Project 35:

Sustainable Highways Through The Use of Carbon Sequestering Construction Materials

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1.0 Executive Summary

Exploratory research at UNH has demonstrated that spontaneous reactions between carbon dioxide and recycled concrete have a significant potential to permanently sequester CO_2 from the atmosphere. This characteristic in addition to the large quantity of concrete in construction and demolition waste streams add an additional beneficial value to utilizing recycled concrete as an aggregate in highway construction. The goal of this research is to observe the carbonation trends of recycled concrete in pilot scale berm applications under various aeration methods. Additional monitoring equipment was also placed within the piles to observe other controlling parameters which may control the rate of carbonation.

Several trends were observed during the analysis of this research which coincide with previous research performed on alkaline materials by the University of New Hampshire. Notable observations include:

1) The diffusion tube used to a increase the material/atmospheric interface of the passive aeration system in Pile B did not appear to have any beneficial carbonation impact compared with a passive aeration system without the diffusion tube (Pile A).

2) Active aeration increased the carbon dioxide concentrations within sections of that pile to near atmospheric concentrations. Other locations within the same pile had much lower concentrations however.

3) Higher percentages of calcium were carbonated in locations which experienced higher CO_2 concentrations during the period of this study.

4) Calcium below the surface of the aggregate experienced less carbonation than observed on the aggregate surfaces.

2.0 Introduction

The fourth report on climate change by the Intergovernmental Panel on Climate Change (IPCC) establishes the ignition of fossil fuels as the primary cause of elevated carbon dioxide concentrations in the earth's atmosphere and human activity in the past 250 years as a very likely cause of the observed global warming trend in the earths atmosphere (ICPP, 2007). In an attempt to offset the anthropogenic release of CO_2, and abate global climate change, carbon sequestration techniques are currently being investigated. Carbon sequestration is the chemical binding of carbon dioxide, achieved through natural and artificial methods, which are able to temporarily or permanently capture carbon dioxide from the atmosphere. Natural methods include biotic and vegetative uptake through respiration and photosynthesis. Artificial methods include processes such as deep well injection into the earth and oceans.

The Recycled Materials Resource Center is investigating the mineral sequestration of CO_2 through the carbonation of recycled concrete. Concrete's sequestration capability is due to the Portland cement component of its mix. Portland cement is the binding agent used in most concretes and is composed primarily of calcium oxide. Calcium oxide in the presence of carbon dioxide and water will carbonate to form calcium carbonate and water following Equations 2.1 through 2.3, and sequester carbon dioxide from the atmosphere.

Eq. 2.1 – Eq. 2.3

$$CO_2 + H_2 0 \rightarrow H_2CO_3 \rightarrow 2H^+ + CO_3^{-2}$$
$$H_2O + CaO \rightarrow Ca(OH)_2 \rightarrow 2(OH)^{-2} + Ca^{+2}$$
$$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$$

The formation of carbonates produces minerals that are stable for geological time scales. Because of their thermodynamic stability and exothermic formation, it is difficult to re-release the carbon dioxide without extreme temperatures. Their stability eliminates the possibility of sudden carbon dioxide releases and also eliminates the risk of gradual leaks (Lackner, 2002).

The carbonation reaction of calcium oxide is controlled by several parameters, which influence the diffusion of aqueous carbon dioxide to calcium hydroxide ions and the ensuing reaction. Four parameters that have been reported in the literature and will be focused on include the surface area, concentration of CO_2, moisture content of the material and temperature (Barnard L.H. et al).

3.0 Objective and Scope

The objective of this research was to observe the carbonation of recycled concrete in a pilot scale berm application under atmospheric conditions. To accomplish this, recycled concrete piles were constructed in windrow fashion with the inclusion of instrumentation stalls to monitor the interior environmental conditions. Monitoring included periodic measurements of carbonate concentrations in the material as well as regular measurements of established controlling parameters, discussed in the introduction.

This research was designed to compare and contrast observations within various locations within a single recovered sample; two different locations within the same pile; three separate piles which employ various aeration techniques as well the change in conditions over time.

4.0 Material

The three windrow piles were all constructed from recycle concrete provided by Pike Industries. The material origin is Pike's Stockyard at Pease Tradeport, located in Portsmouth, New Hampshire. The material was crushed and then stockpiled for an undisclosed period of time by Pike Industries and then transported to UNH on September 7, 2005 by UNH personnel. Construction began on September 21, 2005.

5.0 Instrumentation

This section will provide an overview of the instruments used in the monitoring of this project along with the sampling schedule that was followed and the limitations of the equipment that were found.

5.1 Carbonation of Recycled Concrete

A primary focus of this research was to quantify the amount carbon dioxide recycled concrete would be able to sequester from the atmosphere in a given application. This quantification was accomplished by identifying the percentage of reactive calcium that has carbonated over time. Thermo-Gravimetric Analysis (TGA) analyzes precise weight changes in a material over a specified temperature range. Because the temperature at which carbon dioxide will volatilize from calcium carbonate is known, the mass of carbonated calcium can be quantified within a sample. Similarly, the volatilization of bound hydroxide from calcium occurs at a known temperature range, allowing for the quantification of uncarbonated reactive calcium. Assuming that carbonation occurs uniformly for material within the same pile and location, the ratio of carbonated calcium to total reactive calcium can be applied to different samples over time, yielding the rate at which carbon dioxide is being sequestered.

Samples were analyzed between a temperature range of 20°C and 1000°C. Mass loss between this temperature range is associated with the processes listed in Table 5.1. Any mass loss associated with the vaporization of bound hydroxides was assumed to be calcium hydroxide (reactive calcium) and any mass loss between 500°C and 1000°C was defined as carbonated calcium. Temperature ranges for these processes vary in the literature, however, the ranges presented in Table 5.1 were confirmed through a mass spectrophotometer analysis addition to the thermo-gravimetric analysis (Appendix A).

Table 5.1- Thermo-Gravimetric Temperature Ranges

Process	***Temperature Range (°C)***
Vaporization of Unbound Water	20° – 200°
Vaporization of Bound Hydroxide	200° - 500°
Vaporization of CO_2	500° - 1000°

Samples recovered from the piles were first freeze dried and stored in air tight HDPE containers and stored until analysis. Subsamples were removed from each sample recovered from the pile immediately prior to analysis and analyzed independently. Sub samples focused on three main fractions of the sample: the loose fine grain material recovered (fines); the surface of the larger aggregates (surface); and material below the aggregate surface (deep). Subsamples were analyzed independently to observe the effect surface area and diffusion have on the carbonation of recycled concrete.

Some limitations were observed during this performance of this analysis. Due to the limited sample size for each analysis, it is difficult to ensure the material analyzed is representative of the greater material within the sample. A number of subsamples were analyzed in triplicate however a more complete statistical model will be required to determine statistical significance for the material. In addition a dual beam thermo gravimetric model was used for this analysis which limited productivity due to processing time and requirement necessary to analyze a sample.

5.2 Moisture Content

The moisture content of the recycled concrete was monitored by time domain reflectometry (TDR) supplied by MESA Systems. Probes were placed at both deep and shallow monitoring locations (≈ 2.1ft. and ≈ 0.7 ft from the pile/atmosphere interface). Moisture readings were conducted every half hour interval for a three month period. Data logging was conducted by an independent CPU and uploaded periodically. The TDR system preformed well and was reliable.

5.3 Carbon Dioxide Concentration

The carbon dioxide concentration of the air within the three piles was sampled using a GM-70 hand held carbon dioxide meter manufactured by Vaisala. Data was recorded at two levels within the pile, shallow and deep, on a weekly basis. Atmospheric CO_2 concentrations were also recorded over the same time interval. Initially carbon dioxide measurements were going to be conducted continuously; however moisture negatively affected the probes performance and continuous measurements were found to be inaccurate.

5.4 Temperature

Temperature and relative humidity were measured and recorded using a thermohygrometer, manufactured by Digi-Sense. Data was logged continuously every 30 minutes within the deep and shallow locations of all three piles. The equipment performance was acceptable.

6.0 Construction Design

To observe the carbon sequestering capabilities of recycled concrete three piles were constructed at the University of New Hampshire. The piles were constructed in windrow fashion and stand 3 feet tall, stretch 12 feet in length and are 6 feet wide. Instrumentation stalls were built into the side of the pile to house monitoring probes at two levels within the pile. The top level is designed to provide data at a shallow depth approximately 0.7 feet from the interface between the piles surface and the atmosphere. The bottom level provides readings at a deeper location within the pile approximately 2.1 feet from the free surface of the pile. Common pile dimensions and the location if the instrumentation is shown in Figure 5.1.

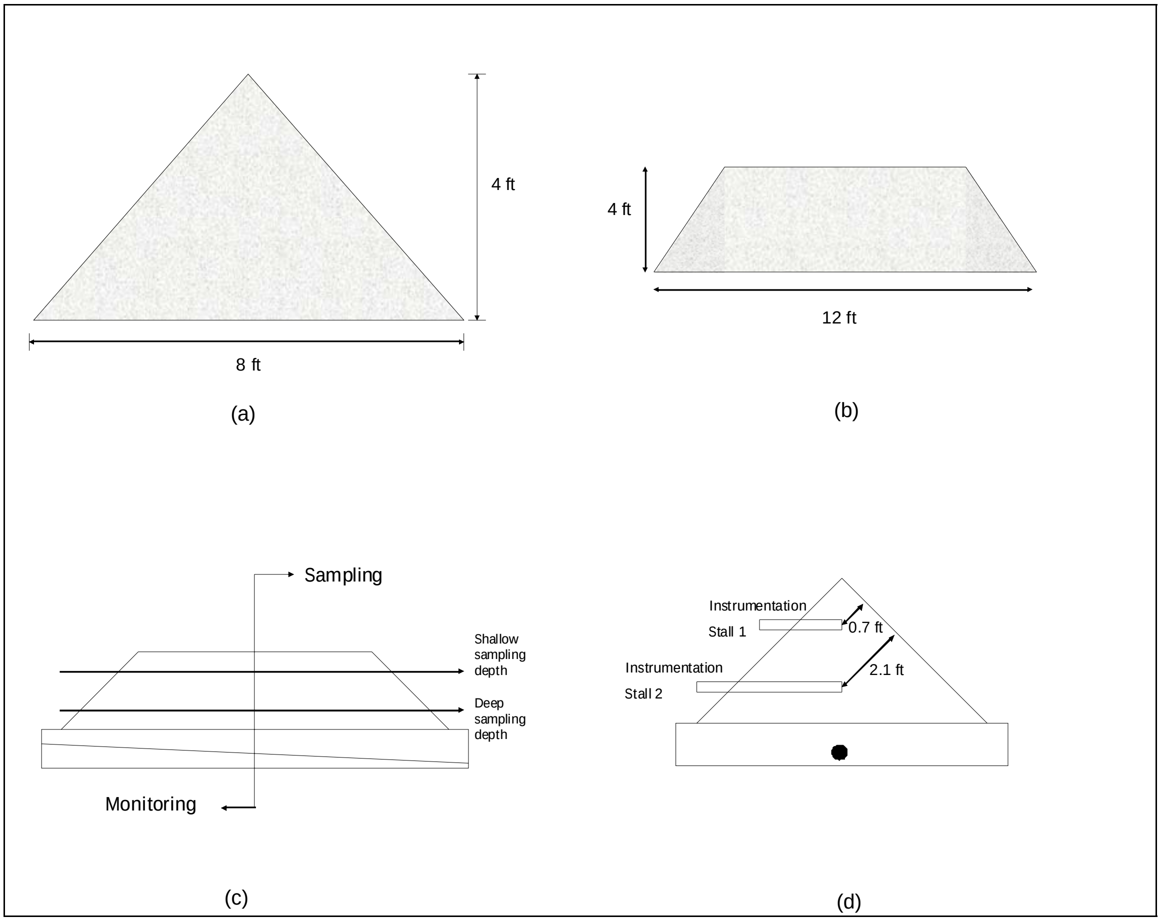

Figure 6.1 – Diagrams of Pile Dimensions and Structural Layout
- **(a) Pile Cross Section with Dimensions**
- **(b) Pile Profile with Dimensions**
- **(c) Sampling and Monitoring Layout**
- **(d) Instrumentation Stall Locations**

In accordance with the location of the instrumentation stalls, small random samples of RC were placed into nylon mesh nets outfitted with extraction cords. The samples were placed at 24 locations within the pile, 12 at the shallow depth and 12 at the deeper location. This material was extracted from the pile periodically to measure the progression of the carbonation process within the pile.

The windrows share common dimensions and were fabricated from the same material but differ in the method that they are aerated and their date of construction. Pile A was constructed on September 21, 2005 and is a passive aeration method. The surface of the windrow is exposed to the atmosphere; however there is no active air exchange to pull fresh air into the center of the pile where the majority of the material is located. Pile B was constructed the following day on September 22, 2005 and also utilizes a passive aeration system but is outfitted with an aeration tube. This tube increases the surface area and distance between the two samplings locations to the atmosphere. The third pile, Pile C, was constructed almost a month later on October 19, 2005. This system utilizes an active aeration method. Ambient air is pulled through the pile into a vacuum chamber by mechanical means.

