

ABSTRACT

Charcoal Chemistry: Developing a Proxy for Paleofire Regimes

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Wildfires have occurred over geologic time since the evolution of land plants and affect global biogeochemical cycling and ecosystem processes. Charcoal particles in the geological record may contain information on several aspects of paleowildfire regimes. The fire intensity, the energy produced during a fire, is poorly understood for fires that occurred in the past. I propose that the organic chemical composition of charcoal may be used to approximate the fire temperature. To test this, I used ^{13}C nuclear magnetic resonance (NMR) to quantify the carbon bonding environments in charcoal particles derived from specimens burned during a prescribed fire at the Lake Waco Wetland in Waco, Texas. I compared the NMR data for charcoal to fire temperatures measured by thermocouples and was able to predict the temperature within 89°C . The intrinsic relationship between pyrolysis temperature and charcoal structure may allow for a better understanding of past conditions during fires.

Charcoal Chemistry: Developing a Proxy for Paleofire Regimes

by

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A Thesis

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CHAPTER ONE

Introduction

Significance and Overview

Understanding fire regimes is an important part of biogeochemical cycling and ecosystem evolution throughout Earth history. According to recent work of Bond and Keeley et al., 2005, Conedera et al., 2009, and Moritz et al., 2005, the fire regime consists of many measurable controls, feedbacks, and patterns that influence fires in the landscape. Some examples of these factors include fire frequency, severity, seasonality, fuel consumption, spreading pattern, size, and climate (Bond and Keeley, 2005; Moritz et al., 2005; Conedera et al., 2009). The fire intensity, especially in paleowildfires, has been one of the most difficult aspects of the fire regime to understand and quantify because the only remaining evidence of fires in the geologic past is the presence of charcoal in sediments. A better understanding of fire intensities can have broad implications in carbon cycling and storage, biodiversity, and the evolution of fire-dependent biomes, and atmospheric concentrations of O₂ and CO₂ (Bowman et al., 2009). By characterizing the chemical structure of charcoal carbon using solid state Nuclear Magnetic Resonance (NMR) spectroscopy, the proposed study will explore the feasibility of using the chemical information preserved in charcoal to infer fire intensity and ultimately regime conditions.

Literature Review

Fire intensity is described as the amount of energy released during combustion of organic material by Keeley et al., 2009 and has not been accurately quantified nor has a single intensity metric been agreed upon. Some current metrics of fire intensity include fireline intensity (kW m^{-1}), reaction intensity (kW m^{-2}), radiant intensity ($\text{cal cm}^{-2} \text{sec}^{-1}$), convection intensity ($\text{kcal m}^{-2} \text{min}^{-1}$ or kW m^{-2}), and total fire intensity (Byram, 1959; Chandler, 1991; DeBano et al., 1998; Keeley, 2009). Keeley et al., 2009 summarized how fireline intensity is increasingly substituted as a measurement for fire intensity, but noted that fireline intensity has a weak correlation with maximum temperature and heating duration achieved by the fire. A common metric of fire intensity has also been temperature. Temperature is a measure of the instantaneous kinetic energy present in a given substance. However, neither of the discussed methods can be used to quantify the amount of heat released in past fires where the only remaining information about the fire is that which is recorded in partially combusted organic matter called charcoal.

As temperature increases, the charcoal carbon (C) or pyrogenic C (PyC) chemistry is altered toward increasingly aromatic structures (Preston and Schmidt, 2006). It has been observed that the oxygen limited thermal degradation, or pyrolysis, of plant cell-wall polymers (e.g., cellulose, and lignin) undergo chemical dehydration and condensation reactions resulting in the formation of polyaromatic structures when above 250°C (Boon et al., 1994; Sharma et al., 2004). At temperatures between 400°C and 500°C , new fused ring systems were produced in the pyrolysis of lignin (Sharma et al., 2004). A study of wood pyrolysis by Czimeczik et al., 2002 showed that small clusters or aromatic rings, lacking a high proportion of graphitic characteristics, were evident in

black carbon (BC) formed below 500°C. Freitas et al., 1999 used NMR spectroscopy data to demonstrate that peat heated at temperatures between 800°C and 1000°C showed well-defined aromatic structures in parallel arrangement similar to graphitic planes. Recently, researchers using ¹³C NMR analyses have found that PyC includes a continuum of thermally altered materials from low temperature partially charred (200-400°C) plant biomass containing small clusters of an estimated 2-3 aromatic rings to increasing aromatic cluster sizes in the high-temperature charcoals (400-700°C) made of an extended network of aromatic rings clustered in groups of about 4-13 aromatic rings (Preston and Schmidt, 2006; Knicker, 2007; McBeath et al., 2011). Aromatic structures from wildfire PyC have been identified as quite prevalent in organic matter from soils, sediments, and rock extracts (Masiello, 2004; Preston and Schmidt, 2006; Knicker et al., 2008; Marynowski and Simoneit, 2009).

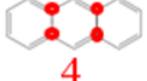
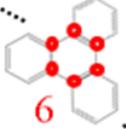
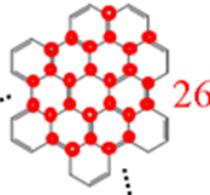
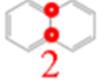
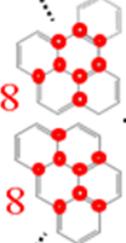
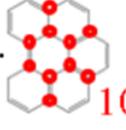
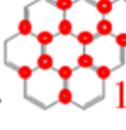
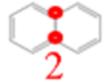
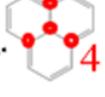
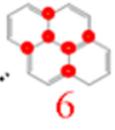
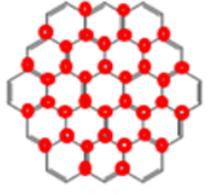
Along with PyC, Polycyclic Aromatic Hydrocarbons (PAHs) are comprised of fused aromatic rings (2-7), which can be used to identify the occurrence of wildfires (Preston and Schmidt, 2006; Marynowski and Simoneit, 2009). The production of PAHs occurs simultaneously with PyC, but are formed in the gas phase during combustion by the combination of two-carbon ions or radicals in the volatiles and are emitted with the smoke plume in close association with soot particles (Masiello, 2004; Preston and Schmidt, 2006). For example, the high-PAH concentrations in the Soltykow exposure of Poland have been interpreted as an indicator of high temperature fires (Marynowski and Simoneit, 2009). It is evident from PyC and PAHs that the aromaticity of a sample is the result of pyrolytic heating and that the number of clustered aromatic rings increases with temperature. Therefore, determining the cluster size of the aromatic ring system may

provide useful information about the thermal degradation of the vegetation, i.e. fire intensity, present during the associated fire regime.

Relationship Between Charcoal Aromaticity and Chemistry

PyC and PAHs are commonly composed of combinations of 6-carbon rings known as the benzene ring (Solum et al., 1989; Preston and Schmidt, 2006; Bourke et al., 2007; Knicker, 2007; McBeath et al., 2011). As these benzene rings fuse together, specific ring linkages or catenations will provide specific ring structures (Table 1). Solum et al., 1989 identified two catenations (primary and circular) as the structural limits of ring catenations and all other arrangements were described as a combination of circular and linear (primary) catenations (Table 1; Figure 1). Table 1 is based upon the catenation models proposed by Solum et al., 1989 and the temperature ranges at which these catenations are likely to form from published values previously discussed by Preston and Schmidt, 2006, Knicker, 2007, and McBeath et al., 2011. The primary catenation includes linear structures represented by a chemistry of $C_{4n+2}H_{2n+4}$ while the circular catenation structures are represented by a chemistry of $C_{6n}^2H_{6n}$ (Solum et al., 1989). With an increasing number of aromatic rings fused into a cluster, the number of shared carbon atoms between neighboring aromatic rings also increases. The shared aromatic carbons located at the junction between two or three aromatic rings are termed “bridgehead” carbons. The location (red dots) and number of bridgehead carbons per catenation structure (red text) are provided in Table 1.

Table 1. Bridgehead carbons (red) as they relate to PyC and PAH catenation structures (adapted from Solum et al., 1989).

Catenation Model ^a	Temperature Range (°C) ^b				
	≤ 250	250 – 400	400 – 500	500 – 700	700 ≤
	≤ 1	2 – 3	4 – 7	8 – 13	14 ≤
Primary	 0	 2	 4	 6	 26
Combined	 0	 2	 8	 10	 14
Circular	 0	 2	 4	 6	 36

^aCatenation Models from Solum et al., 1989 and McBeath et al., 2011 Supplementary info

^bTemperature ranges and # of Aromatic Rings are based off data from Preston and Schmidt 2006, Knicker 2007, and McBeath et al. 2011

Assuming that the clusters of aromatic carbon atoms in charcoal are composed primarily of the benzene rings shown in Table 1, the relative abundance of bridgehead carbons to total sample carbon, or the mole fraction bridgehead carbon, increases logarithmically with the number of aromatic carbons per cluster (Equation 1; Figure 1; Solum et al., 1989). Equation 1 from Solum et al., 1989 demonstrates this relationship.

$$X_b = 1 - \sqrt{6}/\sqrt{C} \quad (1)$$

This is the equation representing the circular catenation type of carbon clusters and the upper dashed curve in Figure 1 from Solum et al., 1989. The amount of bridgehead carbons can be identified in charcoal using ^{13}C NMR spectroscopy as described in detail in the methods section.

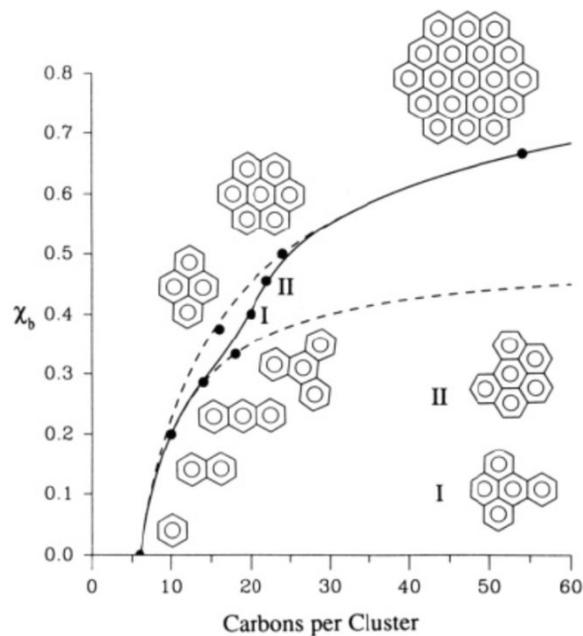


Figure 1. Relationship between the mole fraction bridgehead carbons (X_b) and the number of carbons per cluster (Figure from Solum et al., 1989). The solid line is the combined model of the two catenations while dashed lines indicate circular and primary catenations.

The use of NMR spectroscopy to quantify bridgehead carbons should allow for the identification of formation temperatures in charcoals and provide a means to investigate the nature of the relationship between charcoal formation temperature and the number of aromatic carbons per cluster (referred to as C/C here after).

¹³C NMR Spectroscopy of Charcoal

Basic concepts for the use of ¹³C NMR spectroscopy of charcoal are introduced here and are elaborated further in the Methods section. The ¹³C NMR spectrometer measures the charcoal carbon structure and degree of aromatic ring catenation by measuring the resonance frequencies of ¹³C in an electromagnetic field. A shift in the electromagnetic resonance frequency is produced by carbon nuclei in different chemical bonding environments, denoted as the chemical shift. These chemical bonding environments or carbon functional groups can be identified based upon a specific range of chemical shift values, which are displayed in parts-per-million along the x-axis of the ¹³C NMR spectrum. As an example of the possible differences in fresh (not pyrolyzed) biomass and charcoal, Figure 2A represents a spectrum of fresh Willow biomass while Figure 2B represents Willow biomass pyrolyzed at 500°C. The height of the peaks along the y-axis, or intensity of these peaks, indicates relative amounts of each carbon functional group found in the sample. Figure 2A has a greater intensity at about 70 ppm than any other region while the greatest intensity in Figure 2B is at 130 ppm. The peak area of these signals on the spectrum, identified by integration, can provide the relative proportions of each carbon functional group in the charcoal sample (Brewer, 2010; Figure 2A-B). By using a spectral editing technique called dipolar dephasing (DDMAS),

followed by a three-step integration strategy outlined in Brewer, (2010), the mole fraction bridgehead carbons (grey line in Figure 2B) can be quantified (see Methods).

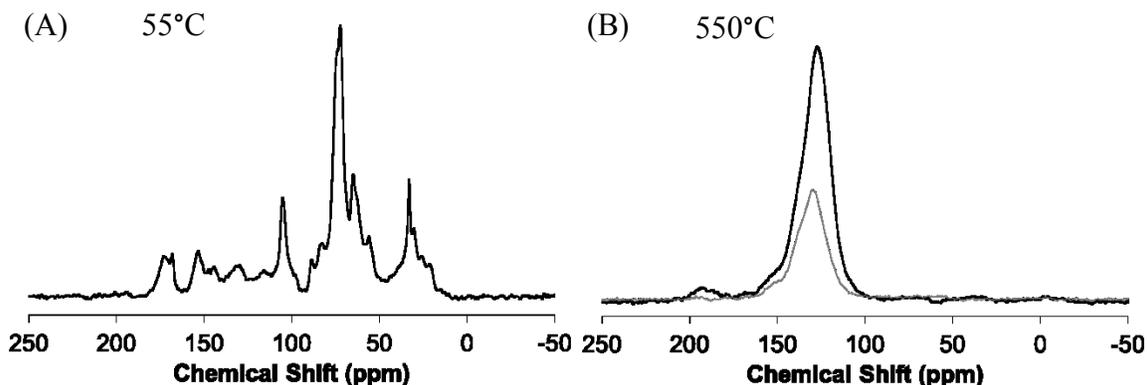


Figure 2. Examples of ^{13}C NMR spectrum. (A), dry fresh Willow sample spectra; (B), Willow pyrolyzed at 550°C (black) and with DDMAS (grey).

Basis for a Lab Charcoal Thermometer using ^{13}C NMR

Based on previously discussed information on X_b , Equation 1, and ^{13}C NMR spectroscopy, Hockaday et al., (*in prep*) analyzed charcoals produced by pyrolysis in a muffle furnace to calibrate a lab charcoal thermometer using the ^{13}C NMR spectroscopy technique. The pyrolysis of biomass is an oxygen-limited reaction capable of producing larger quantities of charcoal as oxygen is minimized. Concomitantly, combustion is when oxygen is abundant and will oxidize and volatilize organic matter leaving only mineral ash (Browne et al., 1963; Tang and Eickner, 1968). To accomplish adequate charcoal formation by pyrolysis in a laboratory setting, pulverized plant biomass was placed in a stainless steel crucible and covered with a loose-fitting lid, to permit the escape of gases. The entire crucible was then placed near the bottom of a stainless steel bucket and buried with sand to restrict the diffusion of oxygen, while allowing gases to

escape. Temperatures ranging from 250°C to 600°C at 50°C intervals were used. Charcoals were heated at a rate of 5°C per minute, and held at the maximum heating temperature (250 to 600°C) for 4 hours and allowed to cool to room temperature before removing them from the muffle furnace. Hockaday et al., (*in prep*) produced 13 charcoal samples from 5 different biomass sources, including: woody tissues (*Malus domestica*, *Prosipis glandulosa*, and *Carya illinoensis*) leaf tissues (*Pinus resinosa*, *Magnolia grandiflora*), and grass tissue (*Zea mays*). These calibration charcoals were pulverized to a fine powder and analyzed by ¹³C NMR spectroscopy for X_b and C/C values.

Bridgehead carbons identified by ¹³C NMR and represented as the mole fraction of bridgehead carbon (X_b) for each of the calibration samples were plotted against the pyrolysis temperature (°C) of formation in Figure 3 by Hockaday et al., *in prep*. A strong linear correlation ($r^2 = 0.96$) and significance ($p = 0.0001$) were achieved (Figure 3).

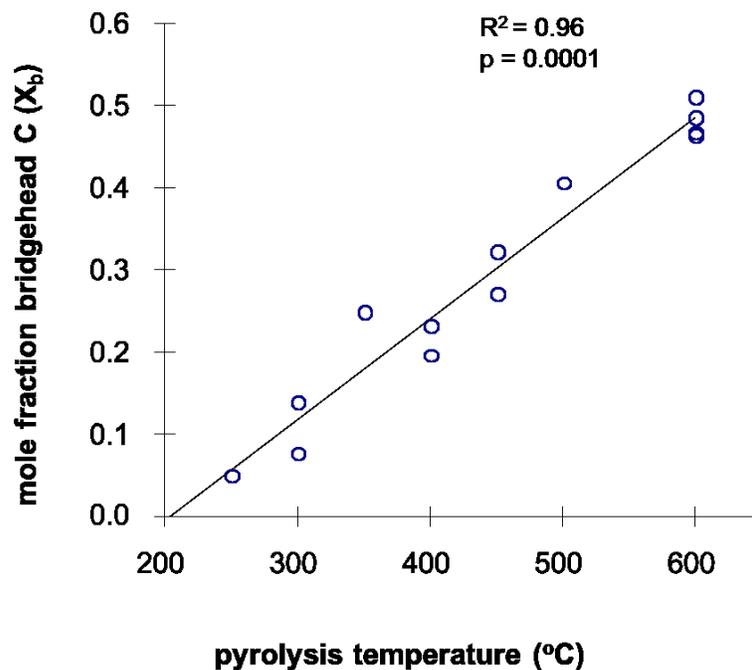


Figure 3. The relationship between the mole fraction bridgehead carbons and furnace pyrolysis temperature for charcoals produced by from Hockaday et al., (*in prep*).

The mole fraction bridgehead carbon values of Figure 3 were converted to aromatic ring condensation (carbons per cluster) by using Equation 1 from Solum et al. (1989). The calculated total aromatic carbon per cluster values for each pyrolysis temperature was plotted in Figure 4 and an exponential relationship was identified (Hockaday et al., *in prep*). A strong linear correlation ($r^2 = 0.97$) and significance ($p = 0.001$) were achieved (Figure 4).

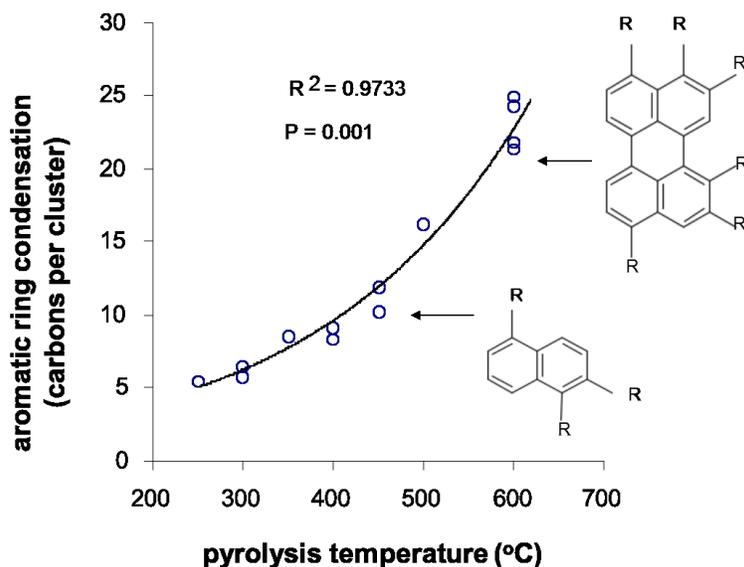


Figure 4. The relationship between the aromatic ring condensation in charcoal (using Equation 1) and the pyrolysis temperatures for charcoals from Hockaday et al., (*in prep*).

Proxy Justification and Utilization

Although many indicators of paleofires exist across many fields of study, few are able to accurately identify the temperature of past fires and even fewer can relate this temperature to the chemistry of the charcoal formed from the fire. Conedera et al., 2009 compiled a list of available proxies including some of the more common proxies such as dendrochronology, marine and lacustrine sediment charcoal analyses, soil charcoal quantification, fire induced pollen changes, magnetic susceptibility of sediment layers, and chemical markers (i.e. BPCAs, levoglucosan, etc.). Charcoal is recognized in many settings as being one of the most resistant forms of carbon to diagenesis, especially the aromatic structures within charcoal, making it a good marker for understanding past environments and changes experienced by those environments (Masiello, 2004; Preston and Schmidt, 2006). More recently, charcoal reflectance has been proven to be able to

estimate formation temperature in present and past charcoal (Ascough et al., 2010). Some limitations such as the sample porosity, alkalinity altering reflectance values, unknown method of vitrification, and inaccuracy at low (< 300°C) temperatures hinder this proxy (Ascough et al., 2010; McParland et al., 2010). The need for further development of novel proxies and integration of these proxies into a multi-proxy approach has been stressed by many authors (Masiello, 2004; Conedera et al., 2009; Ascough et al., 2010).

Carbon-13 NMR spectroscopy is an ideal technique to develop a new charcoal molecular proxy. The NMR technique can provide information about many different compounds and their relative concentrations under the same analysis. The NMR does not require the charcoal sample to be robust (sample sizes of less than 1 gram) or retain its original shape (can be broken or pulverized). Even so, macroscopic charcoal (> 100 – 200 µm in length) was suggested by Conedera et al., 2009 for charcoal proxies because the larger pieces most likely represent the local fire conditions since they are not likely to be transported very far from the source (few hundred meters at most) and Masiello, 2004 highlighted recent works discussing how charcoal with a diameter greater than 60 µm was more indicative of local fire systems since larger particles are less likely to be transported or modified due to pedogenesis and erosion. Furthermore, based on suggestions from Conedera et al., 2009, it is suggested that elongated and angular macroscopic charcoal located in relatively undisturbed soils rather than in sediments be used for proxies for the effects of reworking or remixing due to bioturbation or hydrologic transport most likely have not occurred in these settings. However, I would

argue that the most advantageous characteristic of the NMR is its non-destructive method of analysis. The NMR allows for subsequent analyses of the same sample with different experiments without alteration of the original sample and should allow for more multi-proxy approaches.

Hypotheses and Objectives

Hypothesis 1: Average fire temperature is directly correlated to increasing charcoal cluster size measured by ^{13}C NMR.

Objective 1: Produce charcoals at known temperatures (muffle furnace) and measure their carbon chemistries with ^{13}C NMR to make laboratory calibration.

Objective 2: Record sensor temperatures (thermocouples) at field calibration (prescribed burn) and sample charcoal in close association with the sensors.

Objective 3: Compare carbon chemistry of field calibration charcoals to the mean sensor temperature data

Hypothesis 2: Differences in pyrolyzed biomass species will cause differences in carbon chemistries.

Objective 1: Identify how the chemistry of charcoal differs for dominant flora in wetland such as Cattail and Willow at temperatures between 250 and 600°C

Objective 2: Determine whether charcoals from a mixture of species causes a bias on the proxy temperature

CHAPTER TWO

Proxy Development Strategy and Methods

Pyrolysis of Lab Calibration Charcoal

A grass and wood species found at the field site was selected to calibrate the proxy. Laboratory calibration charcoals were produced from pieces of Cattail (*Typha*) to represent grasses and Willow (*Salix*) to represent tree species. Fresh (green insides) and recently dried out (brown throughout) stems and leaves from each Cattail and Willow species were collected at the Lake Waco Wetland. Each biomass species sample was chopped separately into centimeter (or less) size pieces by a cutting mill (BelArt Mini Mill, Wayne, NJ) and packed into individual glass beakers. In order to mimic the charcoal samples produced by Hockaday et al., *in prep*, the glass beaker was packed full with the corresponding sample and covered with an inverted beaker to form a loose-fitting lid that allowed pyrolysis gases to vent freely. For each sample, the apparatus was placed in a steel bucket and buried beneath 20 cm of fine sand to limit oxygen exposure. The steel bucket was placed in a muffle furnace (Cole-Palmer Stable Temp 1100°C, Vernon Hills, IL) and heated at the desired temperature for 24 hrs. Cattail charcoals were produced at 300, 400, and 500°C while Willow samples were produced at 250, 350, 450, and 550°C. The pyrolyzed sample was subsequently removed and pulverized to a fine powder post pyrolysis by mortar and pestle and transferred into a 20mL glass scintillation vial for storage. These Cattail and Willow charcoal samples along with the Pine, Pecan, and Magnolia samples produced by Hockaday et al., *in prep* were used to establish a calibration for the NMR-based proxy.

Field Study Site Selection and Preparation

Baylor University professor Dr. Joseph White and local US forest service wildland firefighters conducted a prescribed fire at the Lake Waco Wetland in Waco, TX. The Waco Wetland is a man-made wetland that receives water pumped from the Bosque River (Figure 5A). The dominant plant species found at the Waco Wetland were a mix of Bulrush (*Schenoplectus californicus*) and (Cattail) (*Typha*) with a lesser extent of Willow (*Salix*). The wetland was drained for 24 consecutive days before the fire was initiated on August 27th, 2010. According to the National Weather Service's monthly climate data report, the week leading up to the burn (August 20th to August 27th, 2010) in Waco, TX received 4.826 millimeters (0.19 in.) of precipitation and had an average temperature of 32°C (89°F).

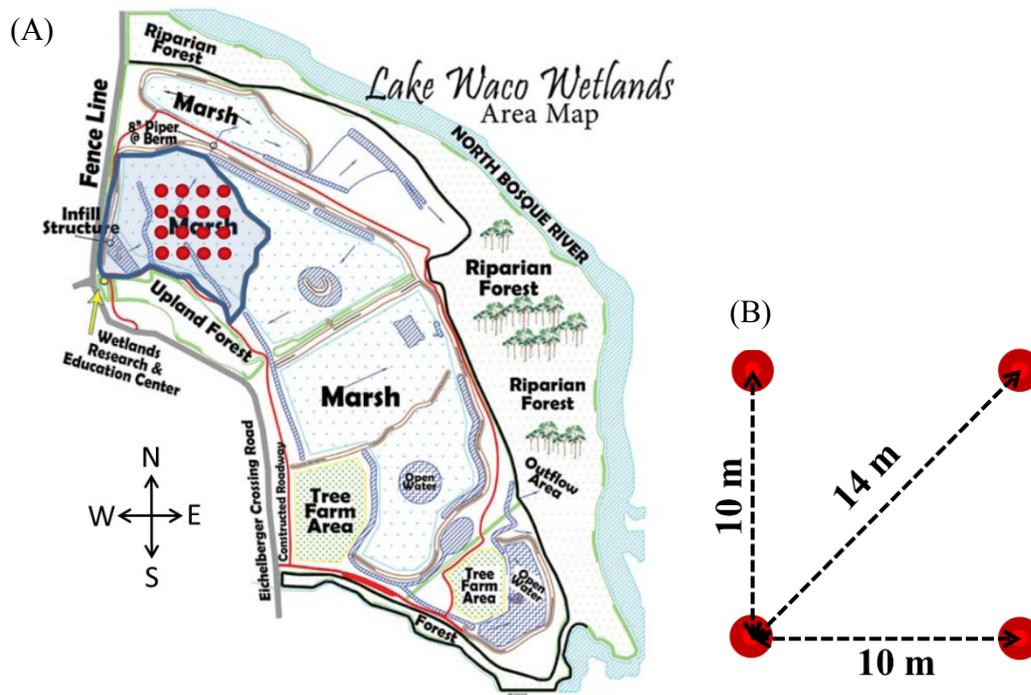


Figure 5. Lake Waco Wetlands area map with sample sites indicated as red circles. (A), Cell 1 highlighted and outlined in blue (modified from <http://www.lakewacowetlands.com/map.html>). (B), Estimated distances between sample sites within cell 1.

In preparation for the prescribed burn sampled in this study, 4 transects of 4 thermocouples each (16 total) were placed in a square grid (Figure 5A). The approximate dimensions of the cells within the thermocouple grid are 10m by 10m, with 14 meters diagonal spacing (Figure 5B). This experimental design provided an opportunity to determine whether charcoals produced under field conditions were related to synoptic fire temperatures.

Field Thermocouple Strategy

Thermocouples were used to capture instantaneous temperatures through time at each sample site. K-type thermocouples with a range of 0-1250°C and resolution of 5-10°C were attached to HOBO data loggers that were buried a few centimeters below the soil surface. The thermocouple temperature sensors were placed ~5cm above the soil surface and were previously programmed to record ambient air temperature every 5 seconds starting a few hours before the fire and ending a few hours after the fire. Given that Boon et al., 1994 and Sharma et al., 2004 suggested 250°C as the temperature at which polyaromatic structures begin forming, only the recorded time and average temperatures above 250°C will be analyzed. Equation 2 describes the average temperature (T_{mean}) recorded by the thermocouple over a given amount of time above 250°C. The variable, t , is the current time of day recorded by the thermocouple.

$$T_{\text{mean}} = \frac{\int_{t_i}^{t_f} T(t) dt}{t_f - t_i} \quad (2)$$

$T(t)$ is the temperature recorded by the thermocouple associated with the specific time of day t . The t_i is the initial time where the temperature was above 250°C and the t_f is the final time where the temperature was above 250°C .

Prescribed Burn Field Parameters

The prescribed fire at the Lake Waco Wetlands (WWF) was initiated by a drip torch at 12:30 p.m. on August 27th, 2010 and ended at approximately 3:30 p.m. (no visible flaming observed, but possible smoldering). Wind speed was 5-10 mph and relative humidity reached 20%. The local air temperature at 12:30 p.m. was 35°C . The fire was calculated to have a spreading rate of 3-7 m/min and flame height was estimated to be up to, but typically less than, 12m above the soil surface. The fire progressed from the initial location in the north corner of the wetland toward the south and was exhausted at the southern border of cell 1 in the wetland (Figure 5A).

Field Charcoal Sampling and Subsampling

Bulk WWF samples including charcoal and uncharred debris were collected 2 hours post-fire with a shovel directly surrounding the thermocouples placed at each site. Two samples, WWF2 and WWF16, were not collected because these sites did not burn. The 14 samples (of 16 total sites) collected were stored in plastic storage bags and later transferred to aluminum dishes for drying and picking. For each sample location, completely black charcoal pieces of various sizes (stem and branch diameters) and tissues (plant species and parts) were picked and ground together with a glass mortar and pestle to a very fine size. The ground sample aliquots were transferred into labeled 4 mL glass vials for storage and later analyses by NMR.

NMR Analytical Method

Four experiments were conducted using NMR on the WWF and calibration samples. Two Cross Polarization (CP) magic angle spinning (MAS) spectroscopy or CPMAS experiments (CPMAS and CPMAS + DD) allowed the identification of carbon nuclei through the transfer of spin from hydrogen nuclei. Two Direct Polarization magic angle spinning spectroscopy or DPMAS experiments (DPMAS and DPMAS + DD) provided the identification of the direct magnetization of carbon, but is more susceptible to paramagnetic materials especially at the centers of high temperature charcoals (McBeath et al., 2011). All four techniques were run on a 300 MHz Bruker Avance III NMR (Billerica, MA) spectrometer with a 7mm solid-state, broadband double resonance MAS (8kHz max) probe in Zirconia (ZrO_2) sample rotors secured with Teflon caps. The four experiments included 4,000 scans of CPMAS, 4,000 scans of CPMAS with dipolar dephasing (DD), 1,000 scans of DPMAS, and 1,000 scans of DPMAS with dipolar dephasing (DD). CPMAS and DPMAS ^{13}C NMR analyses were conducted to identify carbon functional groups present in each charcoal sample.

Procedure for Estimating Mole Fraction Bridgehead Carbon (X_b)

Once the samples were analyzed by NMR, the resulting spectra were used to identify the mole fraction bridgehead carbons per sample for comparison. To estimate the mole fraction bridgehead carbons (X_b) in a sample, I first used the CP and/or DP NMR technique to quantify the mole fraction of carbon in each functional group, including mole fraction aromatic carbon (X_{aro}). Then I performed a second NMR experiment; a spectral editing technique using DD, which uses the dipolar interactions between covalently bonded carbon and hydrogen to selectively dephase (cancel out) the

signal from all carbon atoms involved in a C-H bond. The signal intensities (i.e. peak areas) obtained CP+DD and DP+DD were normalized to the intensity of the corresponding CP or DP spectrum. This normalization process allows for quantification of the non-protonated aromatic carbon ($X_{\text{non-pro-aro}}$). Finally, the mole fraction bridgehead carbon can be estimated by subtracting the contributions from the aromatic carbon atoms with bonding to oxygen or alkyl (non-aromatic) carbon atoms. The oxygen substituted aromatic C is denoted phenolic and aromatic ether carbon ($X_{\text{phe-eth-aro}}$), and alkyl-substituted carbon is denoted $X_{\text{alk-aro}}$. Equation 3 demonstrates the calculation of aromatic bridgehead carbons from integrated NMR peak areas. To calculate X_b in Equation 3, the mole fractions (X) are all normalized to a total carbon (0-220 ppm) value of 1 for the DP NMR spectrum. The non-protonated aromatic carbon (90-145 ppm) from the DP + DD were integrated and normalized to the total DP + DD carbon (0-220 ppm). This ratio is considered the $X_{\text{non-pro-aro}}$ value (Equation 3). The phenolic or ether aromatic carbon (145-165 ppm) from DP were integrated and normalized to the total DP carbon (0-220 ppm). This ratio is considered the $X_{\text{phe-eth-aro}}$ value (Equation 3). The alkyl aromatic (135-145) from the DP + DD were integrated and normalized to the total DP + DD carbon (0-220 ppm). This ratio is considered the $X_{\text{alk-aro}}$ value (Equation 3). As shown in Equation 3, the subtraction of the $X_{\text{phe-eth-aro}}$ and $X_{\text{alk-aro}}$ values from $X_{\text{non-pro-aro}}$ value becomes the X_b value.

$$X_{\text{non-pro-aro}} - X_{\text{phe-eth-aro}} - X_{\text{alk-aro}} = X_b \quad (3)$$

Equation 3 is used for calculating X_b from CP NMR using the same approach. Note that the range of possible X_b values for charcoal is $0 < X_b < 1$ since charcoal must

have at least one bridgehead carbon, but not exclusively bridgehead carbons (edges of rings are not bridgehead carbons). This range is supported by the logarithmic relationship seen in Figure 1 which, for charcoal, may never reach 0 and, in this case, 1 (Solum et al. 1989). The mole fraction bridgehead carbons were then converted to carbons per cluster (C/C) by Equation 1.

Procedure for NMR Spin Counting

A procedure known as spin counting was performed on each NMR spectrum to determine the proportion of the total carbon observed (% C_{obs}) in each charcoal sample. A simple organic molecule, glycine, was selected as a standard for spin counting because the proton and carbon relaxation dynamics have been previously characterized (Smernik and Oades, 2000). The ¹H and ¹³C signal relaxation rates for glycine are relatively slow, and can be easily detected by the spectrometer. My CP and DP NMR experiment parameters were carefully selected to quantitatively detect the glycine signal. Therefore we analyzed a known quantity of glycine carbon (mg C of standard) to determine the signal amplitude (i.e. spectral peak area) generated per milligram of carbon in the standard. The sample's signal amplitude was divided by the previous values to get the mg C^{detected} in the sample as shown in equation 4.

$$\text{mg C}^{\text{detected}}(\text{sample}) = \frac{\text{signal amplitude (sample)}}{\text{signal amplitude (standard)}/\text{mg C (standard)}} \quad (4)$$

To estimate the carbon observed in the charcoal samples, the mg C^{detected} value of the charcoal was divided by the known quantity of C in the charcoal, determined by EA analyses, and multiplied by 100 (Equation 5).

$$\%C_{\text{obs}} = 100 \times \frac{\text{mg C}^{\text{detected}} (\text{sample})}{\text{mg C} (\text{sample})} \quad (5)$$

The % C_{obs} values were calculated for Cattail, Willow, and WWF samples. Pecan, Pine, and Magnolia sample % C_{obs} values have not yet been calculated by Hockaday et al., (*in prep*).

Statistical Methods

Statistical analyses performed on the data set were conducted in the Microsoft Excel program. A linear regression, correlation coefficients (r^2 values), and significances (p-values) were calculated for the linear models used to describe the relationship between the mole fraction bridgehead carbons and measured temperatures (furnace or thermocouple). An exponential regression and correlation coefficients were calculated to model the relationship between the carbons per cluster and measured temperatures (furnace or thermocouple). Residuals of the proxy values were calculated to identify whether the data fit a normal distribution. A nonlinear transformation was conducted on the C/C exponential data ($\log(y) = mx + b$) to increase its linearity so analyses of residuals and p-values may be conducted for C/C. Linear regressions, Root Mean Square Errors (RMSE), and Standard Errors (SE) were calculated to demonstrate the accuracy and precision of the proxy temperatures at estimating the actual temperatures for charcoals formed in the lab and the field. Linear regressions, correlation coefficients, and significances were also calculated to understand the relationships between the accuracy values and ROS/Cellulose Loss values for the field samples.

A Dixon Q-test was performed on the lab and field calibration datasets with a 90% confidence level to identify outlier data points for rejection in each regression

(Appendix A). Under the 90% confidence level, the CP lab calibration data were analyzed with a Q_{crit} of 0.306 ($n = 19$), the DP lab calibration data were analyzed with a Q_{crit} of 0.300 ($n = 20$), and the CP and DP field (WWF) calibration data were analyzed with a Q_{crit} of 0.349 ($n = 14$). Two data points were rejected from the lab calibration data set based on the 90% confidence level (DP C/C technique Cattail 500 and Willow 550 reburn data points; Appendix A) and were not included in regression analyses. No data were rejected from the field calibration (WWF) data set (Appendix A).

The statistical probabilities of significance (p-value) in the relationship between pyrolysis temperature and NMR-based temperature proxies (X_b and C/C) were obtained using the Microsoft excel analyses tool kit for data analyses. The data was considered statistically significant at the 5% significance level ($\alpha = 0.05$). Any data with p-values exceeding 0.05 were considered consistent with the null hypothesis, meaning it can be described by chance alone, and were not considered for further analyses such as the Accuracy vs. ROS data in Figure 22. Each individual proxy temperature's accuracy was calculated as the difference in the estimated (proxy) and actual (furnace or thermocouple) temperature values. The overall accuracy of the proxy temperature models at estimating the actual temperatures is described as the Root Mean Squared Error (RMSE). The standard error (SE) of the mean was calculated using the Microsoft Excel function STEYX to estimate the calibration and field proxy temperature data precision. Statistical values were reported on the corresponding figure and/or table.

Reynolds Creek Sampling

In addition to the field sampling at the Lake Waco Wetland, another prescribed fire at Reynolds Creek provided an opportunity to better understand the spatial patterns of

sensible heat flux (i.e. temperature). Reynolds Creek is a campground located on the North Arm of the Waco Lake reservoir. Sampling was conducted in grassland that was dominated by dry Johnsongrass (*Sorghum halepense*) with lower abundances of Muhlygrass (*Muhlenbergia lindheimeri*) and Little Bluestem (*Schizachyrium scoparium*). In contrast to the Lake Waco Wetland site, thermocouples were deployed to potentially capture the vertical variability in fire temperature within a small volume of 0.3m³ (1 m x 1 m x .3 m). The thermocouple recorders were sealed in a 9cm section of pvc tubing (9cm in diameter) and buried a few cm beneath the soil while the thermocouple sensors were attached to aluminum poles in a 1 meter by 1 meter square plot at each corner and at three different heights (5, 15, and 30cm) before the burn (Figure 6A). Two tiers of metal funnels and buckets were co-located with thermocouples, with the intent of collecting charcoal produced at the 15 and 30 cm thermocouple locations (Figure 6A). Unfortunately, insufficient charcoal (a few pieces to none) was captured at each height for comparison by NMR analysis (Figure 6B). The Reynolds Creek fire was observed as being a fast ground fire with very little charcoal formation (Figure 6B).



Figure 6. Reynolds Creek Sampling apparatus. (A), Before the burn; (B), After the burn. Note one of the poles had melted partway up during the burn and is lying on the ground.

CHAPTER THREE

Results

Proxy Calibration: ^{13}C NMR Analysis of Laboratory Charcoals

The ^{13}C CPMAS NMR spectra of uncharred dry Cattail and Willow are presented in Figure 7A-B. These samples showed the uncharred chemical composition and relative amounts of each for two of the dominant plant species at the Waco Wetland site. The spectra show similar carbon functional group abundances. The Cattail sample is dominated by 60 to 110 ppm range, characteristic of cellulose and hemi-cellulose which are the dominant component of cell walls (Figure 7A). The Willow sample has higher relative abundances of carbon at 130 and 150 ppm (Figure 7B). The 120 to 165 ppm range is characteristic of lignin, the second most common organic compound in plants (Freitas et al., 1999; Baldock et al., 2004; Killops and Killops, 2005).

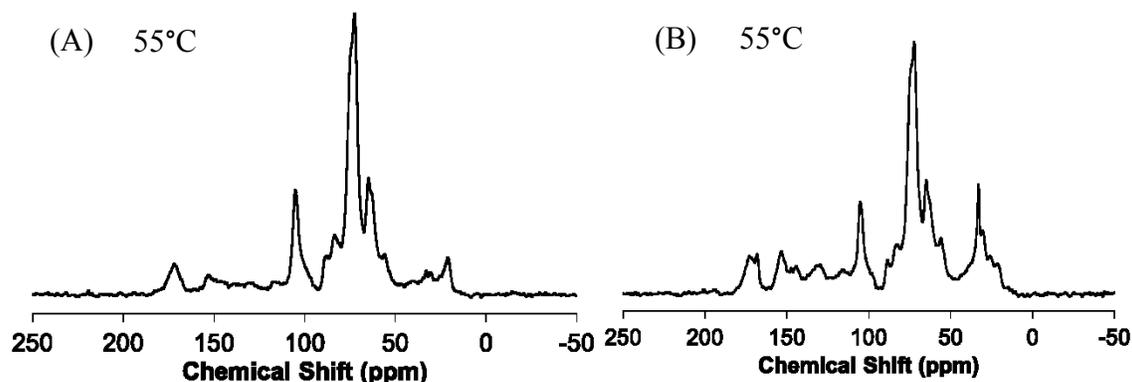


Figure 7. Dry (55°C) calibration sample ^{13}C NMR spectra. (A), Cattail sample spectra using CPMAS; (B), Willow sample spectra using CPMAS.

