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Retention Time Effect on Metal Removal By Peat Columns (U)

by
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Executive Summary

The potential use of a peat bed to treat the H-12 Outfall discharge to bring it to new compliance limits was previously investigated and reported utilizing a 7 hour retention time. The influence of retention time (contact time) of water with peat moss on the removal of copper from the water was investigated under laboratory conditions using vertical flow peat moss columns. Reduction of the necessary retention time has a large influence on the design sizing of any peat bed that would be constructed to treat the H-12 discharge on a full scale basis.

Retention times of 5 hours, 3 hours and 1 hour were tested to determine the copper removal by the peat columns using vertical flow. Water samples were collected after 4, 8, 12, and 16 water volumes had passed through the columns and analyzed for a suite of metals, with quantitative emphasis on copper. Laboratory results indicated that copper removal was very high at each of the 3 retention times tested, ranging from 99.6 % removal at 5 and 3 hours to 98.8% removal at 1 hour. All these values are much lower than the new compliance limit for the outfall. The results also indicated that most divalent metals were removed to their normal reporting detection limit for the analytical methods used, including zinc. Lead levels in the H-12 discharge used in this study were below PQL in all samples analyzed.

While each of the retention times studied removed copper very well, there were indications that 1 hour is probably too short for an operational, long-term facility. At that retention time, there was about 6% compaction of the peat in the column due to the water velocity, and this may affect long term hydraulic conductivity of the peat bed. At that retention time, copper concentration in the effluent was higher than the other times tested, although still very low. Because of the potential compacting and somewhat reduced removal efficiency at a 1 hour retention time, it would be prudent to design to at least a 3 hour retention time for water in any peat bed system that is proposed for the H-12 Outfall.

A scope to design and install a pilot level study at H-12 is currently under development. This study will be designed to examine some of the engineering issues that are of concern regarding the scaling of an actual peat bed to treat the volumes of water that are typically discharged through the H-12 Outfall. Different hydraulic paths and configurations are expected to be part of that scope.

Introduction

The H-12 National Pollutant Discharge Elimination System (NPDES) Outfall at the Savannah River Site is periodically out of compliance with its revised copper limit in the current NPDES permit. As part of the solution to avoid future exceedences, the construction of a peat bed to treat a portion of the normal outfall discharge is being considered, both to remove copper from the water and to improve the water characteristics by addition of organic carbon to the waste stream. The new limit for copper of 6 µg/L that will go into effect in November 2008, will necessitate actions to bring the outfall into compliance with the new permit. A preliminary peat bed study was conducted to confirm metal removal from H-12 effluent (Nelson and Specht 2005),

Peat moss has a very high affinity for removing and holding metals and other cationic elements in water (Brown et al. 2000; Kratochvil and Volesky 1998; Couillard 1994; Veglio and Beolchini

1997). Metal removal is primarily through ion-exchange and complexation occurring on the surface of the peat material. Peat moss has a very high surface area, is polar, and has a high cation exchange capacity, especially for transition metals (Kadlec and Keoleian 1986; Twardowska and Kyziol 1996). This set of properties has made peat moss an intensively studied material for environmental improvement of aqueous waste streams. It is also a plentiful and inexpensive resource compared to many of the more highly processed or synthetic ion exchange materials.

Equilibration rates of metals in solution with peat moss are very rapid (Crist et al. 1996; Gosset et al. 1986; Gardea-Torresdey et al. 1996). In experimental systems, copper equilibrium is reached within 30 minutes of contact with peat moss. This is also the case with other metals that can be removed. There are differences in the binding strength of divalent metals (Gosset et al. 1986; Brown et al.; Crist et al. 1996). The order can vary slightly, based on the exact conditions of contact, but the usual order of affinity of removal is $Pb > Cu = Ni > Cd = Zn$. Calcium, Mg, Mn, and Na are also weakly held on the peat surface, but easily displaced by metals with greater equilibrium constants for peat moss. The large adsorptive capacity of peat moss, coupled with a low loading rate, ensures that the effectiveness of metal removal from the H-12 effluent stream will not be diminished. It is important for this application that copper is among the most effectively removed of the heavy metals.

