave}$  = average particle size = 0.082 mm

$V_{sc}$  = mini-column hydraulic loading rate = Q/A

$$\frac{1000 \text{ mm}^3}{\text{min}} \frac{1}{16.62 \text{ mm}^2} = 60.2 \frac{\text{mm}}{\text{min}} = \boxed{86.65 \frac{\text{m}}{\text{day}}}$$

$$EBCT_{sc} = \text{mini-column empty bed contact time} = EBCT_{LC} \left[ \frac{dp_{sc}}{dp_{LC}} \right] = 87.4 \text{ seconds}$$

where dp = particle diameter

$$V_{sc} = \text{volume of mini-column} = EBCT_{sc} Q_{sc} = 87.4 \text{ sec} \cdot (1 \text{ mL/min}) \cdot (\text{min}/60 \text{ sec}) = 1.46 \text{ mL}$$

$$H_{sc} = V_{sc} / A_{sc} = (1.46 \text{ mL} / 16.62 \text{ mm}^2) \times (10^3 \text{ mm}^3 / \text{mL}) = 87.85 \text{ mm} = 8.79 \text{ cm}$$

$$PAC_{mass,sc} = EBCT_{LC} \left[ \frac{dp_{sc}}{dp_{LC}} \right]^{(2-x)} Q_{sc} \rho \quad \text{where } x = \text{proportionality constant} = 1$$

$$= 450 \text{ sec} \left[ \frac{0.165}{0.85} \right]^{2-1} \frac{1 \text{ mL}}{\text{min}} \frac{\text{min}}{60 \text{ sec}} \frac{0.6 \text{ g}}{\text{mL}}$$

$$= 0.8735 \text{ g}$$

The following table summarizes the dimensions for the mini-columns of all three EBCT criteria.

EBCT <sub>LC</sub>	EBCT <sub>sc</sub>	H <sub>sc</sub>	PAC <sub>mass,sc</sub>
7.5 min. = 450 sec.	87.4 sec.	8.79 cm	0.8735 g
10.0 min. = 600 sec.	116.5 sec.	11.7 cm	1.1647 g
15.0 min. = 900 sec.	174.7 sec.	17.5 cm	1.7471 g

The following pages outline the design of the chlordane-dieldrin mini-columns from criteria set for the full scale columns of EBCT = 7.5, 10, and 15 minutes.

*Full scale column*

$Q = \text{Volumetric flow rate} = 1 \text{ MGD} = 3785 \text{ m}^3/\text{day}$

GAC particle size = No. 12 x No. 40 mesh

$R = \text{average particle radius} = 0.425 \text{ mm}$

Column dimensions:

$r = \text{column radius} = 1.83 \text{ m}$

$h = \text{carbon bed depth} = 3.05 \text{ m}$

EBCT = empty bed contact time = 7.5 min = 450 seconds

(Also designed and tested: 10 min, 15 min)

$V_{lc} = \text{hydraulic loading rate} = Q/A =$

$$\frac{3785 \text{ m}^3}{\text{day}} \frac{1}{1.83^2 \pi \text{ m}^2} = \boxed{352 \frac{\text{m}}{\text{day}}}$$

$Re = \text{Reynolds Number} = \frac{V_{lc} d \rho}{\mu} = 3.88$

Where  $V_{lc} = \text{hydraulic loading rate (m/d)} = 352 \text{ m/d}$

$d = \text{average particle diameter} = 0.00085 \text{ m}$

$\rho = \text{density of water} = 997 \text{ kg/m}^3$

$\mu = \text{dynamic viscosity of water} = 76.98 \text{ kg/day-m}$

$= 8.909\text{E-}4 \text{ kg/s-m}$

$\epsilon_{lc} = \text{Void fraction} = 0.70$

(Perry's Chemical Engineer's Handbook, 7<sup>th</sup> Ed.)

$$\epsilon_{sc} = \text{void fraction in small column} = (V_{T,sc} - V_{s,sc}) / V_{T,sc}$$

$$V_{T,sc} = \text{total column volume} = 1460.1 \text{ mm}^3$$

$$V_{s,sc} = \text{volume of solids in column} = 1456 \text{ mm}^3$$

$$\epsilon_{sc} = (V_{T,sc} - V_{s,sc}) / V_{T,sc} = 2.81E-3$$

$$Re_{sc} = \frac{V_{sc}}{V_{LC}} Re_{LC} \frac{dp_{sc}}{dp_{LC}}$$

$$= \frac{86.64}{352} \cdot 3.88 \cdot \frac{0.165}{0.85} = 0.185$$

$$\text{check: } Re_{sc} = \frac{V_{sc} d \rho}{\mu} = 0.184 \quad \checkmark \checkmark \checkmark$$

$$Sc_{sc} = \text{Schmidt number (mini-column)} = \frac{\mu}{\rho D_{L,sc}} = 1794.34$$

$$Sc_{LC} = \text{Schmidt number (full-scale column)} = \frac{\mu}{\rho D_{L,LC}} = 151.71$$