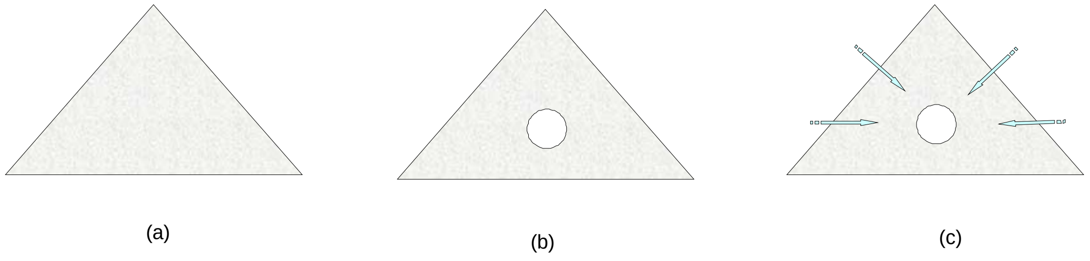

Figure 6.2 – Aeration System for the Three Piles
(a) Pile A - Passive Aeration
(b) Pile B – Passive Aeration with a Diffusion Tube
(c) Pile C – Active Aeration with a vacuum

7.0 Results and Discussion

This section provides selected discussion and analysis which represent observed general trends regarding the performance of recycled concrete in the inspected applications. Data include carbonation analysis of recovered recycled concrete, carbon dioxide measurements within the piles, temperature data and moisture contents of the material. Material was analyzed from the surface, subsurface and fines portion of samples recovered from two locations within three various piles.

7.1 Thermo-gravimetric Analysis

Figure 7.1 provides available carbonation data for Pile A over a 20 month time period. The initial sample analyzed at zero months in Fig 7.1a and 7.1b was recovered during the construction of the piles in September of 2005. Although the sample is included in both graphs only one analysis was conducted at this time. As discussed previously, the evaluation of a material's carbonation is presented in the percent of reactive calcium that has carbonated within the sample. The results reported in a and b are similar. Carbonation concentrations for both locations within Pile A begin between 40% and 60% for the first three samples analyzed in 2005. After this time carbonation levels in the shallow sampling location of Pile A appear to have an increasing trend over the following 17 months to a final carbonation level of 90% carbonated reactive calcium. The material sampled from the deeper location within Pile A has a maximum carbonation concentration closer to 80% however the final reading is 63% which suggests that the deeper location is carbonating at a slower rate.

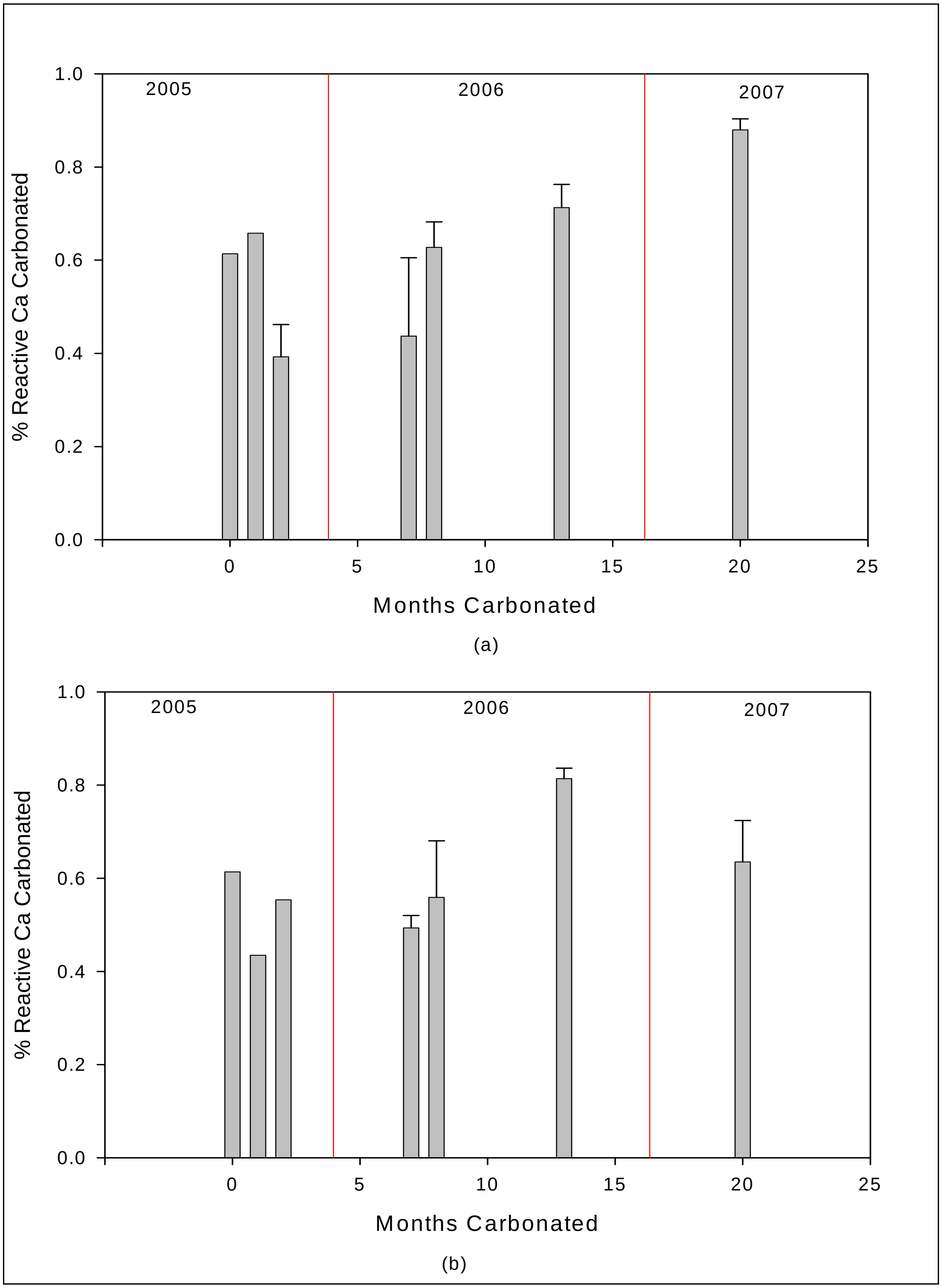

Figure 7.1 – Observed Percent Calcuim Carbonation Concentrations in Pile A over 20 Months
(a) Material Sampled from 0.7 ft below the Pile/Atmospheric interface (Shallow)
(b) Material Sampled from 2.1 ft below the Pile/Atmospheric interface (Deep)

It is also important to recognize that the data only provides insight towards the kinetics of the carbonation after half of the reactive calcium has already achieved carbonation. The period of time from demolition until the piles were constructed at UNH is unknown so kinetic data before 50% of the material is carbonated could possibly follow a much different trend.

Figure 7.2 presents carbonation data at 13 months for both locations in Pile A, Pile B and Pile C. Fig. 7.2a shows the carbonation of material on the pile/atmosphere interface and breaks the carbonation data down into the subsamples that were analyzed: from below the surface of the aggregate; from the surface of the aggregate; and from the independent fine particles loose in the sample. Figure 7.2b and 7.2c present the same sub sample analysis for the shallow sampling depth below the pile/atmosphere interface and the deeper sampling depth below the pile/atmosphere interface.

Several observations can be made from these figures. First, it appears that the material on the pile/atmosphere interface is generally more carbonated than material below that interface. This is likely due to the increased carbon dioxide concentrations at the atmospheric interface. The effect of the same controlling parameter can be witnessed in the generally elevated concentrations of all sub samples for Pile C at the pile/atmosphere interface and shallow sampling level. The deeper sampling level did not appear to

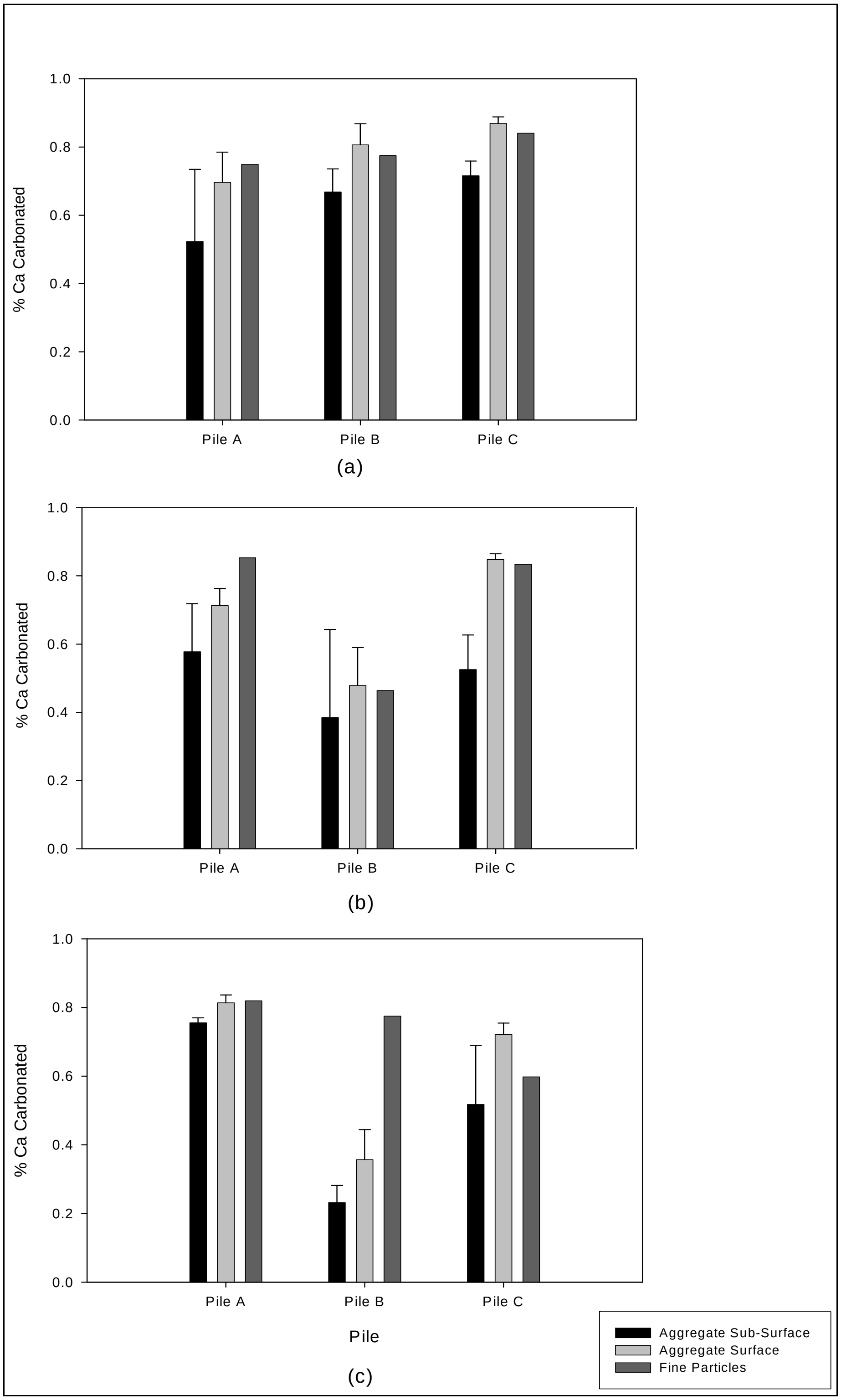

Figure 7.2 – Observed Percent of Rective Ca Carbonated at 13 Months
(a) Pile/Atmosphere Interface Sampling Location
(b) Shallow Sampling Location
(c) Deep Sampling Location

achieve an equivalent level of carbonation, as CO_2 monitoring shows that carbon dioxide concentrations were much lower at this location than above the vacuum tube in Pile C.

Thermo-gravimetric analysis also reveals that carbonation beneath the surface of the aggregate is consistently lower than the carbonation levels of the fine particles in the recycled concrete and the surface are of the aggregate. This suggests the rate limiting behavior of diffusive processes may be significant for the complete carbonation of these materials.

7.2 Carbon Dioxide Concentrations

Single carbon dioxide concentrations were recorded at both the deep and shallow sampling locations within Piles A, B and C, as well as ambient concentrations in the atmospheric. Figure 7.3 shows the average concentrations for these locations over a four month period in the summer.

CO_2 concentrations at the shallow location of Pile A are unavailable due to an equipment malfunction. Concentrations shown do appear to be visually consistent between Pile A and Pile B. Alternatively, Pile C does exhibit elevated concentrations, the shallow monitoring level is consistent with ambient CO_2 concentrations and the deeper level reports concentrations between the passive piles and the atmosphere.