Figure 8A-B and Figure 9A-B include examples of the DPMAS, DPMAS + C-H dephasing, CPMAS, and CPMAS + C-H dephasing ^{13}C NMR techniques to demonstrate how Cattail and Willow samples are altered by pyrolysis at relatively high temperatures (500 and 550 $^{\circ}\text{C}$ respectively). The ^{13}C NMR spectra of all charcoals generated for this study can be viewed in Appendix C. The CPMAS and DPMAS techniques are representative of all the carbon atoms while the DPMAS with dipolar dephasing and CPMAS with dipolar dephasing techniques are representative of only non-protonated carbon atoms, which represent bridgehead carbons if the signals are in the range of 110-135 ppm. The spectra for both plant types (Cattail and Willow) and both techniques (CP and DP) are overwhelmingly dominated by a chemical shift and intense peak within the aromatic region, from 110 to 145 ppm (Figure 8A-B and Figure 9A-B).

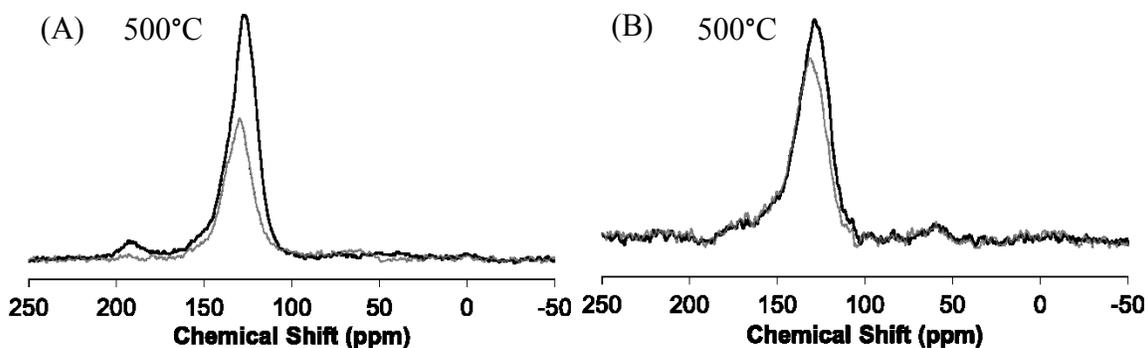


Figure 8. Examples of high temperature Cattail sample ^{13}C NMR spectra (CattailCal_500 sample). Temperature based on pyrolysis furnace. (A), CPMAS (black) and CPMAS with dipolar dephasing (grey) spectra; (B), DPMAS (black) and DPMAS with dipolar dephasing (grey).

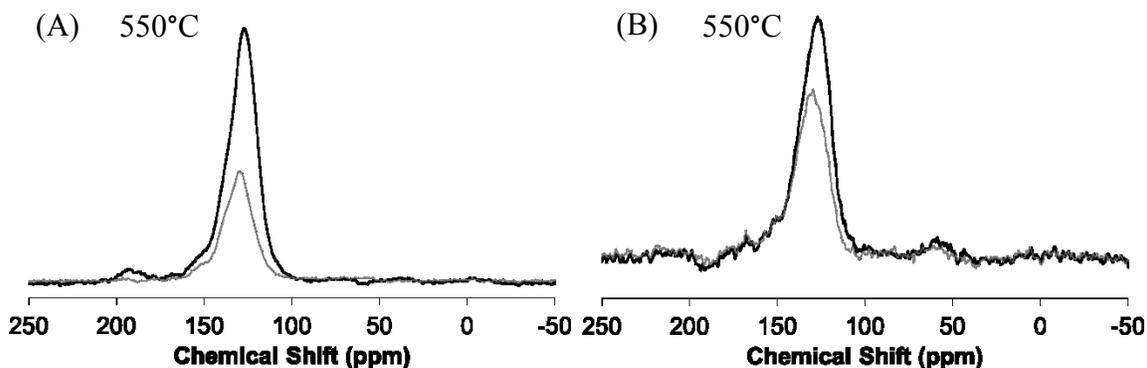


Figure 9. Examples of high temperature Willow sample ^{13}C NMR spectra (WillowCal_550rb sample). Temperature based on pyrolysis furnace. (A), CPMAS (black) and CPMAS with dipolar dephasing (grey) spectra; (B), DPMAS (black) and DPMAS with dipolar dephasing (grey).

Applying the NMR spectra integration techniques described in the Methods to all calibration charcoals (Appendix C), the mole fraction bridgehead carbons (X_b) and carbons per cluster (C/C) (this study and Hockaday et al., *in prep* samples) were calculated in and tabulated (Table 2). The CP X_b values range from 0.00 in uncharred Cattail and Willow samples to 0.72 in a Willow sample that was first pyrolyzed at 250°C and then pyrolyzed a second time at 550°C (sample Willow reburn). The Willow reburn sample was pyrolyzed twice to simulate a wildland setting that undergoes frequent burning, where charcoal particles deposited on the soil surface may experience multiple heating/pyrolysis events. The CP C/C values range from 6 in uncharred Cattail and Willow samples to 78 in the Willow reburn sample. The DP X_b values range from 0.06 in Pecan pyrolyzed at 225°C to 0.89 in the Willow reburn sample. Of the calibration charcoals, the Pecan sample had the lowest X_b values and the Willow reburn sample had the highest X_b values for both the CP and DP techniques. The DP C/C values range from 7 in the Pecan pyrolyzed at 225°C to 90 in the Magnolia pyrolyzed at 600°C.

Table 2. Furnace, mole fraction bridgehead carbon (X_b), and carbons per cluster (C/C) data with associated temperatures and errors from the calibration charcoals analyzed by CP and DP

Calibration Sample Type	Furnace Pyrolysis Temp. (°C)	¹³ C NMR Spectroscopy													
		CP							DP						
		X_b	X_b Temp. (°C) ^a	Accuracy (°C) ^b	C/C	C/C Temp. (°C) ^c	Accuracy (°C) ^b	C_{obs} (%)	X_b	X_b Temp. (°C) ^d	Accuracy (°C) ^b	C/C	C/C Temp. (°C) ^e	Accuracy (°C) ^b	C_{obs} (%)
Cattail	55	0.00	226	-	6	263	-	31	-	-	-	-	-	-	-
	300	0.18	308	8	9	314	14	28	0.22	319	19	10	319	19	105
	400	0.43	422	22	19	406	6	10	0.59	458	58	36	453	53	107
	500	0.48	444	-56	22	428	-72	30	0.84	551	51	f	f	f	110
Willow	55	0.00	226	-	6	263	-	32	-	-	-	-	-	-	-
	250	0.13	284	34	8	298	48	61	0.23	324	74	10	322	72	109
	350	0.24	333	-17	10	331	-19	25	0.38	380	30	16	368	18	102
	450	0.59	492	42	35	485	35	22	0.64	476	26	46	479	29	91
	550	0.56	481	-69	31	471	-79	37	0.74	513	-37	87	546	-4	109
Willow (reburn)	550	0.72	554	4	78	586	36	46	0.89	571	21	f	f	f	100
Pecan ^g	225	0.08	260	35	7	283	58	-	0.06	258	33	7	279	54	-
	350	0.30	361	11	12	352	2	-	0.29	345	-5	12	338	-12	-
	400	0.35	386	-14	14	373	-27	-	0.30	348	-52	12	341	-59	-
	450	0.64	517	67	46	521	71	-	0.55	444	-6	30	435	-15	-
Pine ^g	500	0.58	491	-9	35	485	-15	-	0.73	512	12	85	544	44	-
	300	0.16	299	-1	9	308	8	-	0.16	296	-4	8	303	3	-
	400	0.33	376	-24	13	364	-36	-	0.27	336	-64	11	331	-69	-
Magnolia ^g	450	0.49	448	-2	23	433	-17	-	0.38	380	-70	16	368	-82	-
	300	0.09	268	-32	7	288	-12	-	-	-	-	-	-	-	-
	600	-	-	-	-	-	-	-	0.74	515	-85	90	550	-50	-
RMSE (°C) ^h				34			41			46			46		
SE (± °C) ⁱ				36			43			49			50		

$$^a X_b \text{ Temp.} = 454.43 * X_b + 226.03$$

$$^b \text{Accuracy} = \text{Proxy Temp} - \text{Furnace Pyrolysis Temp.}$$

$$^c \text{C/C Temp} = 126.23 * \ln(\text{C/C}) + 37.088$$

$$^d X_b \text{ Temp.} = 373.84 * X_b + 237.24$$

$$^e \text{C/C Temp} = 104.46 * \ln(\text{C/C}) + 79.857$$

^fRejected by Q-test (see Statistical Methods section in Chapter 2 and Appendix A)

^gfrom Hockaday et al., *in prep*

^hRMSE = Root Mean Square Error; Did not include Cattail 55, Willow 55, or Q-test rejected values

ⁱSE = Standard Error; Did not include Cattail 55, Willow 55, or Q-test rejected values

The observability of charcoal carbon (C_{obs}) in the Willow and Cattail NMR spectra was calculated using Equation 4 and Equation 5 as a means of assessing the quantitative reliability of the NMR data. The DP ^{13}C NMR experiments have a C_{obs} value of $100\% \pm 10\%$ (Table 2). The observability of charcoal carbon in CP ^{13}C NMR experiments was substantially lower than the DP experiments, with C_{obs} values ranging from 9.8 to 60.6% (Table 2).

The mole fraction bridgehead carbons (X_b) were plotted against the pyrolysis temperatures of the calibration charcoals for the CP technique (Figure 10A) and the DP technique (Figure 10B). These figures demonstrate the extent to which the calibration charcoal data are described by a linear regression for each technique. Cattail and Willow samples dried at 55°C were excluded from Figure 10A-B since they are uncharred plant matter. There were no species dependencies in the chemical structure of the different biomass sources in the charcoals. Therefore, I grouped all the samples for subsequent statistical analyses. The CP regression in Figure 10A has a strong linear correlation ($r^2 = 0.88$) and is considered significant ($p < 0.001$). The DP regression in Figure 10B has a strong linear correlation ($r^2 = 0.81$) and is considered significant ($p < 0.001$). These plots demonstrate that X_b responds positively to pyrolysis temperature with the y-intercepts (0.3917 and 0.4261) and the slopes (0.0019 and 0.0022) for CP and DP responding slightly differently (Figure 10A-B).

The X_b proxy temperatures were then calculated from regressions using the data in Figure 10A-B, but with swapped axis, and are provided in the caption of Table 2. Individual accuracies for each sample are also provided to show the difference in each of the proxy temperatures and actual pyrolysis temperatures (Table 2). The overall X_b

model accuracies, the RMSE, are 34°C in the CP technique to 41°C for the DP technique for the calibration charcoals. The precision of the X_b proxy modeled temperatures are provided as the standard error (SE) in Table 2. The CP X_b calculated temperatures are more precise estimates of the actual temperature (SE = ±36°C) than the DP estimates (SE = ±43°C).

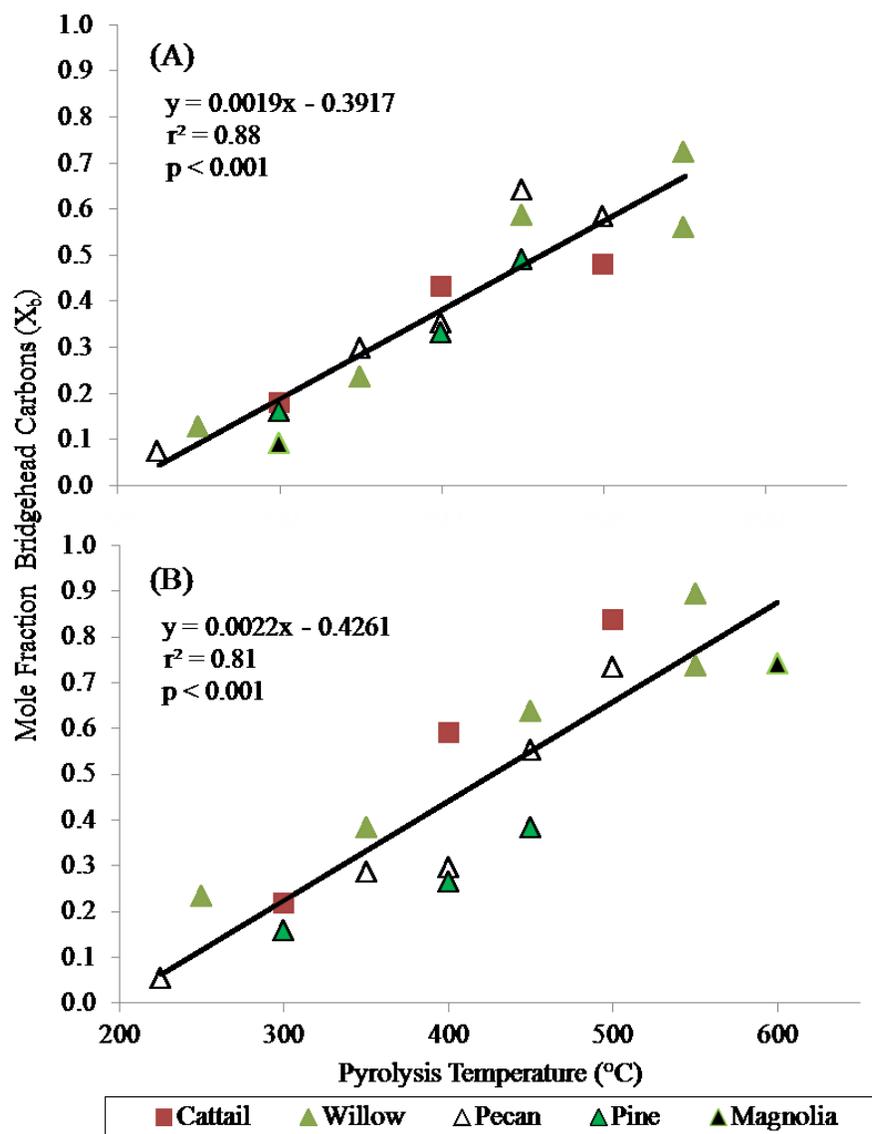


Figure 10. Relationship between ^{13}C NMR X_b values and pyrolysis temperatures for calibration chars. Linear regressions with associated r^2 and p -values are provided in each plot. (A), Results from Cross Polarization technique; (B), Results from Direct Polarization technique.

The carbons per cluster (C/C) are plotted against the pyrolysis temperatures of the calibration charcoals in Figure 11. Figure 11 is shown to demonstrate the extent to which the calibration charcoal data are described by an exponential regression for the CP technique (Figure 11A) and the DP technique (Figure 11B). Cattail and Willow samples dried at 55°C were excluded from Figure 11A-B since they are uncharred plant matter. There were no species dependencies in the chemical structure of the different biomass sources in the charcoals. Therefore, I grouped all the samples for subsequent statistical analyses. The CP regression in Figure 11A has a strong exponential correlation ($r^2 = 0.82$) and is considered significant ($p < 0.001$). The DP regression in Figure 11B has a strong exponential correlation ($r^2 = 0.80$) and is considered significant ($p < 0.001$). These plots demonstrate that C/C responds positively to pyrolysis temperature with the constants (1.2915 and 1.0152) and the rates (0.0065 and 0.0076) for CP and DP responding slightly differently (Figure 11A-B).

The C/C proxy temperatures were then calculated from regressions using the data from Figure 11A-B, but with swapped axis, and are provided in the caption of Table 2. Individual accuracies for each sample are also provided to show the difference in each of the proxy temperatures and actual pyrolysis temperatures (Table 2). The overall C/C model accuracies, the RMSE, are 46°C for both the CP and DP technique for the calibration charcoals. The precision of the C/C proxy modeled temperatures are provided as the standard error (SE) in Table 2. The CP X_b calculated temperatures are slightly more precise estimates of the actual temperature (SE = $\pm 49^\circ\text{C}$) than the DP estimates (SE = $\pm 50^\circ\text{C}$).

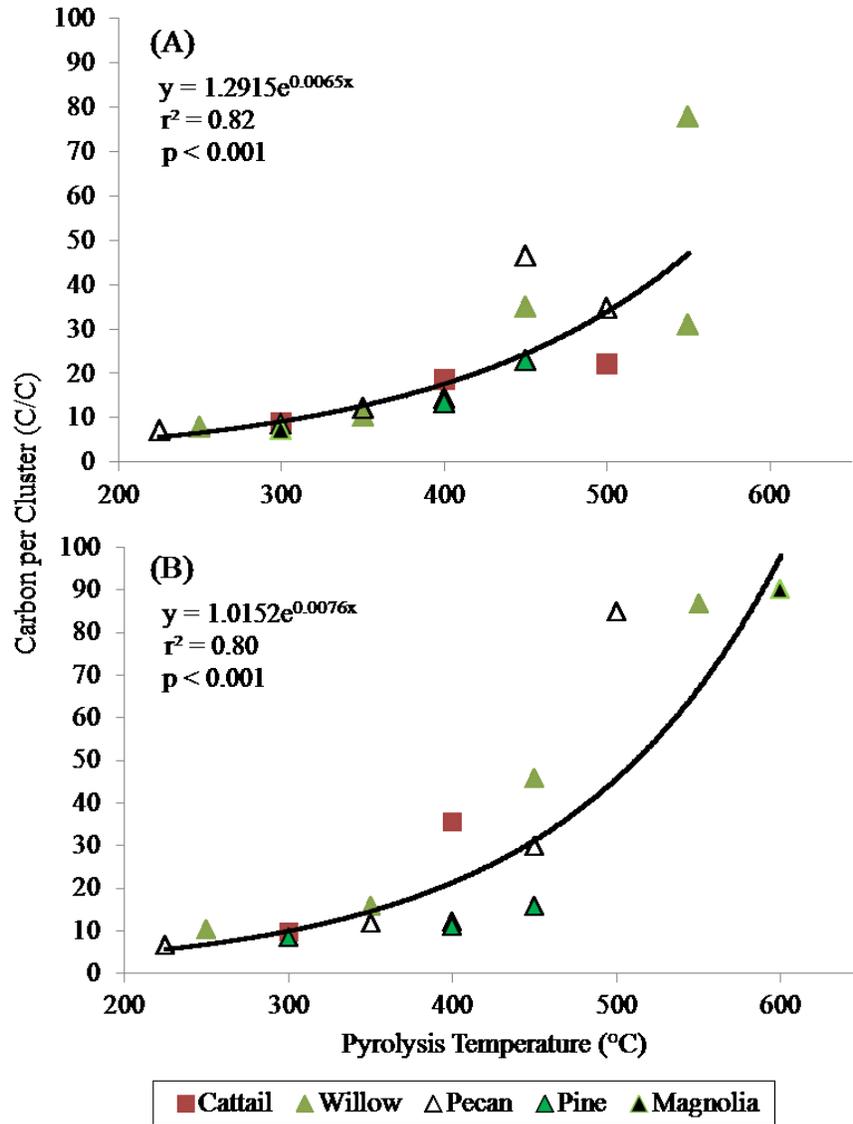


Figure 11. Relationship between ¹³C NMR C/C values and pyrolysis temperatures for calibration chars. Linear regressions with associated r² values are provided in each plot. (A), Results from Cross Polarization technique; (B), Results from Direct Polarization technique. The Cattail 500 and Willow 550 reburn samples were not included since they were rejected with the Q-test (See the *Statistical Methods* in Chapter 2 and Appendix A).

WWF Thermocouple Temperature Analyses

A schematic of the Lake Waco Wetlands is shown in Figure 12 with an expanded view of the area in which the thermocouple array was deployed. The prescribed fire was ignited around the perimeter of the wetland and converged on the middle, where the

thermocouple 6 displays the hottest temperatures. Sample sites 1, 2, 4, 8, 12, and 16 did not achieve maximum thermocouple temperatures above 250°C and were not included in further analyses, for reasons described in Chapter 2.

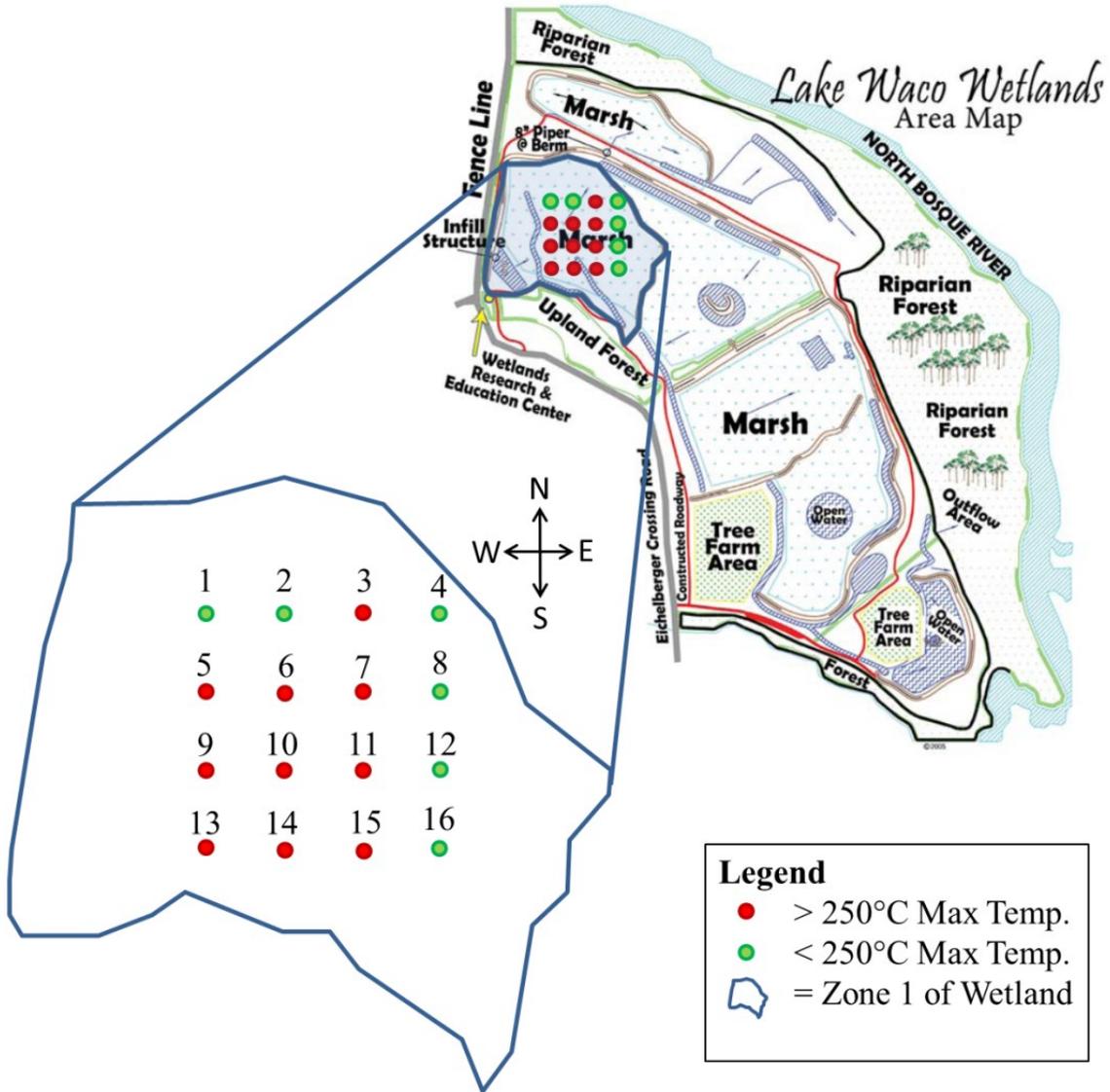


Figure 12. Thermocouple Spatial Map indicating whether temperatures reached above or below 250°C. Red circles indicate locations that reached temperatures above 250°C and green circles indicate locations that did not reach temperatures above 250°C. Cell 1 of WWF is highlighted and outlined in blue (Figure modified from <http://www.lakewacowetlands.com/map.html>).

The thermocouple data in Figure 13 show temperatures as they relate to the time of day during the prescribed burn (from 1:40 pm to 2:40 pm). Peak (maximum) temperatures and Peak Temperature times were determined from Figure 13 as the peaks of each temperature profile (Figure 12; Table 3). Using the times that each thermocouple measured over 250°C, the duration above 250°C was determined (Table 3). The corresponding temperatures for the duration times were used in equation 2 to calculate the mean thermocouple temperatures over 250°C (Table 3).

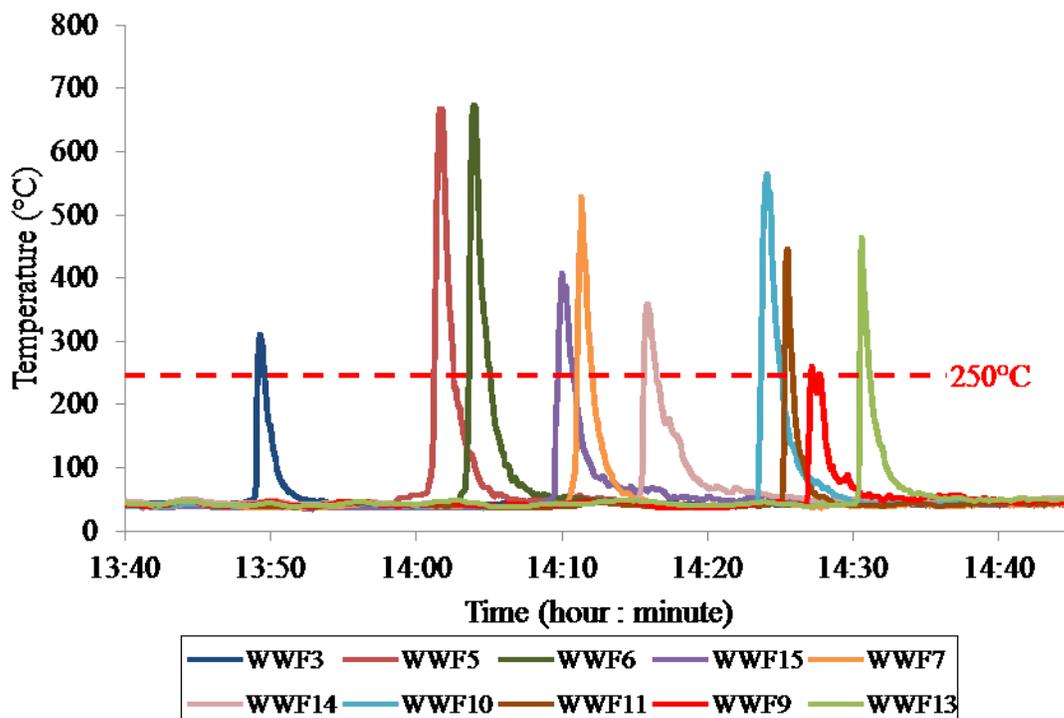


Figure 13. Thermocouple measured temperatures as they relate to time of day (24 hr. time) during the prescribed burn at the Waco Wetlands. The red dashed line indicates the 250°C minimum required for analyses.

By estimating the distance between two thermocouple sample sites and dividing this distance by the amount of time between peak temperatures at these sites, the rate of spread (ROS) can be calculated. Distance estimates are shown in Figure 5B. Peak times

can be obtained from Figure 13. ROS calculations were done between charcoal forming sites (ones that reached a maximum temperature above 250°C). These ROS values can be found in Appendix B. The greatest ROS value between a charred sample site and all the adjacent charred sample sites was identified as the true ROS value that the charcoals at a sample site experienced (Appendix B; Table 3). Table 3 shows all the thermocouple analyses and the true ROS values for each sample site. The ROS values range from 0.016 m sec⁻¹ to 0.118 m sec⁻¹.

Table 3. Thermocouple data from Waco Wetland prescribed burn. Sample sites, duration, and mean temperature values reaching values above 250°C are included. Peak temperature and ROS parameters are included for each site as well.

Waco Wetland Fire Site	Duration above 250°C (sec.)	Mean Temperature above 250°C (°C)	Peak (Max) Temperature (°C)	Peak Temperature Time (hh:mm:ss) ^a	True (max) ROS (m/sec) ^b	Affiliated True ROS site
WWF3	25	290.3	310.3	13:49:15	0.016	WWF6
WWF5	80	472.2	667.5	14:01:35	0.071	WWF6
WWF6	85	463.8	674.3	14:03:55	0.071	WWF5
WWF7	65	394.9	528.7	14:11:20	0.022	WWF6
WWF9	5	260.0	260.0	14:27:10	0.054	WWF10
WWF10	75	426.3	565.0	14:24:05	0.118	WWF11
WWF11	30	363.2	445.3	14:25:30	0.118	WWF10
WWF13	40	347.1	463.1	14:30:35	0.049	WWF9
WWF14	50	314.0	359.2	14:15:50	0.029	WWF15
WWF15	55	343.0	406.9	14:10:00	0.029	WWF14

^aTimes of Peak Temperature are from the peak temperatures in Figure 13

^bTrue ROS values were calculated with the estimated sample site distances from Figure 5B and the difference in Peak Temperature Times in column 5

Waco Wetland Fire Charcoal Proxy Analyses

Examples of Waco Wetland Fire charcoal CP, CP + DD, DP, and DP + DD spectra are shown in Figure 14A-B, Figure 15A-B, and Figure 16A-B. More Waco Wetland Fire charcoal spectra can be viewed in Appendix C. According to the Waco Wetland Fire proxy analyses, Figure 14 is an example of a lower (~300°C) temperature

charcoal, Figure 15 is an example of a moderate ($\sim 325^{\circ}\text{C}$) temperature charcoal, and Figure 16 is an example of a higher ($\sim 350^{\circ}\text{C}$) temperature charcoal produced during the burn. Figure 14 (site WWF4) has a lower proportion of aromatic carbon functional groups (110 to 145 ppm) and higher proportion of non-aromatic carbon (0-110 ppm and 145-220 ppm) than Figure 15 (WWF10). The same goes for Figure 15 (site WWF10) when compared to Figure 16 (site WWF15).

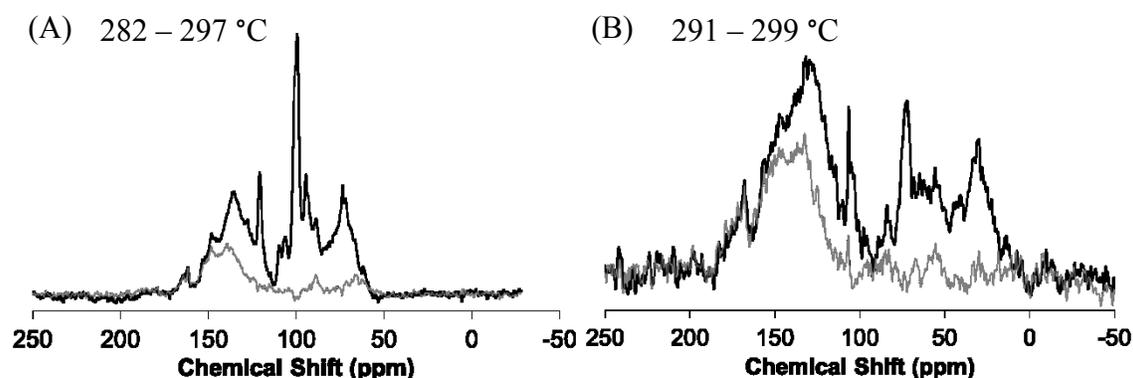


Figure 14. WWF4 sample site ^{13}C NMR spectra indicative of a relatively lower fire temperature. Temperature range based on proxies (X_b and C/C) for CP and DP techniques. (A), CPMAS (black) and CPMAS with dipolar dephasing (grey) spectra; (B), DPMAS (black) and DPMAS with dipolar dephasing (grey).

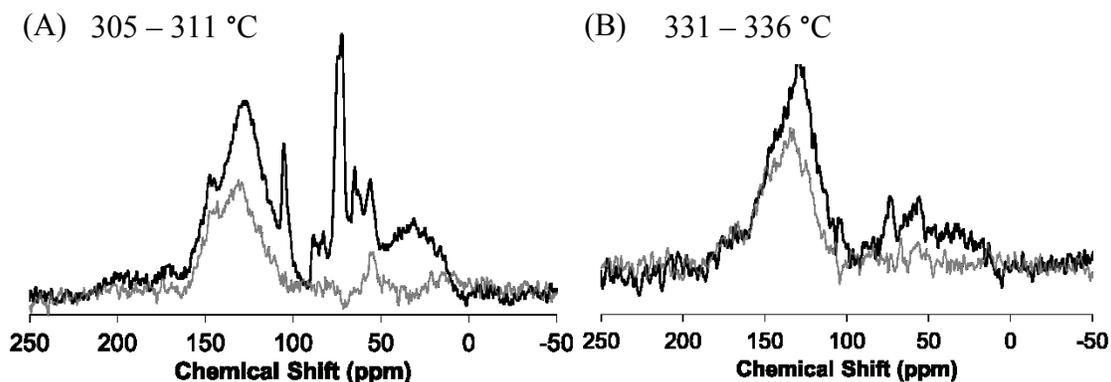


Figure 15. WWF10 sample site ^{13}C NMR spectra indicative of a relatively moderate fire temperature. Temperature range based on proxies (X_b and C/C) for CP and DP techniques. (A), CPMAS (black) and CPMAS with dipolar dephasing (grey) spectra; (B), DPMAS (black) and DPMAS with dipolar dephasing (grey).

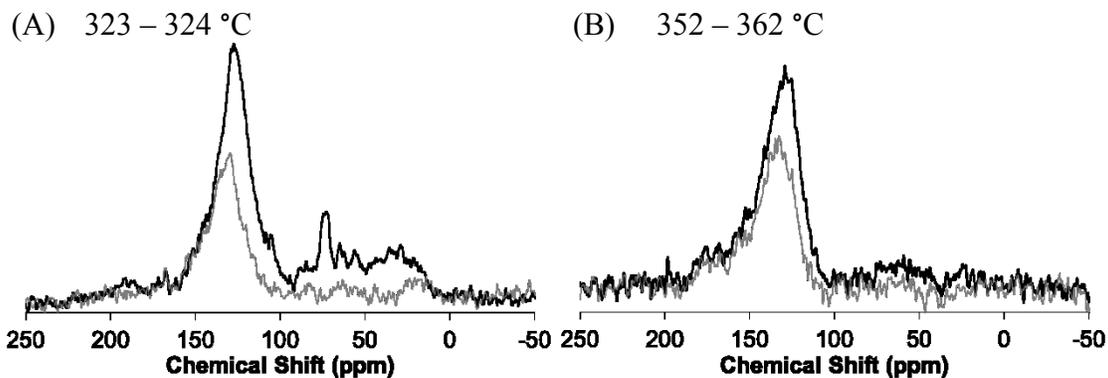


Figure 16. WWF15 sample site ¹³C NMR spectra indicative of a relatively high fire temperature. Temperature range based on proxies (X_b and C/C) for CP and DP techniques. (A), CPMAS (black) and CPMAS with dipolar dephasing (grey) spectra; (B), DPMAS (black) and DPMAS with dipolar dephasing (grey).

The relative peak intensities in the spectra were treated with the algorithm described previously in Chapter 2 to estimate the mole fraction bridgehead carbons (X_b) in each sample just as the calibration charcoals were. The results are shown in Table 4. The X_b values were converted to C/C using equation 1 and are provided in Table 3. Using the proxy calibration in Figure 10A-B and Figure 11A-B, the proxy (X_b and C/C) temperatures are provided in Table 4. Associated individual accuracies, root mean square error, and standard error values are provided for each proxy (Table 4). The RMSE values were between 86 and 106°C for the four techniques (Table 4). The SE had a much smaller range of 71°C to 72°C in Table 4.

Table 4. Mean thermocouple temperature, mole fraction bridgehead carbon (X_b), and carbons per cluster (C/C) data with associated temperatures and errors from the Waco Wetland Fire sensors and charcoals analyzed by CP and DP

Waco Wetland Fire Sample	Mean Thermo. Temp. (°C)	¹³ C NMR Spectroscopy													
		CP							DP						
		X_b	X_b Temp. (°C) ^a	Accuracy (°C) ^b	C/C	C/C Temp. (°C) ^c	Accuracy (°C) ^b	C_{obs} (%)	X_b	X_b Temp. (°C) ^d	Accuracy (°C) ^b	C/C	C/C Temp. (°C) ^e	Accuracy (°C) ^b	C_{obs} (%)
WWF3	290	0.16	298	8	8	307	16	20	0.29	345	55	12	338	48	95
WWF5	472	0.08	264	-208	7	285	-187	51	0.11	277	-195	8	291	-182	100
WWF6	464	0.13	287	-177	8	300	-164	40	0.29	344	-120	12	337	-126	97
WWF7	395	0.13	286	-108	8	299	-96	43	0.18	306	-89	9	309	-86	106
WWF9	260	0.12	281	21	8	296	36	32	0.22	321	61	10	320	60	100
WWF10	426	0.17	305	-122	9	311	-115	28	0.26	336	-91	11	331	-96	106
WWF11	363	0.12	282	-81	8	296	-67	33	0.29	345	-18	12	338	-25	100
WWF13	347	0.13	284	-63	8	298	-50	33	0.15	294	-53	8	302	-45	94
WWF14	314	0.21	320	6	10	321	7	18	0.30	348	34	12	340	26	102
WWF15	343	0.21	323	-20	10	324	-19	20	0.33	362	19	14	352	9	94
RMSE (°C) ^f				106			97				89			86	
SE (± °C) ^g				71			71				71			72	

$$^a X_b \text{ Temp.} = 454.43 * X_b + 226.03$$

$$^b \text{Accuracy} = \text{Proxy Temp} - \text{Furnace Pyrolysis Temp.}$$

$$^c \text{C/C Temp} = 126.23 * \ln(\text{C/C}) + 37.088$$

$$^d X_b \text{ Temp.} = 373.84 * X_b + 237.24$$

$$^e \text{C/C Temp} = 104.46 * \ln(\text{C/C}) + 79.857$$

^fRMSE = Root Mean Square Error

^gSE = Standard Error

CHAPTER FOUR

Discussion and Conclusions

Lab Calibration X_b and C/C Values Increase with Mean Temperature

I have shown that Figures 10A-B and 11A-B convincingly demonstrate charcoal chemistry as a faithful record of the temperature at which charcoal is formed. The X_b and C/C regressions in Figure 10 and Figure 11 were considered significant with p-values less than 0.001 and had r^2 values greater than 0.80 suggesting that each method is viable for estimating charcoal formation temperature under furnace conditions. The C/C r^2 values indicate that the conversion does not strengthen the proxy – temperature relationship, but actually weakens it. Of the charcoal chemical parameters, correlations are stronger in the CP than the DP technique with the strongest correlation between proxy and furnace temperature occurring in the CP X_b regression.

Having demonstrated that the temperature response of X_b is adequately described by a linear model ($p < 0.001$), and C/C is adequately described by an exponential model ($p < 0.001$), the next step is to investigate whether the residuals fit a normal distribution. Residuals are the difference between the actual proxy variable (X_b or C/C) and the estimated or fitted proxy variable (X_b' or C/C') based upon the regressions in Figure 10 and Figure 11 (Appendix D). The normal distribution of the X_b residuals in Figure 17A confirms that the linear model is appropriate for the data. Once the exponential C/C data was transformed to increase linearity, the distribution of the residuals shown in Figure 17B became random, confirming the exponential model as appropriate for the C/C data.