Where  $\mu$  = dynamic viscosity of water  $[L^2/T] = 8.909 E-4 \text{ m}^2/\text{s}$

$\rho$  = density of water at 25°C = 997 kg/m<sup>3</sup>

$D_L$  = free liquid diffusivity

$$= \frac{1.173E-16 (\phi M)^{1.2} T}{\mu v_{sc,LC}^{0.6}}$$

$$D_{L,sc} = 4.98E-10$$

$$D_{L,LC} = 5.89E-9$$

$$\begin{aligned} v_{sc} &= V_{sc}/\epsilon_{sc} = 0.357 \text{ m/s} \\ v_{LC} &= V_{LC}/\epsilon_{LC} = 5.82E-3 \text{ m/s} \\ M &= 18.02 \text{ g/mol} \\ \phi &= 2.6 \end{aligned}$$

$$St_{i(sc,LC)} = \text{Stanton number} = \frac{k_{Gi(sc,LC)} EBCT_{sc,LC} (1-\epsilon_{sc,LC})}{R_{sc,LC} \epsilon_{sc,LC}}$$

Where  $i$  = contaminant, chlordane (c) or dieldrin (d)

$$k_{Gi(sc,LC)} = (D_L/2R_{sc,LC}) (2 + 1.1 Re_{sc,LC}^{0.6} Sc^{1/3})$$

CHLORDANE CONTAMINANT (Full scale EBCT = 7.5 min. = 450 secs)

Small Column

$$\begin{aligned}
 k_{c-s} &= \frac{D_{Lc}}{2R_{sc}} \left[ 2 + 1.1 R_{sc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.37E-10}{2(0.000082)} \left[ 2 + 1.1 (0.185)^{0.6} (1794.34)^{1.3} \right] \\
 &= 1.83E-5
 \end{aligned}$$

$$\begin{aligned}
 St_{s,c} &= \frac{k_{c-s} EBCT_{sc} (1-\epsilon_{sc})}{R_{sc} \epsilon_{sc}} \\
 &= \frac{1.83E-5 (87.4) (1-2.81E-3)}{(0.000082)(2.81E-3)} = 6921.82
 \end{aligned}$$

Large (full-scale) column

$$\begin{aligned}
 k_{c-lc} &= \frac{D_{Lc}}{2R_{lc}} \left[ 2 + 1.1 R_{lc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.37E-10}{2(0.000425)} \left[ 2 + 1.1 (3.88)^{0.6} (151.71)^{1.3} \right] \\
 &= 7.83E-6
 \end{aligned}$$

$$\begin{aligned}
 St_{l,c} &= \frac{k_{c-lc} EBCT_{lc} (1-\epsilon_{lc})}{R_{lc} \epsilon_{lc}} \\
 &= \frac{7.83E-6 (450) (1-0.70)}{(0.000425)(0.70)} = 3.55
 \end{aligned}$$

$$St_{s,c} \gg St_{l,c}$$

$$6921.82 \gg 3.55$$

///



DIELDRIN CONTAMINANT (Full scale EBCT = 7.5 min. = 450 secs)

Small Column

$$\begin{aligned}
 k_{cd-sc} &= \frac{D_{Ld}}{2R_{sc}} \left[ 2 + 1.1 Re_{sc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.74E-10}{2(0.000082)} \left[ 2 + 1.1 (0.185)^{0.6} (1794.34)^{1.3} \right] \\
 &= 1.98E-5
 \end{aligned}$$

$$\begin{aligned}
 St_{sc,d} &= \frac{k_{cd-sc} EBCT_{sc} (1 - e_{sc})}{R_{sc} \epsilon_{sc}} \\
 &= \frac{1.98E-5 (87.4) (1 - 2.81E-3)}{(0.000082)(2.81E-3)} = 7489.18
 \end{aligned}$$

Large (full-scale) column

$$\begin{aligned}
 k_{cd-ic} &= \frac{D_{Ld}}{2R_{ic}} \left[ 2 + 1.1 Re_{ic}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.74E-10}{2(0.000425)} \left[ 2 + 1.1 (3.88)^{0.6} (151.71)^{1.3} \right] \\
 &= 8.5E-6
 \end{aligned}$$

$$\begin{aligned}
 St_{ic,d} &= \frac{k_{cd-ic} EBCT_{ic} (1 - e_{ic})}{R_{ic} \epsilon_{ic}} \\
 &= \frac{8.5E-6 (450) (1 - 0.70)}{(0.000425)(0.70)} = 3.86
 \end{aligned}$$

$$St_{sc,d} \gg St_{ic,d}$$

$$7489.18 \gg 3.86$$

✓✓✓

CHLORDANE CONTAMINANT (Full scale EBCT = 10.0 min. = 600 secs)