There is a clear potential to use peat moss as a treatment media for the H-12 Outfall at SRS. It has a high affinity for the metals that need to be removed, has a high capacity to hold them once removed, removes them rapidly, and is relatively inexpensive to acquire and maintain. A study to assess the potential of a peat bed at the bench-scale was established to document performance and effluent characteristics of the system was previously reported (Nelson and Specht, 2005). That study clearly confirmed the removal characteristics of peat moss that were central to the possible use as a treatment media for the H-12 outfall discharge. Preliminary discussions with South Carolina DHEC personnel indicated that use of peat technology would be acceptable as a treatment method if appropriate design and engineering data were part of the permit process.

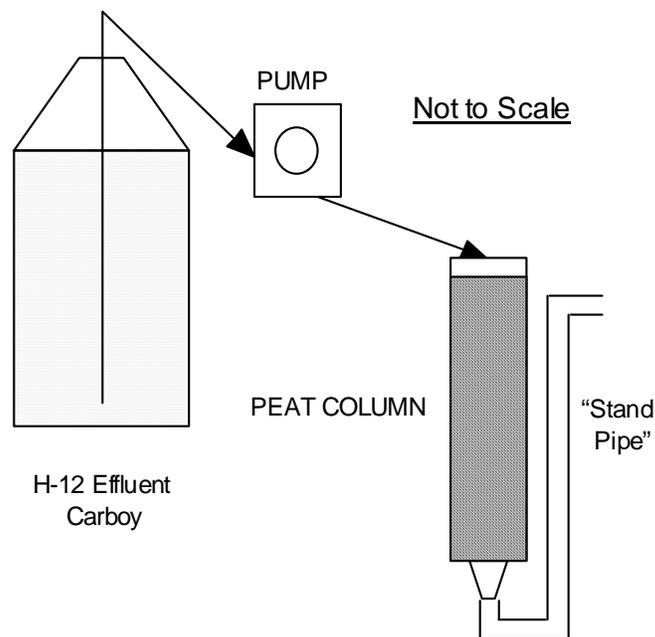
If peat moss is to be used as the treatment media, the speed at which that the water/peat mixture reaches an equilibrium with regard to metals in the solution is an important design and operation characteristic. The water must be in contact with the peat for a sufficient amount of time for the metal to be adsorbed by the peat and removed from the water phase. However, as the contact time becomes longer, the required volume of a peat bed to treat a given volume of water also increased. Therefore, establishment of the retention time necessary to assure metal removal performance of the peat can significantly impact the design size of the system. This report examined the influence of retention time (contact time) of water with the peat moss on metal removal, thereby defining that variable for design of a system.

Retention Time Column Study Methods

Bench-scale peat bed columns were constructed using a circular plastic tube (test column) containing commercial peat moss (Premier Peat, Quebec Canada). This vendor was contacted by members of the design team and the specifications received on the vendors peat moss are included in Appendix A. This project was an extension of the previous peat bed study, and conducted under EEC (TC-A-2005-119) and HAP (SRNL-EST-2005-00174) documents that were prepared previously.