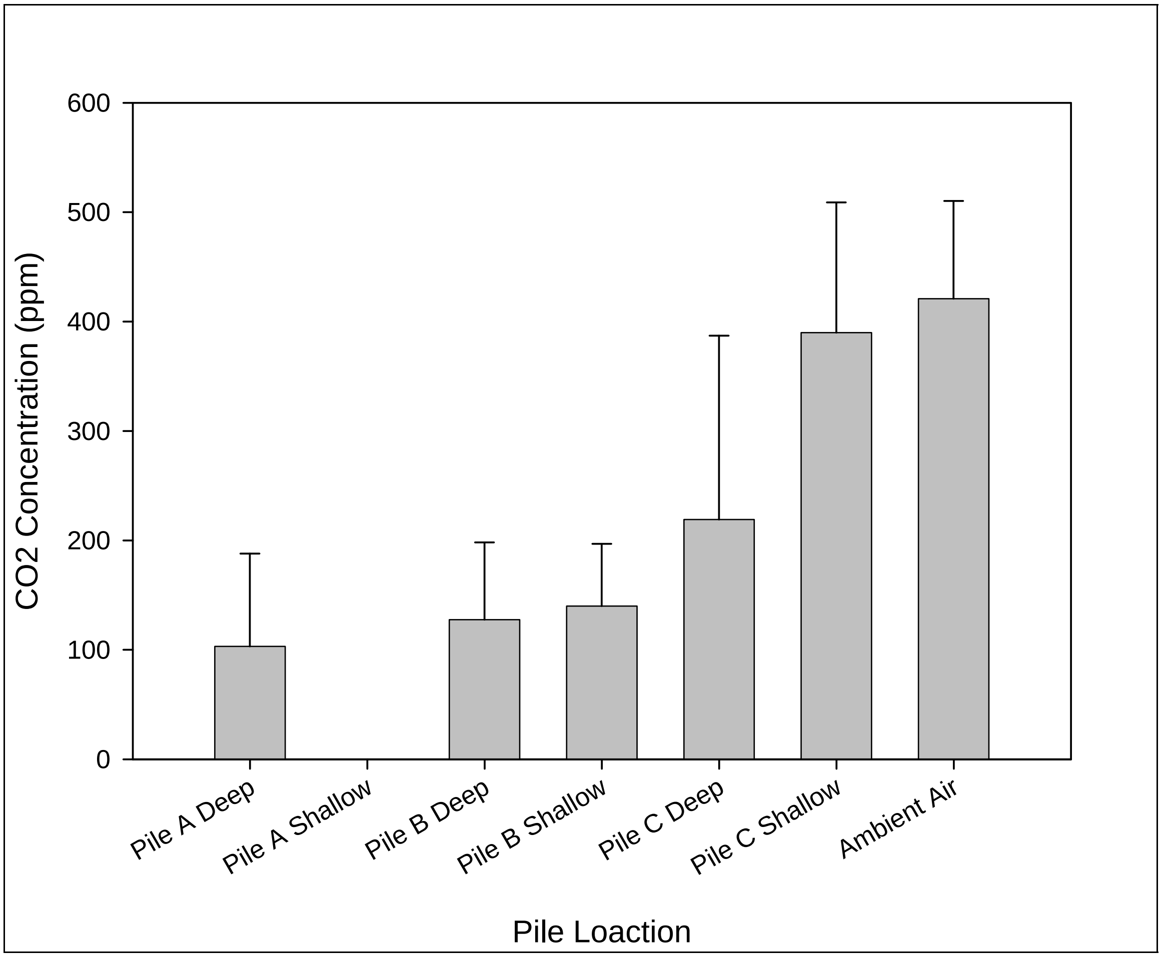

Figure 7.3 – Average Carbon Dioxide Concentrations within Piles A, B,C and the Ambient Air

This data demonstrates that the diffusion tube design in Pile B didn't increase the CO_2 concentration within the passive piles significantly, and therefore the inclusion of a diffusion tube of this design would do little to increase CO_2 concentrations within a berm. Active aeration will have a large effect on the CO_2 concentration within the pile however. It has also been demonstrated that attention should be given to how the vacuum tube is applied to the berm so that air distribution is maximize over the greatest amount of material possible.

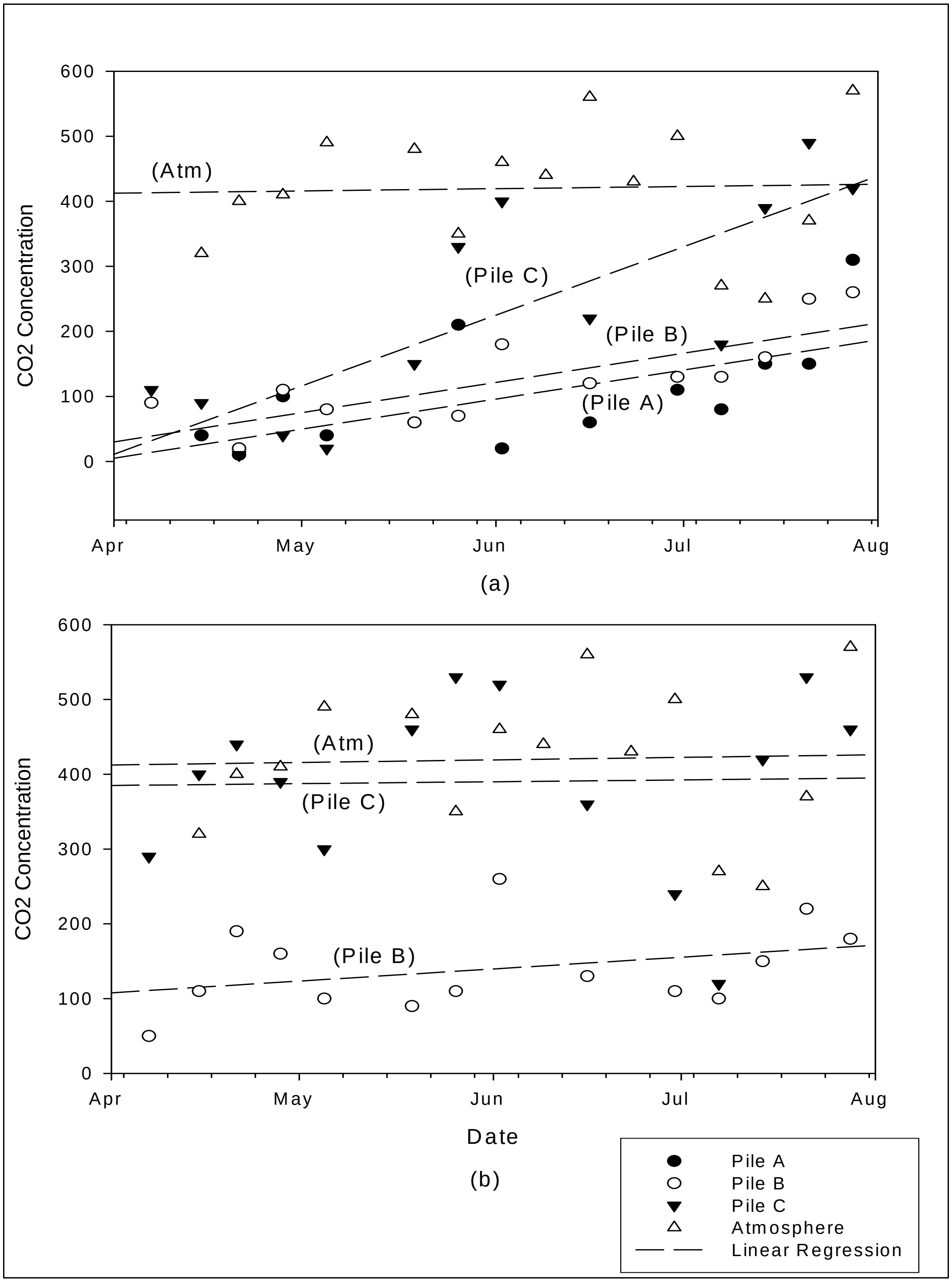

Figure 7.4 – Weekly CO2 Concentrations within Piles A, B and C with Linear Regression

(a) Deep Sampling Location

(b) Shallow Sampling Location

Lastly, active aeration will require power which will need to be generated by traditional or carbon neutral methods. Power generation by the burning of fossil fuels will offset the net carbon that is sequestered through mineralization; an analysis of net carbon sequestration using the active aeration method has not been performed for this project.

Figure 7.4 shows the point concentrations measured at different locations within the piles over a period of four months in the summer of 2006. Linear regression lines were also included in the figure to better display the data and observe the different CO_2 trends between the deep monitoring and shallow monitoring locations. The average concentrations on the pile locations can be observed in Figure 7.4 as they are in Figure 7.3. In addition however an increasing trend in the CO_2 concentration is visible particularly in the deeper location of all three piles. This trend may be due to the large change in the percentage of reactive calcium carbonated during this period. Figure 7.5 compares the carbon dioxide concentrations within the shallow and deep locations of Pile C with the percentage of calcium carbonated in that time period. The figure shows a large change in TGA results between the deep location analyzed in May and October of 2006 correlating with the increasing trend in CO_2 concentration within that same area. Conversely the shallow monitoring location remain fairly consistent in CO_2 concentration over this same time period as does the percentage of calcium that has been carbonated.

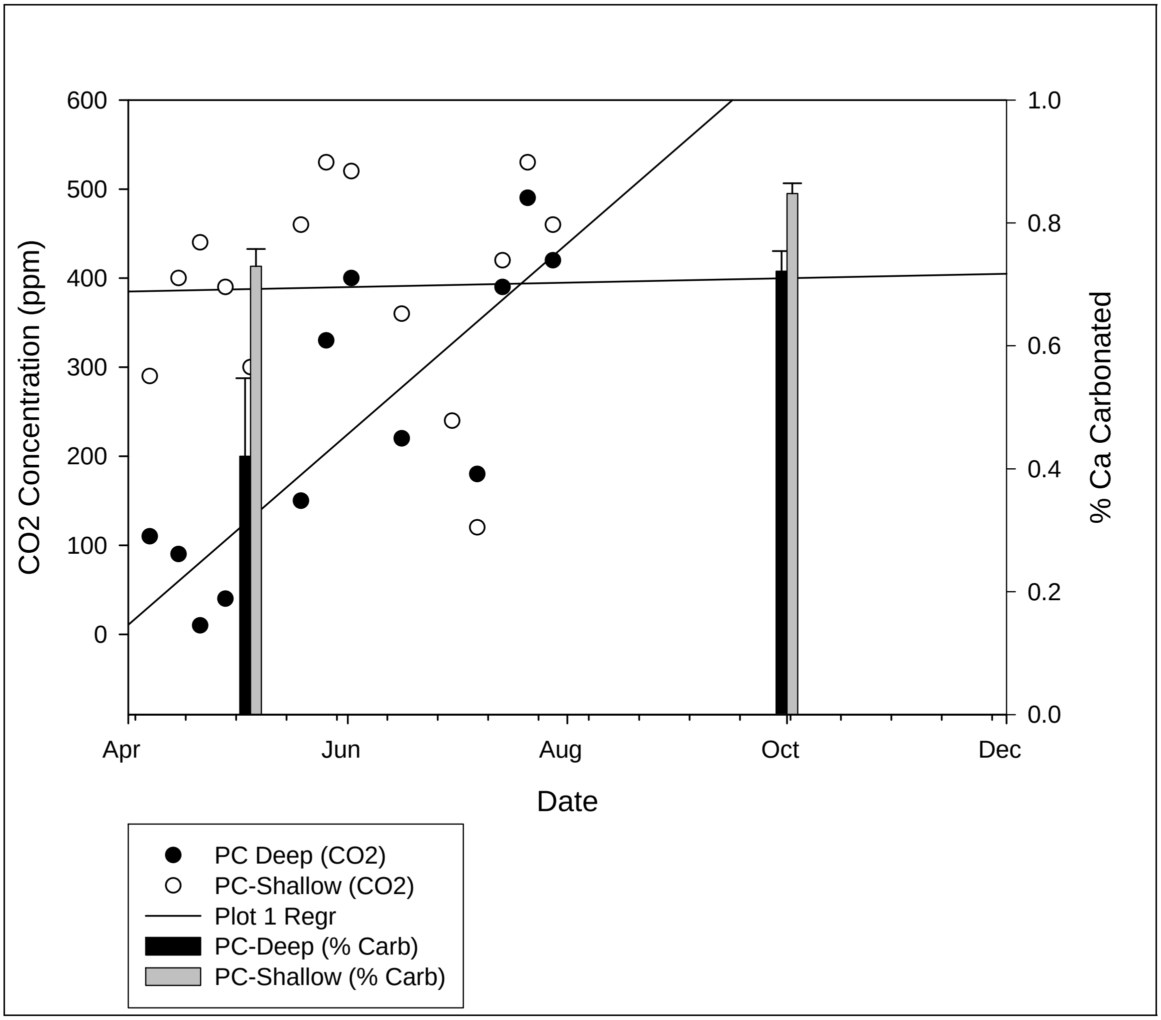

Figure 7.5 - TGA and CO_2 Concentrations of Pile C between April and October of 2006

7.3 Moisture Content

Moisture content (MC)of the recycled concrete was measured by Time Domain Reflectometry (TDR), located in the shallow and deep monitoring locations within the three piles. Continuous data is displayed in Figure 7.6 between the months of September 2005 and November 2005, Pile C was only monitored for a portion of this time due to its late construction. Moisture observations reinforce the carbon dioxide monitoring that was conducted. The shallow monitoring location within Pile C is reported to have a much lower MC than the other locations. This is likely due to the constant vacuum applied to the pile, which will evaporate the moisture off the shallow location where the majority of the airflow is concentrated. The moisture content was relatively consistent between the three piles otherwise, depicted by the bar chart in Figure 7.5. Behavior was similar between the deep and shallow locations of Pile A and B as well.