Small Column

$$\begin{aligned}
 k_{c-s} &= \frac{D_{Lc}}{2R_{sc}} \left[ 2 + 1.1 Re_{sc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.37E-10}{2(0.000082)} \left[ 2 + 1.1 (0.185)^{0.6} (1794.34)^{1.3} \right] \\
 &= 1.83E-5 \\
 St_{sc,c} &= \frac{k_{c-s} EBCT_{sc} (1-\epsilon_{sc})}{R_{sc} \epsilon_{sc}} \\
 &= \frac{1.83E-5 (116.5) (1-2.81E-3)}{(0.000082)(2.81E-3)} = 9327.29
 \end{aligned}$$

Large (full-scale) column

$$\begin{aligned}
 k_{c-lc} &= \frac{D_{Lc}}{2R_{lc}} \left[ 2 + 1.1 Re_{lc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.37E-10}{2(0.000425)} \left[ 2 + 1.1 (3.88)^{0.6} (151.71)^{1.3} \right] \\
 &= 7.83E-6 \\
 St_{lc,c} &= \frac{k_{c-lc} EBCT_{lc} (1-\epsilon_{lc})}{R_{lc} \epsilon_{lc}} \\
 &= \frac{7.83E-6 (600) (1-0.70)}{(0.000425)(0.70)} = 47.37
 \end{aligned}$$

$$St_{sc,c} \gg St_{lc,c}$$

$$9327.29 \gg 47.37$$

✓✓✓

DIELDRIN CONTAMINANT (Full scale EBCT = 10.0 min. = 600 secs)

Small Column

$$\begin{aligned}
 k_{cd-sc} &= \frac{D_{L,d}}{2R_{sc}} \left[ 2 + 1.1 Re_{sc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.74E-10}{2(0.000082)} \left[ 2 + 1.1 (0.185)^{0.6} (1794.34)^{1.3} \right] \\
 &= 1.98E-5 \\
 St_{sc,d} &= \frac{k_{cd-sc} EBCT_{sc} (1-\epsilon_{sc})}{R_{sc} \epsilon_{sc}} \\
 &= \frac{1.98E-5 (116.5) (1-2.81E-3)}{(0.000082)(2.81E-3)} = 9982.72
 \end{aligned}$$

Large (full-scale) column

$$\begin{aligned}
 k_{cd-lc} &= \frac{D_{L,d}}{2R_{lc}} \left[ 2 + 1.1 Re_{lc}^{0.6} Sc^{1.3} \right] \\
 &= \frac{4.74E-10}{2(0.000425)} \left[ 2 + 1.1 (3.88)^{0.6} (151.71)^{1.3} \right] \\
 &= 8.5E-6 \\
 St_{lc,d} &= \frac{k_{cd-lc} EBCT_{lc} (1-\epsilon_{lc})}{R_{lc} \epsilon_{lc}} \\
 &= \frac{8.5E-6 (600) (1-0.70)}{(0.000425)(0.70)} = 5.14
 \end{aligned}$$

$$St_{sc,d} \gg St_{lc,d}$$

$$9982.72 \gg 5.14$$

✓✓✓

CHLORDANE CONTAMINANT (Full scale EBCT = 15.0 min. = 900 secs)

Small Column

$$\begin{aligned}
 k_{t_c-t_c} &= \frac{D_{t_c}}{2R_{t_c}} \left[ 2 + 1.1 Re_{t_c}^{0.6} Sc^{1/3} \right] \\
 &= \frac{4.37E-10}{2(0.000082)} \left[ 2 + 1.1 (0.185)^{0.6} (1794.34)^{1/3} \right] \\
 &= 1.83E-5 \\
 St_{t_c,e} &= \frac{k_{t_c-t_c} EBCT_{t_c} (1-\epsilon_{t_c})}{R_{t_c} \epsilon_{t_c}} \\
 &= \frac{1.83E-5 (174.7) (1-2.81E-3)}{(0.000082)(2.81E-3)} = 13,835.72
 \end{aligned}$$

Large (full-scale) column

$$\begin{aligned}
 k_{t_c-t_c} &= \frac{D_{t_c}}{2R_{t_c}} \left[ 2 + 1.1 Re_{t_c}^{0.6} Sc^{1/3} \right] \\
 &= \frac{4.37E-10}{2(0.000425)} \left[ 2 + 1.1 (3.88)^{0.6} (151.71)^{1/3} \right] \\
 &= 7.83E-6 \\
 St_{t_c,e} &= \frac{k_{t_c-t_c} EBCT_{t_c} (1-\epsilon_{t_c})}{R_{t_c} \epsilon_{t_c}} \\
 &= \frac{7.83E-6 (900) (1-0.70)}{(0.000425)(0.70)} = 7.11
 \end{aligned}$$

$$St_{t_c,e} \gg St_{t_c,e}$$

$$13,835.72 \gg 7.11$$

✓✓✓