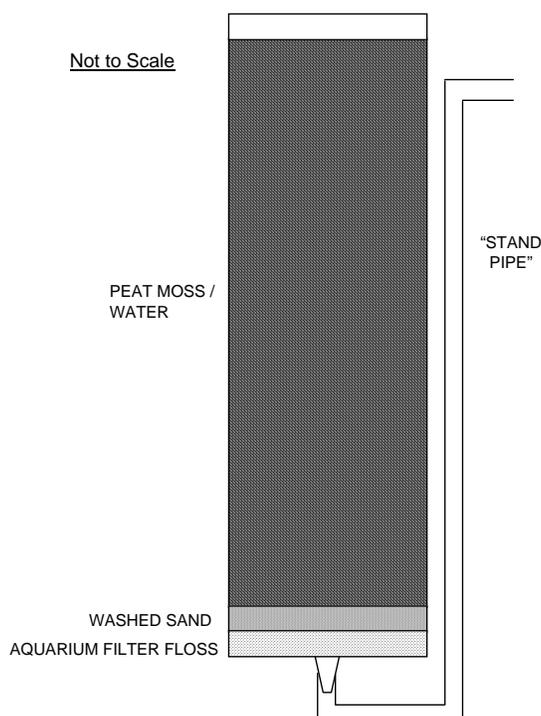
An initial determination of the proportion of space occupied by water at saturated condition of the peat/water mix was calculated gravimetrically to determine the percent water contained in the volume (68%). The water proportion of the peat / water mixture was used to calculate the appropriate flow rate to achieve the targeted retention time by the peat bed columns. It was anticipated that approximately 980 cubic centimeters of peat would be used in each column for the bench-scale systems. The testing apparatus consisted of a reservoir of H-12 effluent, a fluid pump, and test columns containing peat moss (Figures 1 and 2). The columns were clear plastic tube 50 centimeters long and 5 centimeters in diameter. The cap on the bottom of the column had a nipple to allow water to pass out of the column. That nipple was attached to a tygon tube that allowed positioning on the column to simulate a stand pipe and regulate the level of saturation in the column. On top of the nipple is a thin layer of aquarium filter floss covered by approximately 2 millimeter of washed sand. This acted as a filter to maintain the peat in the columns. The peat moss was initially saturated with H-12 effluent prior to placing it into the columns. Actual column volumes after construction were 952 cubic centimeter of water/peat. The test columns were fitted with a tygon inflow line at the top end and a plastic outflow fitting at the other end. The inflow line was connected to a pump that feed H-12 effluent into the test column at a constant rate correlating to the desired retention time on the column. The effluent flowed vertically through the peat column and was collected at the outflow end of the test column discharge tube. Two columns were run at the same time to provide replication, and designated Column A and Column B. Samples for metal testing were collected at intervals of 4, 8, 12, and 16 volumes of water passing through the columns and the remainder of the effluent was discharged to the lab drain.

Figure 1. Schematic of Experimental Design



Effluent at the H-12 Outfall was collected in 25 liter carboys on December 8, 2006 for use in this test. Water from this collection date was used for all retention time trials. The water was maintained under refrigeration until it was needed as source water for the columns. At that point it was allowed to come to room temperature, and copper (in the form of copper sulfate) was added to provide a nominal concentration of 100 micrograms per liter ($\mu\text{g/l}$) to the H-12 effluent. Using a higher concentration of copper in the influent water gave a better estimation of the ability of the peat bed to remove the occasionally higher concentrations of copper that occur in the H-12 effluent and to insure detection of any copper that passed through the column. This served as the source of water to the columns.

Figure 2. Schematic of Peat Column



Three sets of retention times were evaluated based on calculation of the water volume contained in the columns. The original peat bed study utilized approximately a 7 hour retention time. This study evaluated 5, 3, and 1 hour retention times of water on the peat columns. These retention times converted to influent rates of 2.16, 3.60, and 10.79 ml/minute of water on to the columns respectively. The concentration of copper was measured in the influent at the start of the study and effluent was collected for copper analysis after 4, 8, 12, and 16 volumes of water had passed through the column at the tested retention times. Water samples were collected at the specified times and acidified immediately with ultra-pure nitric acid for preservation. Samples were labeled with a 3 character identification, with the first number being the retention time (5, 3, or 1), the second being the column designation (A or B), and the third being the sample sequence (1 through 4). An example would be 3-B-2 and would indicate a 3 hour retention time on column B collected after 8 water volumes.