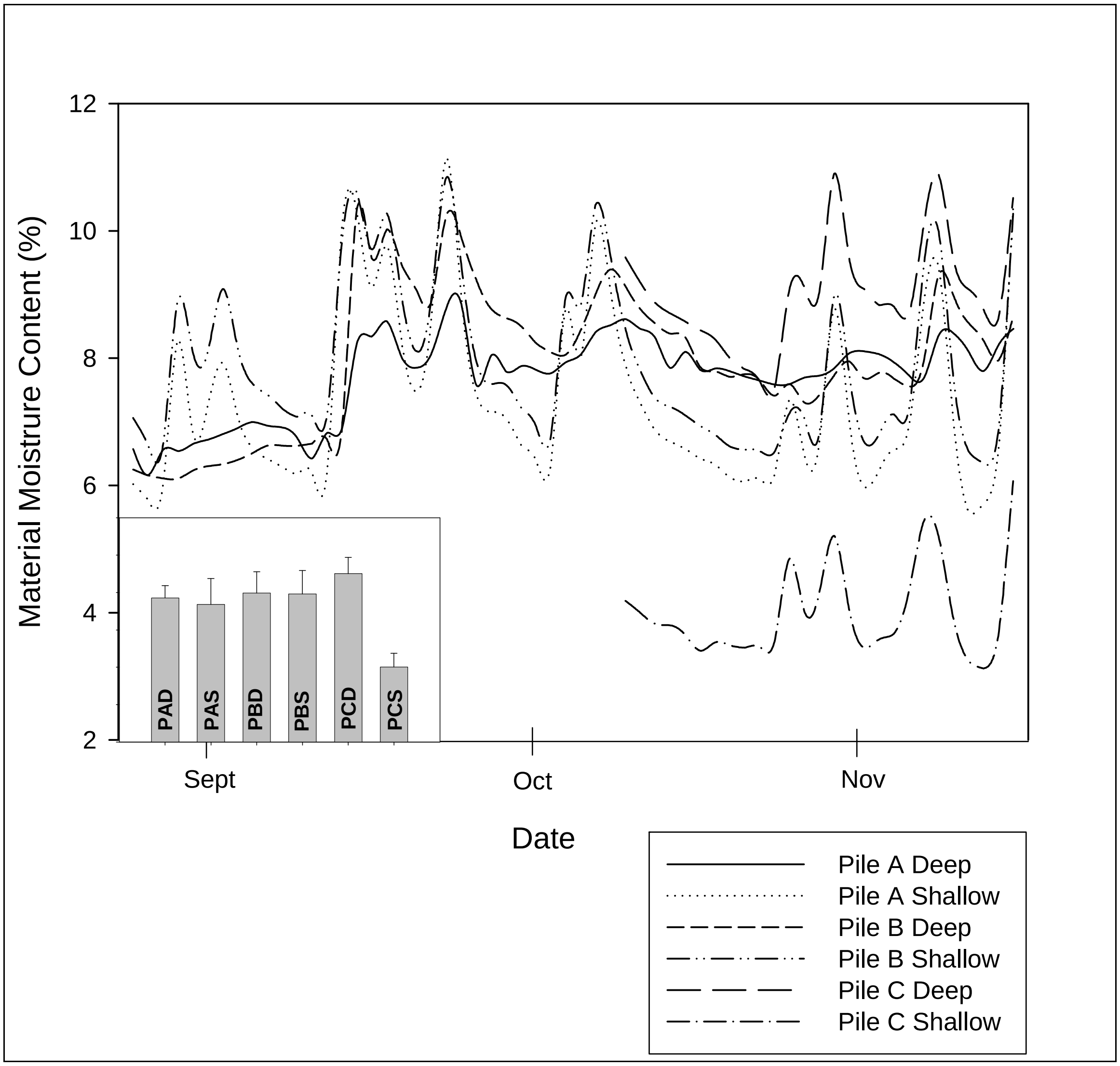

Figure 7.6 – Moisture Content of Piles A,B and C from September to November 2005

A further analysis of the moisture content of Pile A joined with local meteorological data show a correlation between rain events and the moisture peeks of Pile A. In addition to the correlation between precipitation and moisture content, the location of the pile also appears to have an effect on the response to the rain event.

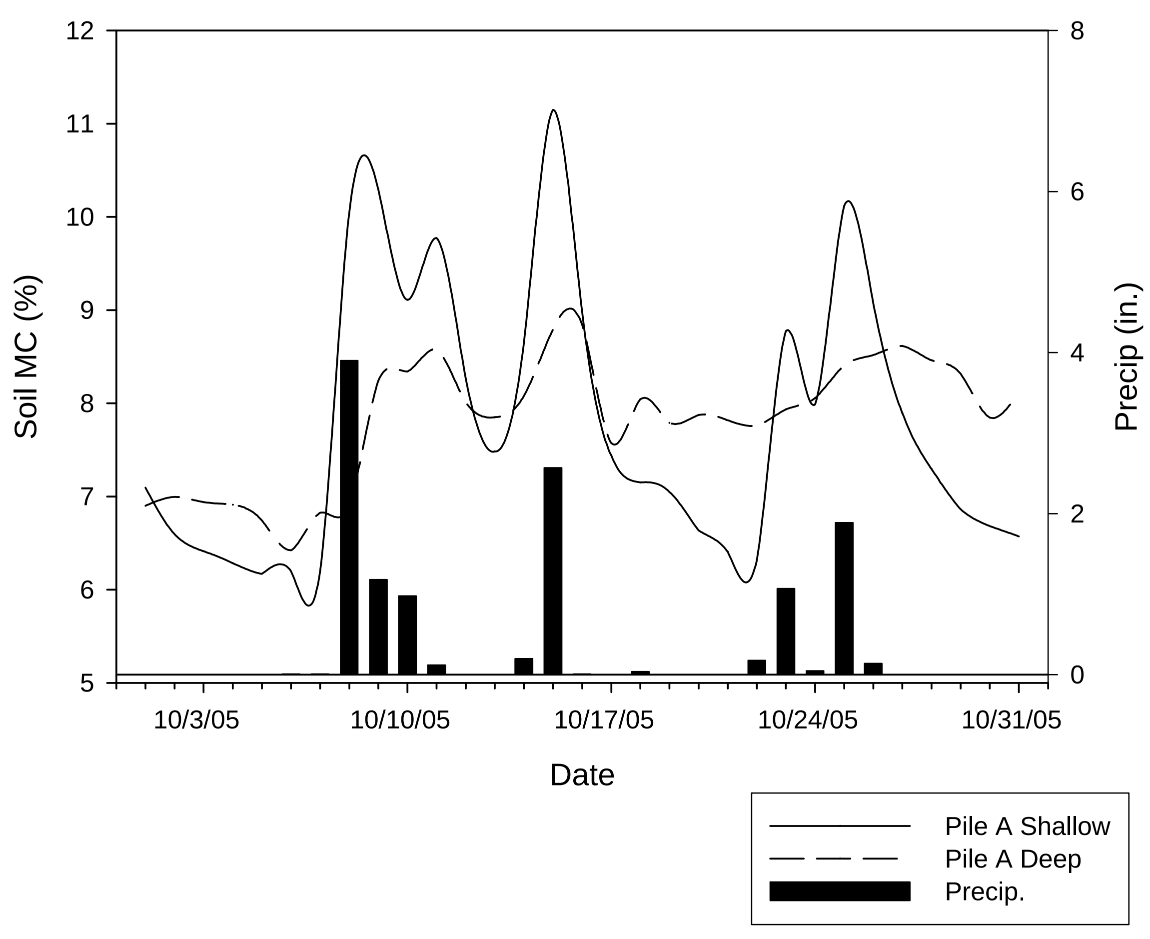

Figure 7.7 – Moisture Content of Pile A in Conjunction with Rain Events between in October, 2005

7.4 Temperature

Temperature measurements were recorded continuously every 30 minutes at the shallow and deep monitoring locations within Piles A, B and C. Measurements for the shallow monitoring location in Pile A are not reported due to equipment malfunction. Figure 7.8 shows the average temperatures in the piles over a four month period in the summer. Temperatures appear to be relatively consistent.

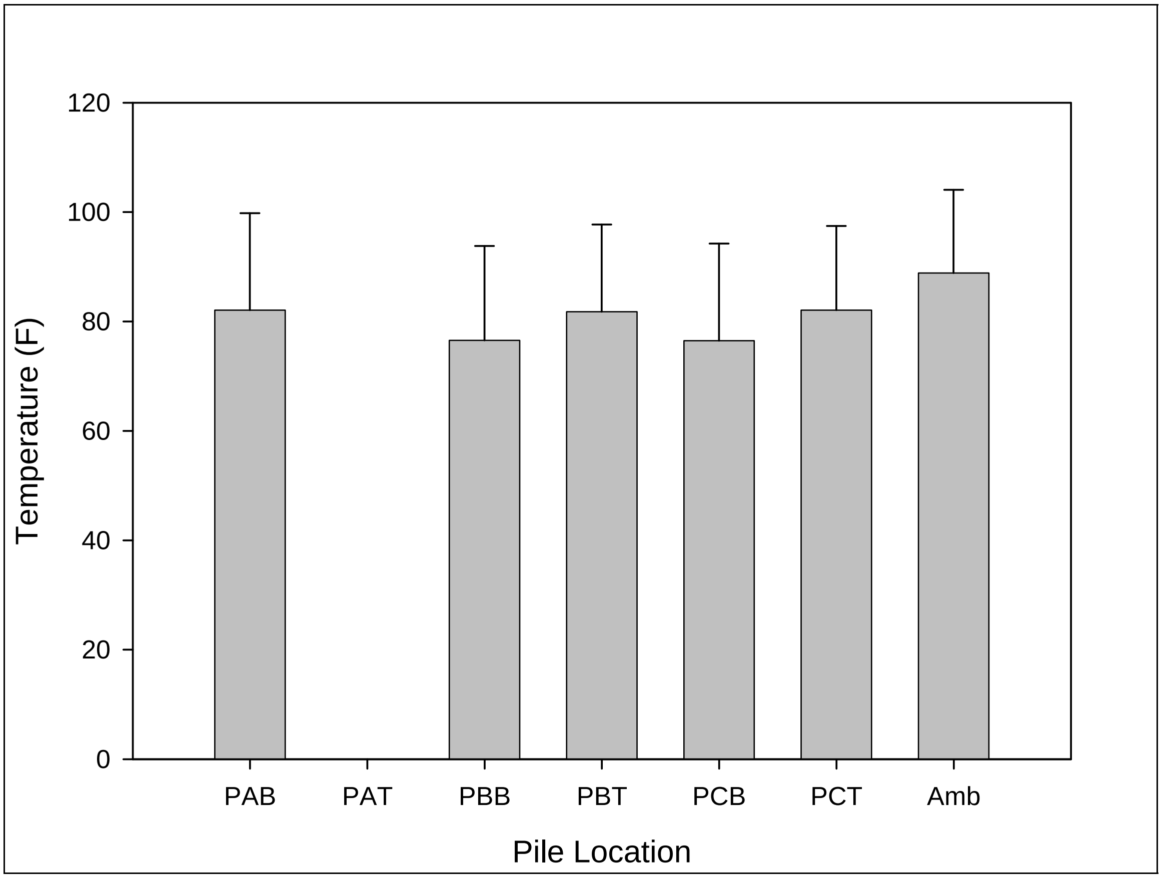

Figure 7.8 – Average Temperature Within Piles A, B and C

References

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IPCC, “AR 4 Report”, Intergovernmental Panel of Climate Change, Working Group I, 2007

Lackner K.S., “A Guide to CO2 Sequestration” Science, Vol 300, # 5626 pp. 1677-1678 June, 2003

Leipold J, “Carbon Sequestration Utilizing Alkaline Waste Materials” Department of Civil Engineering, University of New Hampshire, Durham, NH, not yet published

Appendix A

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THERMAL ANALYSIS LABORATORY

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Customer Name:
Agency/Company: Fisher Gardner
Phone:
Email:
Date of Samples Received: 12/20 /05
Report Date: 12/22/05

ANALYTICAL REPORT (1)

Samples: CFA-7, CKD-17, RCF-49, SLG-RCF

Experimental:

TG-MS Technique:

The samples were analyzed by a TA 2950 TGA interfaced to a Pfeiffer Thermostar Mass Spectrometer by means of a heated capillary transfer line. The samples were heated from room temperature to 1000 °C at a rate of 20 °C/min . The capillary transfer line was heated to 200 °C, and the inlet port on the mass spectrometer was heated to 150 °C. The Thermostar unit is based on a quadrupole design and the mass scan ranged from 0-110 amu. The sample gas from the TGA was ionized at 70eV. The system was operated at a pressure of 1×10^{-5} toor. The experiment took place in a nitrogen gas with flow rate of 60ml/min.

Results and Discussion:

Figure 1: TGA Curve of CFA-7
Figure 2: m/z = 17, 18 MS plot of CFA-7
Figure 3: m/z = 44 MS plot of CFA-7
Figure 4: MS plot of CFA-7
Figure 5: TGA Curve of CKD-17
Figure 6: m/z = 17, 18 MS plot of CKD-17
Figure 7: m/z = 44 MS plot of CKD-17
Figure 8: MS plot of CKD-17
Figure 9: TGA Curve of RCF-49
Figure 10: m/z = 17, 18 MS plot of RCF-49

In the case of CFA-7, there're two weight loss stages in the TGA curve: around 74°C and 575 °C to 700 °C. At the first stage, MS plot showed two peaks: m/z=17 and m/z=18 (Figure 2), which may be the surface water evolved; at the second stage, MS plot showed m/z=44 peak (Figure 3), which may be the CO_2 evolved coming from decomposition of $CaCO_3$.

In the case of CKD-17, there's one obvious weight loss stage in the TGA curve: from 480°C and 800°C and MS plot showed two peaks at the same time: m/z=44 (Figure 7), which may be the CO_2 evolved coming from decomposition of $CaCO_3$. And in the MS plot m/z=17 and m/z=18 (Figure 6)also showed peaks around 60 °C which may be the surface water evolved, and around 245 °C which may be because of releasing of bond water.