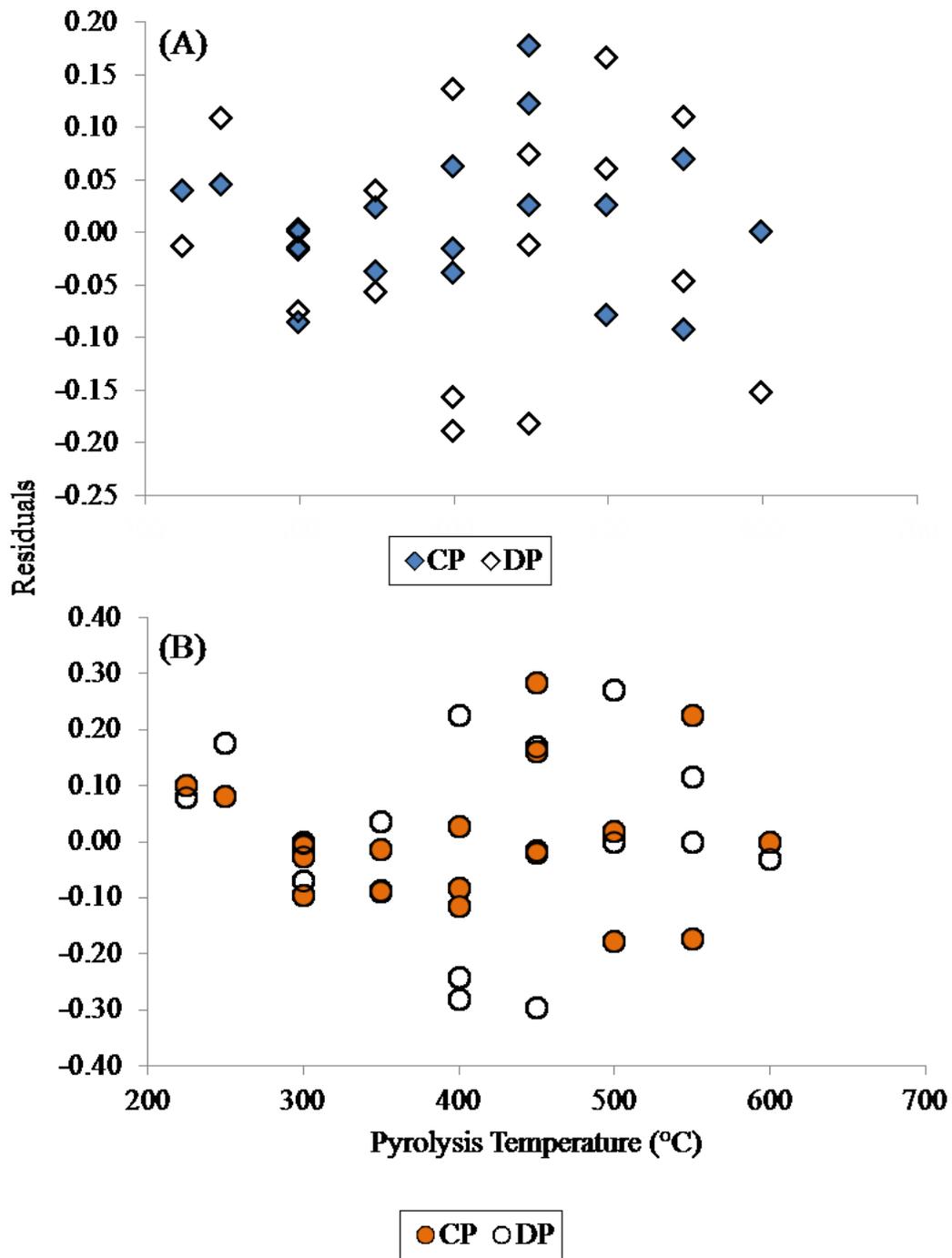


Figure 17. Relationship between proxy value residuals and pyrolysis temperatures. (A), Xb residuals. (B), C/C residuals not including points previously rejected by Q-test (see *Statistical Methods* and Appendix A). A nonlinear transformation ($\log(y) = mx + b$) was performed on the C/C exponential model to achieve linearity for both C/C and C/C'.

After demonstrating the residuals fit a normal distribution for X_b and C/C , the accuracy and precision of the models for the prediction of pyrolysis temperature was assessed. I plotted the X_b and C/C proxy temperature calculated from X_b as a function of the actual furnace temperature in Figure 18A and Figure 18B. The X_b values have y-intercepts closer to zero and slopes closer to 1 than the C/C values for the CP and DP techniques (Figure 18A-B) indicate a higher accuracy for X_b . The X_b CP technique (Figure 18A) also has a lower RMSE value (34°C) than the C/C CP technique (Figure 18A) RMSE value (46°C), making the X_b CP proxy more accurate. The DP proxy values in Figure 18B are of the same accuracy (RMSE = 46°C). In general, the CP technique (Figure 18A) precisions for both X_b (SE = $\pm 36^\circ\text{C}$) and C/C (SE = $\pm 43^\circ\text{C}$) are closer to the 1:1 line than the DP technique (Figure 18B) precisions for X_b (SE = $\pm 49^\circ\text{C}$) and C/C (SE = $\pm 50^\circ\text{C}$). Overall, the CP X_b technique is the most accurate and precise at estimating the actual temperature since it has a regression that has a y-intercept closest to zero (48.028), slope closest to 1 (0.8786), lowest RMSE value (34°C) and smallest SE value ($\pm 36^\circ\text{C}$) of all the regressions.

Field Calibration X_b and C/C Values Estimate Temperature up to 350°C

I used the regression models in Figure 18A-B and described in Table 2 to estimate the pyrolysis temperature for each Waco Wetland charcoal sample. The pyrolysis temperature indicated by the charcoal chemistry for CP (Figure 19A) and DP (Figure 19B) are plotted against the mean air temperature (above 250°C) recorded by the thermocouple located at each sampling site. The regressions in Figure 19 indicate the data are quite linear and both proxies estimate nearly the same temperature based off the

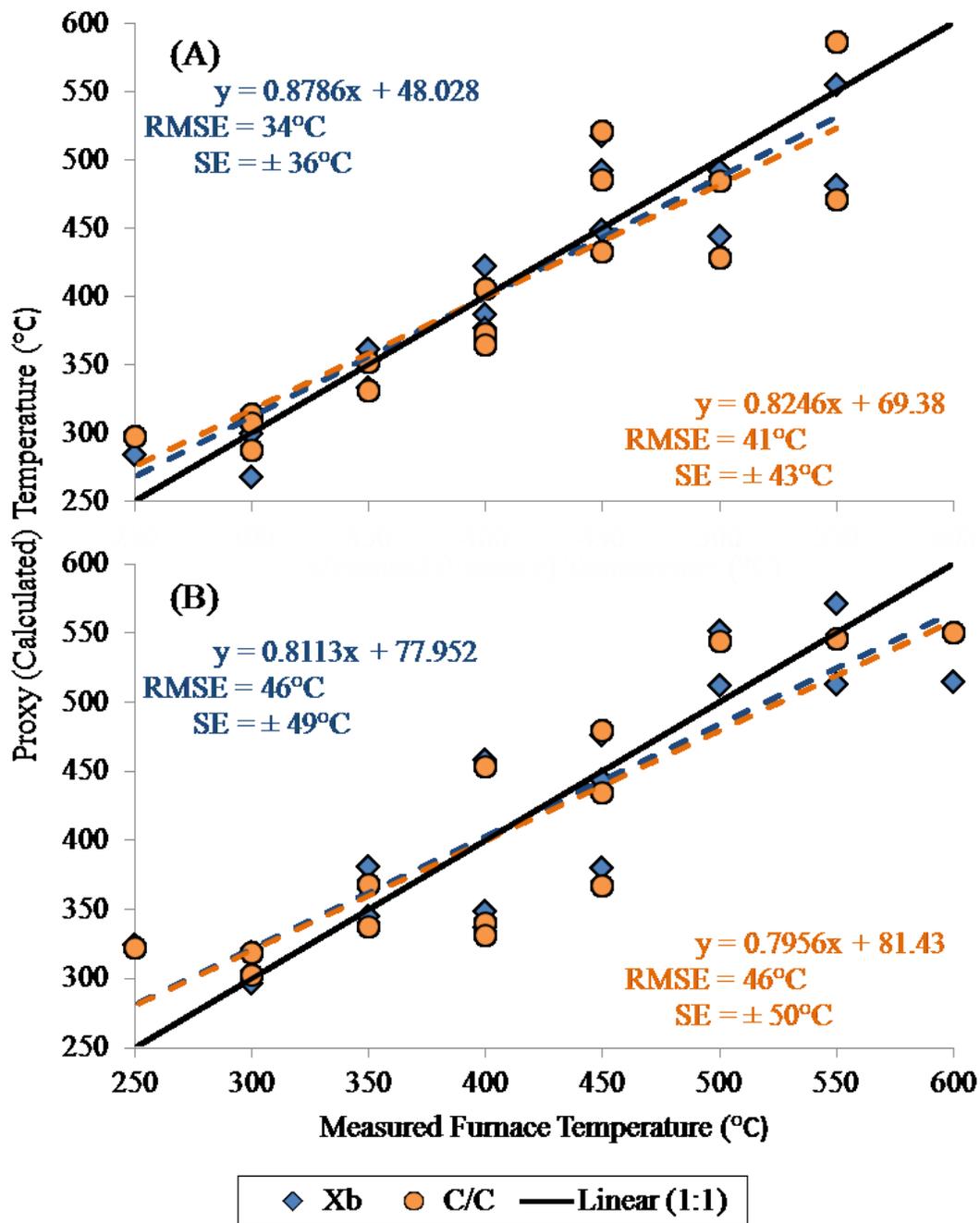


Figure 18. The relationship between the measured (furnace) calibration charcoal temperatures and the proxy (calculated) temperatures. The blue dashed lines and blue text refers to X_b values while the orange dashed lines and orange text refers to C/C values. (A), Cross Polarization technique; (B), Direct Polarization technique.

very small slopes of less than 0.016. The RMSE values of the regressions were all above 86°C which demonstrates much lower accuracy than the calibration charcoals (RMSE values of 46°C or lower). All the SE values are either 71 or 72°C (within 1°C) indicating the models have far less precision than the calibration charcoals (SE values less than 50°C) and are all quite similar in precision. Even so, thermocouple temperatures up to 350°C are estimated accurately by the charcoal-based proxy in Figure 19A (CP technique), but are over-estimated in Figure 19B (DP technique). However, the charcoal pyrolysis temperatures seem to be under-estimating the air temperatures recorded by thermocouples above 350°C for both techniques with the under-estimation becoming larger with increasing air temperature. In the CP technique, the X_b values consistently estimate slightly lower temperatures than the C/C values. The DP technique shows no apparent over or underestimation between proxies. The majority of the estimated charcoal pyrolysis temperatures fall between about 250 and 350°C according to NMR-based proxy. The field samples must be experiencing conditions not experienced in the lab around 350°C for all the proxies to estimate lower than actual temperatures.

Sources of Uncertainty

This section discusses three major sources of uncertainty that may affect the accuracy of the proposed NMR-based temperature proxy: (1) the production of charcoal in the laboratory with accurately-determined production temperatures, (2) the quantitative analysis of charcoals by NMR spectroscopy, and (3) the collection of representative field samples (charcoals) and the measurement of the fire temperature associated with a field charcoal sample.

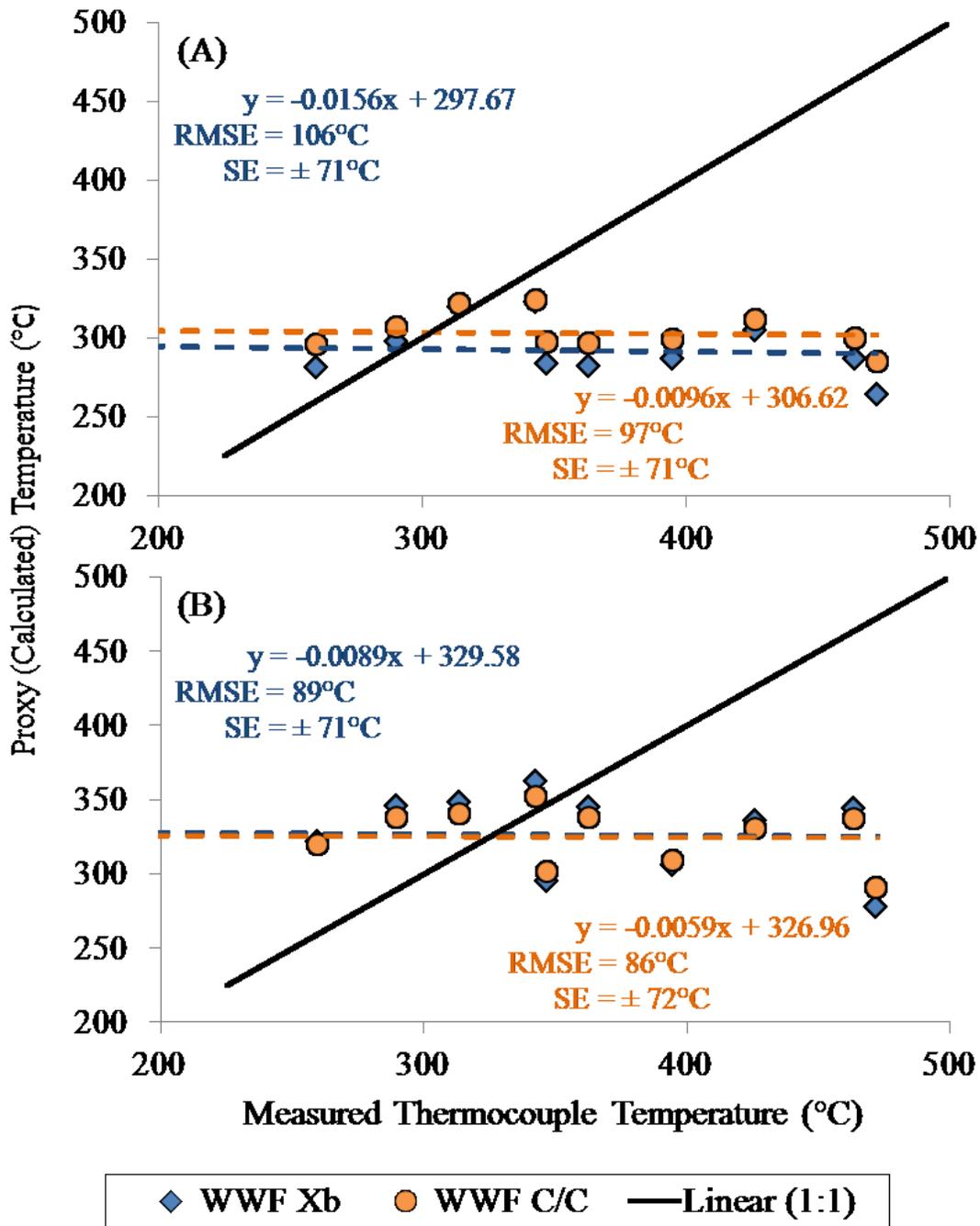


Figure 19. The relationship between the measured (thermocouple) WWF charcoal temperatures and the proxy (calculated) temperatures. The blue dashed lines and blue text refers to X_b values while the orange dashed lines and orange text refers to C/C values. (A), Cross Polarization technique; (B), Direct Polarization technique.

(1) Accuracy of Charcoal Production Temperature for Proxy Calibration

The systematic differences in laboratory charcoal values present in Figure 10A-B, Figure 11A-B, and Figure 18A-B may have been caused by inaccuracies in the muffle furnace temperatures. Even though the muffle furnace sensor is accurate to within 1°C (according to the user's manual), the muffle furnace temperature is based on the air temperature sensed by a thermocouple within the furnace chamber, not in the beaker where the charcoal was being produced. Therefore, it is possible that the charcoal production temperature was not identical to the furnace temperature. It is highly unlikely, that the temperature within the pyrolysis beaker never reached the desired temperature because the isothermal treatment time was 24 hours, allowing sufficient time for thermal equilibrium between the furnace and charcoal temperatures. However, it is possible that temperatures experienced by the charcoal exceeded the set-point of the furnace, during the exothermic phase of biomass pyrolysis reactions. Specifically, the pyrolytic decomposition of the lignin polymer is exothermic at temperatures above 345 degrees C (Tang and Eickner, 1968), and these reactions may add heat to the biomass without affecting the thermostat which regulates furnace temperature. It is also worth mentioning that the natural variability in the biomass composition of different species may have been sources of variability and uncertainty, but the lack of substantial differences in the NMR data in this study make this difficult to impossible to decipher.

(2) Uncertainty in the Analysis of Charcoal by NMR Spectroscopy

The NMR is known to inaccurately identify carbon functional groups when the sample has high contents of paramagnetic and ferromagnetic material (Freitas et al., 2002). The degree of charcoal paramagnetism has been shown to increase at high

pyrolysis temperatures due to the stabilization of free radical electrons within the extended network of aromatic carbons (Bourke et al., 2007). Freitas et al. (2002) found that the aromatic region in charcoals contains large quantities of paramagnetic materials when produced at temperatures above 600°C. McBeath et al., 2011 found the quantitative observability of charcoals produced above 500°C decreased rapidly with DP from 87% at 500°C to 67% at 600°C and 57% at 700°C. This is why only three charcoal samples above 500°C were included in this study with only one at 600°C. Higher temperature charcoals were produced, but issues with probe tuning and observability prevented further analyses.

The quantification of the total carbon observed and the possible under-representation of certain chemical structures is a concern for charcoal samples because the remote protonation of bridgehead carbons can lead to poor polarization transfer during cross-polarization NMR experiments (Smernik and Oades, 2000). Table 2 indicates that the spin counting results for the DP technique has C_{obs} values of $100 \pm 10\%$ for the laboratory and field charcoals produced by this study. The C_{obs} values for the Hockaday et al., *in prep* charcoals (Pine, Pecan, and Magnolia) were not calculated and may contain low observability values. However, the CP technique C_{obs} values calculated in this study are much lower than the DP C_{obs} values. This is common for charcoal (Smernik and Oades, 2000), but the C_{obs} values in this study (61 – 10%) are even smaller than those found by McBeath et al., 2011 in charcoals of chestnut wood (*Castanea sativa*) produced at the same temperatures from 250 to 500°C (87 – 36%). Smernik and Oades, 2000 found a C_{obs} value of 29% for a 450C charcoal of red gum (*Eucalyptus camaldulensis*), while the Willow charcoal in this study has a C_{obs} of only 22%. The

higher apparent observability in the study by Smernik and Oades (2000) is likely due to their use of a variation on the spin counting technique, called spin accounting, which applies a correction for the rapid relaxation of protons in charcoal. Furthermore, Smernik and Oades (2000) tested whether specific carbon functional groups were preferentially under-represented in charcoal and discovered that condensed aromatic region observability can be quite diminished in CP and DP spectra, likely due to paramagnetic centers. Although the Pine, Pecan, and Magnolia charcoals may have low C_{obs} values, the Cattail and Willow charcoals have very low CP C_{obs} values when compared to DP NMR, and highly aromatic structures tend to be under-represented relative to the carbon in the glycine standard, the carbon functional groups seem to be represented well for all the charcoals used in the regressions (Figure 10; Figure 11). This is surprising, but may be a function of reduced observability across the entire spectrum instead of in select functional groups, thus retaining the same relative carbon ratios in CP and DP for charcoals. Low concentrations of paramagnetic centers in the 250 to 600°C charcoals relative to higher temperature charcoals may also lead to identical functional group observability in the DP and CP techniques.

(3) Uncertainty in Field Calibrations

The field calibrations have much weaker overall accuracy (up to 106°C versus only 34°C for RMSE when using the CP Xb technique) and precision ($\pm 71^\circ\text{C}$ versus $\pm 36^\circ\text{C}$ for SE when using the CP Xb technique) values than the lab calibrations owing to more sources of uncertainty (Table 2; Table 4; Figure 18; Figure 19). Since the scale of the pyrolysis volume is much larger in a prescribed burn such as the Waco Wetland Fire than the inside of a muffle furnace, charcoal production has the potential to be more

heterogeneous structurally and chemically. Indeed, the range of peak temperatures recorded by the thermocouples suggests that it is possible to have a variety of charcoal ranging from amorphous composite derivatives of lignin and cellulose to turbostratic crystallites comprised of fused aromatic rings (Keiluweit et al., 2010). Furthermore, the conditions or fire regime in which the charcoal formed can be quite variable even within a single fire event suggesting that charcoal formed relatively close to each other may vary dramatically. Some possible sources of this uncertainty include the picking and sampling strategy, spatial differences within the fire regimes (such as moisture, density, wind speed variability, rate of spread, and fire behavior), reaction kinetics, and thermal lag. The remainder of the discussion is devoted to the treatment of each of these issues in detail.

Picking and Sampling Strategy

Charcoal collection and picking from the Waco Wetland sample locations may not have provided appropriate charcoal aliquots to be analyzed by NMR. Even though all effort was made to make sure only black, variable plant part, multiple species charcoals were picked to replicate true charcoal preservation, true preservation charcoal may not have been represented. Picked charcoal may have been visibly black on the outside, but may have contained uncharred “fresh green” tissues inside thus biasing the charcoal NMR response to lower values. Charcoal preserved in the rock record is assumed to be of many species, plant parts, and degrees of charring, however, degradation may remove the less recalcitrant (partially charred or lower temperature) charcoal pieces (Masiello, 2004; Conedera et al., 2009; McParland et al., 2009). Also, woody or stem tissues may be persevered better than grassy or leafy tissues due to their higher contents of

lignocellulosic material. The samples picked at the Waco Wetland sample sites may have also included species not used in the calibration proxy that react to pyrolysis differently.

Fuel Moisture

Differences in starting material moisture may have caused differences in calculated Waco Wetland charcoal X_b values. Dimitrakopoulos et al., 2010 observed percent fuel moisture contents of prescribed burns at the botanical garden of the School of Forestry and Natural Environment at Aristotle University, Thessaloniki to range from 8 to 114% with ignitions above 30% being dependent on variables other than moisture. Latent heat loss (related to moisture content) of the specific plant biomass would require the charcoal to experience a greater intensity or longer duration of heating in order to produce the same amount of X_b as a dry piece of biomass. Given the conditions described in the Methods for the prescribed burn at the Waco Wetland (the wetland was drained for 24 consecutive days before the fire was initiated, the week leading up to the burn received 4.826 millimeters (0.19 in.) of precipitation and had an average temperature of 32°C (89°F)), moisture differences are possible, but unlikely since the high temperatures and low precipitation amounts were probably enough to dry out all the standing biomass to near moisture levels.

Fuel Density

Thermocouples were able to provide precise temperature readings (every 5 seconds) and could show how the temperature changed with time, but may not have been able to accurately record the ambient temperature around each sampled charcoal piece. Even though the thermocouples are rated for temperatures much lower (0°C) and greater

(1250°C) than the recorded WWF prescribed burn temperatures (30°C and 675°C respectively), single-point thermocouple measurements may not accurately sample the pyrolysis volume at the field site because they only record temperatures ~5 centimeters above the soil surface and the majority of the heat involved in charcoal production can be above this height. A more extensive 3-dimensional sampling method may be needed to discern the localized pyrolysis conditions.

The Reynolds Creek Burn is a good example of such a situation. Figure 20 shows how the maximum temperature recorded by thermocouples can vary laterally and vertically within a 1 meter by 1 meter plot area and within 30 cm height. Based off Figure 20, charcoal collected within a 1m² area at Reynolds Creek could have experienced temperatures up to 250°C in difference (East corner) or no difference at all (West corner).

The curves in Figure 20 demonstrates how the density of the vegetation in a given space will alter the amount of internal energy available per unit volume. The spatial geometry or shape of the biomass is also important since it too can provide variability to the fuel load. These changes in energy could affect the amount of heat produced at any given sample location causing different temperatures to be recorded in the charcoal chemistry.

Wind Speed Variability

Wind speeds are especially unpredictable and may occur in gusts up to 40 km hr⁻¹ or ~25 mph during a prescribed burn (Dimitrakopoulos et al., 2010). Convective heating, or the transfer of energy through gases, would have preferentially heated biomass downwind of the dominant wind direction. This charcoal may have experienced a greater

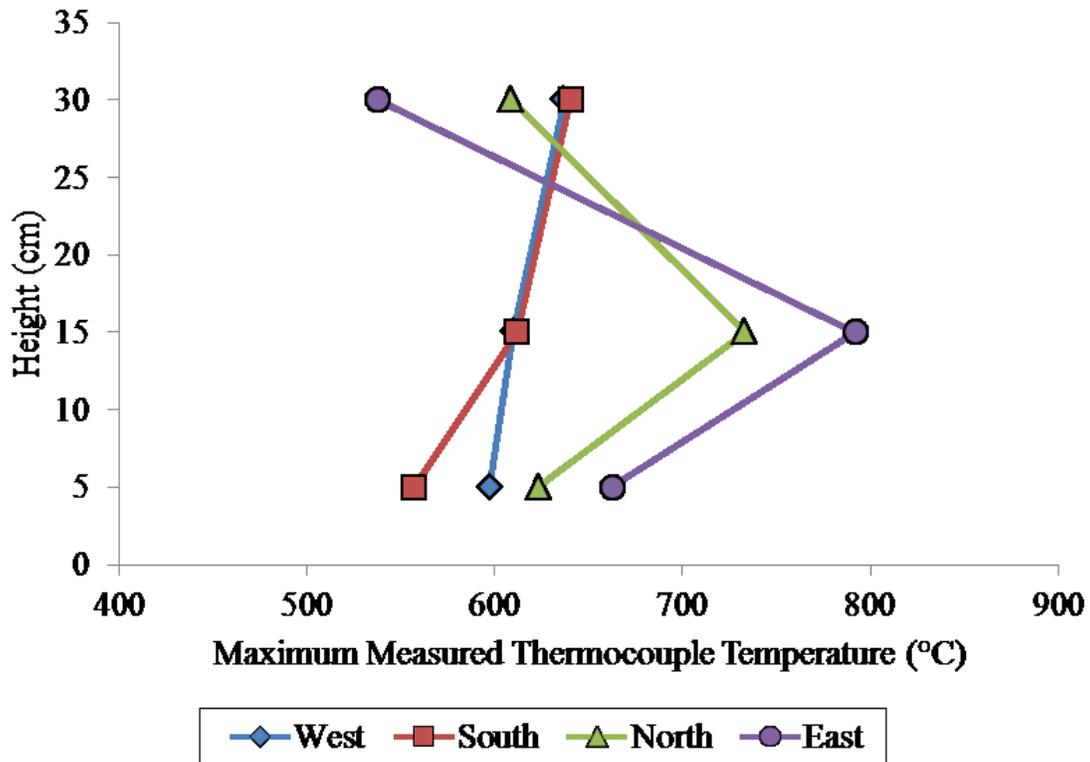


Figure 20. Reynolds Creek Thermocouple Temperatures with height.

“pre-heating” than other charcoal. Charcoal may have also been blown from another location containing different fire regime conditions to the location in which it was collected. Spot fires in wildfires are commonly started by such a method. The presence of charcoal in sample sites not achieving a maximum temperature of 250°C at the WWF sites is evidence for lateral transport of charcoal not represented by the sample site’s thermocouple. This transported energy or charcoal could have caused inaccurate measured bridgehead carbon values at one or more of the WWF sample sites.

ROS and Fire Behavior

Along with changing wind speeds, the Rate of Spread (ROS) and fire behavior (based on wind direction) may have altered charcoal chemistry by changing available

oxygen content (pyrolysis or combustion), the heating rate (thermal lag), and/or the duration of temperatures above 250°C (thermal lag). Figure 21 utilizes peak temperature times and the calculated ROS values between each site from Table 3 and Appendix B to estimate fire behavior during the Waco Wetland prescribed burn. Thermocouple locations that experienced the greatest true ROS values and more than one fire behavior direction also experienced the greatest fire temperatures (Table 3 and Figure 13). This is most likely due to an increase in available oxygen for combustion (exothermic reaction) and more heat transfer (less thermal lag) from multiple wind directions and speeds.

Relative wind speed and direction were also estimated from Table 3 and Figure 21. The fire behavior direction with the highest ROS values most likely had the greatest wind speed for that day and the fire behavior with the lowest ROS values most likely had the lowest wind speed for that day. The Eastward fire behavior direction (purple arrows) had the two highest ROS values for that day (0.071 m sec^{-1} and 0.118 m sec^{-1}) while the Southwestward fire behavior (yellow arrows) had the two lowest ROS values for that day (0.016 m sec^{-1} and 0.018 m sec^{-1}) according to Table 3, Figure 13, and Appendix B. According to the National Weather Service's monthly climate report for August, 2010, the maximum wind speed for the prescribed burn reached 20 mph in the 80°ENE direction. This validates our estimate for the greatest relative wind speed and direction based on the ROS and peak temperature times.

The data in Figure 22 show the ROS values from Table 3 plotted as a function of the proxy temperature accuracy (from Table 4) for each respective field sample. The linear correlation in Figure 22 is most likely due to some sort of moisture-induced or thermally-induced temperature lag between the thermocouple and the charcoal particles.

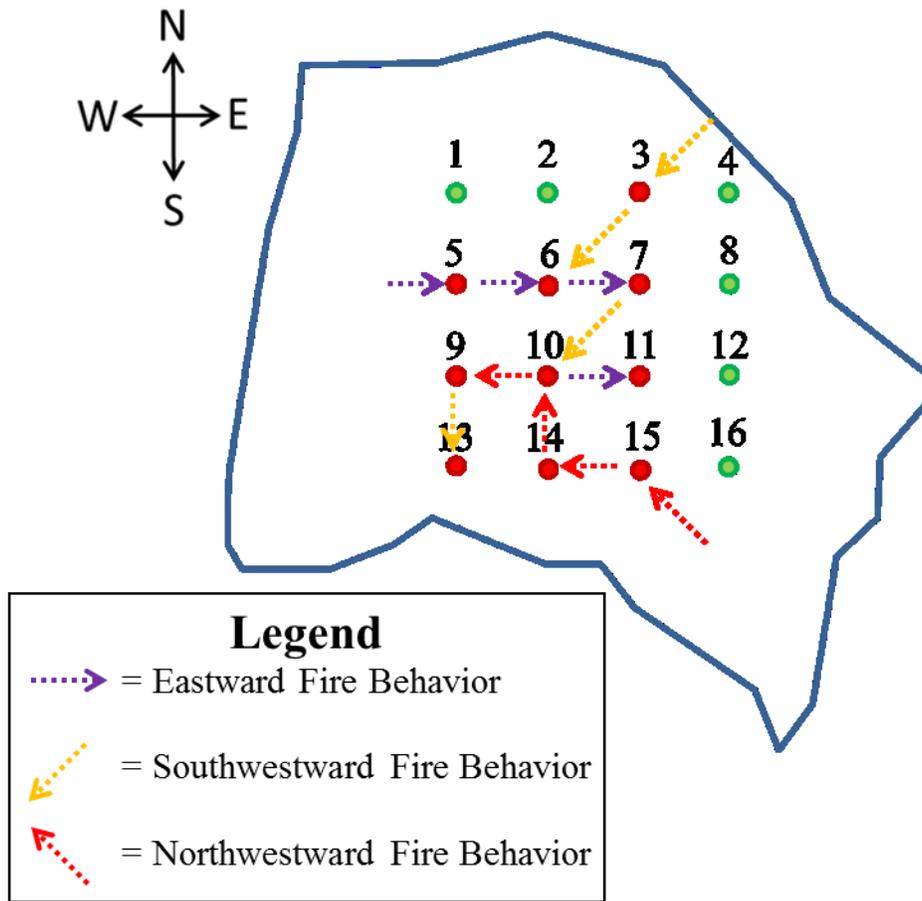


Figure 21. Fire behavior map for the Waco Wetland prescribed burn. The three directions of fire behavior (colored arrows) based on the peak temperature times and ROS values in Table 3, Figure 13, and Appendix B.

A linear correlation ($r^2 = 0.24$) and significance ($p = 0.15$) was observed between the accuracy and the ROS experienced at each charcoal sample location from the WWF (Figure 22). Only the X_b CP accuracy data are shown for it had the greatest correlation coefficient value and lowest p-value. It is probable that thermodynamics could be used to reconcile these differences.

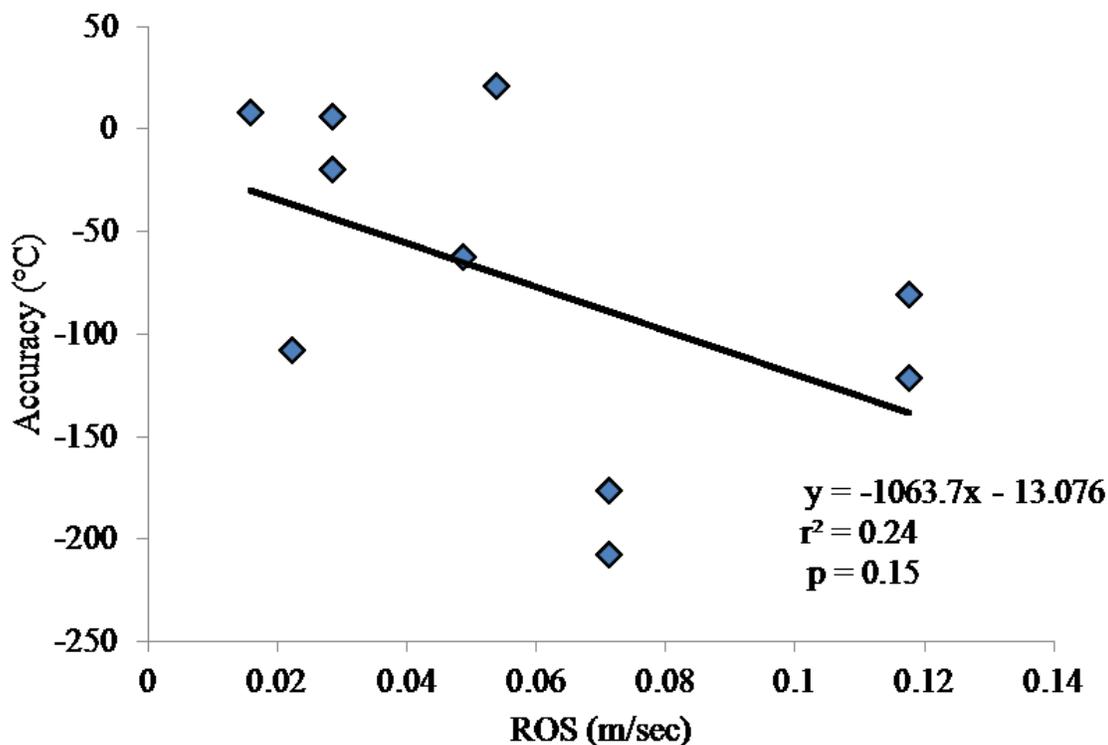


Figure 22. Relationship between Accuracy and ROS values for WWF samples. Linear regressions with associated X_b CP technique. The r^2 and p-value are provided. The black line is the X_b CP linear regression.

Reaction Kinetics and Thermal Lag

When creating the lab calibration, sufficient time and thermal energy was provided to the biomass that was pyrolyzed in the muffle furnace to drive all reactions to completion at their respective temperatures (i.e. equilibrium). As shown in Figure 13, Table 3, and Figure 22, a relatively short duration, or amount of energy was experienced by the field samples. Unlike the lab calibration charcoals, the field charcoals were probably rate-limited and did not undergo all the reactions the calibration charcoals experienced. This idea led me to investigate what might be the cause off the offset between the thermocouple temperatures and the temperatures estimated by the NMR-based proxy. To do so, I consider the thermodynamic properties of primary and

secondary reactions of charcoal formation to derive a correction factor for incomplete (non-equilibrium) pyrolysis.

Fortunately, Mok and Antal, 1983 reported the thermal lag in biomass samples undergoing rapid heating, where they document a substantial time lag in the temperature rise of the biomass particles relative to the temperature rise of the air surrounding the biomass. They identified the 1st order endothermic cellulose pyrolysis reaction as the cause of the thermal lag during pyrolysis. Upon rapid heating, cellulose pyrolysis reactions are predominant from 240 to 450°C with a maximum rate at 335°C, during which cellulose is efficiently converted into vapors and leaves little to no charred residue behind (Tang and Eickner, 1968). Narayan and Antal, 1996 further described endothermic cellulose pyrolysis thermal lag as having heat demand that increases with heating rate, and demonstrated that temperature lags caused by the endotherm also increase as a function of heating rate. Lignin on the other hand is slightly endothermic during pyrolysis from 190 to 345°C, but is highly exothermic from 345 to 500°C (Tang and Eickner, 1968). If thermal lag due to a 1st order endothermic cellulose reaction is affecting the WWF samples, the field temperature offsets between thermocouple and NMR-based proxy should correspond to the amount of cellulose lost from the sample.

An advantage of the NMR method is its ability to identify the relative contributions of specific organic molecules (i.e. cellulose) to the bulk sample mass by analyzing the relative concentrations of carbon functional groups in a sample. As described earlier in the results, Frietas et al., 1999 and Baldock et al., 2004 identified the 60-110 ppm region of the NMR spectrum as the cellulose (carbohydrate) signal for plant biomass. If thermal lag due to endothermic cellulose pyrolysis is affecting the samples,

the loss of cellulose carbon content from the field charcoals relative to a fresh uncharred sample should reflect this. In order to explain this loss quantitatively and to relate it to thermodynamics, the relative amounts of cellulose carbon for uncharred biomass (represented by the average 60-110 ppm value of the 55°C Willow and Cattail samples) and each field sample (represented by the 60-110 ppm range for each WWF sample) were converted into percent mass in grams of the total sample mass by normalizing to a bulk sample of 100 grams. This normalization allowed for the conversion of each functional group into grams and the relative masses to be a percentage of the total mass (100 grams). The difference in the normalized masses between the uncharred biomass and the field sample provided the mass of Cellulose Carbon Loss due to endothermic cellulose pyrolysis. Equation 6 shows how the mole fraction cellulose in the field sample (60-110 ppm), $X_{cel-field}$, is normalized to 100 and subtracted from the mole fraction cellulose in uncharred biomass (60-110 ppm), $X_{cel-uncharred}$, normalized to 100 to get the cellulose carbon loss in grams for each field sample sample.

$$Cellulose\ Carbon\ Loss = (100)X_{cel-uncharred} - (100)X_{cel-field} \quad (6)$$

The $X_{cel-uncharred}$ value is the average value for mole fraction cellulose in Cattail and Willow samples and may be modified based on assumptions for species presence. By assuming the relative mass of cellulose carbon loss from Equation 6 is equivalent to the relative mass of molecular cellulose loss in a 100 gram bulk sample, the cellulose loss in grams per sample can be identified and related to thermodynamics. Figure 23 shows the amount of cellulose loss from the WWF field calibration samples versus the proxy temperature error for each respective field sample. Equation 6 and Figure 23 use only

the CP X_b technique since the uncharred Cattail and Willow samples were only analyzed by the CPMAS NMR technique. The linear correlation in Figure 23 is most likely a product of the 1st order endothermic cellulose thermal lag. A strong linear correlation ($r^2 = 0.69$) and significance ($p = 0.0029$) were observed between the accuracy (from Table 4) and the cellulose loss in the charcoal samples from the WWF (Figure 23). Theoretical estimated accuracies due to endothermic cellulose pyrolysis thermal lag were calculated to try to explain this relationship.

I have attempted to calculate an “idealized” thermal lag, using basic thermodynamic principles as a means of explaining this relationship in Figure 23. The theoretical lag is based upon the temperature at which endothermic cellulose pyrolysis is at its maximum rate (335°C), and the thermal energy that is consumed (T_{consumed}) per gram of cellulose during the reaction.

In order to calculate the amount of heat energy in the form of temperature removed or consumed from the pyrolysis of one gram of cellulose (T_{consumed}), some thermodynamic parameters must be known. The specific enthalpy (ΔH_c), or energy involved during pyrolysis, of cellulose was described by Mok and Antal, 1983 to be 210,000 J kg⁻¹. The positive ΔH_c value indicates it is an endothermic reaction. The specific heat (c_c) of cellulose, or amount of energy needed to raise a specific mass of cellulose by 1°C, value of 1670 J kg⁻¹ °C⁻¹ was determined by Pyle and Zaror, 1984. Equation 7 takes the cellulose heat of pyrolysis value (ΔH_c) for 1 gram of cellulose ($m_c = .001\text{kg}$) and divides it by the specific heat of cellulose (c_c) to get the mass of cellulose consumed by endothermic absorption of 1°C from the reaction (T_{consumed}). About 0.125

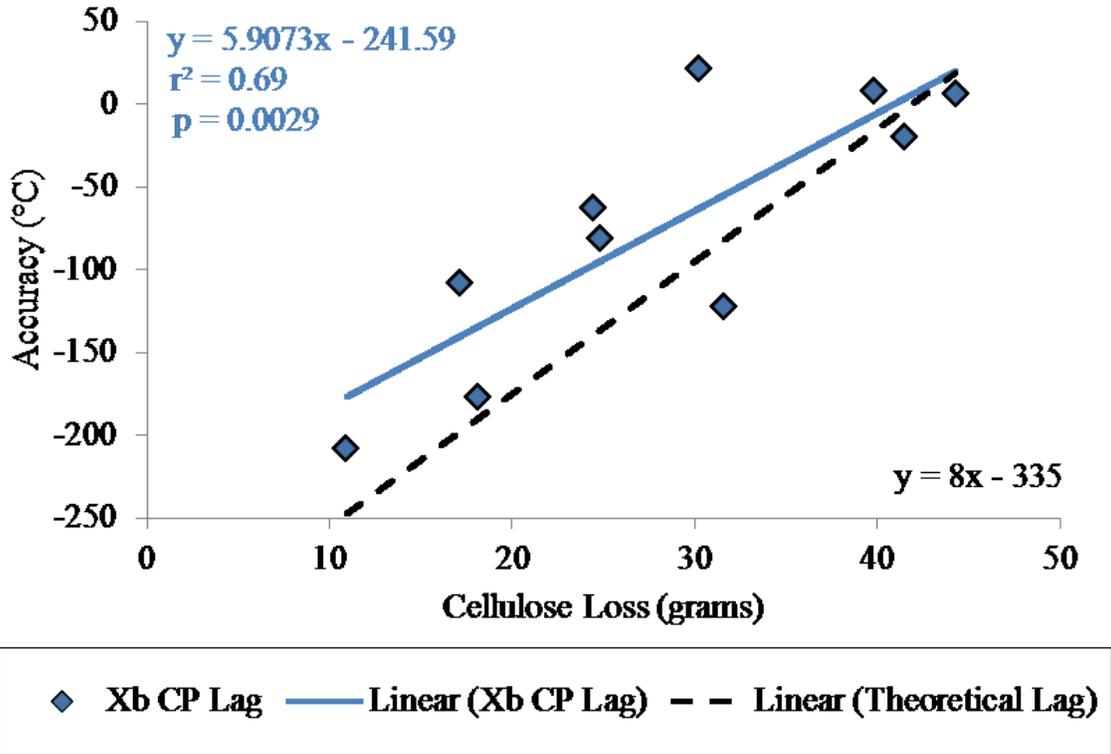


Figure 23. Relationship between Accuracy and the Cellulose Loss in grams for WWF samples. Linear regressions with associated X_b CP technique. r^2 and p-values are provided in each plot. The blue line is the X_b CP linear regression and the dashed black line is the theoretical lag linear regression.

grams of cellulose will consume 1°C in endothermic cellulose pyrolysis. Thus, the pyrolysis of 1 gram of cellulose will consume 8°C in endothermic cellulose pyrolysis.

$$T_{consumed} = \frac{\Delta H_c m_c}{c_c} \quad (7)$$

By using the $T_{consumed}$ value as the slope and assuming the y-intercept to be the temperature of cellulose pyrolysis (335°C from Tang and Eickner, 1968), the theoretical thermal lag regression was developed for Figure 23.