The samples were submitted to EMS Analytical Laboratory for analysis (SC DHEC Certification 02550001). Since copper concentrations were expected to be below the usual PQL (0.005 mg/L) that the laboratory uses for detection, a quantitative estimate of copper concentration was requested for reporting purposes. Periodic duplicate samples were collected and sent to the University of Georgia Analytical Laboratory for confirmation and actual values for the low levels of copper that were expected to be present in the effluent. Columns were started on December 19, 2006.

Results

While conducting the series of retention time studies, no disruptions in flow through the columns were experienced. The 5 hour retention time series was conducted first, followed by the 3 hour and 1 hour series. Results of analysis for elements that were present in the influent water and their subsequent concentrations after passage through the columns are included in Appendix B of this report. Elements that were below PQL values in all analyses, both influent and effluent, are not included here (e.g. lead, nickel, chromium, cobalt, manganese, aluminum, and tin). Results from the two columns for a given retention time and column volume were very similar, and an average of all eight samples is therefore discussed as the retention time result. The results for copper are listed in Table 1. The H-12 discharge used in this series of retention time trials was characteristic of the copper level currently being reported in the H-12 Outfall DMR data. Spiking of the influent used in the study brought the copper concentration to slightly greater than the planned increase of 100 µg/L, but was within the value expected based on the degree of precision used in adding the spike to the carboys of H-12 discharge.

Table 1. Copper concentration in effluent after different retention times on the peat columns (Mean ±SD).

Sample	Copper Conc (µg/L)	Removal (%)
H-12 Discharge Used	8.30	
H-12 Spiked Influent	118.90	
5 Hour Retention Effluent	0.51 ± 0.22	99.6
3 Hour Retention Effluent	0.49 ± 0.24	99.6
1 Hour Retention Effluent	1.41 ± 0.25	98.8

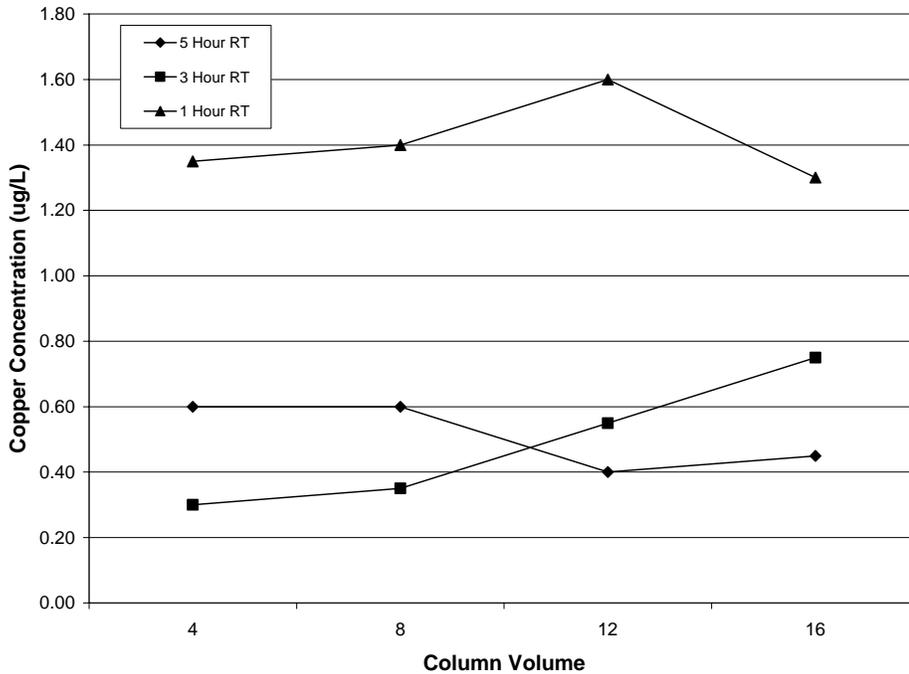
All retention times tested removed nearly 100% of the influent copper in the water supplied to the columns. These reported values of copper are below the normally reported detection limit for the instrument and method used, so they should be viewed with some caution. The low levels of the 5 and 3 hour samples were, however, very consistent in their value (Figure 3). While the 1 hour retention time was slightly higher in reported copper, this value was also very consistent among the eight samples collected. All samples collected in this study removed in excess of 98% of the influent copper mass and results were best at 5 and 3 hour retention times. At 1 hour retention time on the column a slight increase in the amount of copper eluting from the column was seen, but is insignificant given the influent concentration. All retention times brought the spiked influent to far below the new compliance limit for the H-12 Outfall.