In the case of RCF-49, there're two weight loss stages in the TGA curve: around 70°C and 465 °C to 750 °C. At the first stage, MS plot showed two peaks: m/z=17 and m/z=18 (Figure 10), which may be the surface water evolved; at the second stage, MS plot showed m/z=44 peak (Figure 11), which may be the CO_2 evolved coming from decomposition of $CaCO_3$. And after 900 °C, there's still CO_2 coming out from the sample.

In the case of SLG-RCF, there're three weight loss stages in the TGA curve: around 68°C, from 385°C to 460 °C, and 565°C to 700°C. At the first stage, MS plot showed two peaks: m/z=17 and m/z=18 (Figure 14), which may be the surface water evolved; at the second stage, MS plot showed m/z=17 and m/z=18 peaks again, (Figure 14), which may be due to the releasing of bond water; at the third stage, MS plot showed m/z=44 peak (Figure 15), which may be the CO_2 evolved coming from decomposition of $CaCO_3$. And in the MS plot m/z=17 and m/z=18 also showed peaks around 421 °C which may be because of releasing of bond water.

Wei-Ping Pan,
Sumpter Professor of Chemistry

Table 1 Summary of TGA Data

Sample ID	Weight loss, %			Residue, %
	First stage	Second stage	Third stage	
CFA-7	1.27	----	1.55	95.36
CKD-17	----	----	30.04	66.60
RCF-49	0.50	----	7.96	89.39
SLG-RCF	4.26	2.10	1.43	89.32

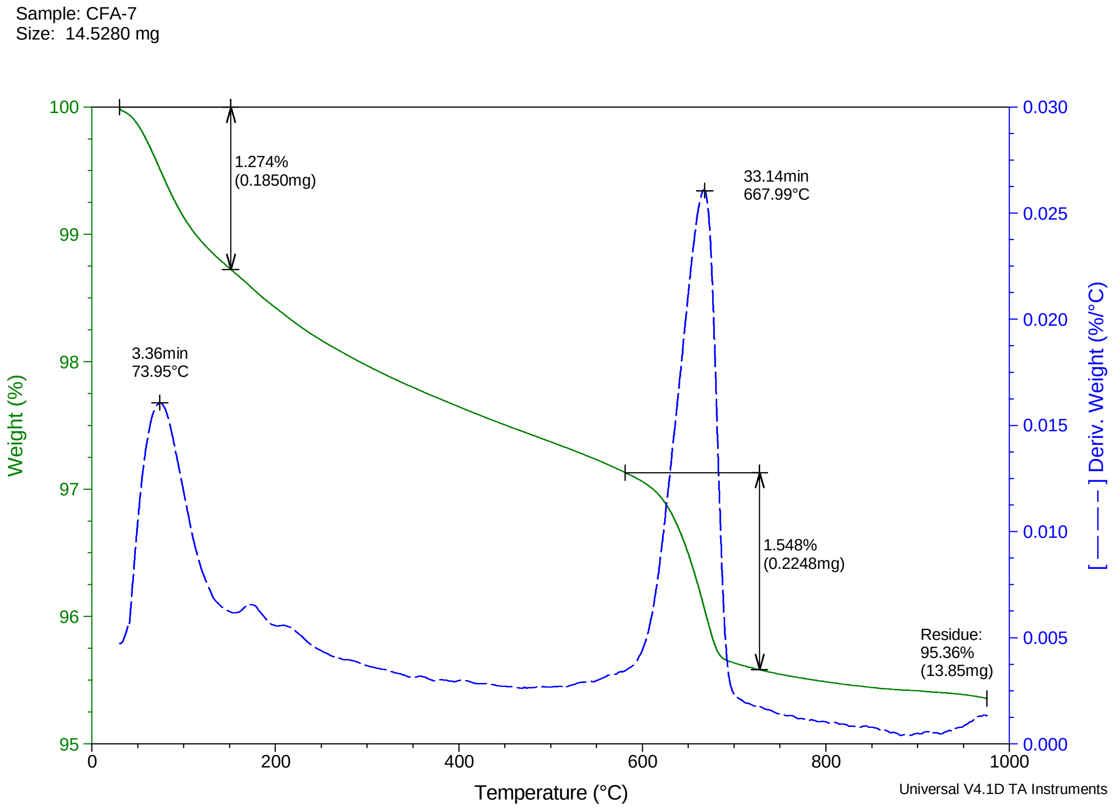
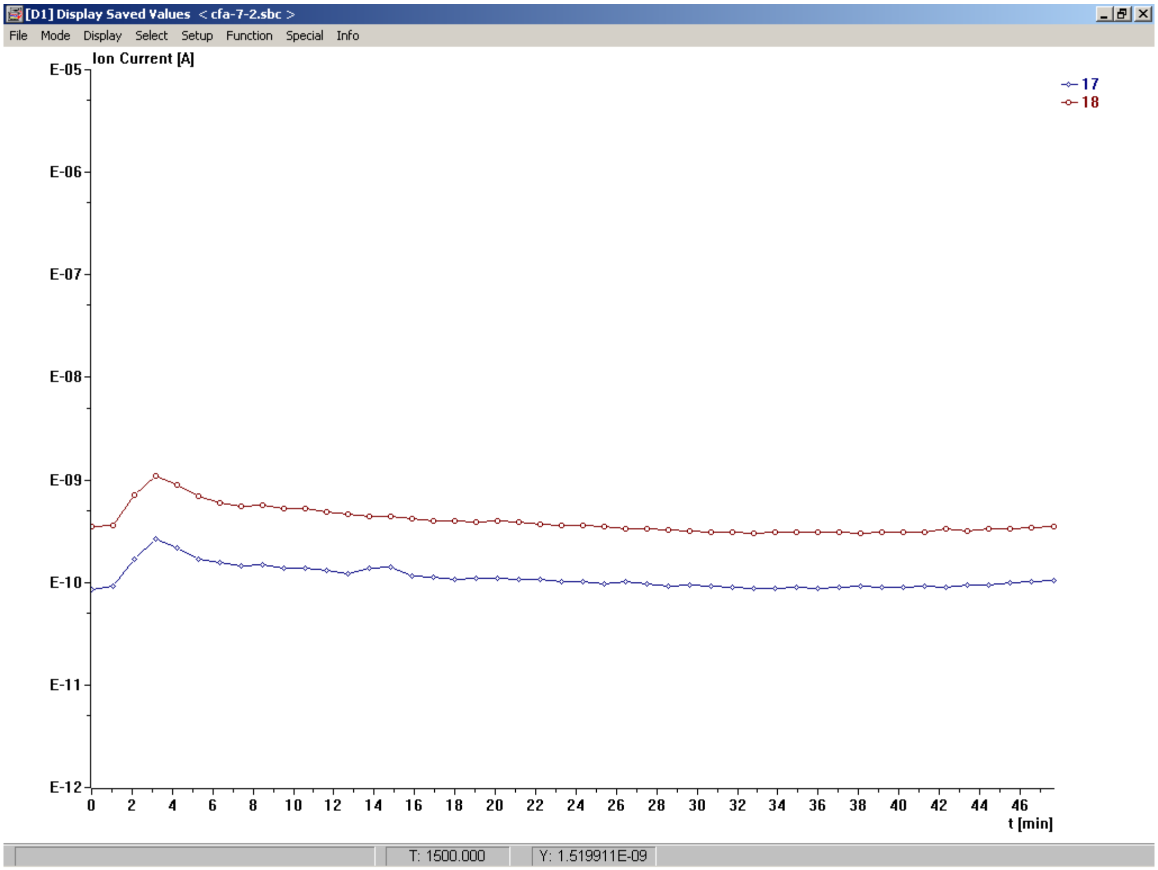