Table 5 presents the estimated theoretical accuracy correction and theoretical calculated temperatures based upon the endothermic cellulose pyrolysis thermal lag

regression in Figure 23. Table 5 also includes previously identified (thermocouple) and calculated (CP X_b technique) temperatures for comparison. Theoretical estimated accuracy correction values were calculated based off the theoretical lag regression in Figure 23. Three WWF sites had no correction for they were not observed by thermocouples or proxy to reach the minimum value for endothermic cellulose pyrolysis (335°C). The thermal lag corrected temperatures are more accurate (RMSE = 46°C) than the uncorrected CP X_b temperatures (RMSE = 106°C) in Table 5. The precision values decrease from ± 71°C in the uncorrected values to 42°C in the corrected values (Table 5).

Table 5. Mean thermocouple, proxy (CP X_b), and thermal lag corrected temperatures and accuracies for the Waco Wetland Fire samples

Waco Wetland Fire Sample	Mean Thermocouple Temperature (°C)	Proxy Calculated		Theoretical Thermal Lag Corrected		
		Temperature (°C) ^a	Accuracy (°C) ^b	Correction (°C) ^c	Temperature (°C) ^d	Accuracy (°C) ^e
WWF3	290	298	8	0	298	8
WWF5	472	264	-208	-248	511	39
WWF6	464	287	-177	-190	477	13
WWF7	395	286	-108	-198	484	89
WWF9	260	281	21	0	281	21
WWF10	426	305	-122	-82	387	-40
WWF11	363	282	-81	-136	418	55
WWF13	347	284	-63	-139	423	76
WWF14	314	320	6	0	320	6
WWF15	343	323	-20	-3	326	-17
RMSE (°C) ^f			106			46
SE (± °C) ^g			71			42

^aTemperature values for CP X_b from Table 3

^bAccuracy values for CP X_b from Table 3

^cCorrection = (8) x (Cellulose Loss) – 335; Temperature must be above 335°C

^dTemperature = CP X_b Temperature value – Theoretical Estimated Error value

^eAccuracy = Thermal Lag Corrected Temp. – Mean Thermocouple Temp.

^fRMSE = Root Mean Square Error

^gSE = Standard Error

Figure 24 uses the measured thermocouple temperatures in Table 5 plotted against the proxy calculated and corrected temperatures from Table 5 to show how well the

calculated and corrected temperatures estimate the actual measured temperatures of charcoal formation. Both calculated and corrected temperatures accurately estimate the actual temperatures up to about 350°C. However, the estimated temperatures corrected for thermal lag do a better job at estimating the actual temperature above 350°C. It appears that thermal lag due to cellulose endotherm was a major cause of error in the proxy-based temperature estimates for fire temperatures above 335°C.

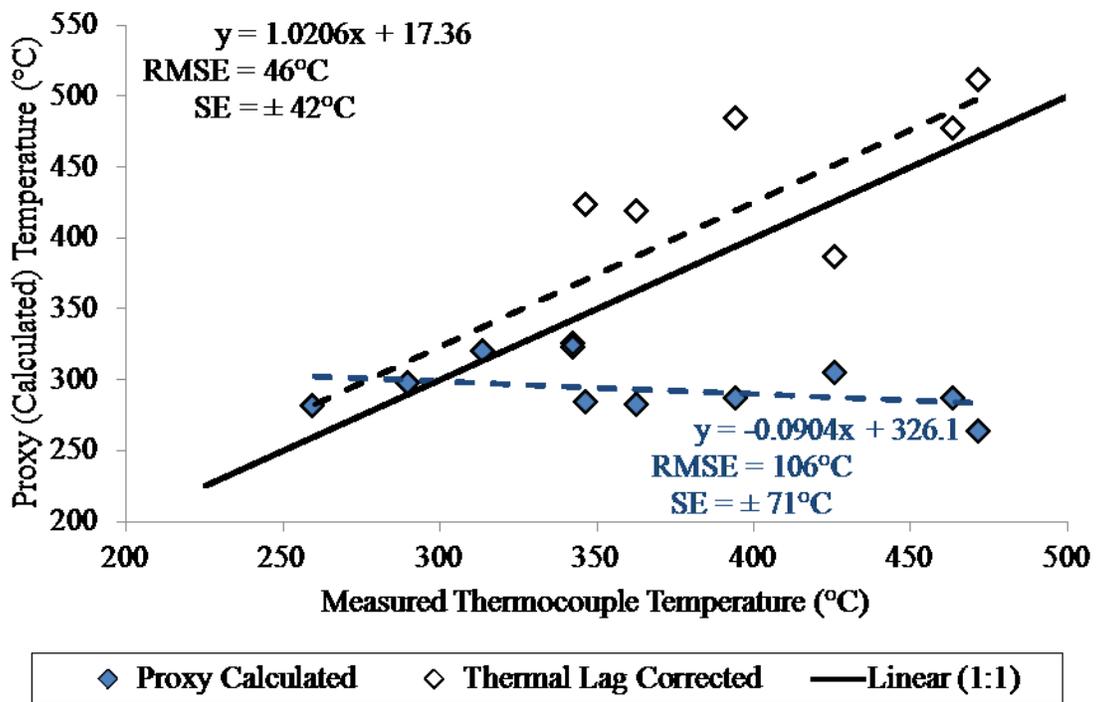


Figure 24. Relationship between the measured thermocouple WWF charcoal temperatures and the proxy (calculated and corrected) temperatures using the CP X_b technique.

As proposed in Hypothesis 1, when using the cellulose loss correction as in Figure 24, the NMR-based proxy can estimate the average fire temperature based off the chemistry of the charcoal. With the CP X_b technique, the thermal lag corrected proxy is nearly as accurate and precise in the field (46 and $\pm 42^\circ\text{C}$ respectively) as it is in the lab

(34 and $\pm 36^{\circ}\text{C}$ respectively) at estimating charcoal formation temperature (Table 2; Table 5). Further analyses and studies are needed to increase the accuracy of the CP X_b technique and the accuracy of other techniques (CP C/C, DP X_b , and DP C/C) can be increased. The thermal lag correction presented here is a good starting point for developing more comprehensive corrections of field data when using the X_b and C/C proxies.

It is Unclear Whether Species Type Affects Accuracy of Proxies

Given the data, hypothesis 2 is inconclusive whether species type made a significant difference on the proxy's ability to estimate mean temperature. Many of the calibration species types overlap each other and fit an overall linear regression calibration line well. A larger sample size with more grass species is required to discern this.

Conclusions and Implications

^{13}C NMR has been shown to be able to identify charcoal-specific carbon functional groups in fire residues. These groups when tested in a laboratory setting can calculate two carbon chemistry parameters (X_b and C/C) that provide the foundation of a proximate paleo-charcoal thermometer. Field calibration of the proxy has provided promising results. ROS calculations allowed for a better understanding of fire behavior and thermal lag offsets in field samples. A thermal lag correction was developed to help alleviate the offset seen in field samples due to the thermal heat consumption of endothermic cellulose pyrolysis. Further development of field calibration sampling and understanding of fire behavior may lead to more accurate field calibrations in the future. Utilization of this proxy in the rock record will initially require abundant macroscopic

charcoal pieces in combination with a multi-proxy approach (such as GC/MS) to identify and verify the various fire regime conditions.

APPENDICES

APPENDIX A

Q-test

Lab Calibration Data Q-test

DP					CP				
Sample type	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
Xb					Xb				
-	-	-	-	-	0	-	-	-	-
0.055	-	-	-	-	0	0.000	0.000	0.300	1
0.158	0.103	0.123	0.306	1	0.075	0.075	0.104	0.300	1
0.219	0.061	0.073	0.306	1	0.092	0.017	0.024	0.300	1
0.232	0.013	0.016	0.306	1	0.124	0.032	0.044	0.300	1
0.265	0.033	0.039	0.306	1	0.128	0.004	0.006	0.300	1
0.287	0.022	0.026	0.306	1	0.161	0.033	0.046	0.300	1
0.297	0.010	0.012	0.306	1	0.181	0.02	0.028	0.300	1
0.382	0.085	0.101	0.306	1	0.236	0.055	0.076	0.300	1
0.383	0.001	0.001	0.306	1	0.297	0.061	0.084	0.300	1
0.552	0.169	0.202	0.306	1	0.33	0.033	0.046	0.300	1
0.561	0.009	0.011	0.306	1	0.353	0.023	0.032	0.300	1
0.59	0.029	0.035	0.306	1	0.431	0.078	0.108	0.300	1
0.632	0.042	0.050	0.306	1	0.479	0.048	0.066	0.300	1
0.638	0.006	0.007	0.306	1	0.489	0.01	0.014	0.300	1
0.734	0.096	0.115	0.306	1	0.56	0.071	0.098	0.300	1
0.737	0.003	0.004	0.306	1	0.584	0.024	0.033	0.300	1
0.742	0.005	0.006	0.306	1	0.585	0.001	0.001	0.300	1
0.839	0.097	0.116	0.306	1	0.64	0.055	0.076	0.300	1
0.893	0.054	0.064	0.306	1	0.722	0.082	0.114	0.300	1

Lab Calibration Data Q-test

DP					CP				
Sample type	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
Xb Temp. (°C)					Xb Temp. (°C)				
-	-	-	-	-	206	-	-	-	-
219	-	-	-	-	206	0.000	0.000	0.300	1
266	46.818	0.123	0.306	1	246	39.474	0.104	0.300	1
293	27.727	0.073	0.306	1	255	8.947	0.024	0.300	1
299	5.909	0.016	0.306	1	271	16.842	0.044	0.300	1
314	15.000	0.039	0.306	1	274	2.105	0.006	0.300	1
324	10.000	0.026	0.306	1	291	17.368	0.046	0.300	1
329	4.545	0.012	0.306	1	301	10.526	0.028	0.300	1
367	38.636	0.101	0.306	1	330	28.947	0.076	0.300	1
368	0.455	0.001	0.306	1	362	32.105	0.084	0.300	1
445	76.818	0.202	0.306	1	380	17.368	0.046	0.300	1
449	4.091	0.011	0.306	1	392	12.105	0.032	0.300	1
462	13.182	0.035	0.306	1	433	41.053	0.108	0.300	1
481	19.091	0.050	0.306	1	458	25.263	0.066	0.300	1
484	2.727	0.007	0.306	1	464	5.263	0.014	0.300	1
527	43.636	0.115	0.306	1	501	37.368	0.098	0.300	1
529	1.364	0.004	0.306	1	514	12.632	0.033	0.300	1
531	2.273	0.006	0.306	1	514	0.526	0.001	0.300	1
575	44.091	0.116	0.306	1	543	28.947	0.076	0.300	1
600	24.545	0.064	0.306	1	586	43.158	0.114	0.300	1

Lab Calibration Data Q-test

DP					CP				
Sample type C/C	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type C/C	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
-	-	-	-	-	6.000	-	-	-	-
6.719	-	-	-	-	6.000	0.000	0.000	0.300	1
8.463	1.744	0.005	0.306	1	7.012	1.012	0.003	0.300	1
9.837	1.374	0.004	0.306	1	7.277	0.265	0.001	0.300	1
10.173	0.336	0.001	0.306	1	7.819	0.541	0.001	0.300	1
11.106	0.934	0.002	0.306	1	7.891	0.072	0.000	0.300	1
11.802	0.696	0.002	0.306	1	8.524	0.633	0.002	0.300	1
12.141	0.338	0.001	0.306	1	8.945	0.421	0.001	0.300	1
15.710	3.569	0.009	0.306	1	10.279	1.334	0.004	0.300	1
15.761	0.051	0.000	0.306	1	12.141	1.861	0.005	0.300	1
29.895	14.134	0.037	0.306	1	13.366	1.225	0.003	0.300	1
31.133	1.238	0.003	0.306	1	14.333	0.967	0.003	0.300	1
35.693	4.560	0.012	0.306	1	18.532	4.199	0.011	0.300	1
44.305	8.612	0.023	0.306	1	22.104	3.572	0.009	0.300	1
45.786	1.481	0.004	0.306	1	22.978	0.874	0.002	0.300	1
84.798	39.012	0.102	0.306	1	30.992	8.014	0.021	0.300	1
86.744	1.946	0.005	0.306	1	34.671	3.679	0.010	0.300	1
90.139	3.395	0.009	0.306	1	34.838	0.167	0.000	0.300	1
231.473	141.334	0.371	0.306	0	46.296	11.458	0.030	0.300	1
524.063	292.591	0.768	0.306	0	77.636	31.339	0.082	0.300	1

Lab Calibration Data Q-test

DP					CP				
Sample type C/C Temp. (°C)	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type C/C Temp. (°C)	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
-	-	-	-	-	236	-	-	-	-
263	-	-	-	-	236	0.000	0.000	0.300	1
286	23.314	0.061	0.306	1	260	23.988	0.063	0.300	1
301	15.193	0.040	0.306	1	266	5.707	0.015	0.300	1
305	3.391	0.009	0.306	1	277	11.039	0.029	0.300	1
314	8.873	0.023	0.306	1	278	1.408	0.004	0.300	1
320	6.139	0.016	0.306	1	290	11.870	0.031	0.300	1
323	2.853	0.007	0.306	1	298	7.424	0.020	0.300	1
349	26.034	0.068	0.306	1	319	21.390	0.056	0.300	1
349	0.327	0.001	0.306	1	345	25.603	0.067	0.300	1
414	64.662	0.170	0.306	1	360	14.794	0.039	0.300	1
418	4.100	0.011	0.306	1	370	10.748	0.028	0.300	1
432	13.807	0.036	0.306	1	410	39.528	0.104	0.300	1
453	21.833	0.057	0.306	1	437	27.117	0.071	0.300	1
457	3.321	0.009	0.306	1	443	5.963	0.016	0.300	1
519	62.252	0.163	0.306	1	489	46.029	0.121	0.300	1
521	2.291	0.006	0.306	1	506	17.258	0.045	0.300	1
525	3.878	0.010	0.306	1	507	0.741	0.002	0.300	1
620	95.264	0.250	0.306	1	551	43.746	0.115	0.300	1
703	82.541	0.217	0.306	1	630	79.533	0.209	0.300	1

Waco Wetland Field Calibration Data Q-test

DP					CP				
Sample type Xb	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type Xb	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
0.107	-	-	-	-	0.083	-	-	-	-
0.143	0.036	0.159	0.349	1	0.121	0.038	0.292	0.349	1
0.153	0.010	0.044	0.349	1	0.123	0.002	0.015	0.349	1
0.183	0.030	0.132	0.349	1	0.124	0.001	0.008	0.349	1
0.204	0.021	0.093	0.349	1	0.127	0.003	0.023	0.349	1
0.224	0.020	0.088	0.349	1	0.133	0.006	0.046	0.349	1
0.263	0.039	0.172	0.349	1	0.134	0.001	0.008	0.349	1
0.286	0.023	0.101	0.349	1	0.149	0.015	0.115	0.349	1
0.288	0.002	0.009	0.349	1	0.158	0.009	0.069	0.349	1
0.289	0.001	0.004	0.349	1	0.165	0.007	0.054	0.349	1
0.295	0.006	0.026	0.349	1	0.172	0.007	0.054	0.349	1
0.297	0.002	0.009	0.349	1	0.173	0.001	0.008	0.349	1
0.305	0.008	0.035	0.349	1	0.206	0.033	0.254	0.349	1
0.334	0.029	0.128	0.349	1	0.213	0.007	0.054	0.349	1

Waco Wetland Field Calibration Data Q-test

DP					CP				
Sample type Xb Temp. (°C)	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type Xb Temp. (°C)	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
242	-	-	-	-	250	-	-	-	-
259	16.364	0.159	0.349	1	270	20.000	0.292	0.349	1
263	4.545	0.044	0.349	1	271	1.053	0.015	0.349	1
277	13.636	0.132	0.349	1	271	0.526	0.008	0.349	1
286	9.545	0.093	0.349	1	273	1.579	0.023	0.349	1
296	9.091	0.088	0.349	1	276	3.158	0.046	0.349	1
313	17.727	0.172	0.349	1	277	0.526	0.008	0.349	1
324	10.455	0.101	0.349	1	285	7.895	0.115	0.349	1
325	0.909	0.009	0.349	1	289	4.737	0.069	0.349	1
325	0.455	0.004	0.349	1	293	3.684	0.054	0.349	1
328	2.727	0.026	0.349	1	297	3.684	0.054	0.349	1
329	0.909	0.009	0.349	1	297	0.526	0.008	0.349	1
332	3.636	0.035	0.349	1	315	17.368	0.254	0.349	1
346	13.182	0.128	0.349	1	318	3.684	0.054	0.349	1

Waco Wetland Field Calibration Data Q-test

DP					CP				
Sample type C/C	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type C/C	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
7.524	-	-	-	-	7.135	-	-	-	-
8.169	0.645	0.108	0.349	1	7.766	0.630	0.247	0.349	1
8.363	0.194	0.032	0.349	1	7.801	0.035	0.014	0.349	1
8.989	0.625	0.104	0.349	1	7.819	0.018	0.007	0.349	1
9.469	0.481	0.080	0.349	1	7.873	0.054	0.021	0.349	1
9.964	0.494	0.082	0.349	1	7.982	0.109	0.043	0.349	1
11.046	1.082	0.180	0.349	1	8.000	0.018	0.007	0.349	1
11.769	0.723	0.120	0.349	1	8.285	0.285	0.111	0.349	1
11.836	0.066	0.011	0.349	1	8.463	0.178	0.070	0.349	1
11.869	0.033	0.006	0.349	1	8.606	0.142	0.056	0.349	1
12.072	0.203	0.034	0.349	1	8.752	0.146	0.057	0.349	1
12.141	0.069	0.011	0.349	1	8.773	0.021	0.008	0.349	1
12.422	0.281	0.047	0.349	1	9.517	0.744	0.292	0.349	1
13.527	1.105	0.184	0.349	1	9.687	0.170	0.067	0.349	1

Waco Wetland Field Calibration Data Q-test

DP					CP				
Sample type C/C Temp. (°C)	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)	Sample type C/C Temp. (°C)	Gap	Q _{cal}	Q _{crit} (90% conf. level)	(If Q _{cal} < Q _{crit} , then 1)
274	-	-	-	-	263	-	-	-	-
283	8.313	0.140	0.349	1	276	13.022	0.277	0.349	1
285	2.371	0.040	0.349	1	277	0.701	0.015	0.349	1
292	7.285	0.123	0.349	1	277	0.351	0.007	0.349	1
298	5.261	0.089	0.349	1	278	1.056	0.022	0.349	1
303	5.141	0.087	0.349	1	280	2.122	0.045	0.349	1
313	10.417	0.176	0.349	1	281	0.355	0.008	0.349	1
320	6.405	0.108	0.349	1	286	5.376	0.114	0.349	1
320	0.567	0.010	0.349	1	289	3.271	0.070	0.349	1
320	0.284	0.005	0.349	1	292	2.569	0.055	0.349	1
322	1.712	0.029	0.349	1	294	2.590	0.055	0.349	1
323	0.574	0.010	0.349	1	295	0.372	0.008	0.349	1
325	2.312	0.039	0.349	1	307	12.530	0.266	0.349	1
334	8.611	0.145	0.349	1	310	2.725	0.058	0.349	1

APPENDIX B
ROS Calculations

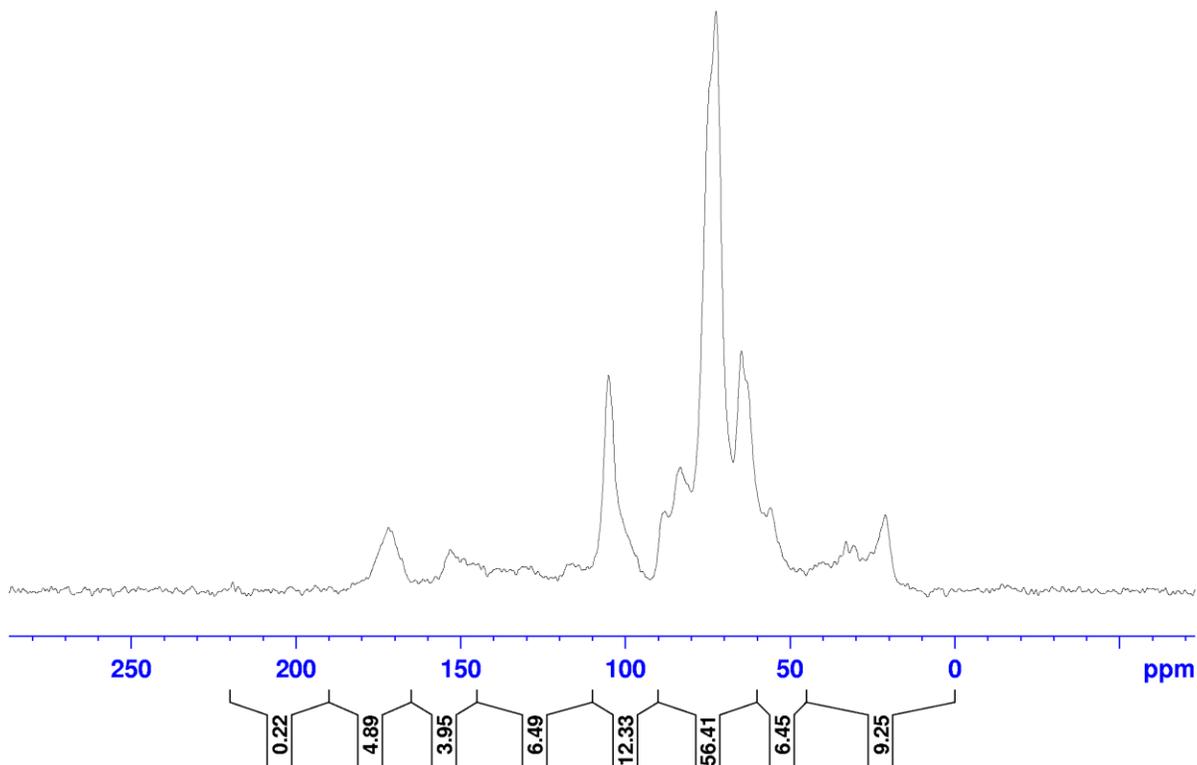
ROS Calculations for the Waco Wetland Fire samples

Sample Site	Adjacent Sample Site	Distance (m)	Time Difference (sec)	ROS (m/sec)
WWF3	WWF6	14	880	0.0159
	WWF7	10	1325	0.0075
WWF5	WWF6	10	140	0.0714
	WWF9	10	1535	0.0065
	WWF10	14	1350	0.0104
WWF6	WWF3	14	880	0.0159
	WWF5	10	140	0.0714
	WWF7	10	445	0.0225
	WWF9	14	1395	0.0100
	WWF10	10	1210	0.0083
	WWF11	14	1295	0.0108
WWF7	WWF3	10	1325	0.0075
	WWF6	10	445	0.0225
	WWF10	14	765	0.0183
WWF9	WWF11	10	850	0.0118
	WWF5	10	1535	0.0065
	WWF6	14	1395	0.0100
WWF10	WWF10	10	185	0.0541
	WWF13	10	205	0.0488
	WWF14	14	680	0.0206
	WWF5	14	1350	0.0104
	WWF6	10	1210	0.0083
WWF11	WWF7	14	765	0.0183
	WWF9	10	185	0.0541
	WWF11	10	85	0.1176
	WWF13	14	390	0.0359
	WWF14	10	495	0.0202
	WWF15	14	845	0.0166
	WWF6	14	1295	0.0108
WWF13	WWF7	10	850	0.0118
	WWF10	10	85	0.1176
	WWF14	14	580	0.0241
	WWF15	10	930	0.0108
	WWF9	10	205	0.0488
WWF14	WWF10	14	390	0.0359
	WWF14	10	885	0.0113
	WWF9	14	680	0.0206
WWF15	WWF10	10	495	0.0202
	WWF11	14	580	0.0241
	WWF13	10	885	0.0113
	WWF15	10	350	0.0286
	WWF10	14	845	0.0166
WWF15	WWF11	10	930	0.0108
	WWF14	10	350	0.0286

APPENDIX C
NMR Spectra

Cattail Calibration charcoal sample dried at 55
 129.1 mg
 CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands
 1 ms contact pulse
 Probe: 7 mm 5kHz MAS

72



```

Current Data Parameters
NAME      VonBargenCattailCal55 092612
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20120926
Time      13.56
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_wch
TD         1024
SOLVENT   CDC13
NS         1104
DS         0
SWH        34722.223 Hz
FIDRES     33.308421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D31        0.00020000 sec
TD0        1
ZGOPINS

===== CHANNEL f1 =====
NUC1       13C
P2         8.00 usec
P15        1000.00 usec
PLW1       180.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

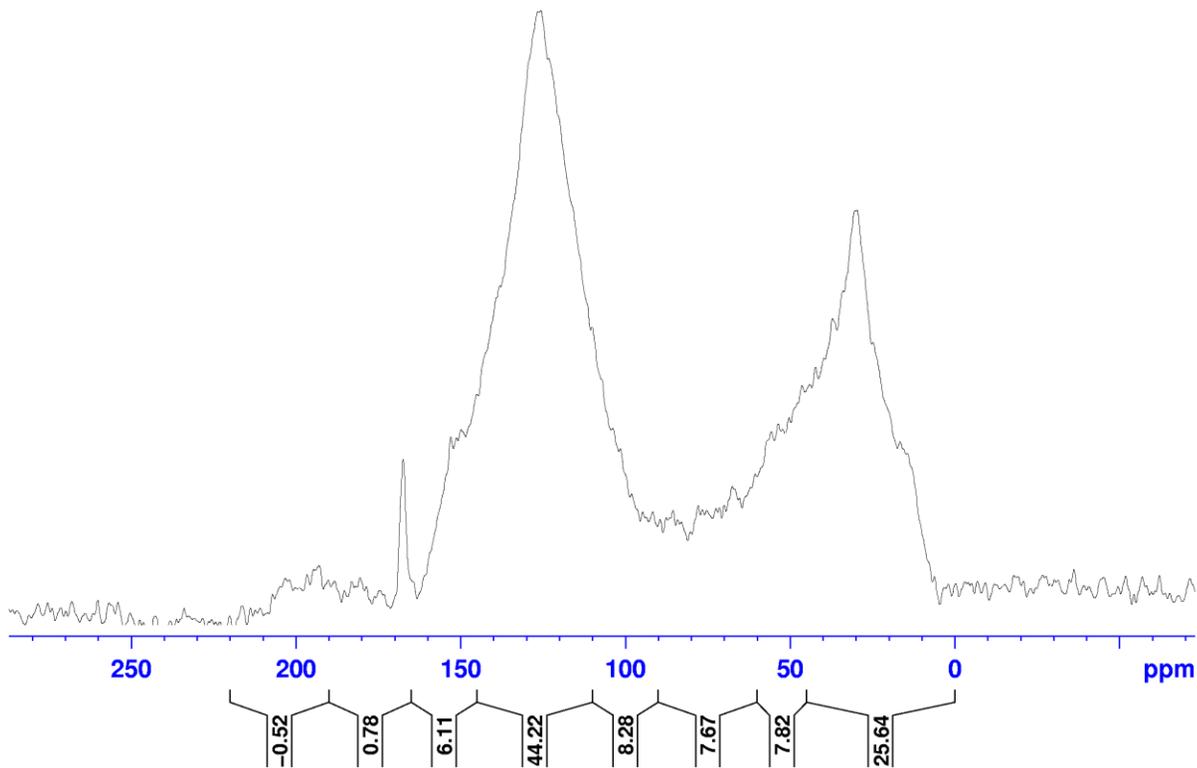
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2        1H
P3          2.85 usec
PCPD2       5.50 usec
PLW2        0 W
PLW2        260.00000000 W
SFO2        300.1312605 MHz
SPNAM0      Squa100.1000
SPOAL0      0.500
SPOFFS0     0 Hz
SPWD        85.00000000 W

F2 - Processing parameters
SI          16384
SF          75.4679759 MHz
WDW         EM
SSB         0
LB          50.00 Hz
GB          0
PC          0.20
  
```



Cattail Calibration Char at 300C
 178.0mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

73



```

Current Data Parameters
NAME      VonBargenCattailCal300 111112
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20121111
Time      20.18
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D31        0.00020000 sec
TDO        4
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

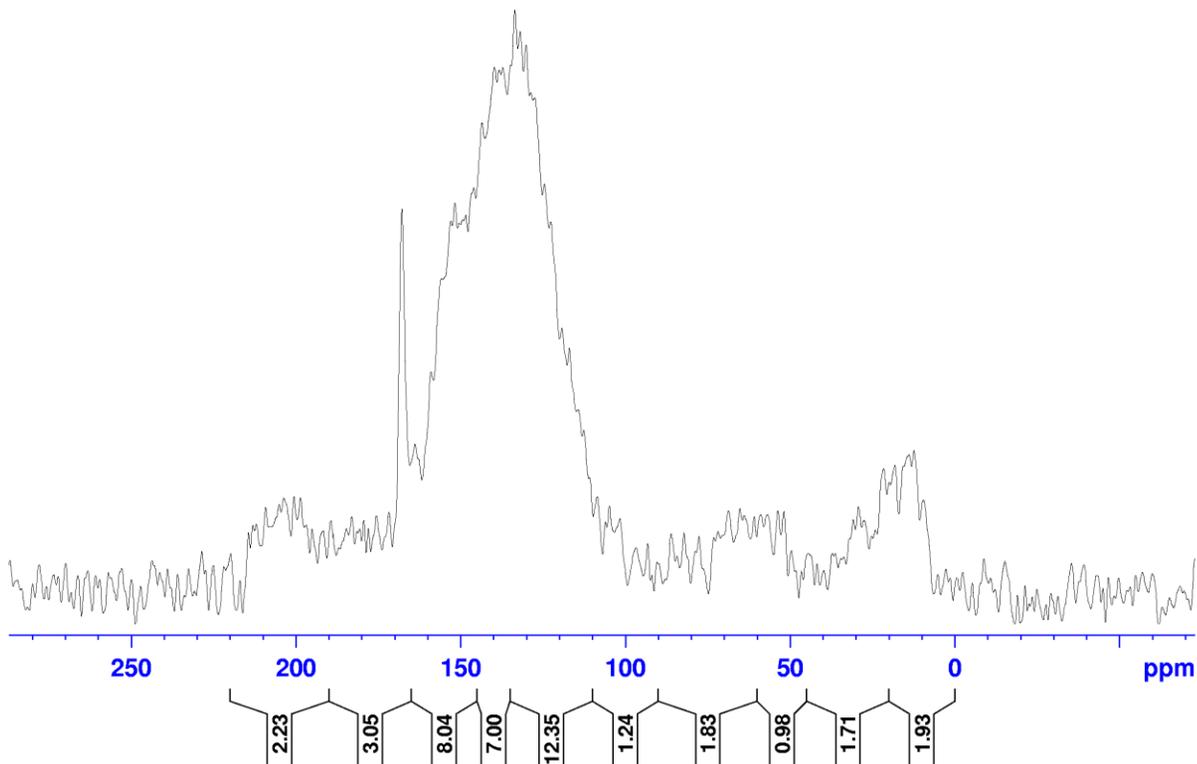
----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2     5.50 usec
PLW2       260.00000000 W
PLW12     260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squal00.1000
SPOAL0     0.500
SPOFFS0    0 Hz
SPWD       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Cattail Calibration Char at 300C
 178.0mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

74



```

Current Data Parameters
NAME      VonBargenCattailCal300 111112
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20121112
Time      0.03
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqa_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

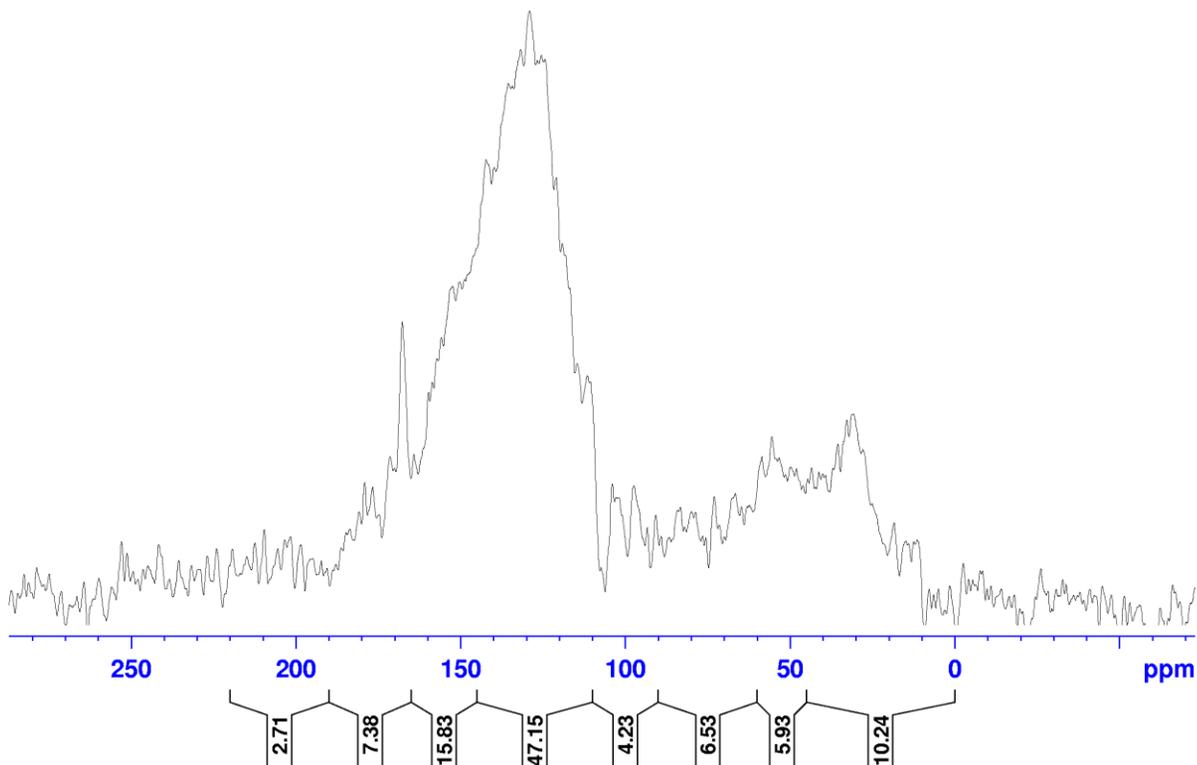
----- CHANNEL f2 -----
CPDPRG2    tppm15
NUC2       1H
P3         2.85 usec
PCPD2      5.50 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squal00.1000
SPOAL0     0.500
SPOFFS0    0 Hz
SPWD       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Cattail Calibration Char at 300C
 try with digital filter
 178.0mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

75



```

Current Data Parameters
NAME      VonBargenCattailCal300 111112
EXPNO     5
PROCNO    2

F2 - Acquisition Parameters
Date_     20121113
Time      20.51
INSTRUM   spect
PROBHD    7 mm MAS 5B/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
TDO        10
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



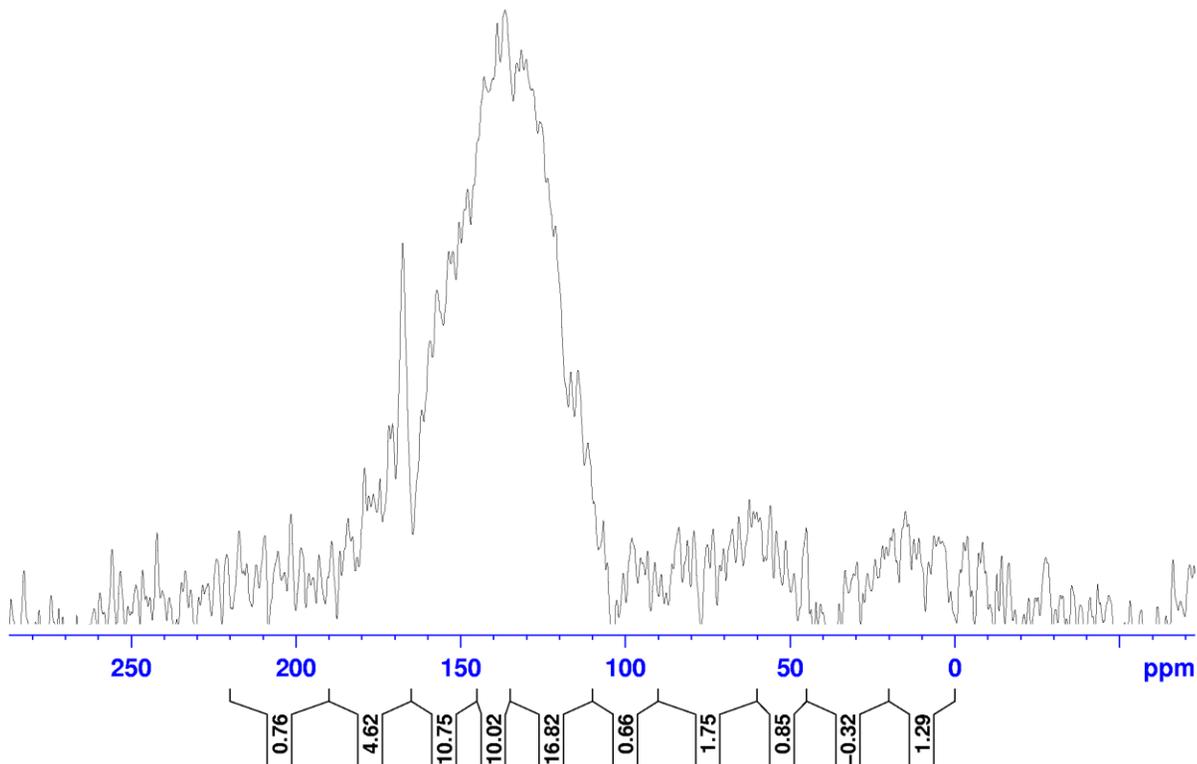
Cattail Calibration Char at 300C

178.0mg

Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling

Probe: 7 mm MAS 5kHz MAS

76



Current Data Parameters
NAME VonBargenCattailCal300 111112
EXPNO 7
PROCNO 2

F2 - Acquisition Parameters
Date_ 20121122
Time 11.10
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdec_toss_ngs
TD 1024
SOLVENT CDCl3
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TDD 1
ZCOPTNS

===== CHANNEL f1 =====
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

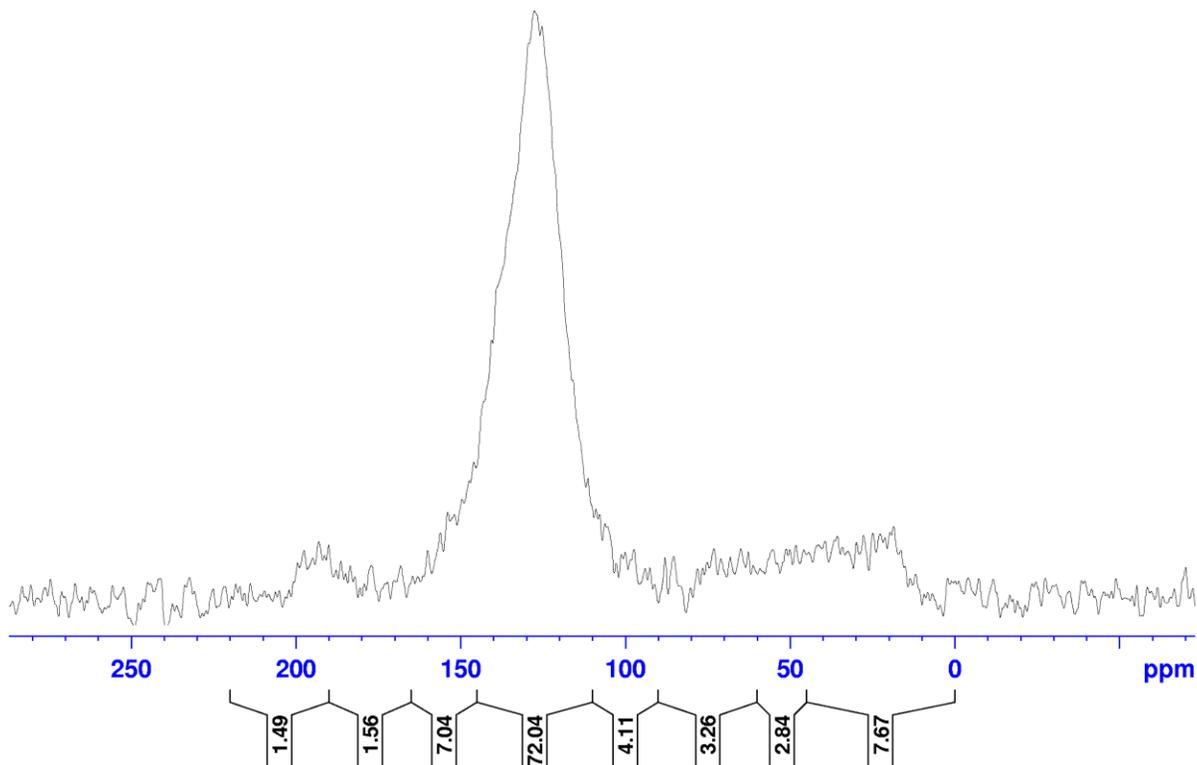
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4679928 MHz
WDW EM
SSB 0
LB 60.00 Hz
GB 0
PC 0.20



Cattail Calibration Char at 400C
 194.8mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

77