Duplicate samples of 4 selected collections that were sent to the University of Georgia Analytical Laboratory confirmed the magnitude of reduction and the trend of an increase in copper concentration of the 1 hour retention time samples (Table 2).

Table 2. Comparison of copper concentration ($\mu\text{g/L}$) reported by laboratories for duplicate samples. Note that EMS samples are below the PQL for the method of analysis.

Sample ID	EMS	U Ga
5-A-2	0.7	1.110
3-B-2	0.4	1.065
1-A-2	1.5	1.999
1-B-4	1.3	1.957

Figure 3. Copper concentration in effluent during the 16 water volumes eluted from the peat columns at different retention times (RT). Values are the average for the two columns.



The columns also removed a wide variety of positively charged ions from the influent water, as was the case previously reported in the original peat bed study (Nelson and Specht, 2005). Lead concentration in the influent was below the laboratory PQL and was not detected in any of the samples analyzed. The divalent ions that were in the source water were generally removed from the water after passage through the columns. All zinc ($36 \mu\text{g/L}$) and calcium ($2,388 \mu\text{g/L}$) in the influent was removed to the laboratory PQL in all samples as well. Iron ($104 \mu\text{g/L}$) was reduced by approximately 80% after retention of five or three hours on the column, and by 50%

after retention for 1 hour. Many monovalent ions were removed from the influent during the retention time trials due to the large adsorption capacity of the peat. These ions were displacing hydrogen ions present in the peat structure when the study was started, and are only weakly bound by the peat. Magnesium and potassium were reduced by approximately 50% and sodium was reduced by approximately 33% at all retention times. These monovalent ions will be displaced by ions with higher binding affinities when hydrogen ions bound to the peat are depleted. This early removal of large quantities on monovalent ions will not affect the long term ability of peat to continue removal of heavy metals of concern that are divalent and possess much higher binding affinities with the substrate.

The pH of the influent used in the study (H-12 discharge spiked with copper) was 6.78 and the pH of the effluent from the columns was typically 4.25 during the retention time trials. The retention time study only followed the first 50 column volumes that passed through the columns. During this time, hydrogen ions originally occupying exchange sites are being displaced by any positively charged ion, and are responsible for the low pH. The study is continuing using one of the peat columns to examine the loading capacity of the peat, and the pH of the effluent has risen over time to stabilize near a pH of 6.0.

During the running of the different retention time trials, no difference in column characteristics were noted at the 5 and 3 hour rates. However, when the water flow rate was increased to provide a 1 hour retention, there was obvious turbulence in the surface of the peat layer associated with the pumping rate. This disturbance only appeared to affect the upper one centimeter of the column, but during the 1 hour retention time trial sequence the column length was reduced by approximately 3 centimeters (approximately 6% decrease in height of peat column). This is believed to be due to compaction of the peat in the column due to the velocity of the water that was required to meet the 1 hour retention criteria. The discharge height of the tubing from the column during the run had to be lowered approximately 4 centimeters to maintain the slight water head on the column. This is expected to be reflective of a slightly reduced hydraulic conductivity of the peat in the column due to the compaction of the peat. When one of the columns was subsequently used for the loading study using a 3 hour retention time, the discharge height had to be maintained at this lower height to keep column head at the desired level. The compaction that had occurred during the 1 hour trial continued to affect the hydraulic conductivity of the column when a longer retention time was resumed.