Figure 1 TGA Curve of CFA-7



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Y: 1.519911E-09

Figure 2: m/z=17,18 MS plot of CFA-7

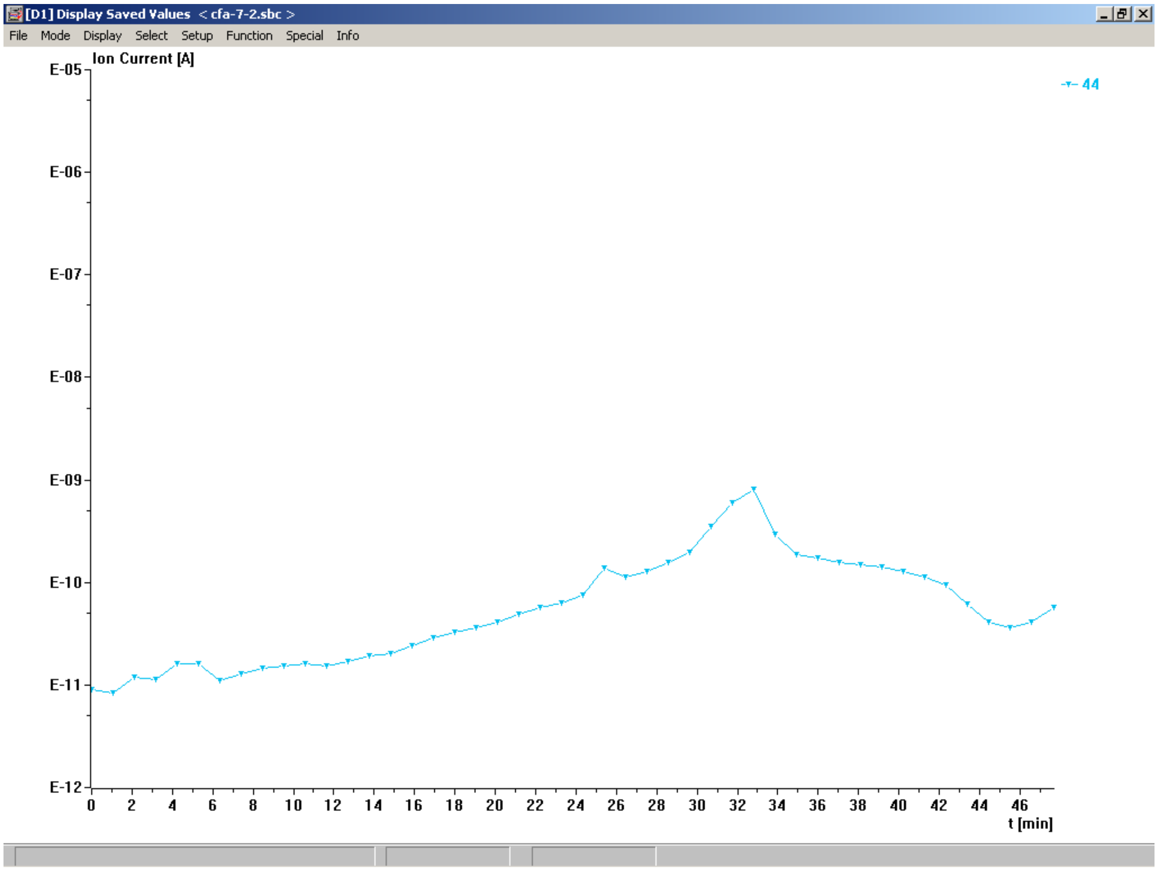

Figure 3: m/z=44 MS plot of CFA-7

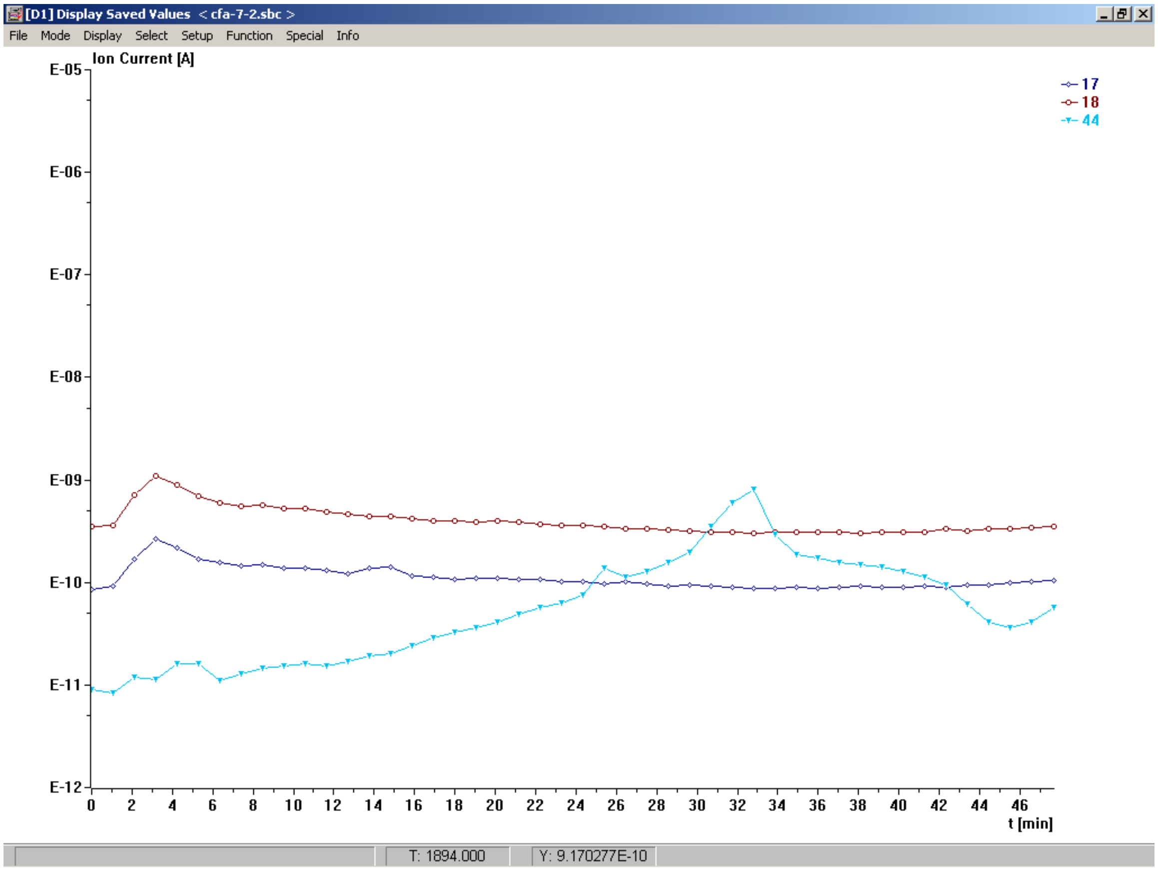

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Figure 4: MS plot of CFA-7

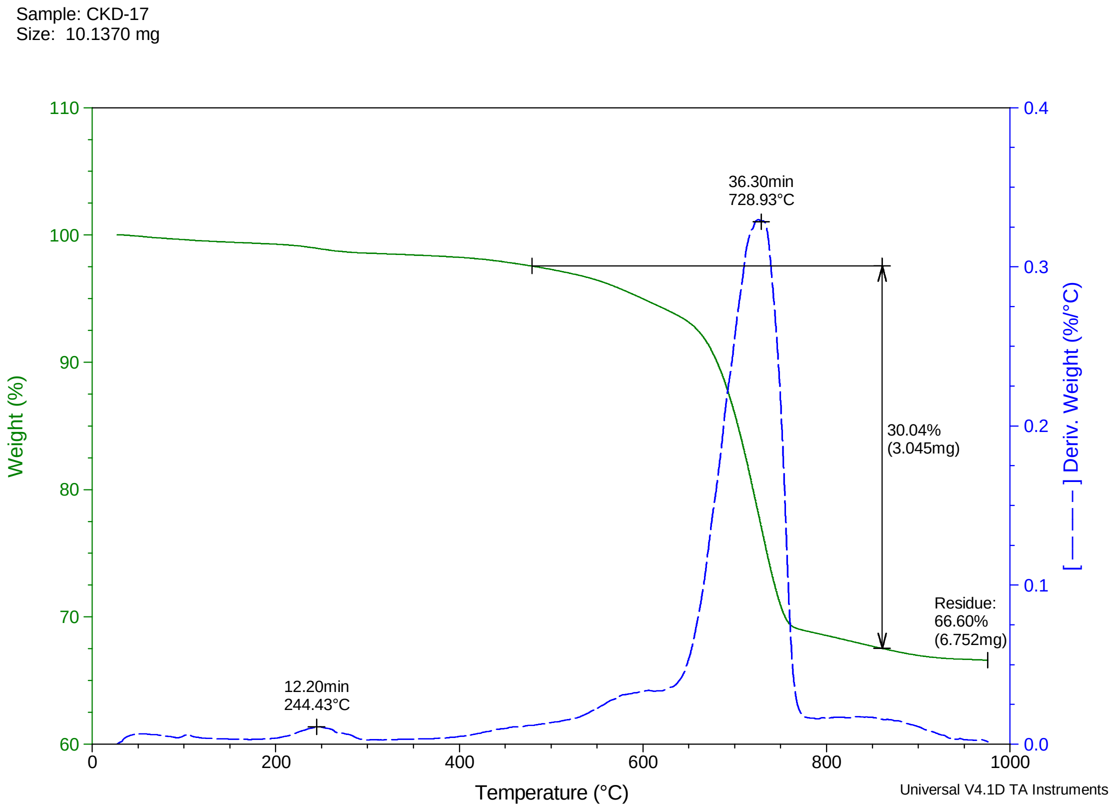

Figure 5 TGA Curve of CKD-17

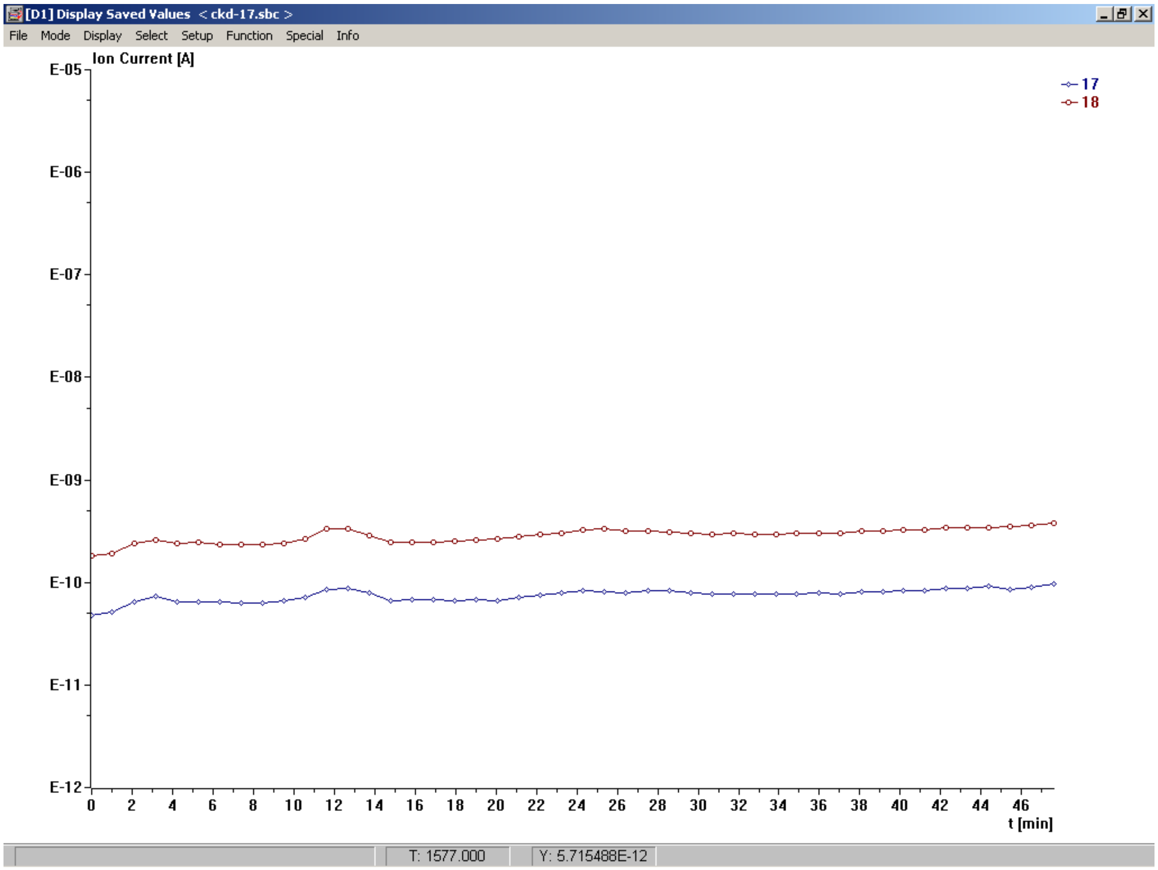

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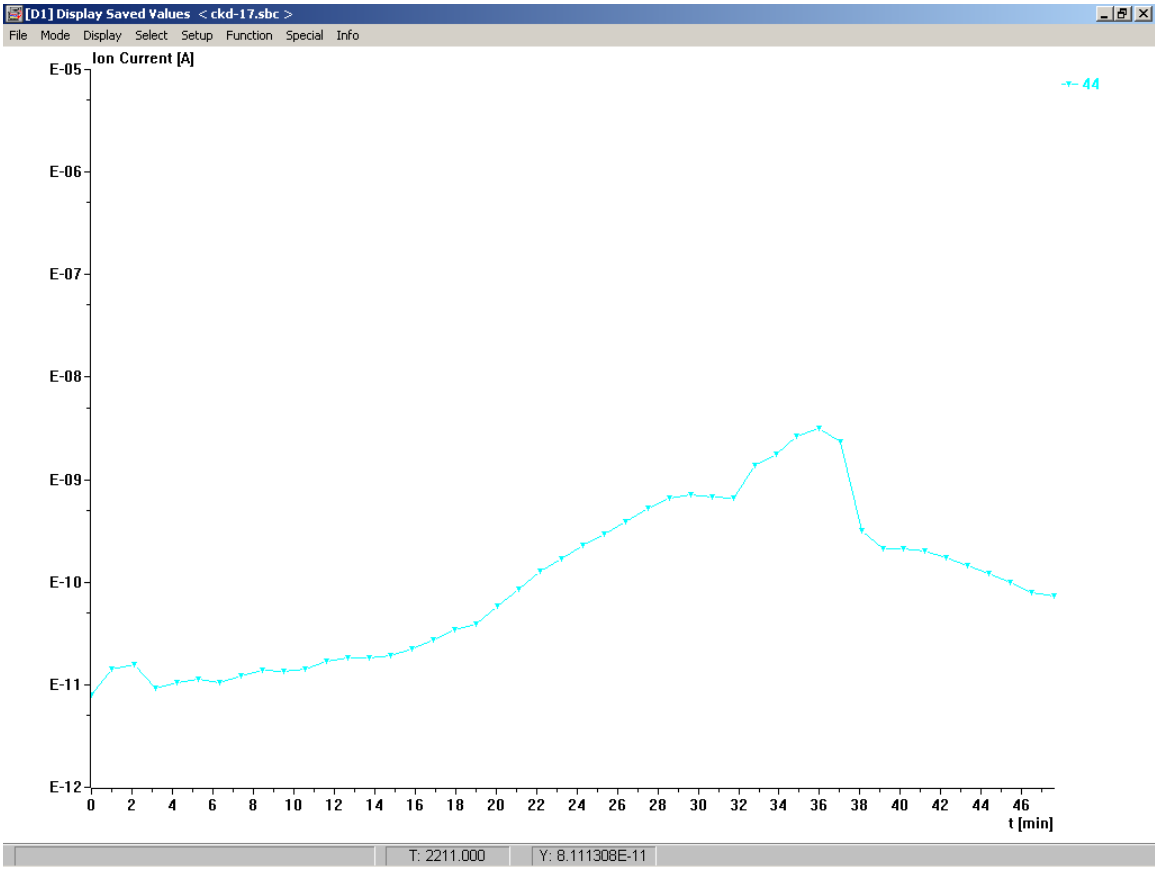
Figure 6: m/z=17,18 MS plot of CKD-17