```

Current Data Parameters
NAME      VonBargenCattailCal400 110812
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20121108
Time      20.36
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D31        0.00020000 sec
TDO        4
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2     5.50 usec
PLW2       260.00000000 W
PLW12     260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squal00.1000
SPOAL0     0.500
SPOFFS0    0 Hz
SPWD       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



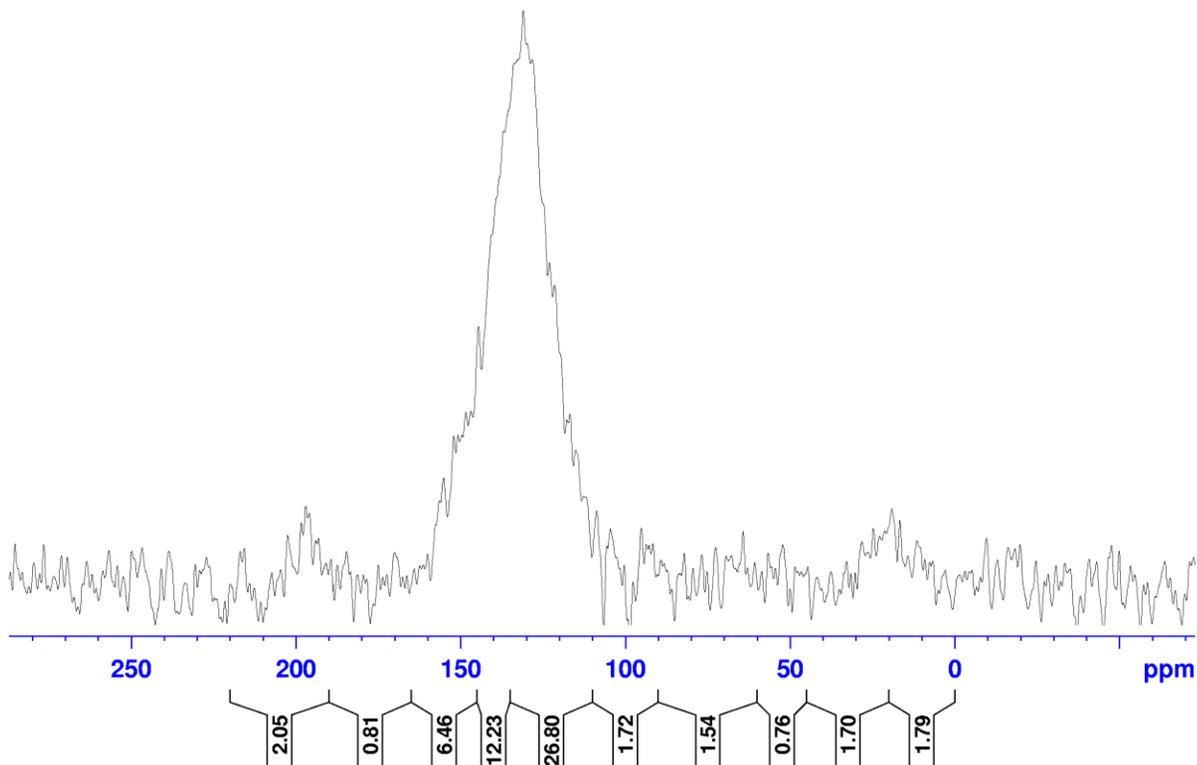
Cattail Calibration Char at 400C

194.8mg

CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)

Probe: 7 mm 5kHz MAS

78



```
Current Data Parameters
NAME      VonBargenCattailCal400 110812
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20121109
Time      7.57
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqa_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

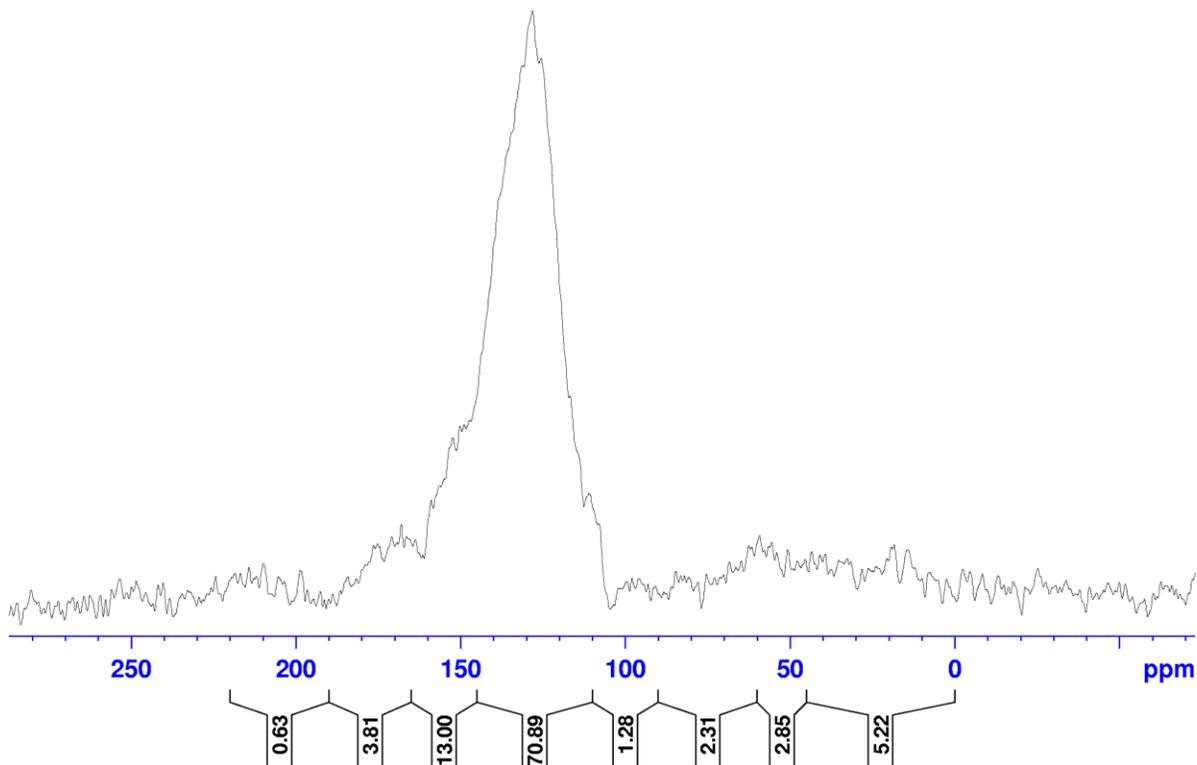
----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2     5.50 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squal00.1000
SPOAL0     0.500
SPOFFS0    0 Hz
SPWD       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
```



Cattail Calibration Char at 400C
 194.8mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

79



```

Current Data Parameters
NAME      VonBargenCattailCal400 110812
EXPNO     3
PROCNO    3

F2 - Acquisition Parameters
Date_     20121109
Time      13.49
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
TDO        10
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



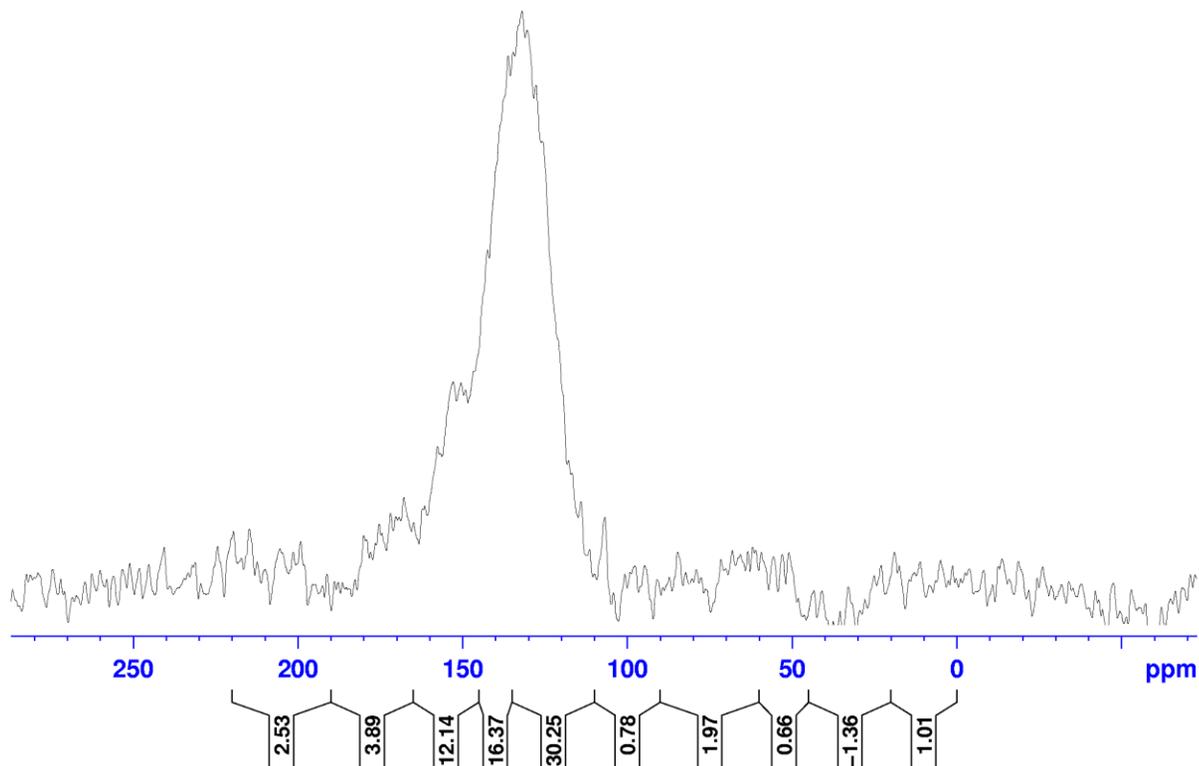
Cattail Calibration Char at 400C

194.8mg

Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling

Probe: 7 mm MAS 5kHz MAS

80



Current Data Parameters
NAME VonBargenCattailCal400 110812
EXPNO 4
PROCNO 3

F2 - Acquisition Parameters
Date_ 20121111
Time 9.27
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdec_toss_nga
TD 1024
SOLVENT CDCl3
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
ZGOPTNS

----- CHANNEL f1 -----
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

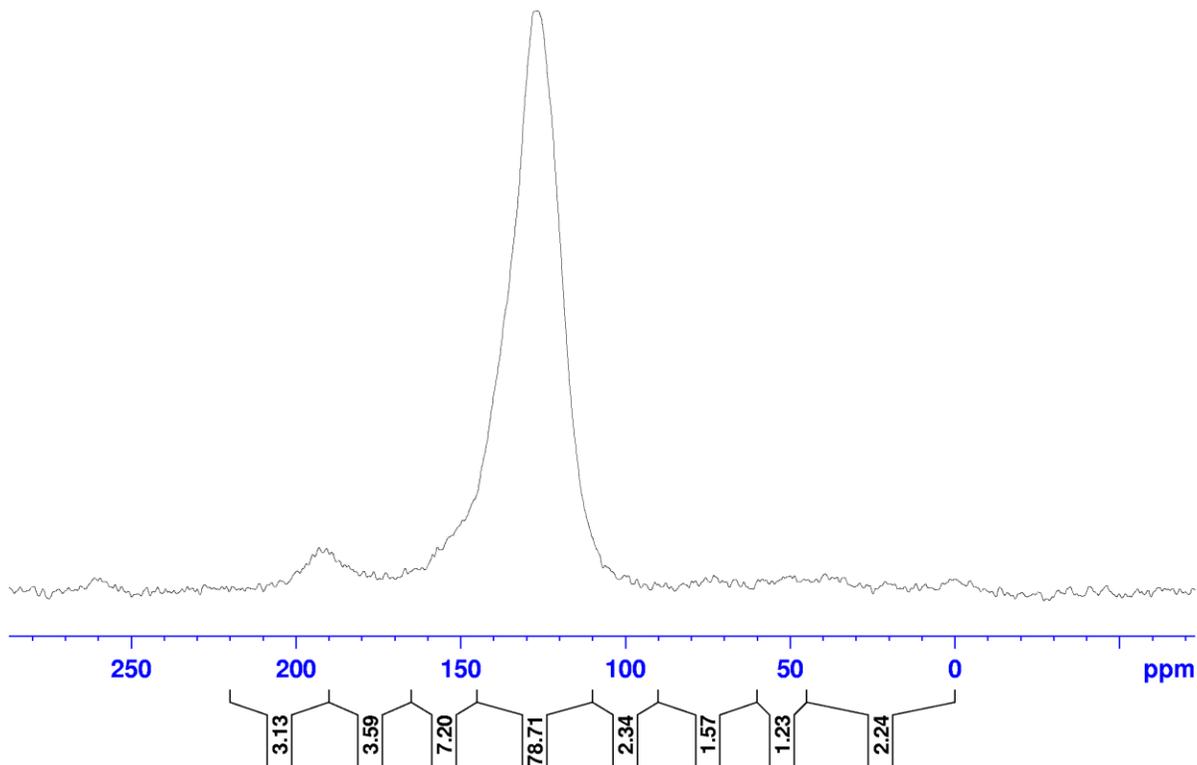
----- CHANNEL f2 -----
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4679928 MHz
WDW EM
SSB 0
LB 60.00 Hz
GB 0
PC 0.20



Cattail Calibration Char at 500C
 187.9mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

18



```

Current Data Parameters
NAME      VonBargenCattailCal500 110412
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20121104
Time      9.17
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D31        0.00020000 sec
TDO        4
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2     5.50 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squal00.1000
SPOAL0     0.500
SPOFFS0    0 Hz
SPWD       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```

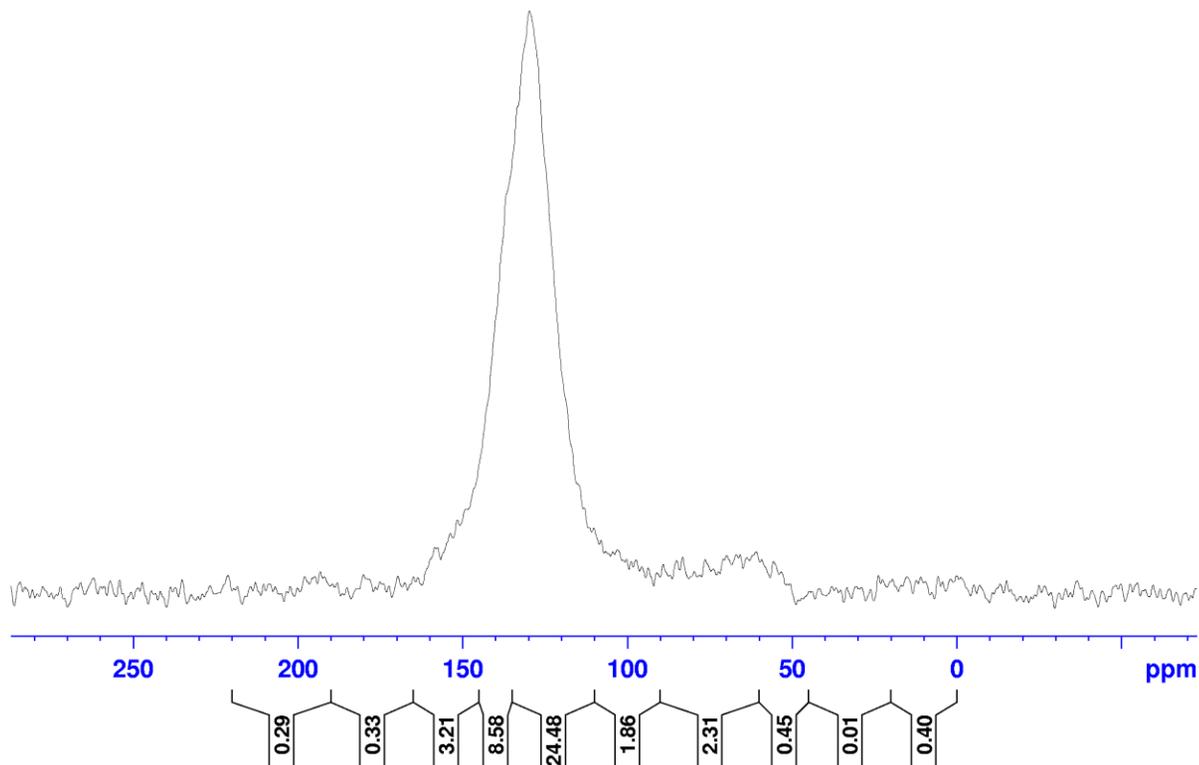


Cattail Calibration Char at 500C

187.9mg

CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)

Probe: 7 mm 5kHz MAS



Current Data Parameters
NAME VonBargenCattailCal500 110412
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121104
Time 13.27
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_nqa_WCH
TD 1024
SOLVENT CDCl3
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
ZGOPTNS

----- CHANNEL f1 -----
NUC1 13C
P2 7.90 usec
P15 2000.00 usec
PLW1 110.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squal00.1000
SPOAL0 0.500
SPOFFS0 0 Hz
SPWD 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679911 MHz
WDW EM
SSB 0
LB 60.00 Hz
GB 0
PC 0.20



Cattail Calibration Char at 500C
 187.9mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

```

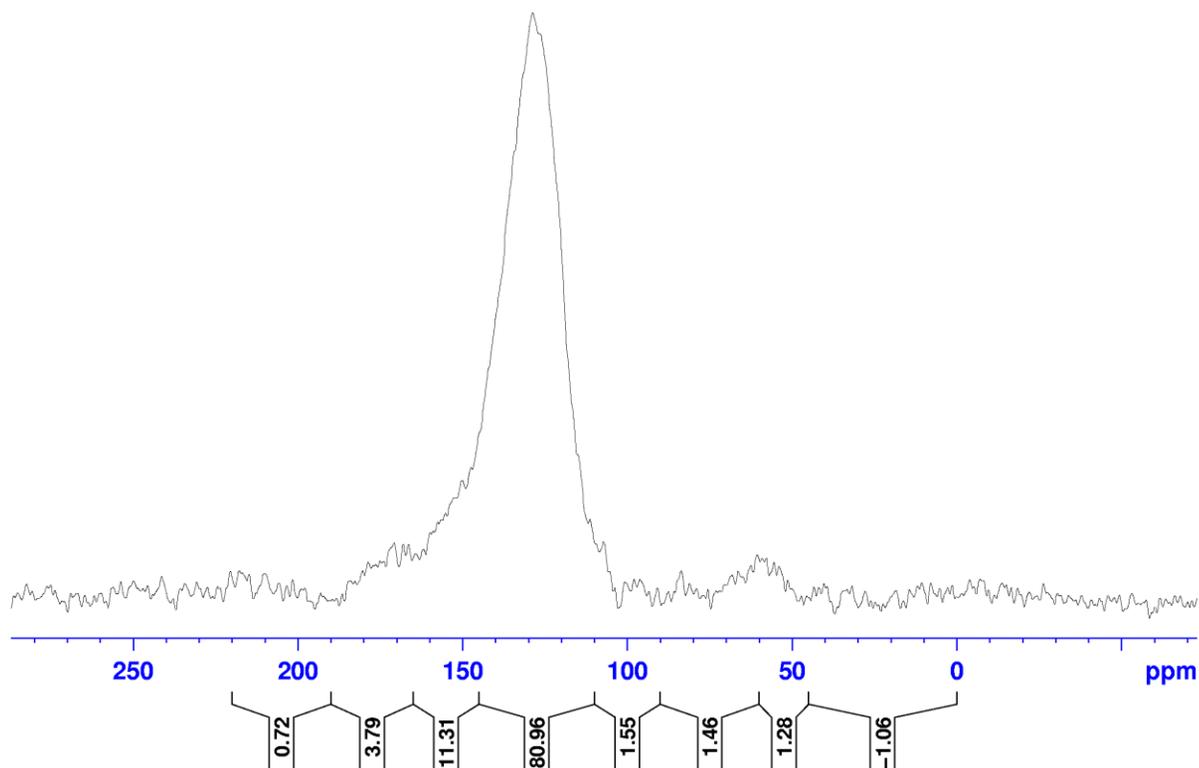
Current Data Parameters
NAME      VonBargenCattailCal500 110412
EXPNO     3
PROCNO    3

F2 - Acquisition Parameters
Date_     20121104
Time      17.51
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ        0.0147956 sec
RG         45.2
DW        14.400 usec
DE         8.08 usec
TE        303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
TDO        10
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



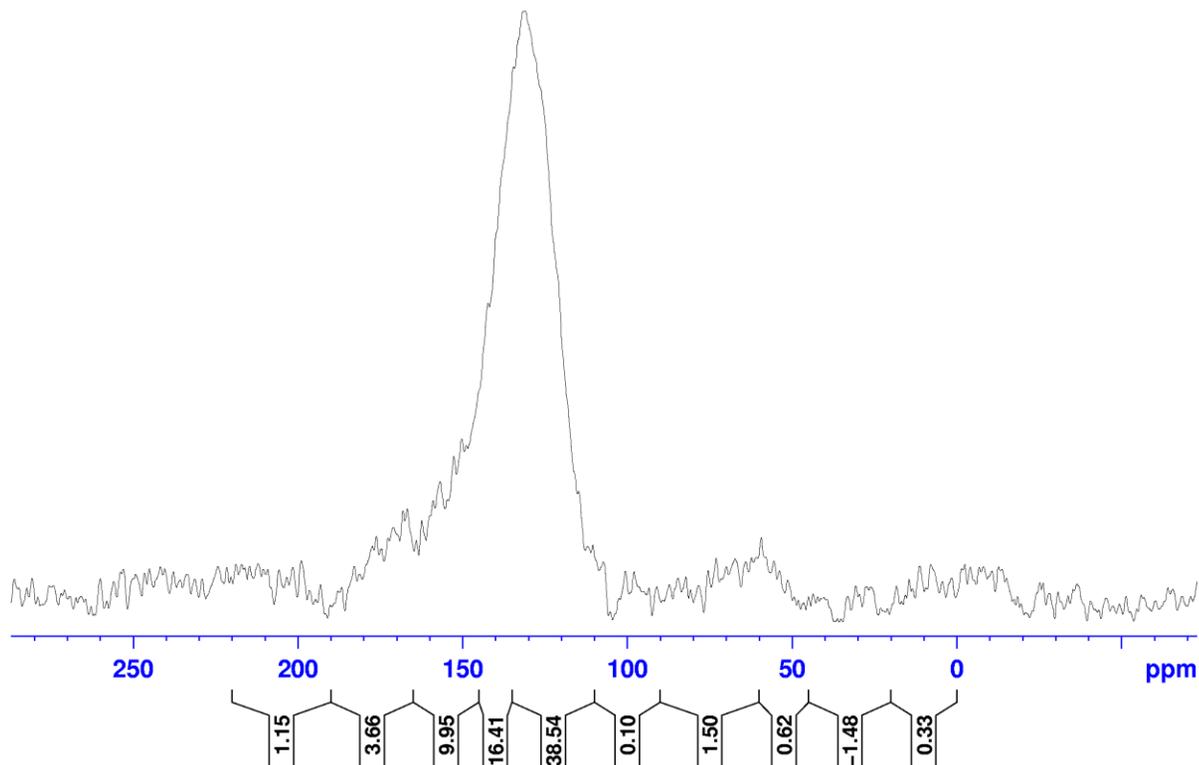
Cattail Calibration Char at 500C

187.9mg

Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling

Probe: 7 mm MAS 5kHz MAS

84



Current Data Parameters
NAME VonBargenCattailCal500 110412
EXPNO 4
PROCNO 3

F2 - Acquisition Parameters
Date_ 20121106
Time 10.58
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdec_toss_nga
TD 1024
SOLVENT CDCl3
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
ZGOPTNS

----- CHANNEL f1 -----
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

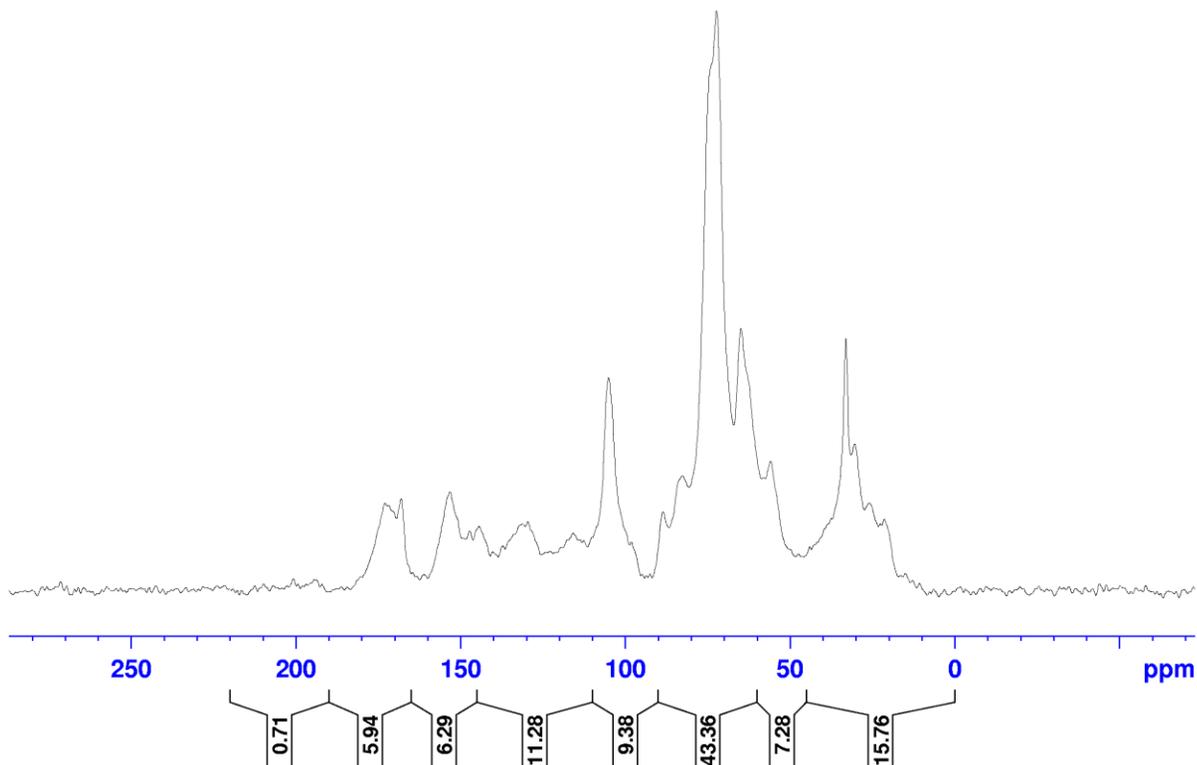
----- CHANNEL f2 -----
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4679928 MHz
WDW EM
SSB 0
LB 60.00 Hz
GB 0
PC 0.20



Willow Calibration sample dried at 55
 170.1 mg
 CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands
 1 ms contact pulse
 Probe: 7 mm 5kHz MAS

85



Current Data Parameters
 NAME VonBargerWillowCal55 101612
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20121016
 Time 16.08
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG cptoss_WCH
 TD 1024
 SOLVENT CDCl3
 NS 1365
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.0000000
 D1 3.00000000 sec
 D31 0.00020000 sec
 TD0 20
 ZGOPTNS

===== CHANNEL f1 =====
 NUC1 13C
 P2 8.00 usec
 P15 1000.00 usec
 PLW1 180.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 P3 2.85 usec
 PCPD2 5.50 usec
 PLW2 0 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz
 SPNAM0 Squa100.1000
 SPOAL0 0.500
 SPOFFS0 0 Hz
 SPW0 85.00000000 W

F2 - Processing parameters
 SI 16384
 SF 75.4679759 MHz
 WDW EM
 SSB 0
 LB 50.00 Hz
 GB 0
 PC 0.20



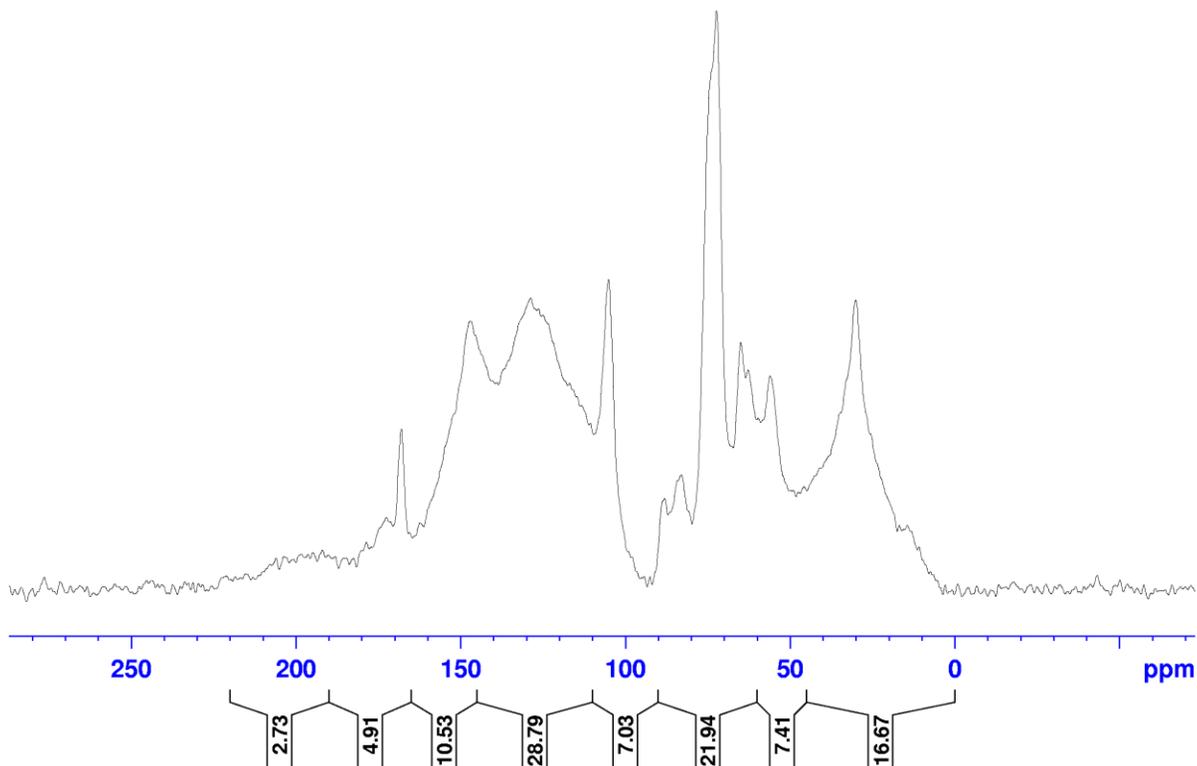
Willow Calibration charcoal sample pyrolysed at 250 degC
154.1mg

CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands

1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOPSS pi pu.
Singificant improvement in TOSS was observed



Current Data Parameters
NAME VonBargenWillowCal250 111812
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121118
Time 10.58
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptomss_wch
TD 1024
SOLVENT CDC13
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.308421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D31 0.00020000 sec
TDO 40
ZGOPINS

===== CHANNEL f1 =====
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squa100.1000
SPOAL0 0.500
SPOFFS0 0 Hz
SPWD 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20

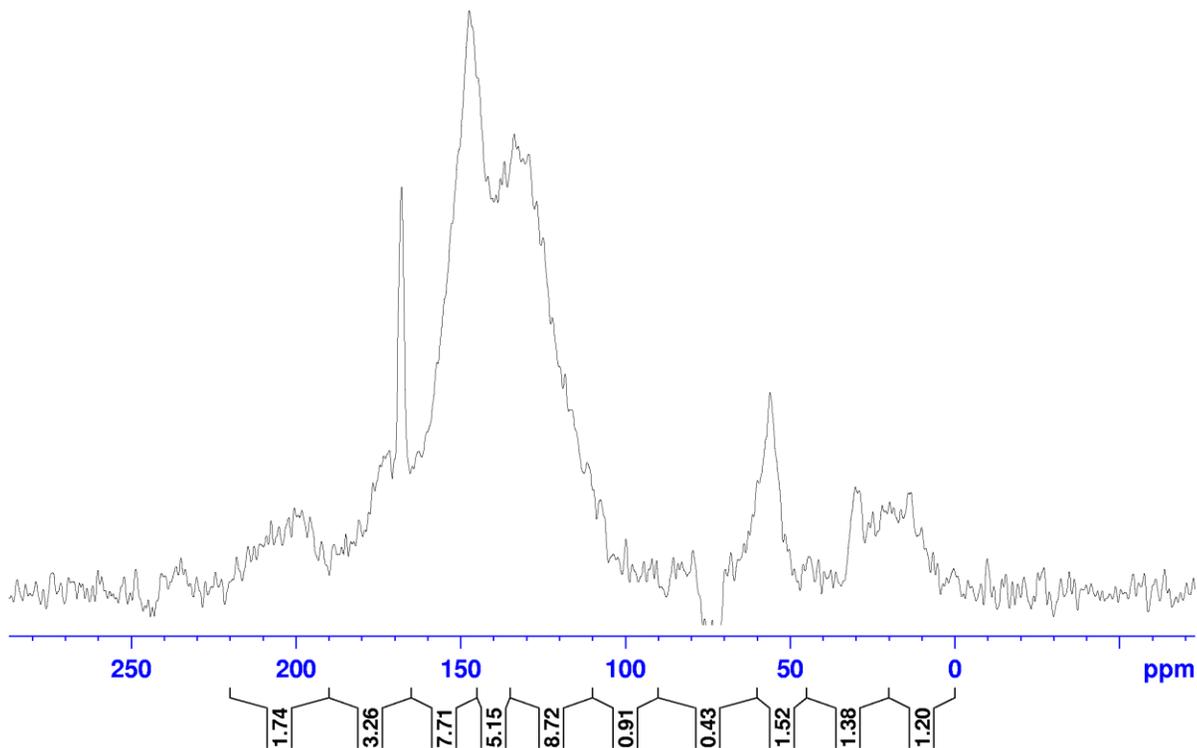


Willow Calibration charcoal sample pyrolysed at 250 degC
154.1 mg

CPMAS square100 with dipolar dephasing and total supression of spinning sidebands, and tppm15 decoupling
1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOSS PI pul:
Singificant improvement in TOSS was observed



Current Data Parameters
NAME VonBargenWillowCal250 111812
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121118
Time 14.19
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_nqs_wch
TD 1024
SOLVENT CDC13
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TD0 40
ZGOPTS

===== CHANNEL f1 =====
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

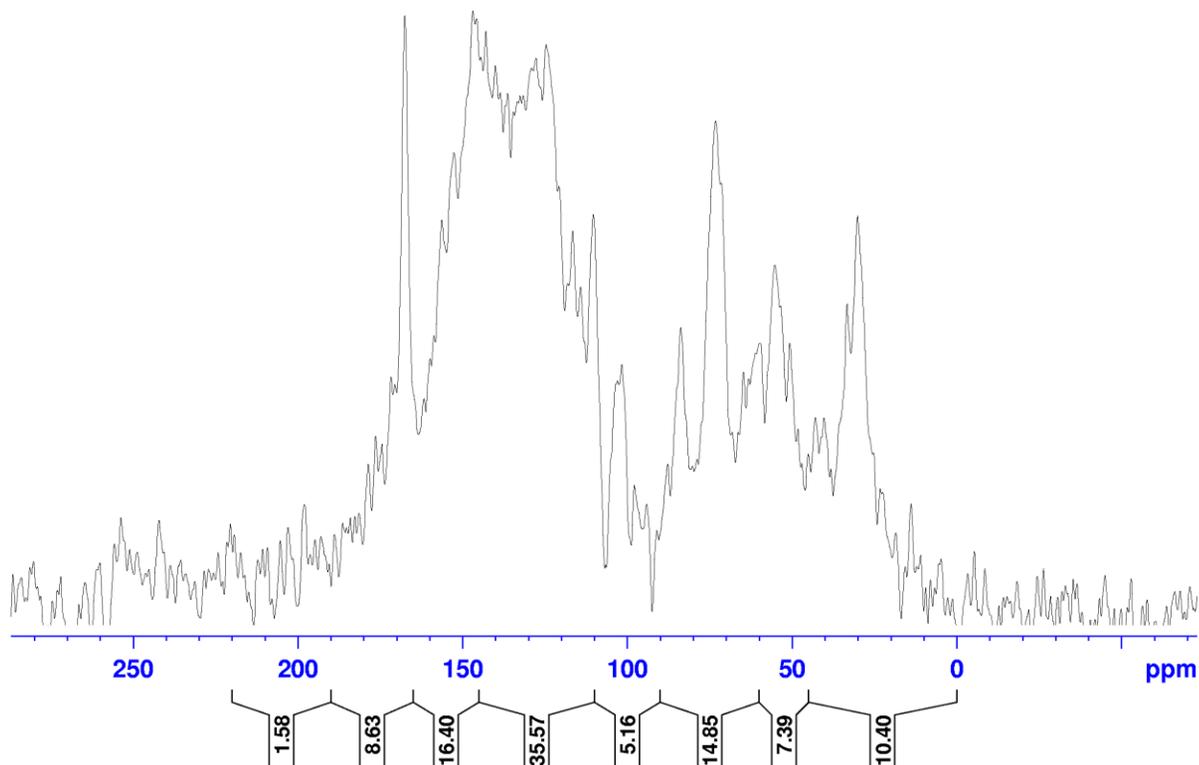
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squa100.1000
SPOAL0 0.500
SPOFFS0 0 Hz
STW0 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20



Willow Calibration charcoal sample pyrolysed at 250 degC
 154.1 mg
 hpdec with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS
 improved TOSS sequence
 added Td0 loops

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```

Current Data Parameters
NAME VonBergenWillowCal250 111812
EXPNO 3
PROCNO 2

F2 - Acquisition Parameters
Date_ 20121118
Time 20.06
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdecTOSS
TD 1024
SOLVENT CDC13
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.308421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D31 0.00020000 sec
TDO 10
ZGOPINS -DTOSSB

===== CHANNEL f1 =====
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

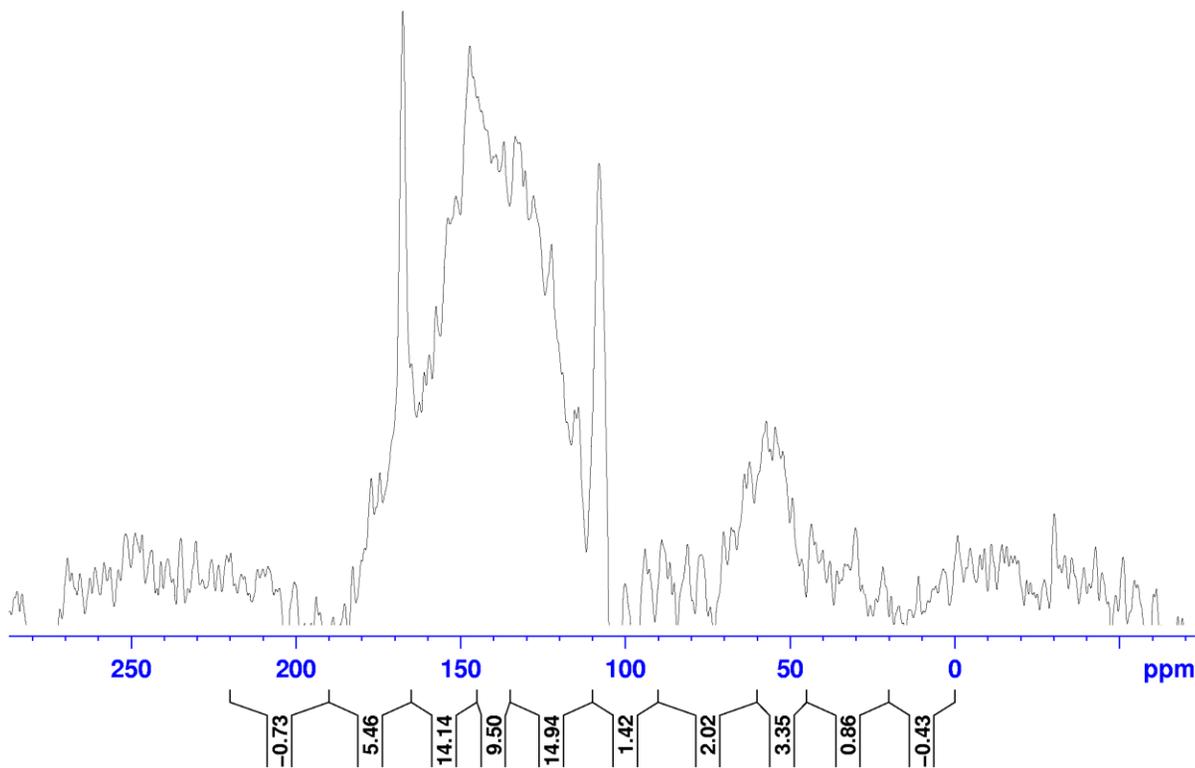
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4680013 MHz
WDW EM
SSB 0
LB 60.00 Hz
GB 0
PC 0.20
  