Conclusions

The potential use of a peat bed to treat the H-12 Outfall discharge to bring it to new compliance limits was previously investigated and reported. Peat moss was found to act as an extremely effective ion exchange substrate for water quality improvement, and removed nearly 100% of heavy metals from the influent water. The retention time of the water in contact with the peat bed in that study was 7 hours. The influence of retention time (contact time) of water with peat moss on the removal of copper from the water was investigated under laboratory conditions using peat moss columns as the experimental apparatus. Reduction of the necessary retention time has a large influence on the design sizing of any peat bed that would be constructed to treat the H-12 discharge on a full scale basis.

Discharge collected at the H-12 Outfall was used as the influent water to the columns and the copper level was increased by approximately 100 µg/L prior to adding it to the columns. Retention times of 5 hours, 3 hours and 1 hour were tested to determine the copper removal by

the peat columns. Water samples were collected after 4, 8, 12, and 16 water volumes had passed through the columns and analyzed for a suite of metals, with quantitative emphasis on copper. Laboratory results indicated that copper removal was very high at each of the 3 retention times tested, ranging from 99.6 % removal at 5 and 3 hours to 98.8% removal at 1 hour. All these values are much lower than the new compliance limit for the outfall. The results also indicated that most divalent metals were removed to their normal reporting detection limit for the analytical methods used, including zinc. Lead levels in the H-12 discharge used in this study were below PQL in all samples analyzed.

While each of the retention times studied removed copper very well, there were indications that 1 hour is probably too short for an operational, long-term facility. At that retention time, there was about 6% compaction of the peat in the column due to the water velocity, and this may affect long term hydraulic conductivity of the peat bed. At that retention time, copper concentration in the effluent was higher than the other times tested, although still very low. Iron removal by the peat column was only 50% at 1 hour compared to 80% at 3 and 5 hour retention times. Because of the potential compacting and somewhat reduced removal efficiency at a 1 hour retention time, it would be prudent to design to at least a 3 hour retention time for water in any peat bed system that is proposed for the H-12 Outfall.

A scope to design and install a pilot level study at H-12 is currently under development. This study will be designed to examine some of the engineering issues that are of concern regarding the scaling of an actual peat bed to treat the volumes of water that are typically discharged through the H-12 Outfall. Different hydraulic paths and configurations are expected to be part of that scope.

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APPENDICES

Appendix A Peat Moss Specifications

technical data

FIBROUS BLOND SPHAGNUM PEAT MOSS

PRO-MOSS 'TBK' is made of a select long-fibered blond Sphagnum peat moss for general commercial use. **PROMOSS 'TBK'** provides a high degree of water retention and air porosity for a wide range of applications. Ideal for use as a major component in horticultural growing media and mushroom casing materials which require high fibrosity.

PRODUCTION FACILITY: Rogersville (New Brunswick), Canada

PACKAGE SPECIFICATIONS:

Code	Size(cu.ft.)	Packing	Weight(lb)	Minimum Yield(cu.ft.)
0010P	55	2/pallet	850 - 1050	113.0
0023P	6.0	18/pallet	85 - 95	12.0

LABORATORY ANALYSIS***CHEMICAL CHARACTERISTICS:**

pH:	3.8 - 4.4 (1:3, v:v water)
Electrical Conductivity:	0.09 - 0.15 mmhos/cm
C/N Ratio:	125 - 135
Cation Exchange Capacity:	150 - 250 meq/100 g
Organic Matter:	95 - 99 %
Ash Content:	1 - 5 %

PHYSICAL CHARACTERISTICS:

Total Porosity:	96 - 97 %
Dry Bulk Density:	3 - 4.5 Lbs./cu.ft. (0.05 - 0.07 g/cm ³)
Fresh Bulk Density:	6 - 8 Lbs./cu.ft. (0.10 - 0.13 g/cm ³)
Water-Holding Capacity:	1200 - 1500 % by weight
Moisture Content:	40 - 55 % (Fresh Basis)

DRY GRANULOMETRY:

<u>Mesh Size</u>	<u>% Passing</u>
10 mesh:	75 - 85 %
20 mesh:	50 - 65 %
50 mesh:	20 - 35 %
100 mesh:	10 - 18 %

** This data is for information purposes only. Peat moss is a natural product; therefore, results for individual samples may vary to a limited degree.*

PHFT12r3

Appendix B. Analytical Results of Retention Time Trials

Sample#	Analyte (mg/l)						
	Cu*	Zn	Fe	Ca	K	Mg	Na
H-12	0.0083	0.0367	0.1036	2.3871	0.7754	0.3540	8.9988
H-12 Sp	0.1189	0.0354	0.1050	2.3883	0.8636	0.3562	9.1441
5-A-1	0.0003	<0.01	0.0382	<0.05	0.7217	0.2104	5.1998
5-B-1	0.0009	<0.01	0.0418	<0.05	0.7212	0.2167	5.2714
5-A-2	0.0007	<0.01	0.0250	<0.05	0.7002	0.2018	5.1239
5-B-2	0.0005	<0.01	0.0232	<0.05	0.7015	0.2010	5.1518
5-A-3	0.0003	<0.01	0.0241	<0.05	0.5901	0.1888	5.9480
5-B-3	0.0005	<0.01	0.0230	<0.05	0.5445	0.1827	5.9724
5-A-4	0.0006	<0.01	0.0223	<0.05	0.4449	0.1581	6.1223
5-B-4	0.0003	<0.01	0.0170	<0.05	0.4108	0.1579	6.2352
<u>AVG</u>	0.00051	<0.01	0.0268	<0.05	0.6044	0.1897	5.6281
<u>St Dev</u>	0.00022		0.0085		0.1269	0.0223	0.4819
3-A-1	0.0003	<0.01	0.0232	<0.05	0.4183	0.1633	6.5578
3-B-1	0.0003	<0.01	0.0240	<0.05	0.4008	0.1631	6.5029
3-A-2	0.0003	<0.01	0.0233	<0.05	0.3804	0.1701	6.3682
3-B-2	0.0004	<0.01	0.0228	<0.05	0.3813	0.1661	6.4605
3-A-3	0.0003	<0.01	0.0222	<0.05	0.3653	0.1578	6.1653
3-B-3	0.0008	<0.01	0.0261	<0.05	0.3721	0.1724	6.5503
3-A-4	0.0008	<0.01	0.0262	<0.05	0.3733	0.1667	6.3744
3-B-4	0.0007	<0.01	0.0261	<0.05	0.3819	0.1727	6.5149
<u>AVG</u>	0.00049	<0.01	0.0242	<0.05	0.3842	0.1665	6.4368
<u>St Dev</u>	0.00024		0.0016		0.0173	0.0051	0.1314
1-A-1	0.0014	<0.01	0.0478	<0.05	0.3689	0.1671	6.4206
1-B-1	0.0013	<0.01	0.0528	<0.05	0.3770	0.1639	6.3803
1-A-2	0.0015	<0.01	0.0507	<0.05	0.3850	0.1583	6.4536
1-B-2	0.0013	<0.01	0.0552	<0.05	0.3983	0.1667	6.6725
1-A-3	0.0012	<0.01	0.0477	<0.05	0.3855	0.1515	6.4084
1-B-3	0.0020	<0.01	0.0564	<0.05	0.3911	0.1556	6.5457
1-A-4	0.0013	<0.01	0.0492	<0.05	0.3750	0.1387	6.2873
1-B-4	0.0013	<0.01	0.0556	<0.05	0.3930	0.1395	6.6034
<u>AVG</u>	0.00141	<0.01	0.0519	<0.05	0.3842	0.1552	6.4715
<u>St Dev</u>	0.00025		0.0036		0.0100	0.0113	0.1267

Sample designation is Ret Time - Column - Sample

*Per Customer request, Cu results are quantitative estimate when <PQL