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Y: 8.111308E-11

Figure 7: m/z=44 MS plot of CKD-17

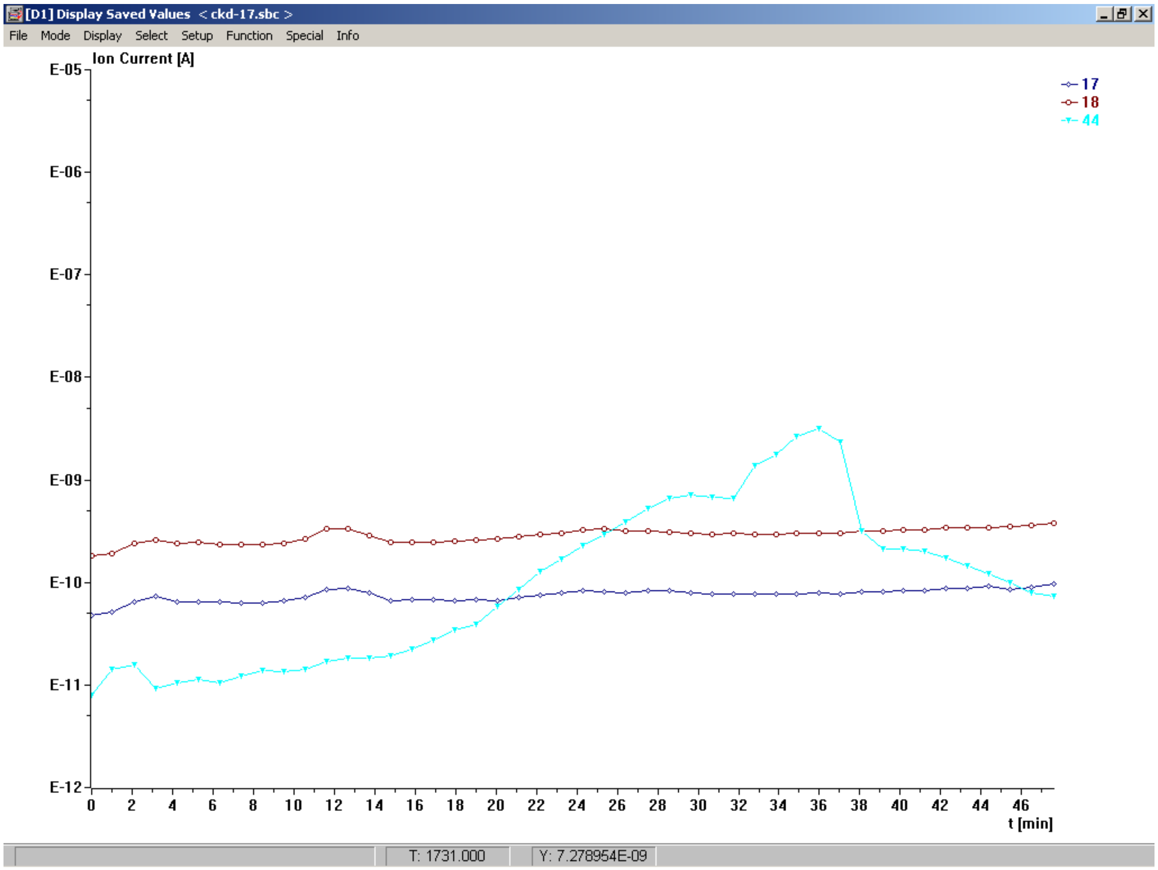

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Figure 8: MS plot of CKD-17

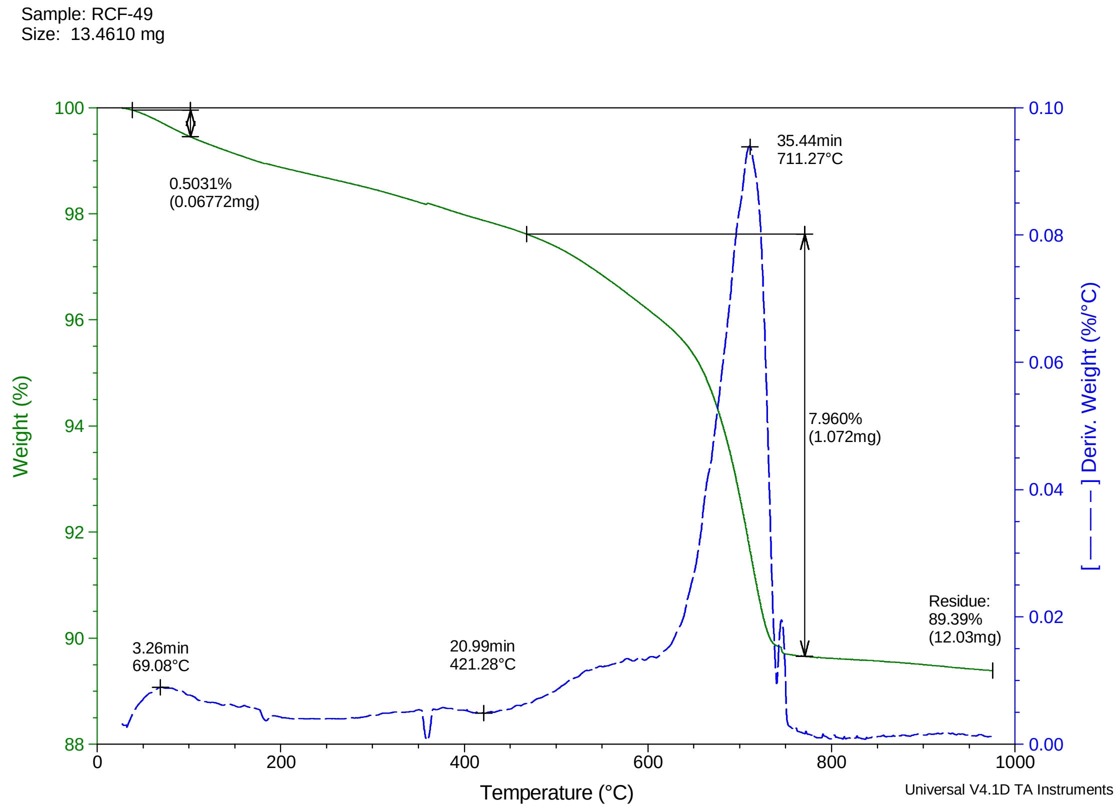
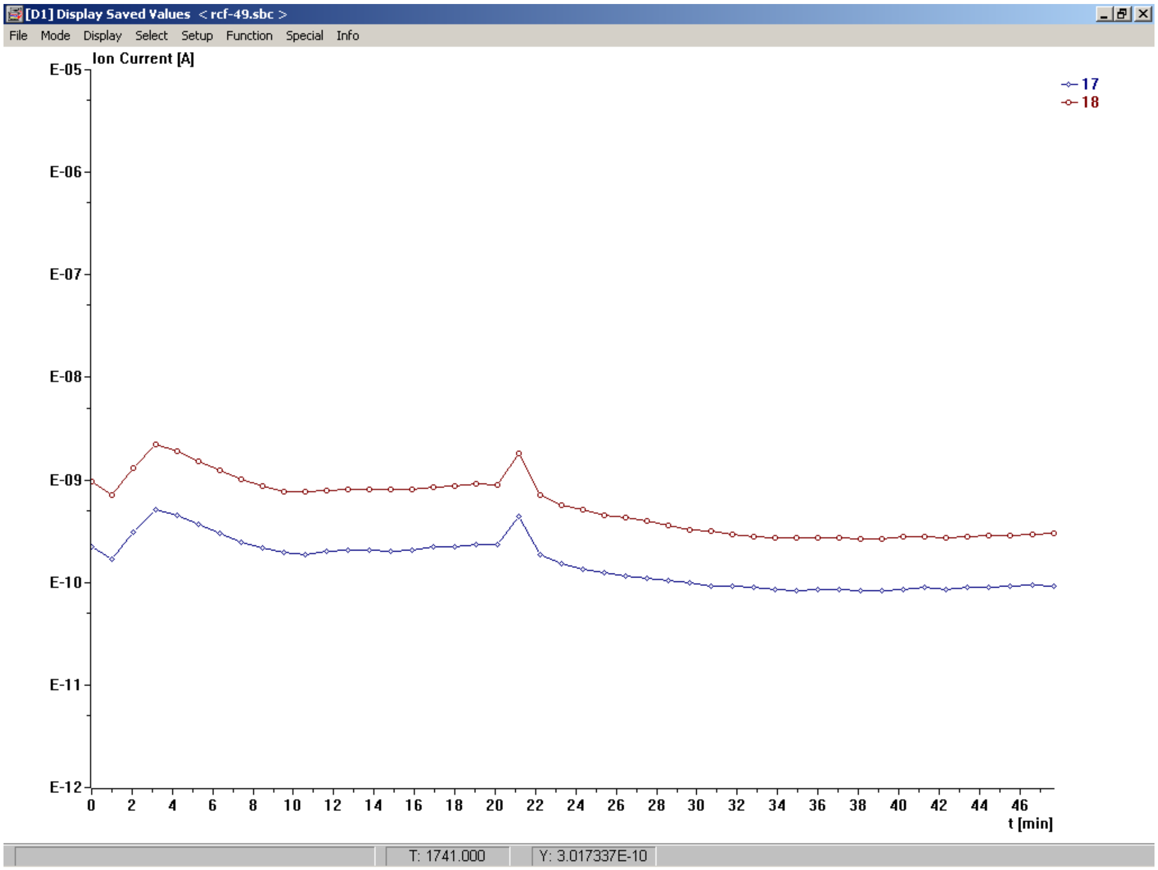