```



Willow Calibration charcoal sample pyrolysed at 250 degC
 154.1 mg
 hpdec (direct polarization) with diplor dephasing, Total Sideband Suppression (TOSS), and TPPM15 decoupling
 Probe: 7 mm , 5kHz MAS
 improved TOSS sequence

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```

Current Data Parameters
NAME VonBergenWillowCal250 111812
EXPNO 4
PROCNO 2

F2 - Acquisition Parameters
Date_ 20121119
Time 21.06
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdec_toss_nps
TD 1024
SOLVENT CDC13
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.308421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TD0 10
ZGOPTNS -DTOSSB

===== CHANNEL f1 =====
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4680013 MHz
WDW EM
SSB 0
LB 70.00 Hz
GB 0
PC 0.20
  
```



Willow Calibration charcoal sample pyrolysed at 350 degC
165.9mg

CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands

1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOPSS pi pu.
Singificant improvement in TOSS was observed

Current Data Parameters
NAME VonBargenWillowCal350 112312
EXPNO 1
PROCNO 1

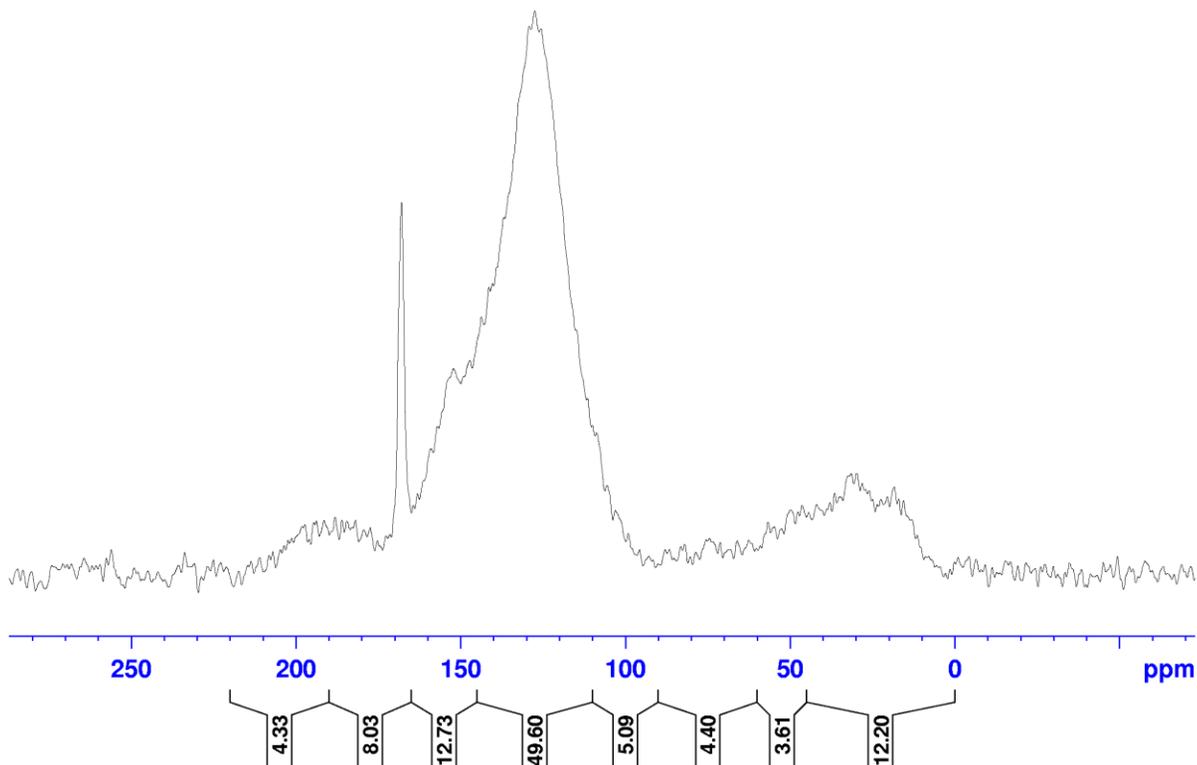
F2 - Acquisition Parameters

Date_ 20121123
Time 13.13
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_wch
TD 1024
SOLVENT CDCl3
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.308421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D31 0.00020000 sec
TDO 40
ZGOPINS

=====
CHANNEL f1
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

=====
CHANNEL f2
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squa100.1000
SPOAL0 0.500
SPOFFS0 0 Hz
SPWD 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20



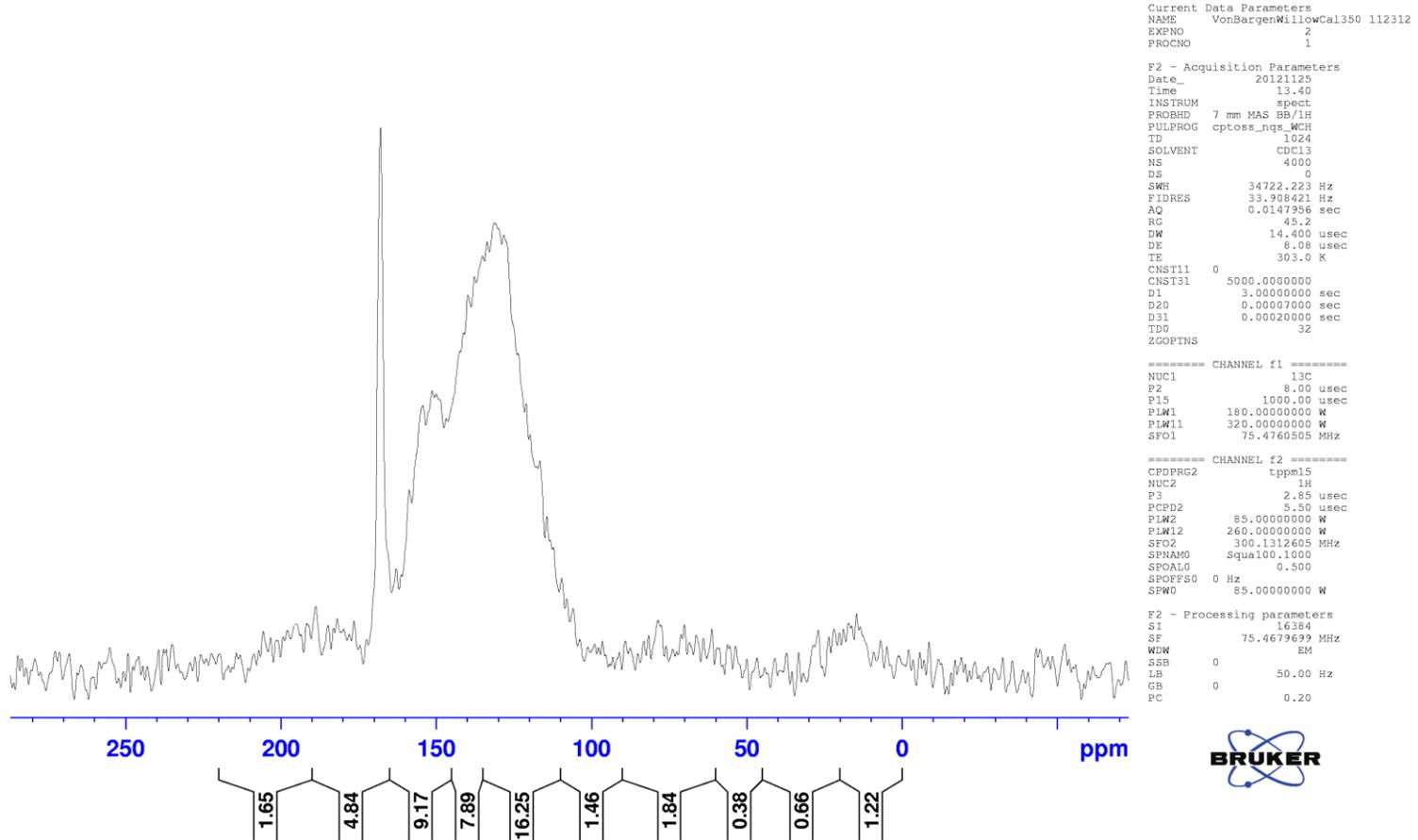
Willow Calibration charcoal sample pyrolysed at 350 degC
165.9 mg

CPMAS square100 with dipolar dephasing and total suppression of spinning sidebands, and tppm15 decoupling

1 ms contact pulse

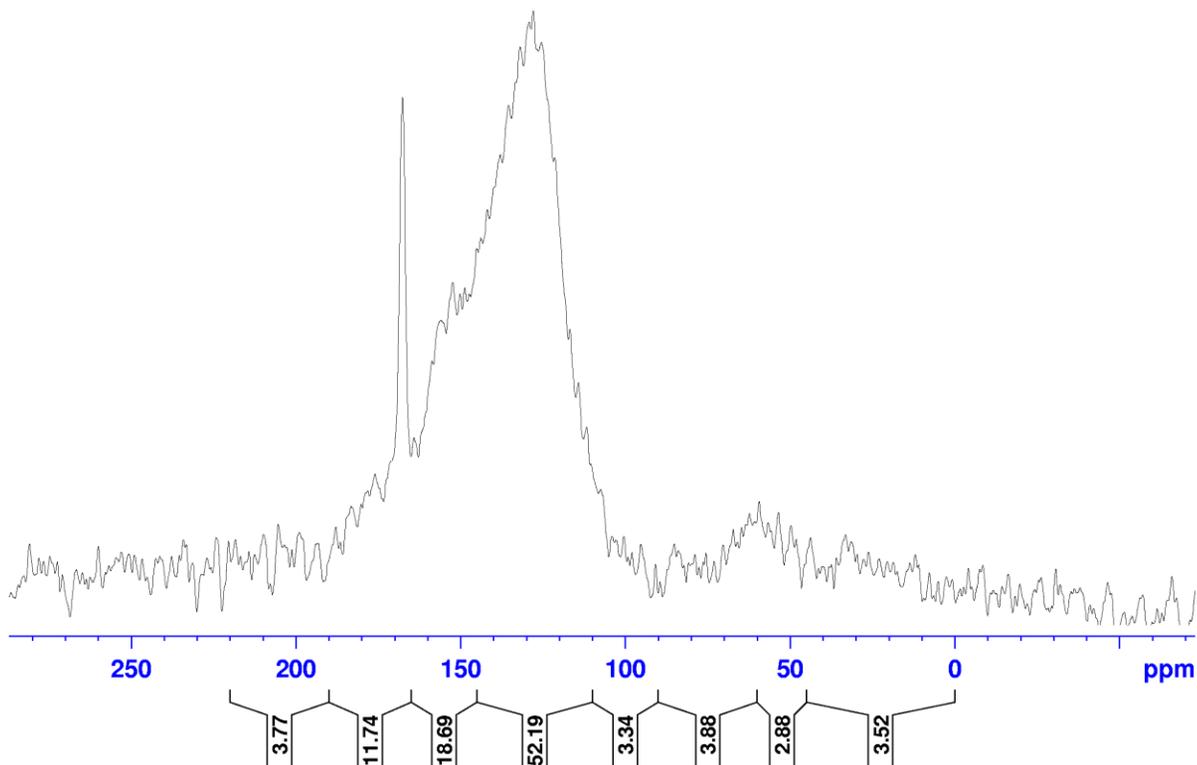
Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOSS PI pul:
Singificant improvement in TOSS was observed



Willow Calibration charcoal sample pyrolysed at 350 degC
 165.9 mg
 hpdec with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS
 improved TOSS sequence
 added Td0 loops

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Current Data Parameters
 NAME VonBergenWillowCal350 112312
 EXPNO 3
 PROCNO 2

F2 - Acquisition Parameters
 Date_ 20121125
 Time 19.04
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG hpdecTOSS
 TD 1024
 SOLVENT CDC13
 NS 1000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 90.00000000 sec
 D31 0.00020000 sec
 TDO 10
 ZGOPINS -DTOSSB

==== CHANNEL f1 =====
 NUC1 13C
 P1 4.00 usec
 P2 8.00 usec
 PLW1 320.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

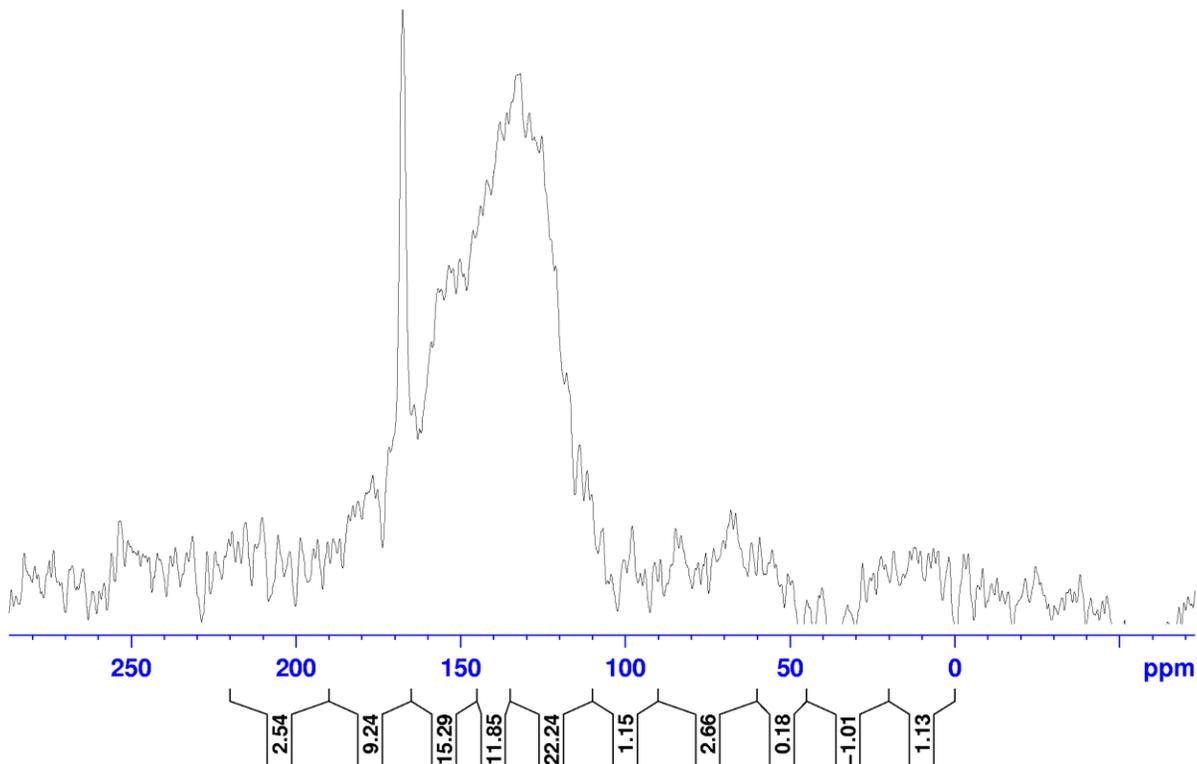
==== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 PCPD2 5.40 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz

F2 - Processing parameters
 SI 16384
 SF 75.4680013 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Willow Calibration charcoal sample pyrolysed at 350 degC
 165.9 mg
 hpdec (direct polarization) with diplor dephasing, Total Sideband Suppression (TOSS), and TPPM15 decoupling
 Probe: 7 mm , 5kHz MAS
 improved TOSS sequence

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```

Current Data Parameters
NAME VonBargenWillowCal350 112312
EXPNO 4
PROCNO 2

F2 - Acquisition Parameters
Date_ 20121126
Time 20.05
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdec_toss_nps
TD 1024
SOLVENT CDC13
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.308421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TD0 10
ZGOPTNS -DTOSSB

===== CHANNEL f1 =====
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4680013 MHz
WDW EM
SSB 0
LB 70.00 Hz
GB 0
PC 0.20
  
```



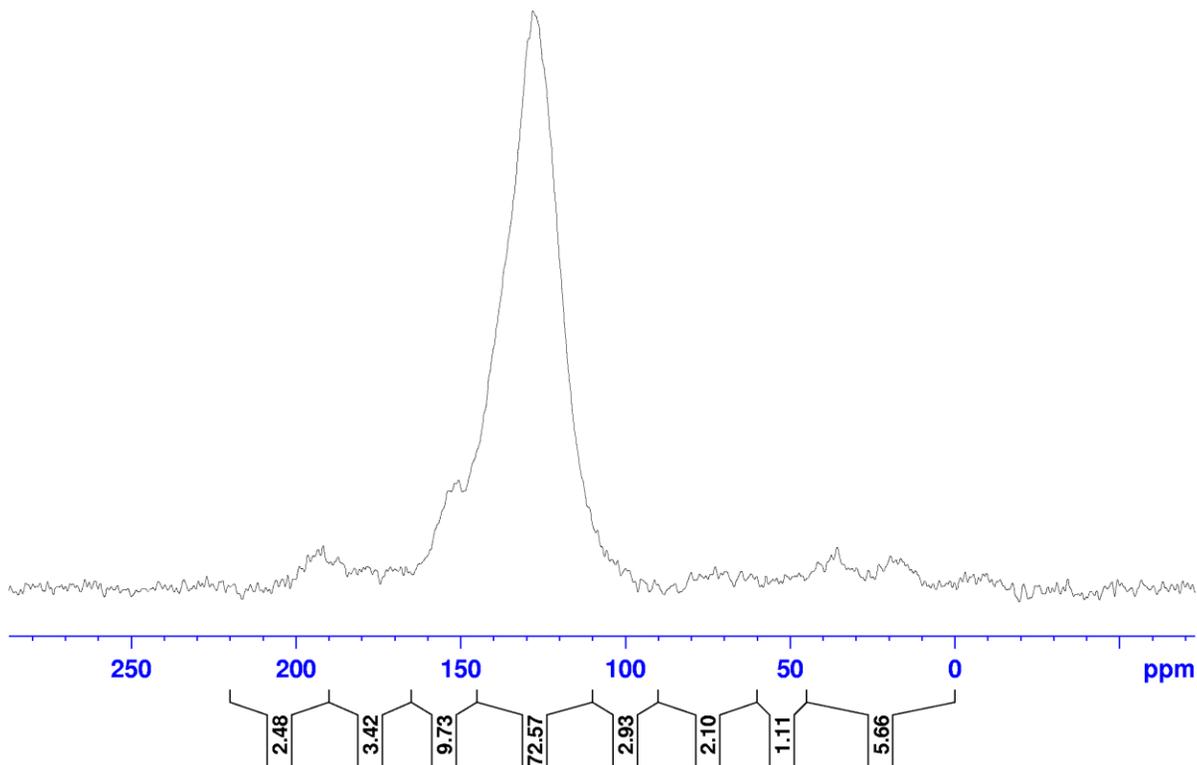
Willow Calibration charcoal sample pyrolysed at 450 degC
148.0mg

CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands

1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOPSS pi pu.
Singificant improvement in TOSS was observed



Current Data Parameters
NAME VonBargenWillowCal450 120212
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121202
Time 10.31
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_wch
TD 1024
SOLVENT CDCl3
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D31 0.00020000 sec
TDO 40
ZGOPINS

==== CHANNEL f1 =====
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

==== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squa100.1000
SPOAL0 0.500
SPOFFS0 0 Hz
SPWD 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20



Willow Calibration charcoal sample pyrolysed at 450 degC
148.0 mg

CPMAS square100 with dipolar dephasing and total suppression of spinning sidebands, and tppm15 decoupling
1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOSS PI pul:
Singificant improvement in TOSS was observed

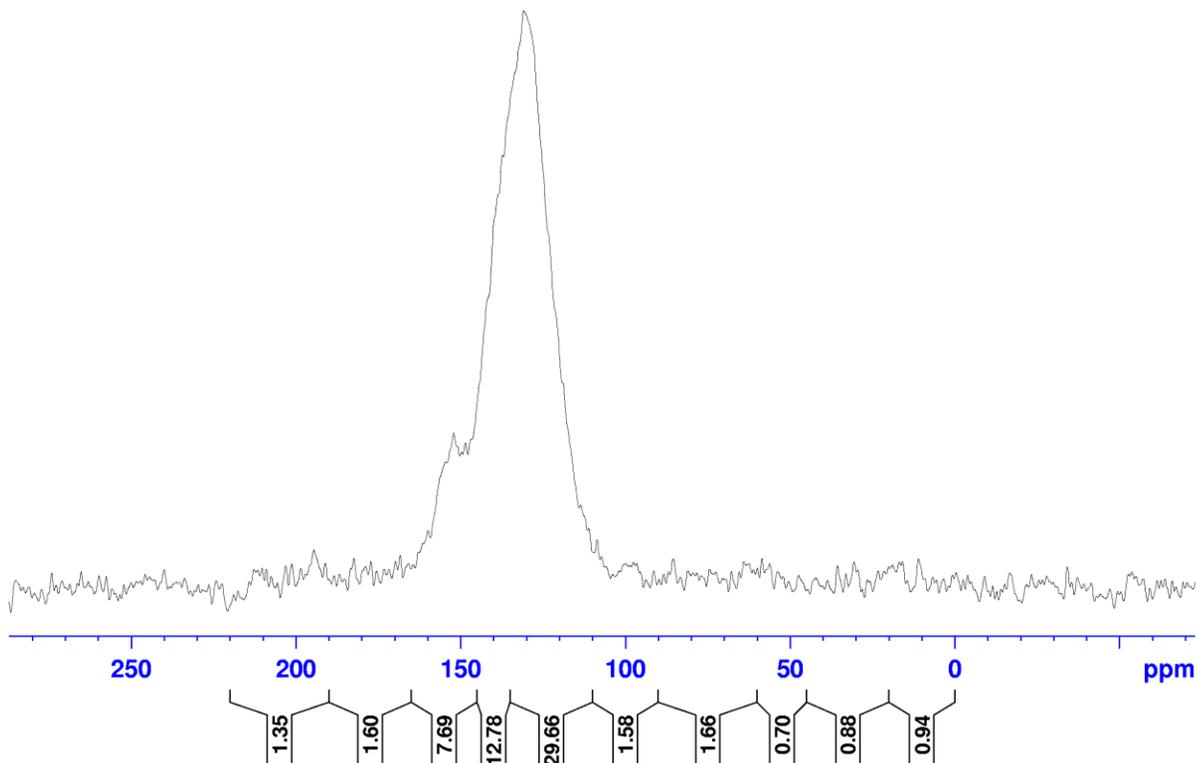
Current Data Parameters
NAME VonBargenWillowCal450 120212
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121203
Time 16.19
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_nqs_wch
TD 1024
SOLVENT CDC13
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.308421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TD0 8
ZGOPTNS

===== CHANNEL f1 =====
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

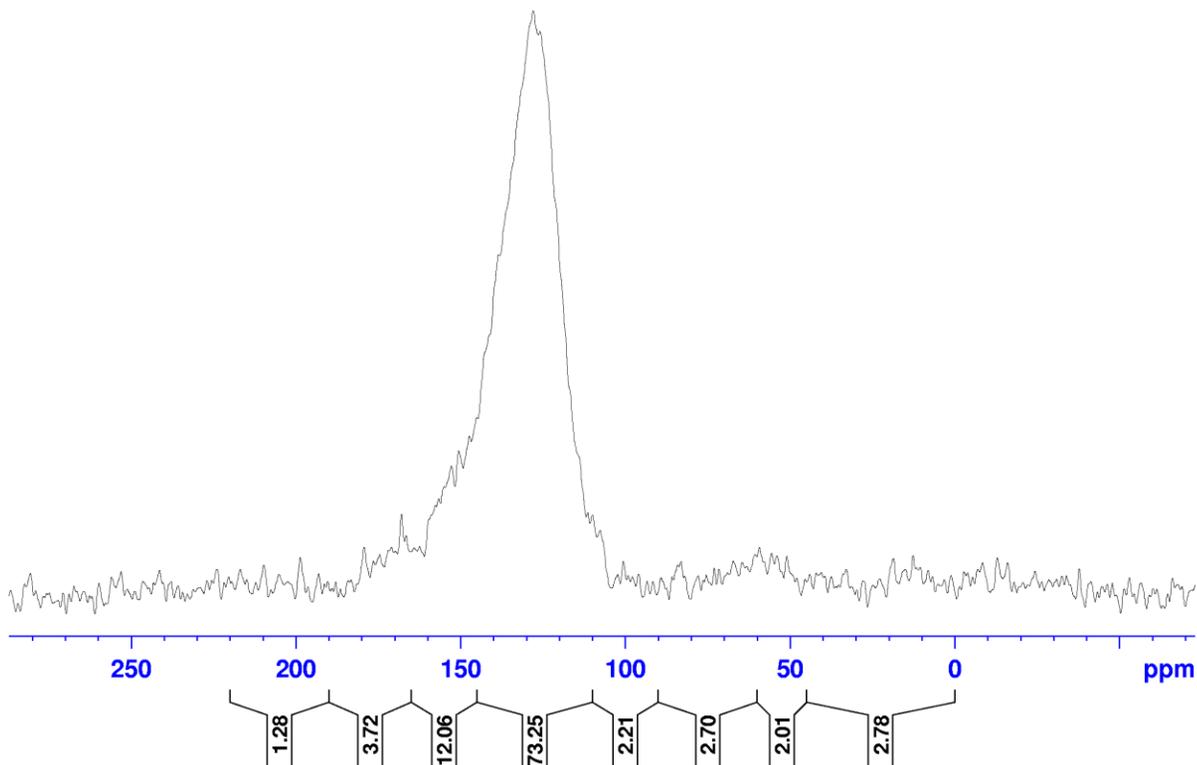
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squal00.1000
SPOALO 0.500
SPOFFS0 0 Hz
STW0 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20



Willow Calibration charcoal sample pyrolysed at 450 degC
 148.0 mg
 hpdec with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS
 improved TOSS sequence
 added Td0 loops

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```

Current Data Parameters
NAME      VonBergenWillowCal450 120212
EXPNO    3
PROCNO   2

F2 - Acquisition Parameters
Date_    20121203
Time     20.15
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdecTOSS
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D31      0.00020000 sec
TD0      5
ZGPGINS  -DTOSSB

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

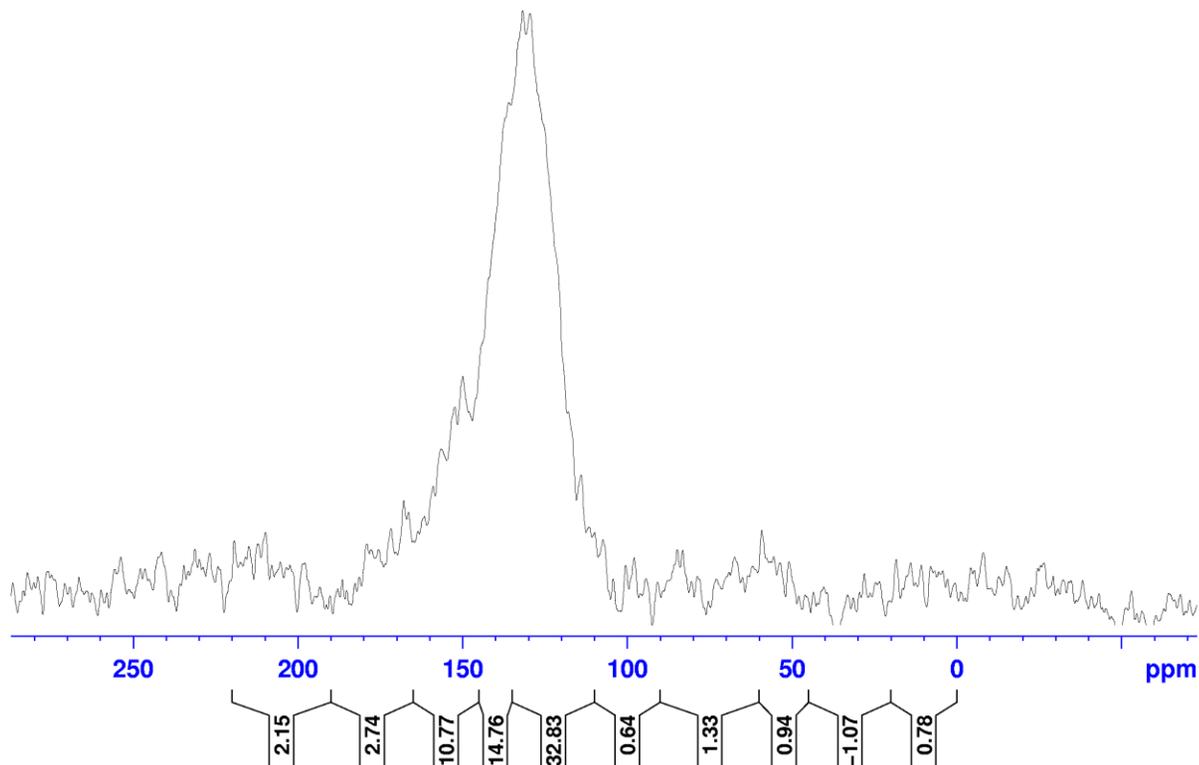
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4680013 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Willow Calibration charcoal sample pyrolysed at 450 degC
 148.0 mg
 hpdec (direct polarization) with diplor dephasing, Total Sideband Suppression (TOSS), and TPPM15 decoupling
 Probe: 7 mm , 5kHz MAS
 improved TOSS sequence

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```

Current Data Parameters
NAME      VonBergenWillowCal450 120212
EXPNO    4
PROCNO   2

F2 - Acquisition Parameters
Date_    20121204
Time     11.47
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nps
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
TD0      10
ZGOPTNS  -DTOSSB

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4680013 MHz
WDW      EM
SSB      0
LB       70.00 Hz
GB       0
PC       0.20
  
```



Willow Calibration charcoal sample pyrolysed at 550 degC (normal)
 156.3 mg
 CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands
 1 ms contact pulse
 Probe: 7 mm 5kHz MAS
 modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOPSS pi pu
 Singificant improvement in TOSS was observed

```

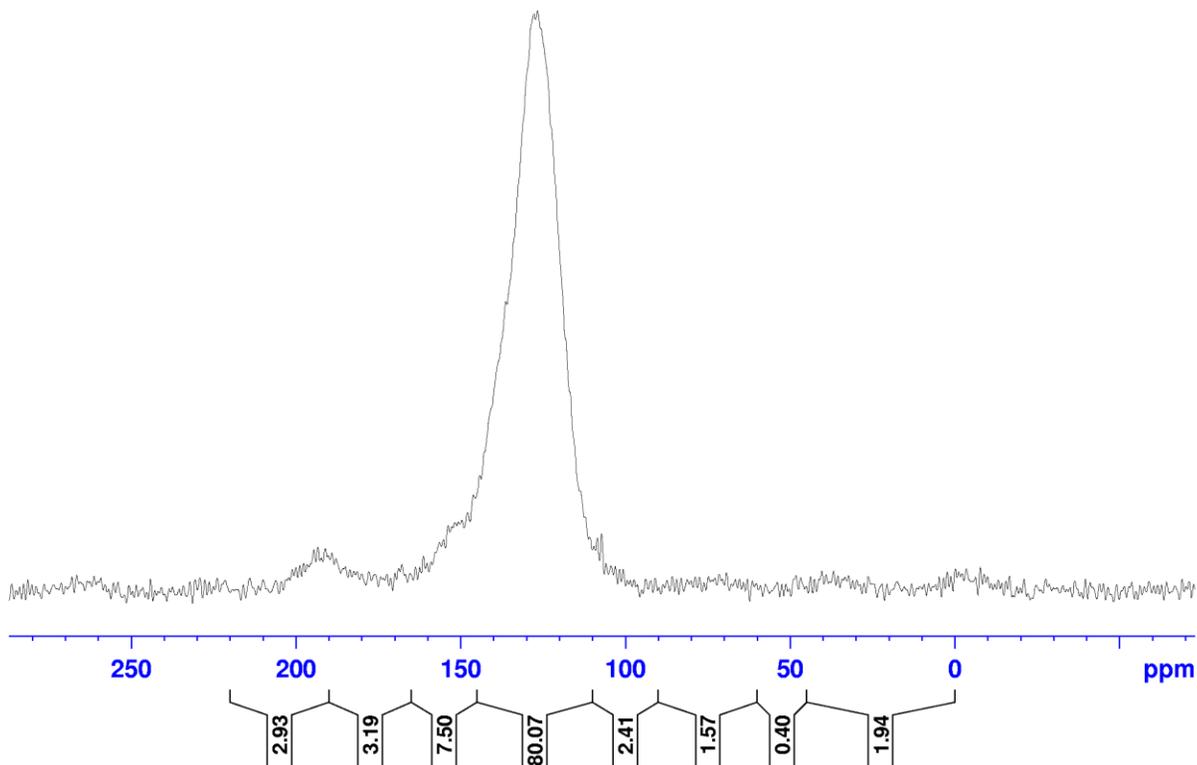
Current Data Parameters
NAME      VonBargenWillowCal550n 111512
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20121115
Time      18.59
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D31        0.00020000 sec
TDO        40
ZGOPTNS

----- CHANNEL f1 -----
NUC1       13C
P2         8.00 usec
P15        1000.00 usec
PLW1       180.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2     5.50 usec
PLW2       85.00000000 W
PLW12     260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squa100.1000
SPOAL0     0.500
SPOFFS0    0 Hz
SPWD       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679699 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         0.20
  
```



Willow Calibration charcoal sample pyrolysed at 550 degC (normal)

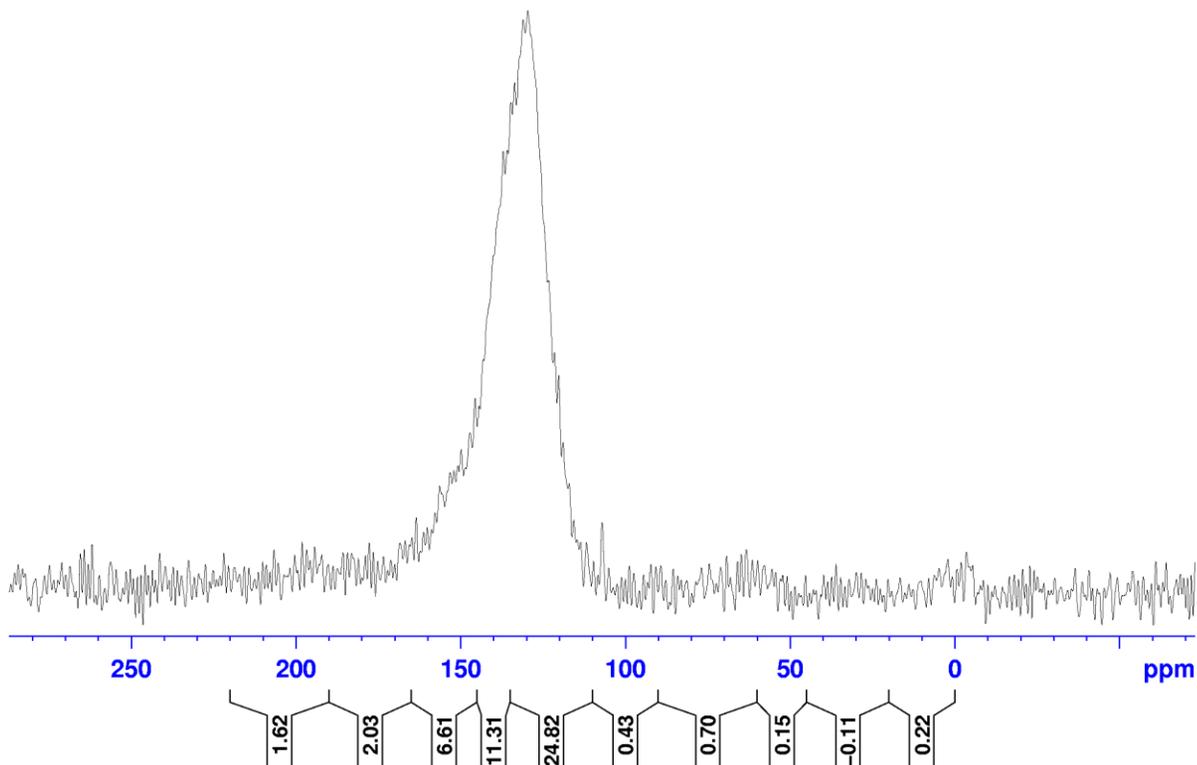
156.3 mg

CPMAS square100 with dipolar dephasing and total supression of spinning sidebands, and tppm15 decoupling

1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOSS PI pul:
Singificant improvement in TOSS was observed



Current Data Parameters
NAME VonBargenWillowCal550n 111512
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121115
Time 22.25
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_nqa_WCH
TD 1024
SOLVENT CDCl3
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TDD 40
ZGOPTNS

===== CHANNEL f1 =====
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

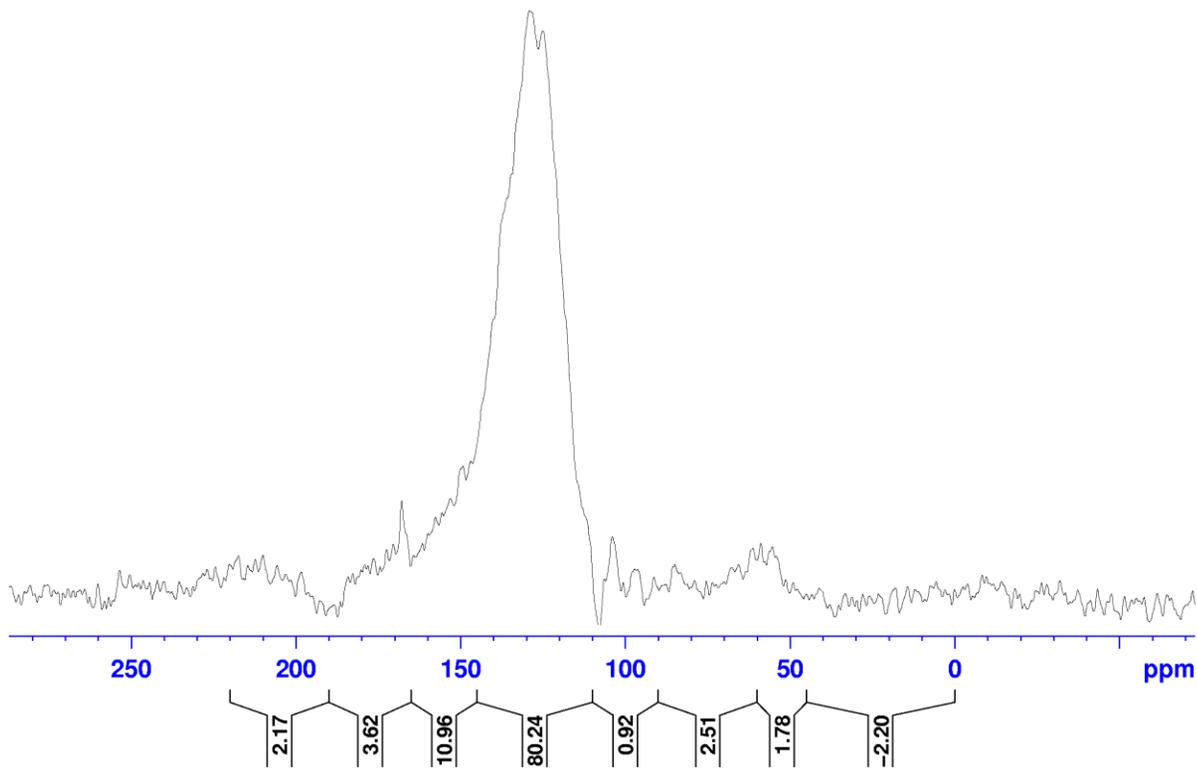
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squal00.1000
SPOALO 0.500
SPOFFS0 0 Hz
SPWO 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.20



Willow Calibration charcoal sample pyrolysed at 550 degC (normal)
 156.3 mg
 hpdec with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS
 improved TOSS sequence
 added Td0 loops

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```

Current Data Parameters
NAME      VonBargenWillowCal550n 111512
EXPNO     3
PROCNO    3

F2 - Acquisition Parameters
Date_     20121116
Time      4.12
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
TDO        10
ZGOPTNS   -DTOSSB

----- CHANNEL f1 -----
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

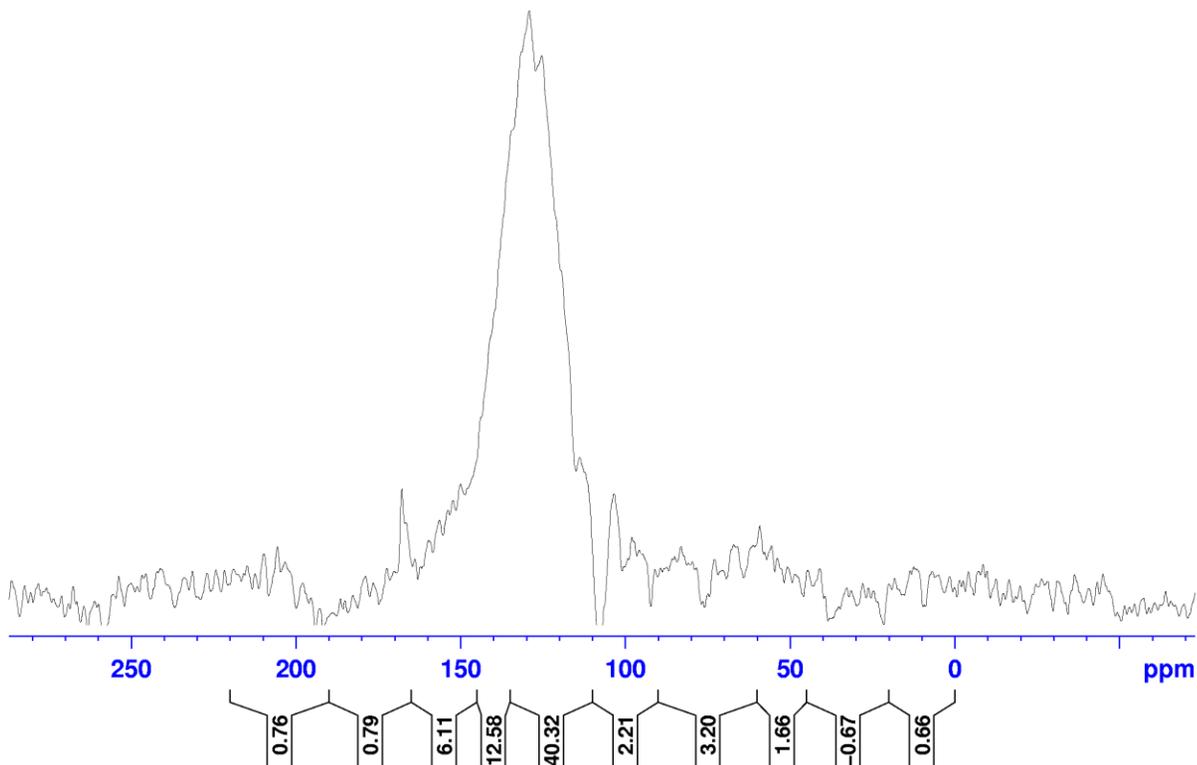
----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2       1H
PCPD2     5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4680013 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Willow Calibration charcoal sample pyrolysed at 550 degC (normal)
 156.3 mg
 hpdec (direct polarization) with diplor dephasing, Total Sideband Suppression (TOSS), and TPPM15 decoupling
 Probe: 7 mm , 5kHz MAS
 improved TOSS sequence

101