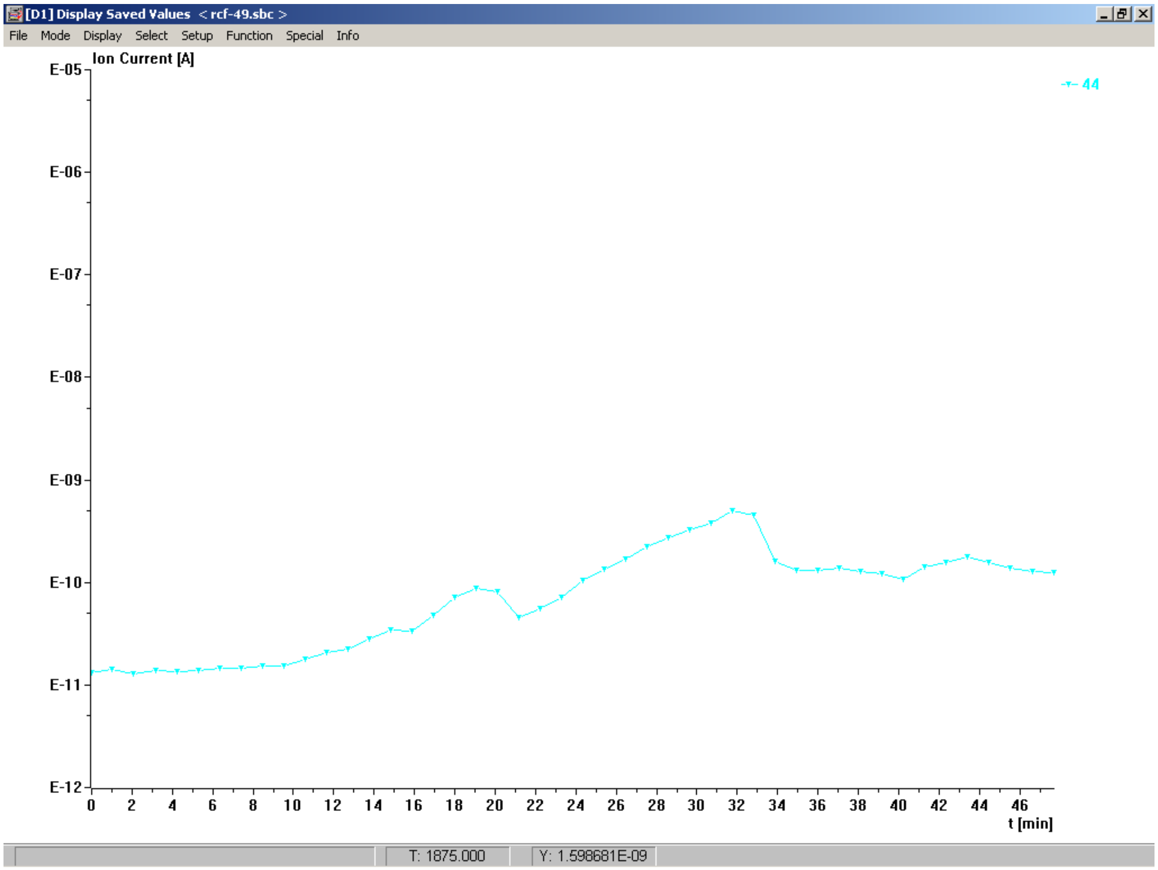
Figure 9 TGA Curve of RCF-49



T: 1741.000

Y: 3.017337E-10

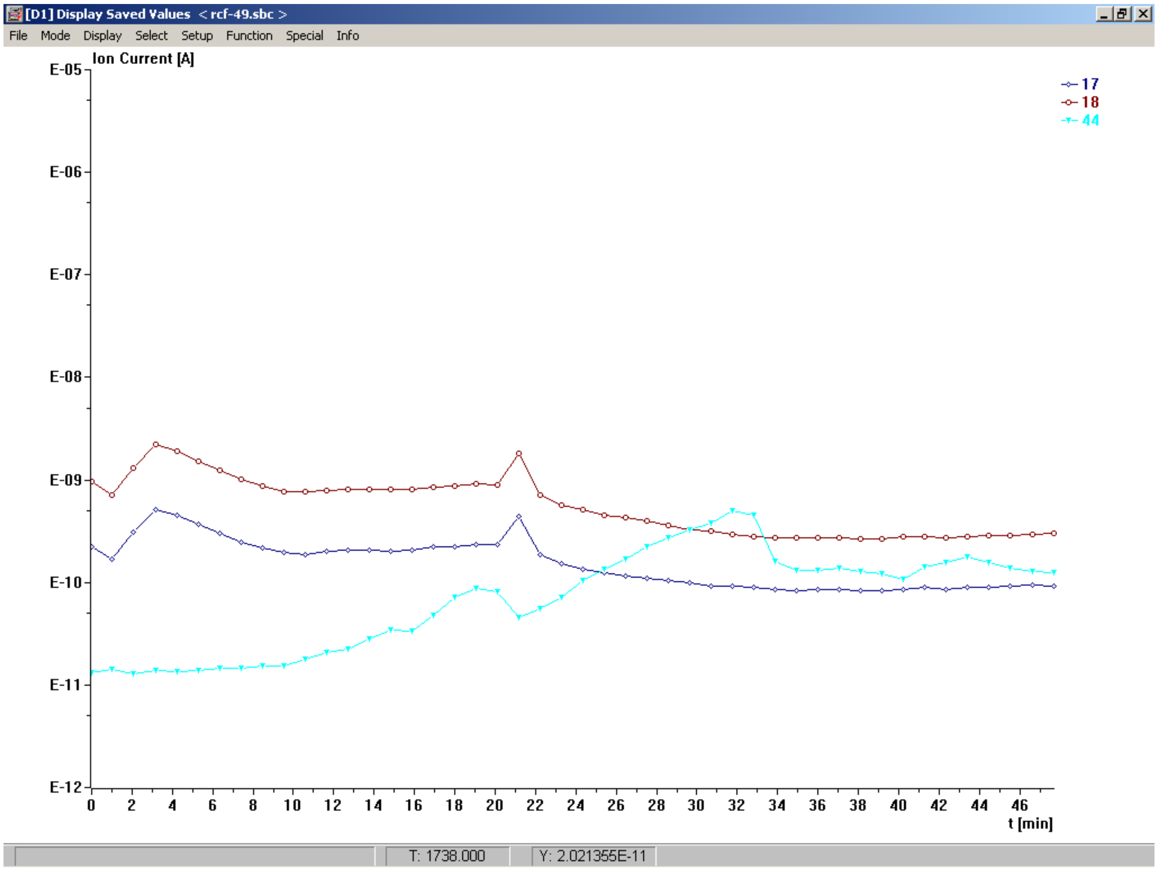
Figure 10: m/z=17,18 MS plot of RCF-49



T: 1875.000

Y: 1.598681E-09

Figure 11: m/z=44 MS plot of RCF-49



T: 1738.000

Y: 2.021355E-11

Figure 12: MS plot of RCF-49

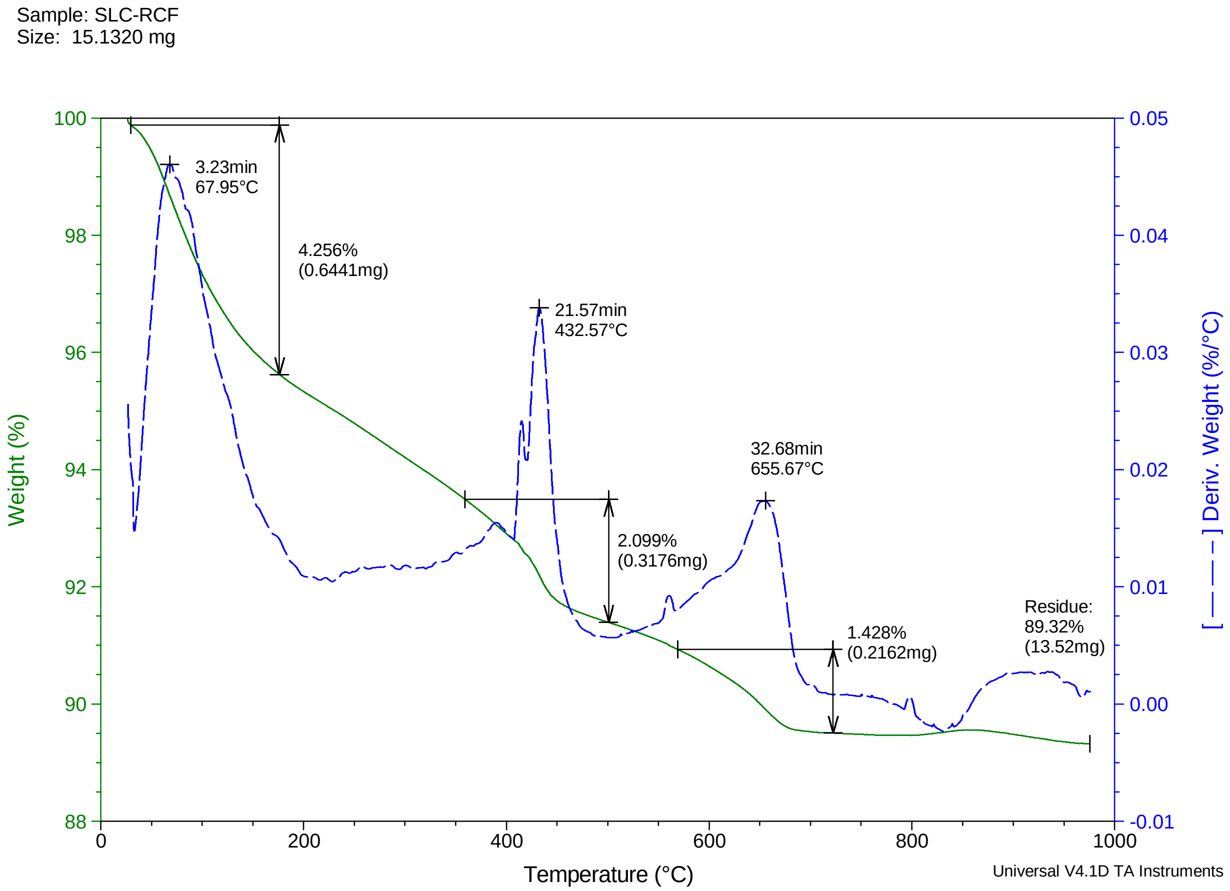


Figure 13 TGA Curve of SLG-RCF

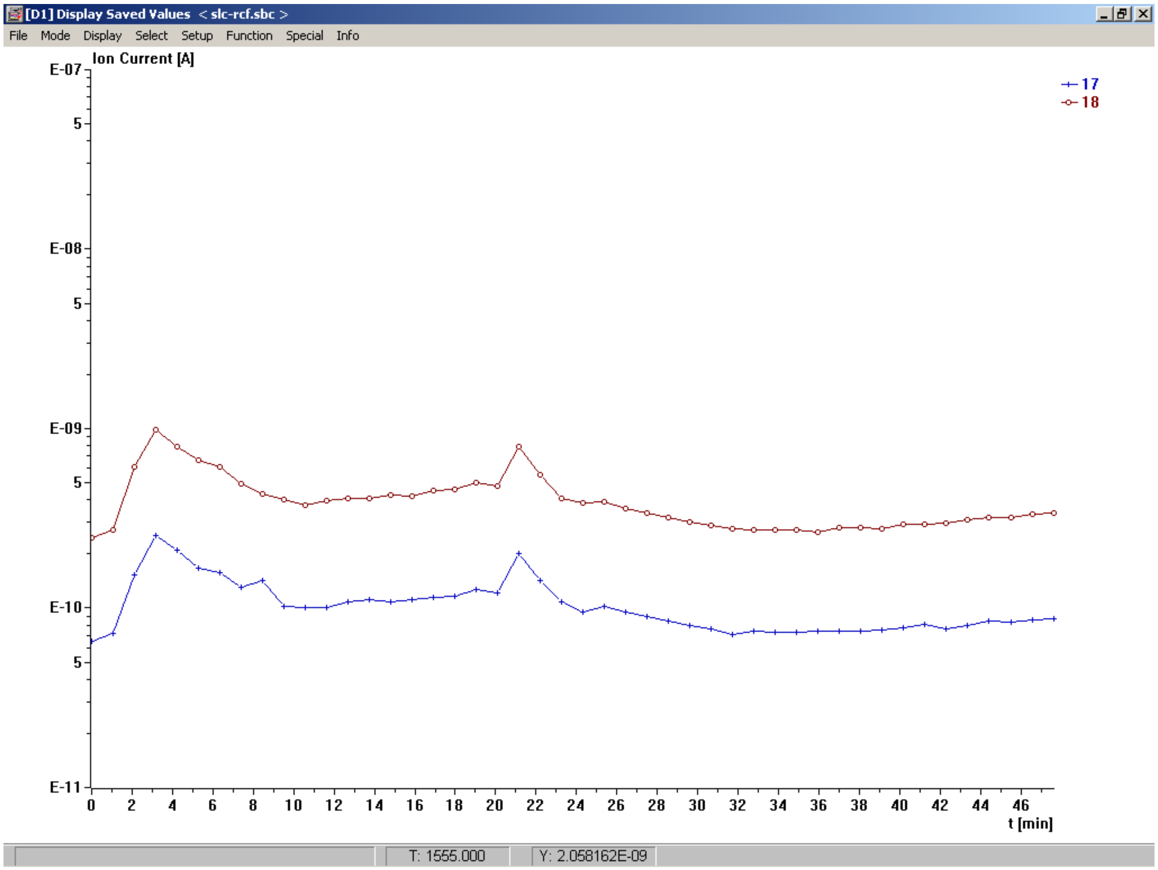
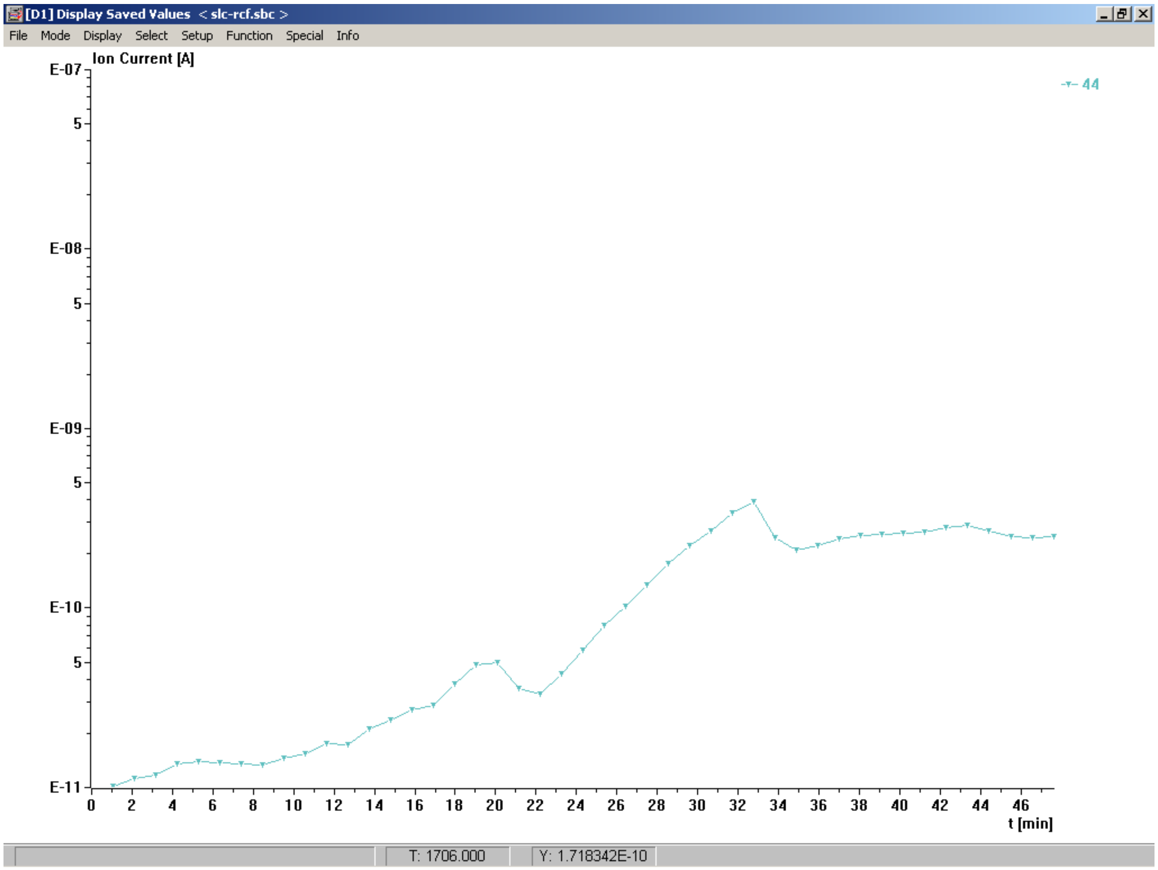


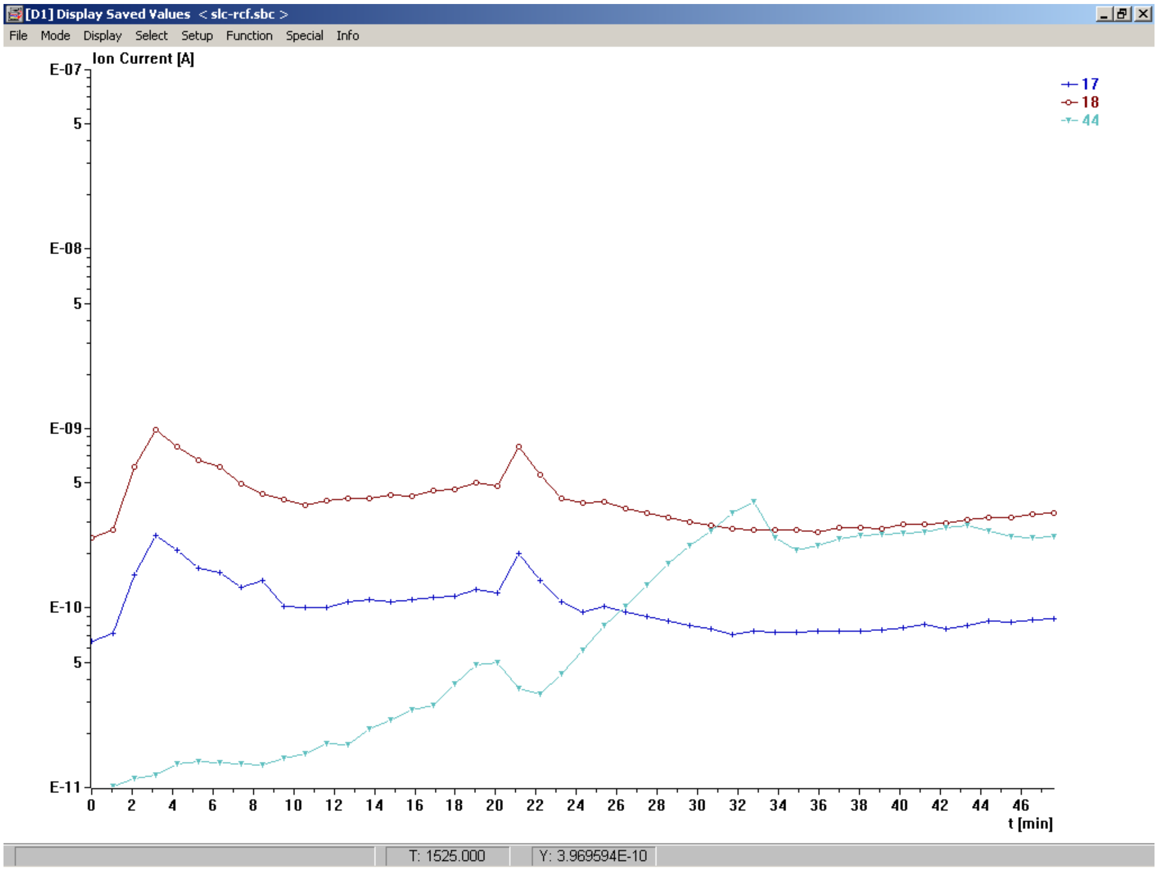
Figure 14: m/z=17,18 MS plot of SLG-RCF



T: 1706.000

Y: 1.718342E-10

Figure 15:m/z=44 MS plot of SLG-RCF



T: 1525.000

Y: 3.969594E-10

Figure 16: MS plot of SLG-RCF