```

Current Data Parameters
NAME      VonBargenWillowCal550n 111512
EXPNO     4
PROCNO    2

F2 - Acquisition Parameters
Date_     20121117
Time      5.12
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_ngs
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
TDD        10
ZCOPTNS   -DTOSSB

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4680013 MHz
WDW        EM
SSB        0
LB         70.00 Hz
GB         0
PC         0.20
  
```



Willow Calibration charcoal sample pyrolysed at 550 degC (reburn)
 154.2 mg
 CPMAS square100 with tppm15 decoupling and total supression of spinning sidebands
 1 ms contact pulse
 Probe: 7 mm 5kHz MAS
 modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOPSS pi pu
 Singificant improvement in TOSS was observed

```

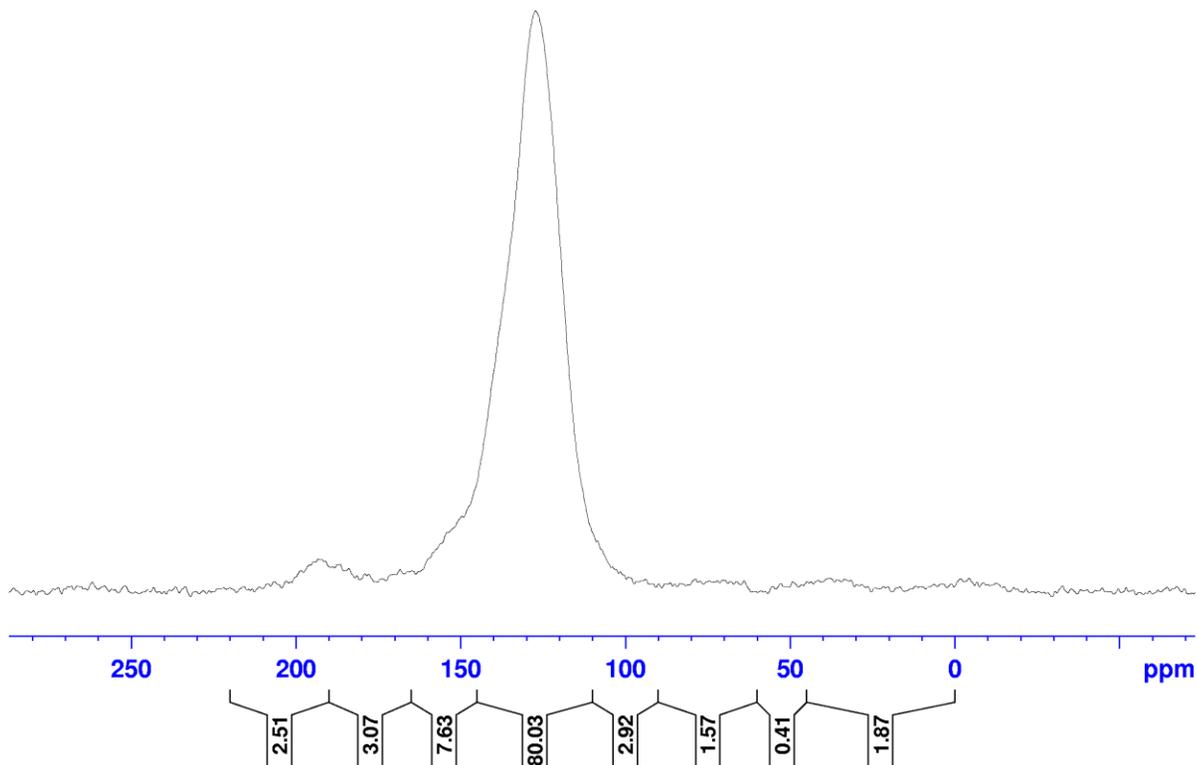
Current Data Parameters
NAME      VonBargerWillowCal550rb 120712
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20121207
Time      20.20
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_WCH
TD        1024
SOLVENT   CDCl3
NS        4000
DS        0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ        0.0147956 sec
RG        45.2
DW        14.400 usec
DE        8.08 usec
TE        303.0 K
CNST11    0
CNST31    5000.000000
D1        3.00000000 sec
D31       0.00020000 sec
TD0       40
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2        8.00 usec
P15       1000.00 usec
PLW1      180.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
P3        2.85 usec
PCPD2     5.50 usec
PLW2      85.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SPNAM0    Squa100.1000
SFOAL0    0.500
SPOFFS0   0 Hz
SPW0      85.00000000 W

F2 - Processing parameters
SI        16384
SF        75.4679699 MHz
WDW       EM
SSB       0
LB        50.00 Hz
GB        0
PC        0.20
  
```



Willow Calibration charcoal sample pyrolysed at 550 degC (reburn)

154.2 mg

CPMAS square100 with dipolar dephasing and total suppression of spinning sidebands, and tppm15 decoupling

1 ms contact pulse

Probe: 7 mm 5kHz MAS

modified the TOSS sequence by inserting the power level command pl11 into each line of code used to control the TOSS PI pul:
Singificant improvement in TOSS was observed

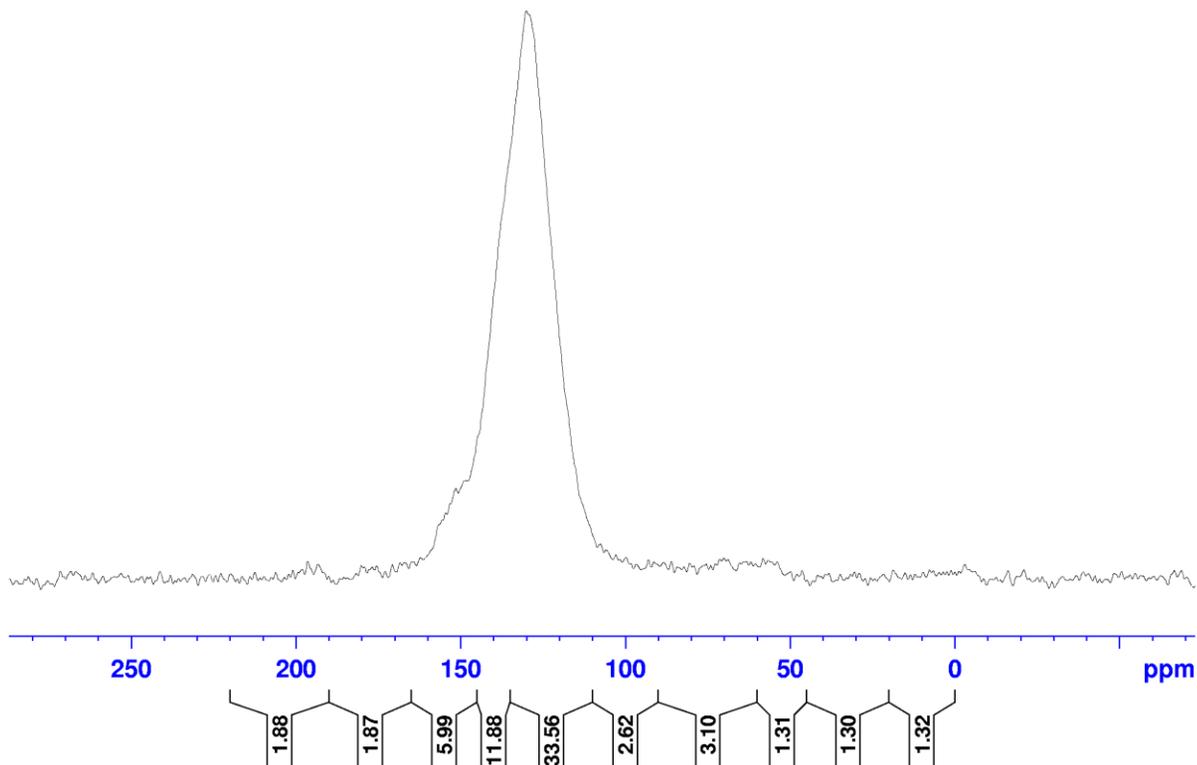
Current Data Parameters
NAME VonBargenWillowCal550rb 120712
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121208
Time 11.02
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_nqs_WCH
TD 1024
SOLVENT CDCl3
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
TDO 20
ZGOPTNS

----- CHANNEL f1 -----
NUC1 13C
P2 8.00 usec
P15 1000.00 usec
PLW1 180.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

----- CHANNEL f2 -----
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.50 usec
PLW2 85.00000000 W
PLW2 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squa100.1000
SFOAL0 0.500
SPOFFS0 0 Hz
SPW0 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4679699 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20



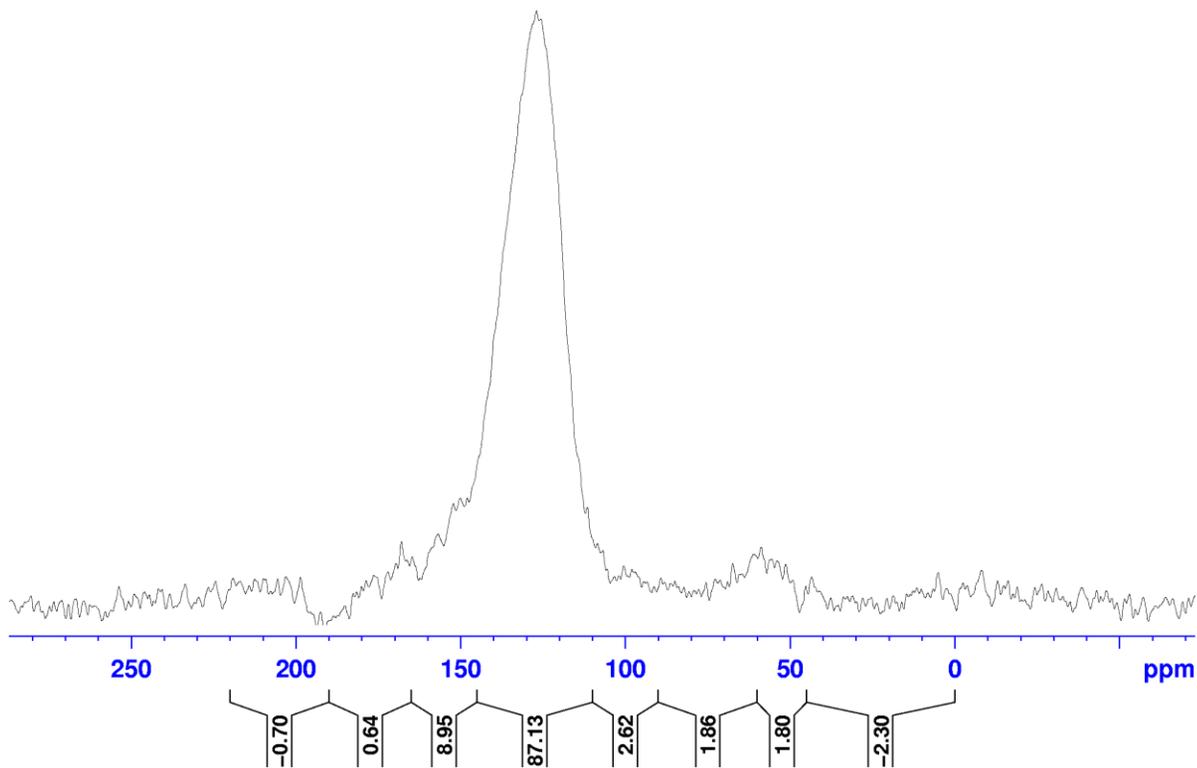
Willow Calibration charcoal sample pyrolysed at 550 degC (reburn)
 154.2 mg
 hpdec with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS
 improved TOSS sequence
 added Td0 loops

Current Data Parameters
 NAME VonBargenWillowCal550rb 120712
 EXPNO 3
 PROCNO 2

F2 - Acquisition Parameters
 Date_ 20121208
 Time 15.13
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG hpdecTOSS
 TD 1024
 SOLVENT CDCl3
 NS 1000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 30.00000000 sec
 D31 0.00020000 sec
 TD0 10
 ZGOPTS -DROSSB

===== CHANNEL f1 =====
 NUC1 13C
 P1 4.00 usec
 P2 8.00 usec
 PLW1 320.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz
 ===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 PCPD2 5.40 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz

F2 - Processing parameters
 SI 16384
 SF 75.4680013 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Willow Calibration charcoal sample pyrolysed at 550 degC (reburn)
 154.2 mg
 hpdec (direct polarization) with diplor dephasing, Total Sideband Suppression (TOSS), and TPPM15 decoupling
 Probe: 7 mm , 5kHz MAS
 improved TOSS sequence

```

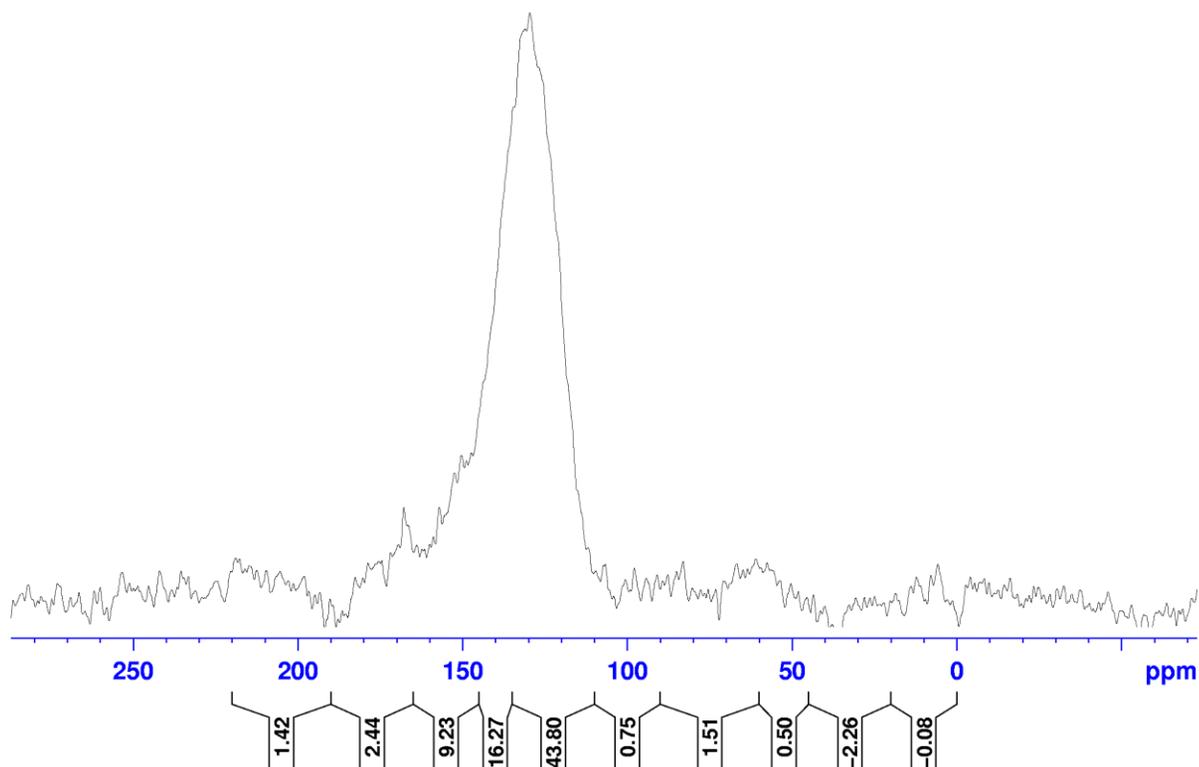
Current Data Parameters
NAME      VonBargenWillowCal550rb 120712
EXPNO     4
PROCNO    2

F2 - Acquisition Parameters
Date_     20121209
Time      16.14
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_nqs
TD        1024
SOLVENT   CDCl3
NS        1000
DS        0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ        0.0147956 sec
RG        45.2
DW        14.400 usec
DE        8.08 usec
TE        303.0 K
CNST11    0
CNST31    5000.0000000
D1        30.00000000 sec
D20       0.00007000 sec
D31       0.00020000 sec
TDO       10
ZGOPTNS   -DTOSSB

----- CHANNEL f1 -----
NUC1      13C
P1        4.00 usec
P2        8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

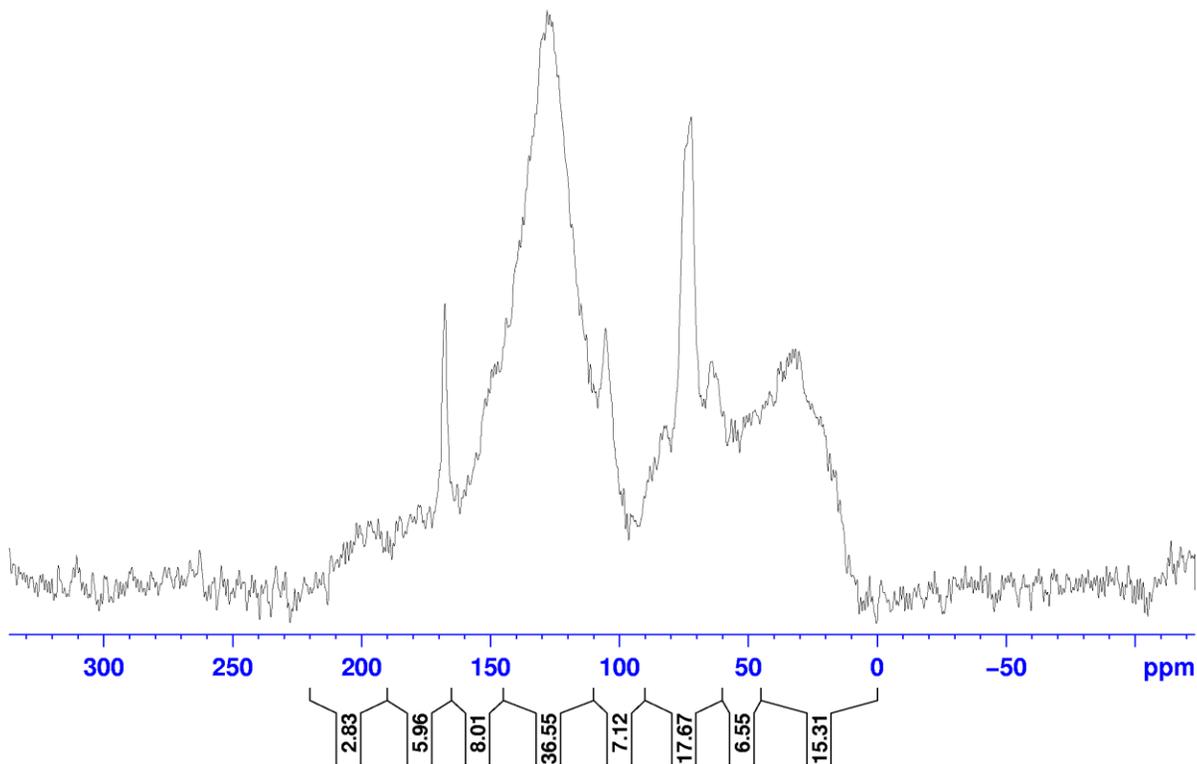
----- CHANNEL f2 -----
CPDPRG2   tppm15
NUC2      1H
PCPD2     5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI        16384
SF        75.4680013 MHz
WDW       EM
SSB       0
LB        70.00 Hz
GB        0
PC        0.20
  
```



Waco Wetland Fire charcoal sample site 1
 177.4mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

106



```

Current Data Parameters
NAME      VonBargen_WWF1Char_110112
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20121101
Time     19.29
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D31      0.00020000 sec
TD0      4
ZGOPTNS  4

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

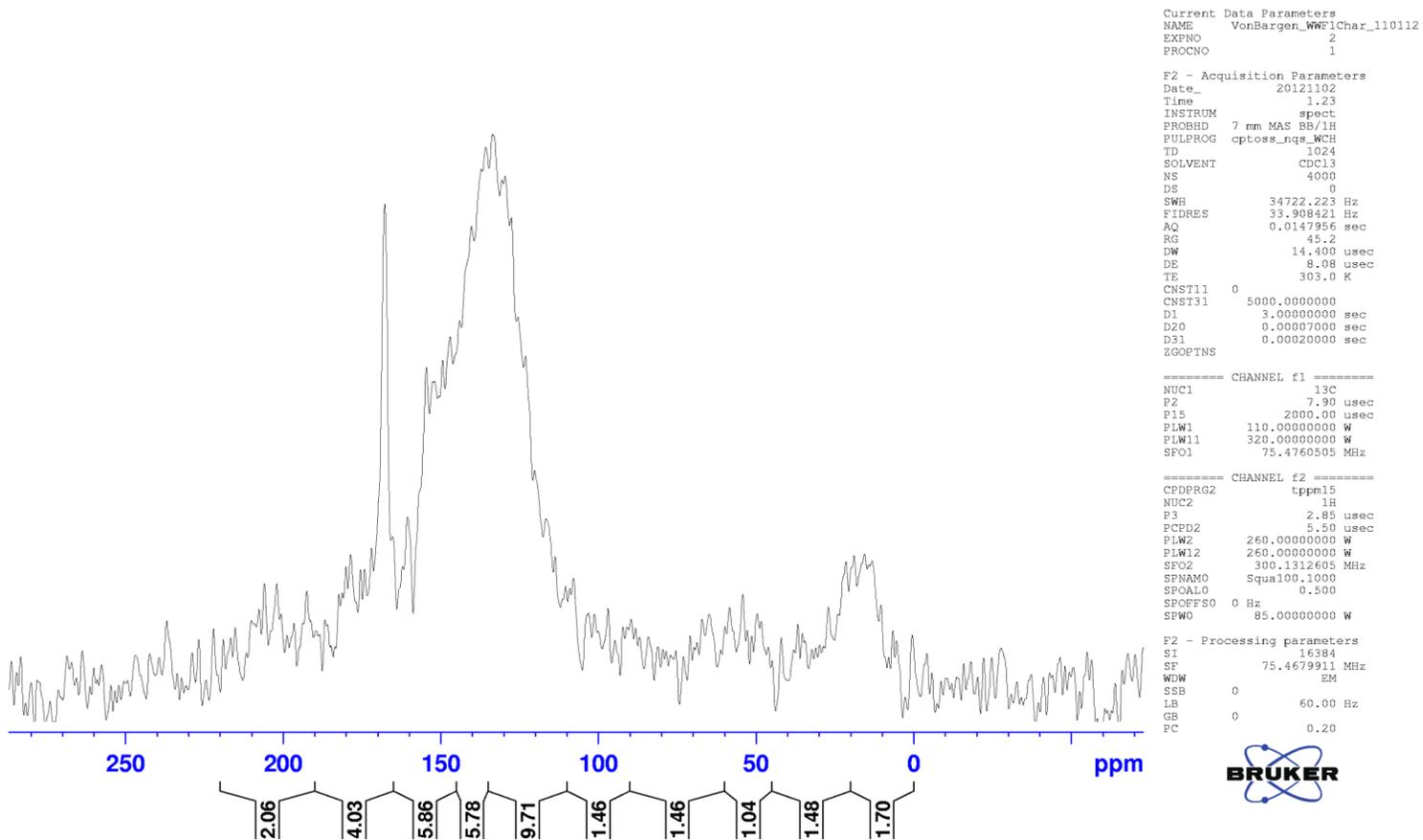
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOALO   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 1
 177.4mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

107



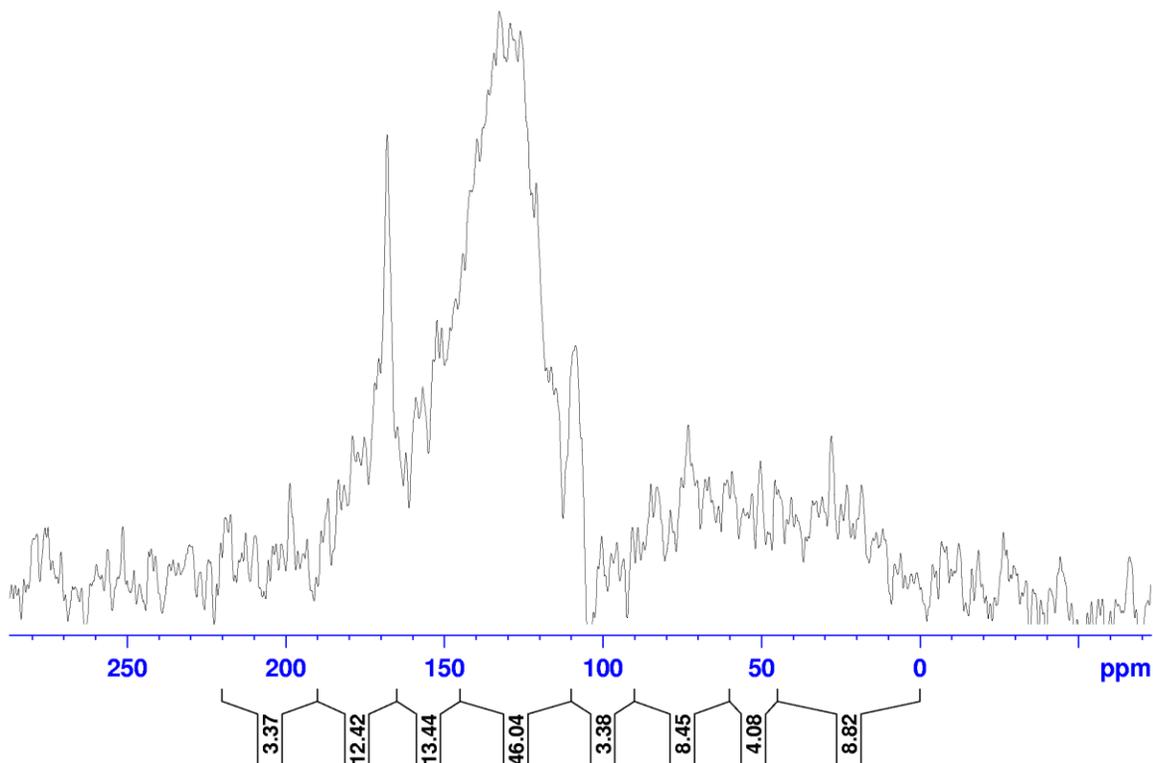
Waco Wetland Fire charcoal sample site 1

177.4mg

hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling

Probe: 7 mm MAS 5kHz MAS

801



Current Data Parameters
NAME VonBargen_WWF1Char_110112
EXPNO 3
PROCNO 4

F2 - Acquisition Parameters
Date_ 20121102
Time 3.53
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG hpdecTOSS
TD 1024
SOLVENT CDCl3
NS 1000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 90.00000000 sec
D31 0.00020000 sec
TD0 10
ZGPTNS

===== CHANNEL f1 =====
NUC1 13C
P1 4.00 usec
P2 8.00 usec
PLW1 320.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

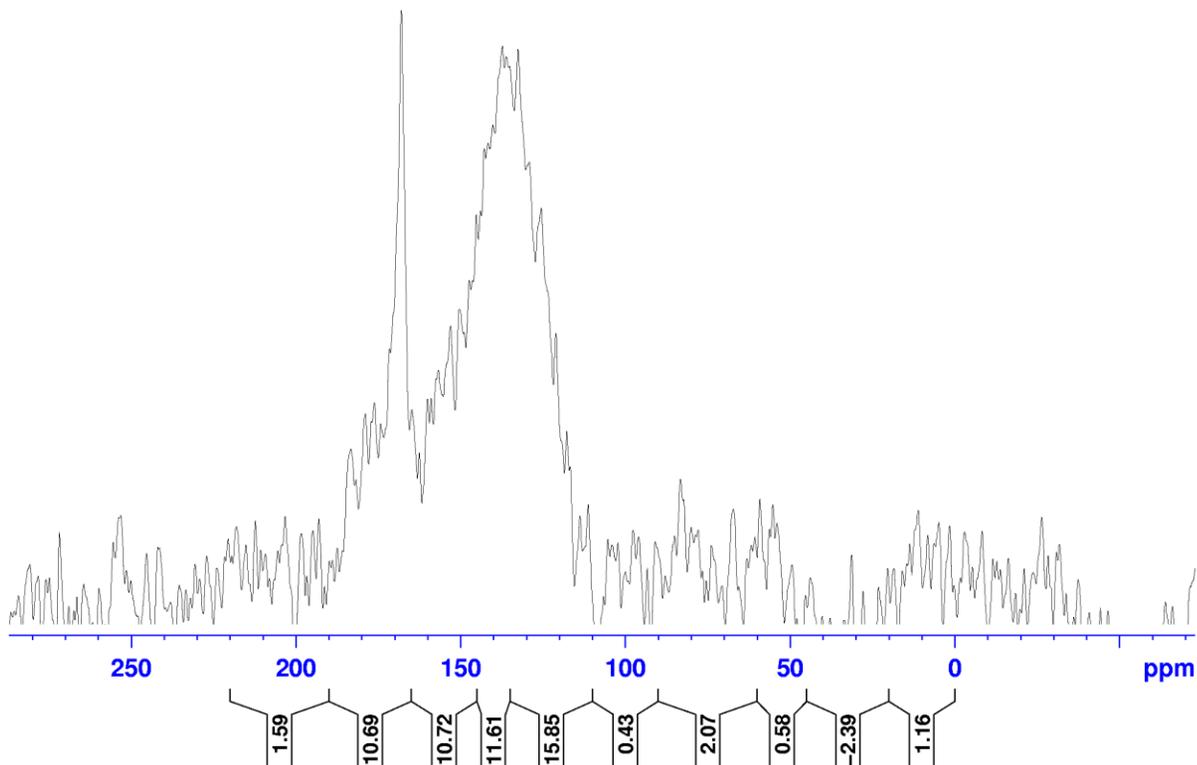
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz

F2 - Processing parameters
SI 16384
SF 75.4679928 MHz
WDW EM
SSB 0
LB 60.00 Hz
GB 0
PC 0.20



Waco Wetland Fire charcoal sample site 1
 177.4mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

109



```

Current Data Parameters
NAME      VonBargen_WWF1Char_110112
EXPNO    4
PROCNO   3

F2 - Acquisition Parameters
Date_    20121104
Time     2.23
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nqs
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOP1NS

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

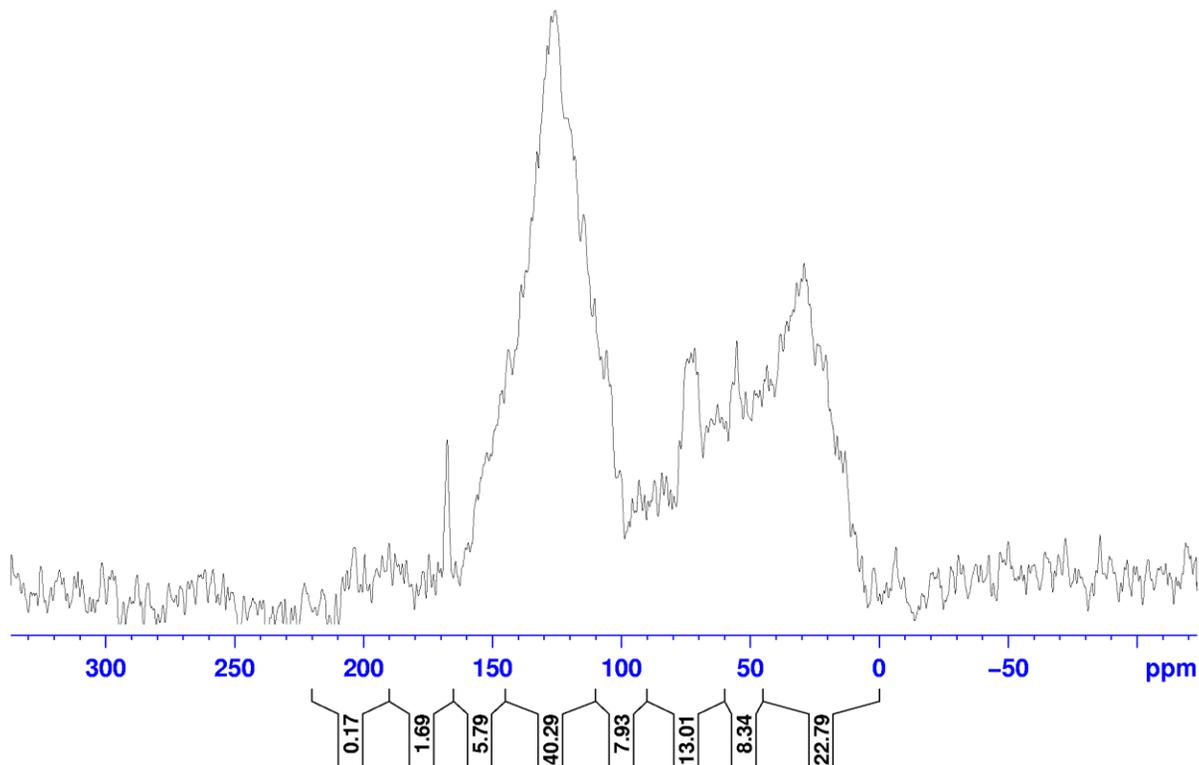
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4679928 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 3
 151.2mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

110



Current Data Parameters
 NAME VonBargen_WWF3Char_102512
 EXPNO 5
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20121128
 Time 7:57
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG cptoss_WCH
 TD 1024
 SOLVENT CDCl3
 NS 4000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 3.00000000 sec
 D31 0.00020000 sec
 TD0 40
 ZGOPTNS

===== CHANNEL f1 =====
 NUC1 13C
 P2 7.90 usec
 P15 2000.00 usec
 PLW1 110.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

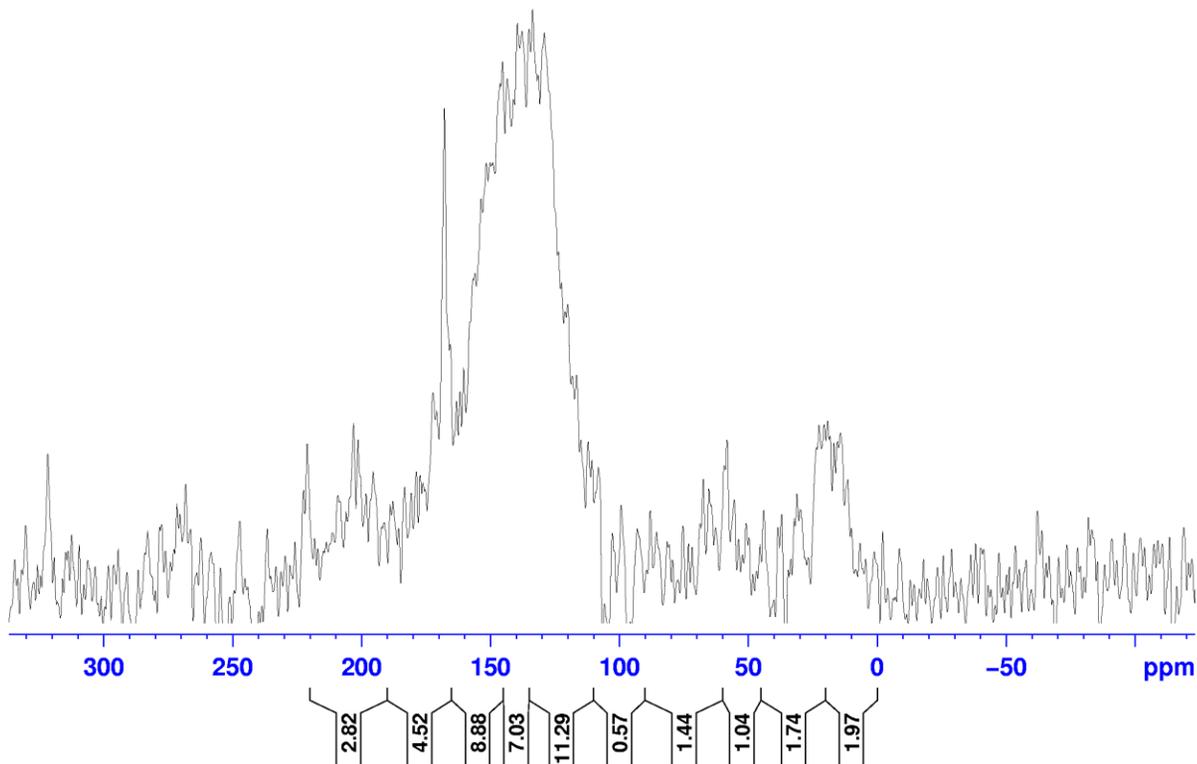
===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 P3 2.85 usec
 PCPD2 5.50 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz
 SPNAME Squal00.1000
 SFOAL0 0.500
 SPOFFS0 0 Hz
 SEW0 85.00000000 W

F2 - Processing parameters
 SI 16384
 SF 75.4679911 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Waco Wetland Fire charcoal sample site 3
 152.9mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

111



```

Current Data Parameters
NAME      VonBargen_WWF3Char_102512
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20121026
Time      10.40
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqs_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2        7.90 usec
P15       2000.00 usec
PLW1      110.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

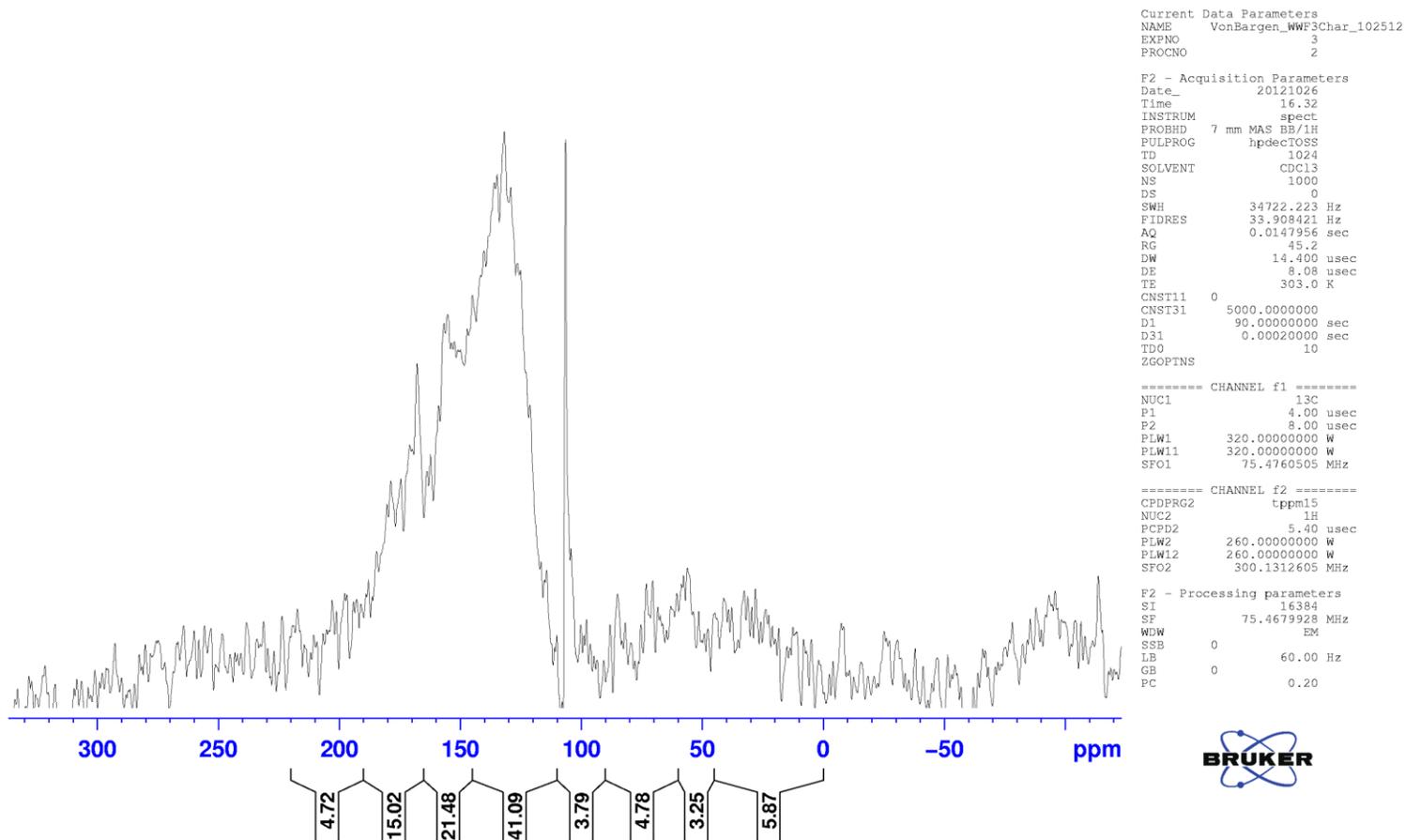
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
P3        2.85 usec
PCPD2     5.50 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SPNAM0    Squa100.1000
SFOAL0    0.500
SPOFFS0   0 Hz
SEW0      85.00000000 W

F2 - Processing parameters
SI        16384
SF        75.4679911 MHz
WDW       EM
SSB       0
LB        60.00 Hz
GB        0
PC        0.20
  
```



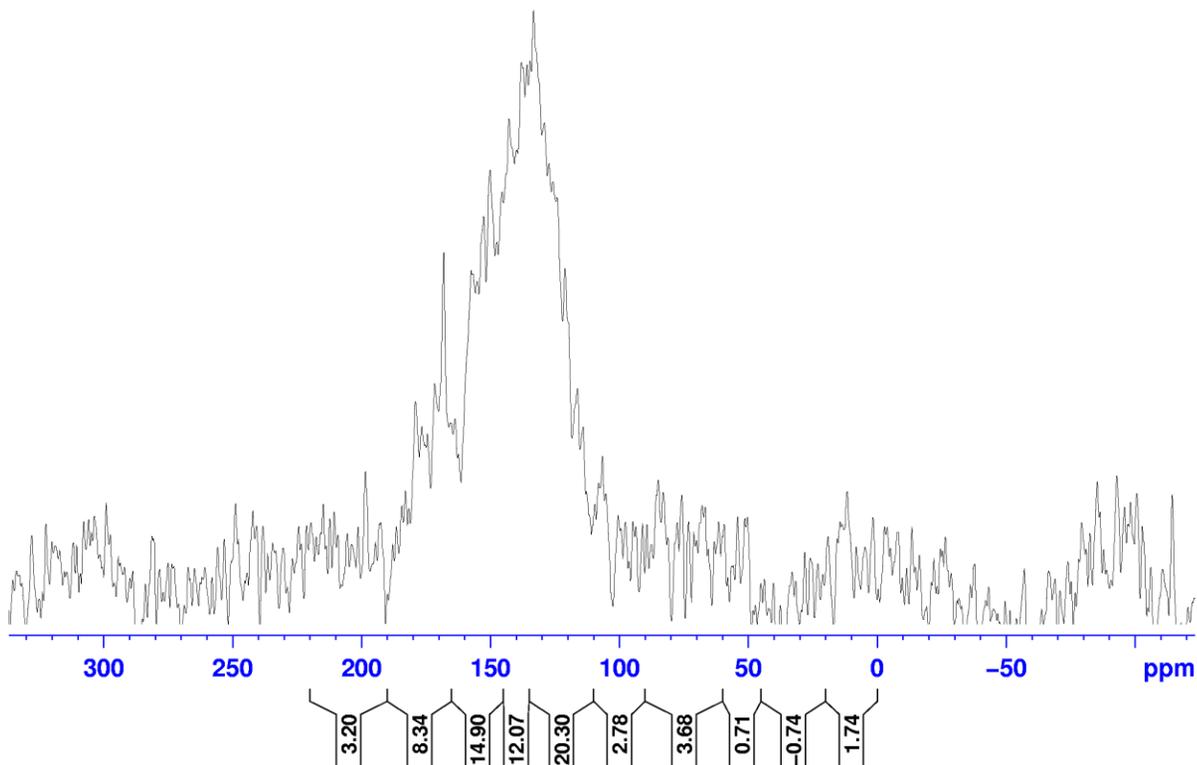
Waco Wetland Fire charcoal sample site 3
152.9mg
hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
Probe: 7 mm MAS 5kHz MAS

112



Waco Wetland Fire charcoal sample site 3
 152.9mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

113



```

Current Data Parameters
NAME      VonBargen_WWF3Char_102512
EXPNO    4
PROCNO   3

F2 - Acquisition Parameters
Date_    20121028
Time     16.02
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nqs
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOP1NS

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

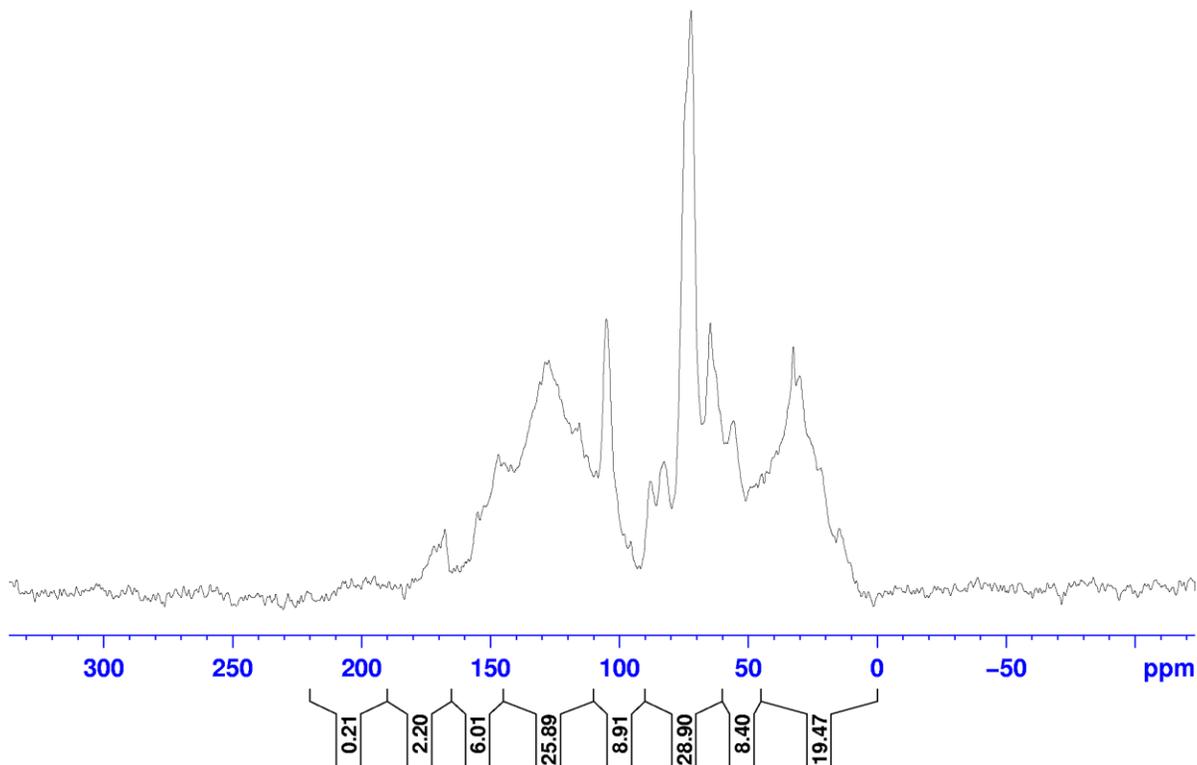
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4679928 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 4
 183.5mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

114



```

Current Data Parameters
NAME      VonBargen_WWF4Char_102112
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20121021
Time     13.34
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D31      0.00020000 sec
TD0      4
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

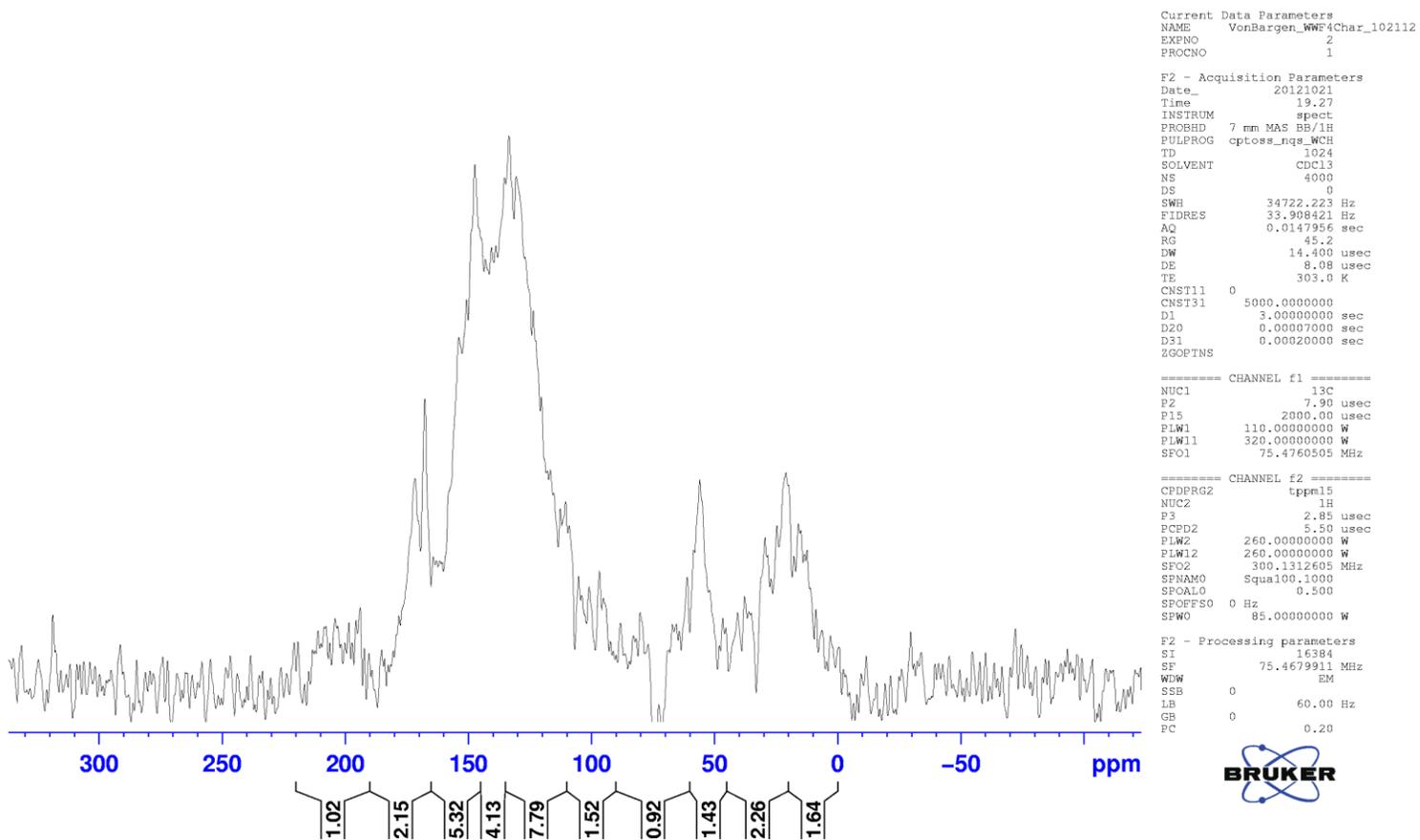
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOALO   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



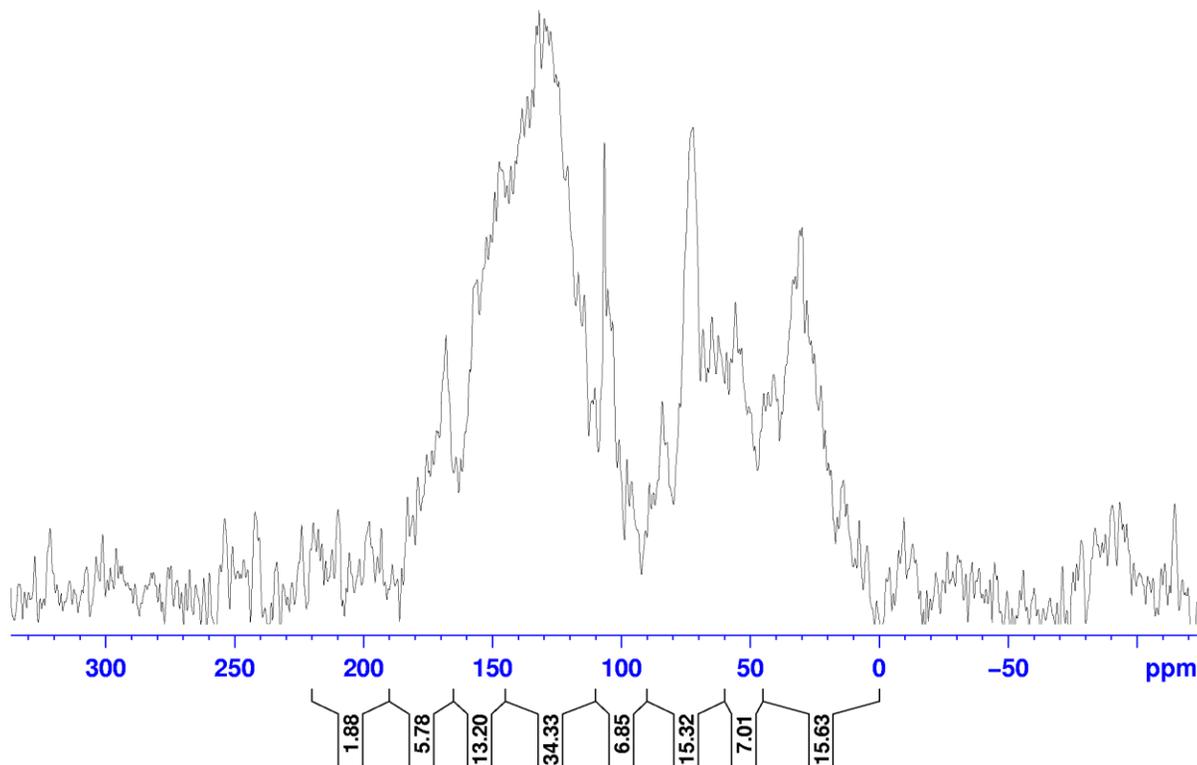
Waco Wetland Fire charcoal sample site 4
 183.5mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

115



Waco Wetland Fire charcoal sample site 4
 183.5mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

116



```

Current Data Parameters
NAME      VonBargen_WWF4Char_102112
EXPNO    3
PROCNO    2

F2 - Acquisition Parameters
Date_     20121021
Time      21.58
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
TD0        10
ZGPTINS

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

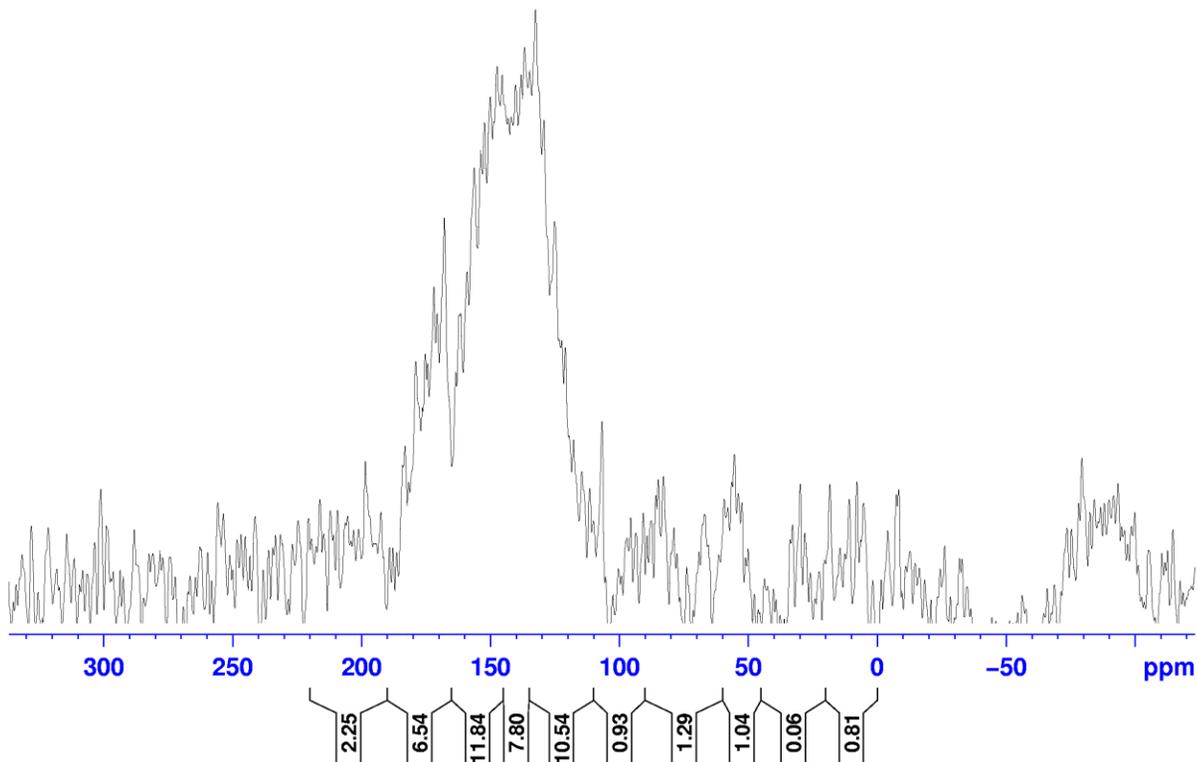
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 4
 183.5mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

117



```

Current Data Parameters
NAME      VonBargen_WWF4Char_102112
EXPNO    4
PROCNO    2

F2 - Acquisition Parameters
Date_     20121023
Time      21.28
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_nqs
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

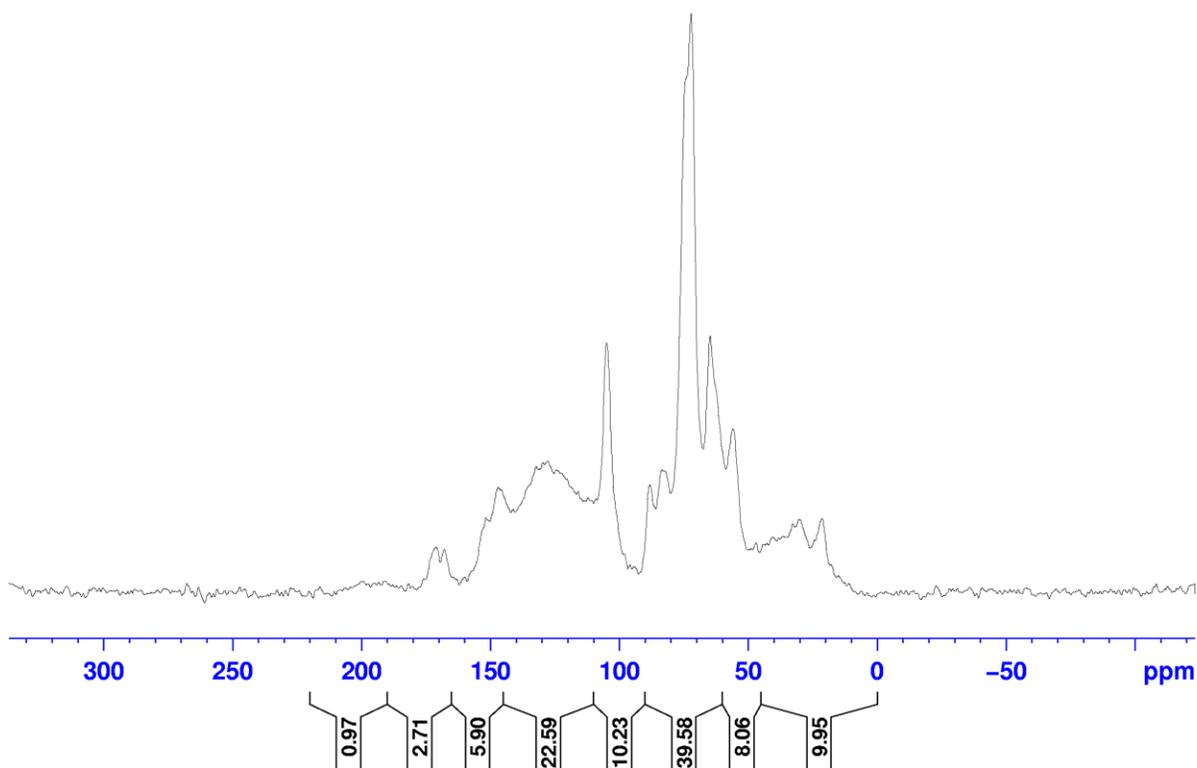
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 5
 234.2mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

118



```

Current Data Parameters
NAME      VonBargen_WWFSChar_101812
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20121018
Time     19.21
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D31      0.00020000 sec
TD0      4
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

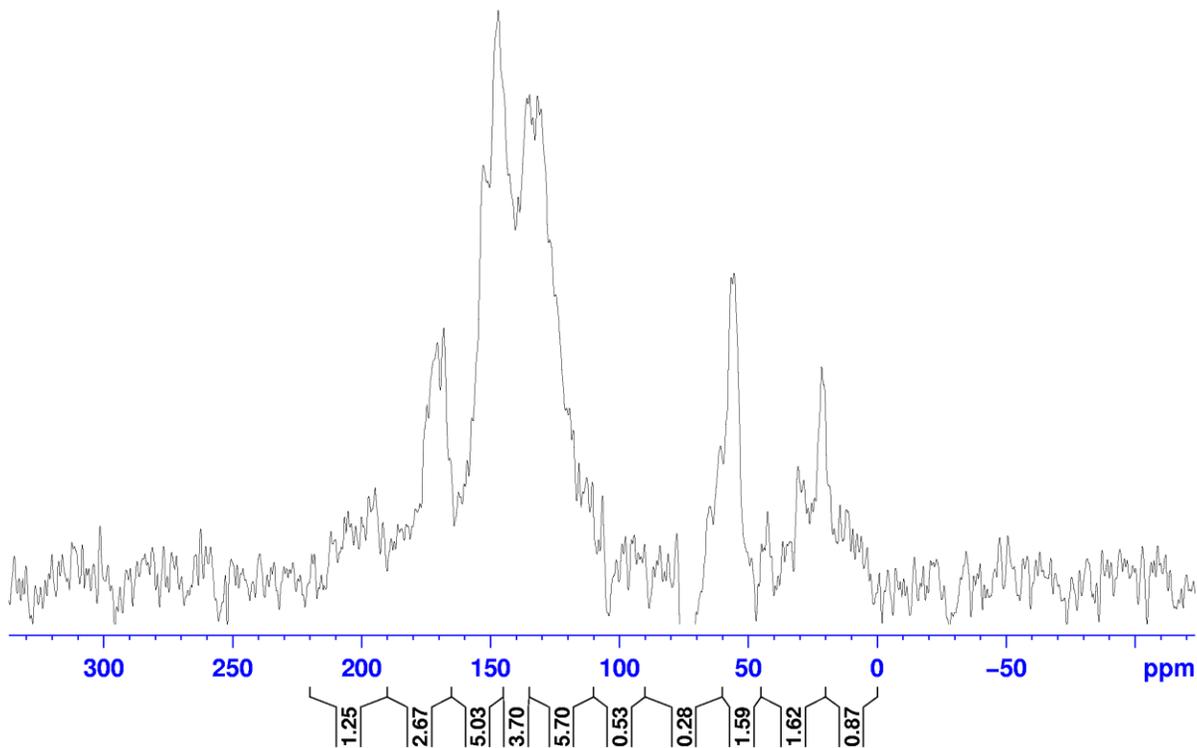
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOALO   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 5
 234.2mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

119



```

Current Data Parameters
NAME      VonBargen_WWFSChar_101812
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20121019
Time      1.14
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqs_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2        7.90 usec
P15       2000.00 usec
PLW1      110.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

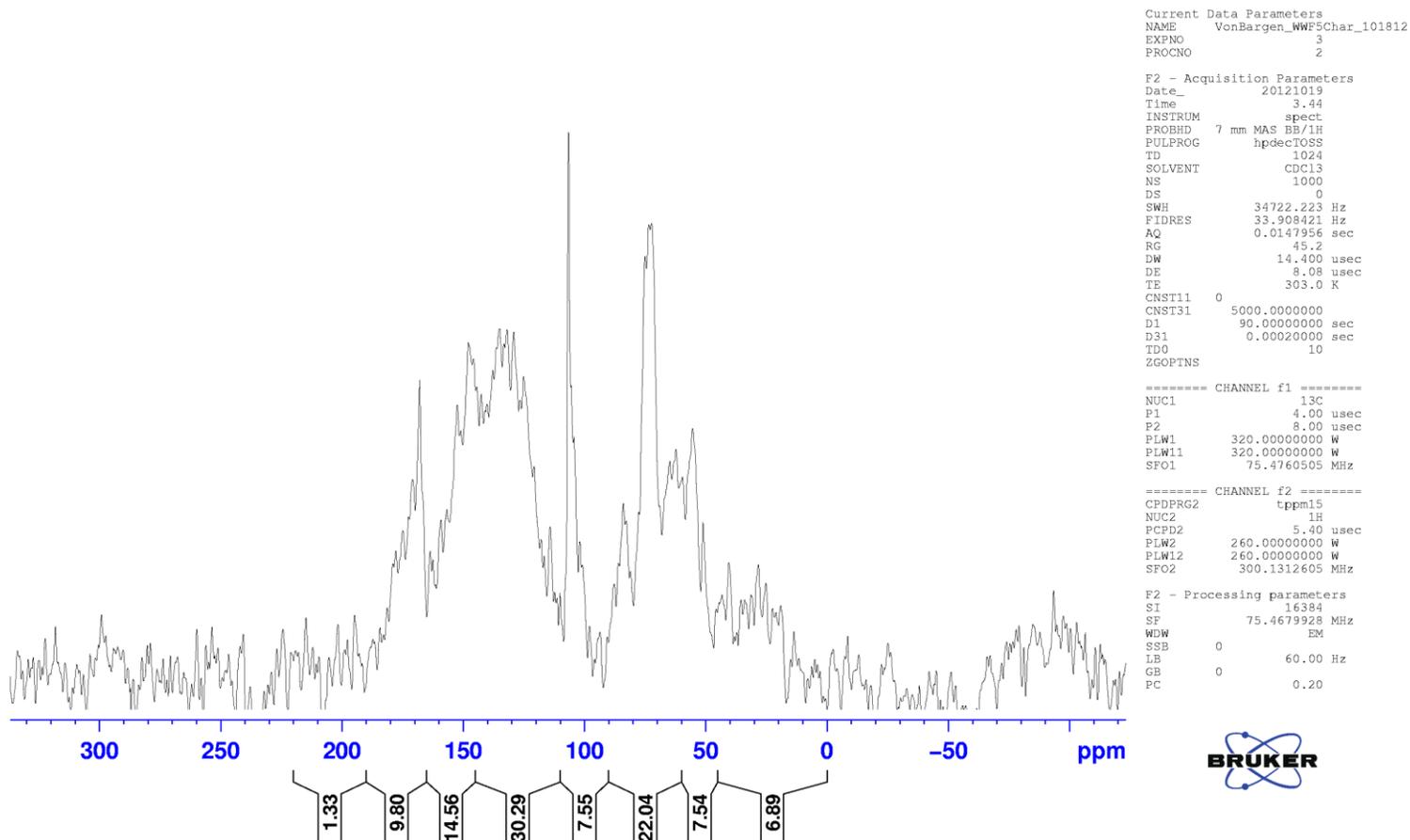
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
P3        2.85 usec
PCPD2     5.50 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SPNAM0    Squa100.1000
SFOAL0    0.500
SPOFFS0   0 Hz
SEW0      85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



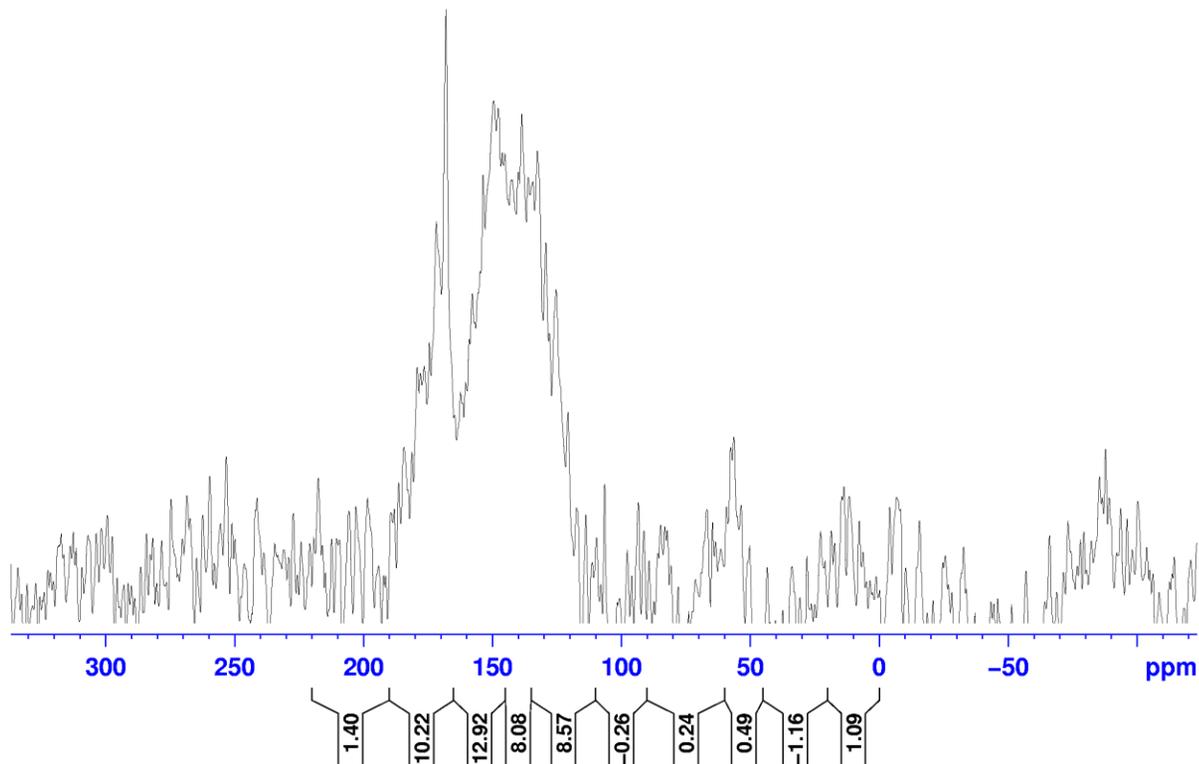
Waco Wetland Fire charcoal sample site 5
234.2mg
hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
Probe: 7 mm MAS 5kHz MAS

120



Waco Wetland Fire charcoal sample site 5
 234.2mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

121



```

Current Data Parameters
NAME      VonBargen_WWF5Char_101812
EXPNO    4
PROCNO   2

F2 - Acquisition Parameters
Date_    20121021
Time     3.15
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nqs
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOP1NS

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

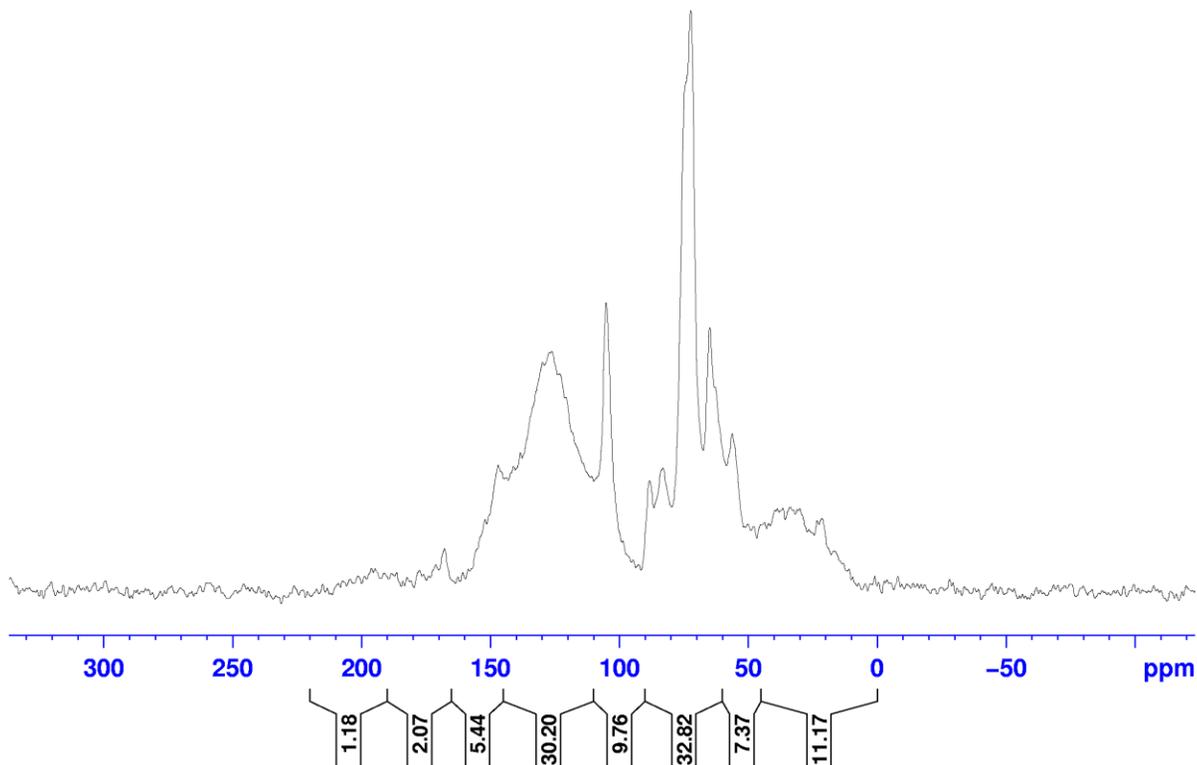
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4679928 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 6
 162.3mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

122



```

Current Data Parameters
NAME      VonBargen_WWF6Char_060712
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120607
Time     9.02
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD        1024
SOLVENT  CDCl3
NS        4000
DS        0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ        0.0147956 sec
RG        45.2
DM        14.400 usec
DE        8.08 usec
TE        303.0 K
CNST11   0
CNST31   5000.000000
D1        3.00000000 sec
D31       0.00020000 sec
ZGOPTS

===== CHANNEL f1 =====
NUC1      13C
P2        7.90 usec
P15       2000.00 usec
PLW1      110.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

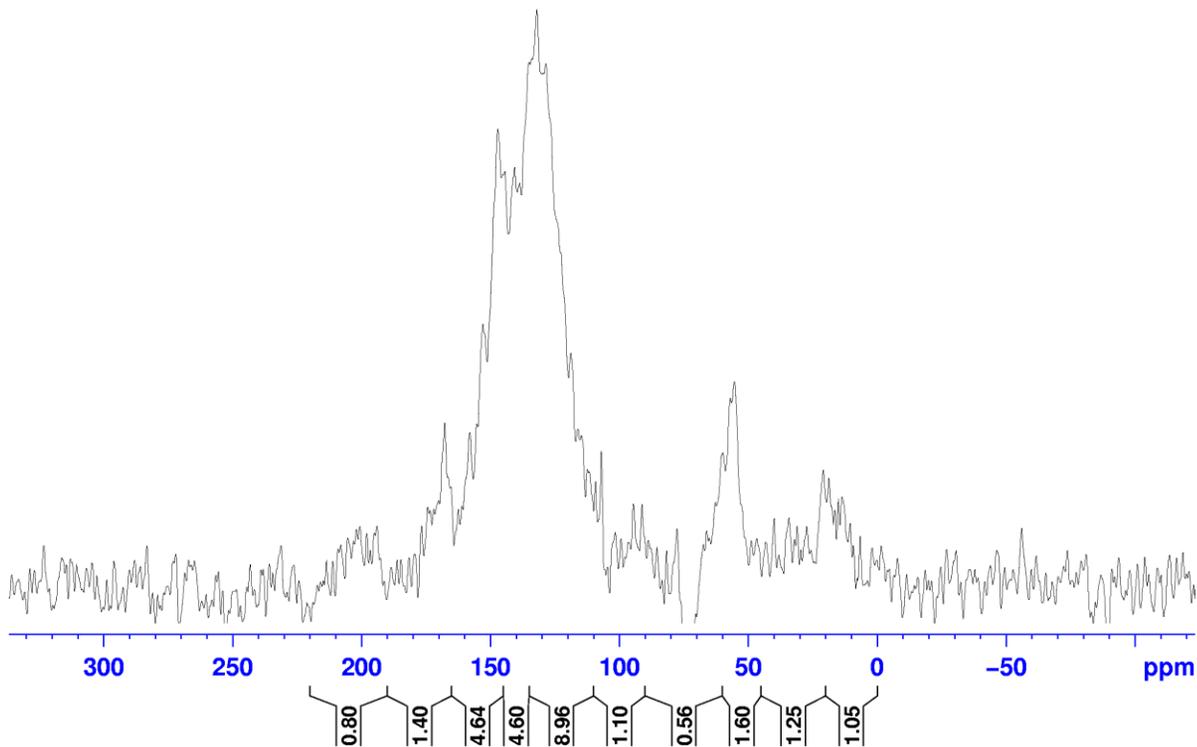
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2     5.50 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SFXAM0    Squal00.1000
SFOAL0    0.500
SPOFFS0   0 Hz
SPW0      85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 6
 162.3mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

123



```

Current Data Parameters
NAME      VonBargen_WW6Char_060712
EXPNO    2
PROCNO    1

F2 - Acquisition Parameters
Date_    20120607
Time     15.44
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_nqs_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

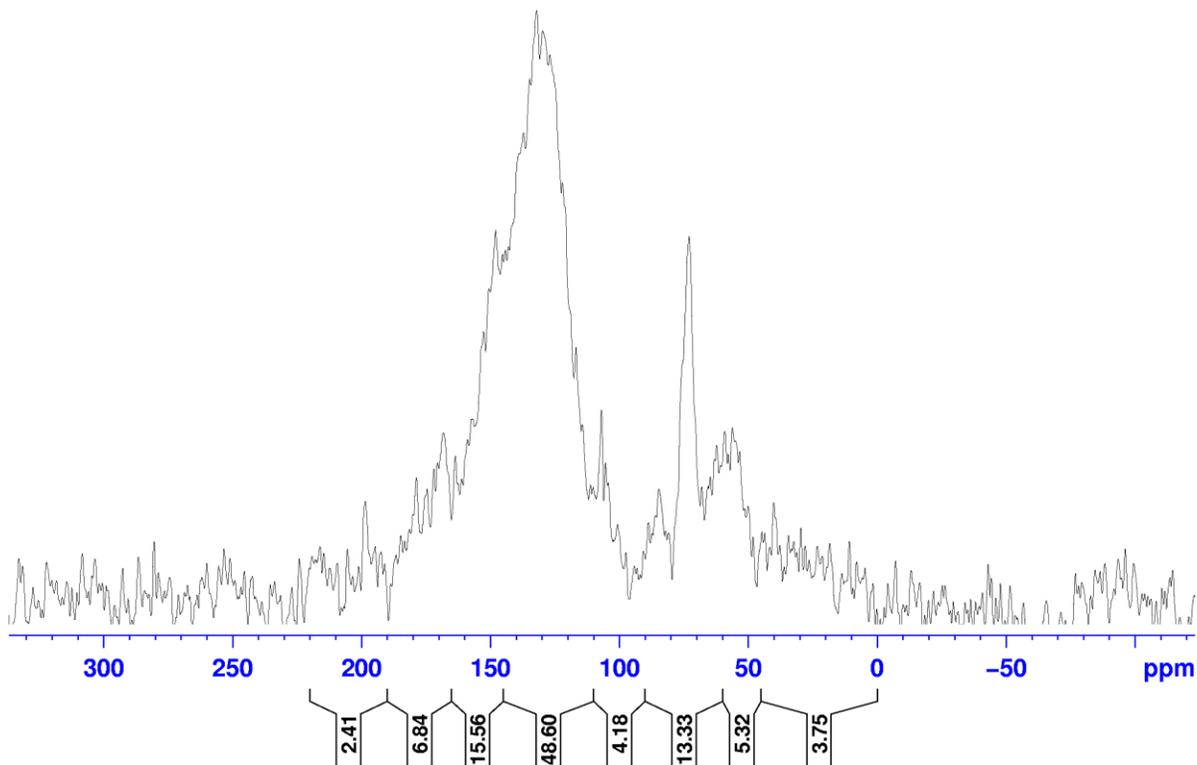
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOALO   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 6
162.3mg
hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
Probe: 7 mm MAS 5kHz MAS

124



```
Current Data Parameters
NAME      VonBargen_WWF6Char_060712
EXPNO     3
PROCNO    3

F2 - Acquisition Parameters
Date_     20120608
Time      16.44
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
ZGOPINS

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

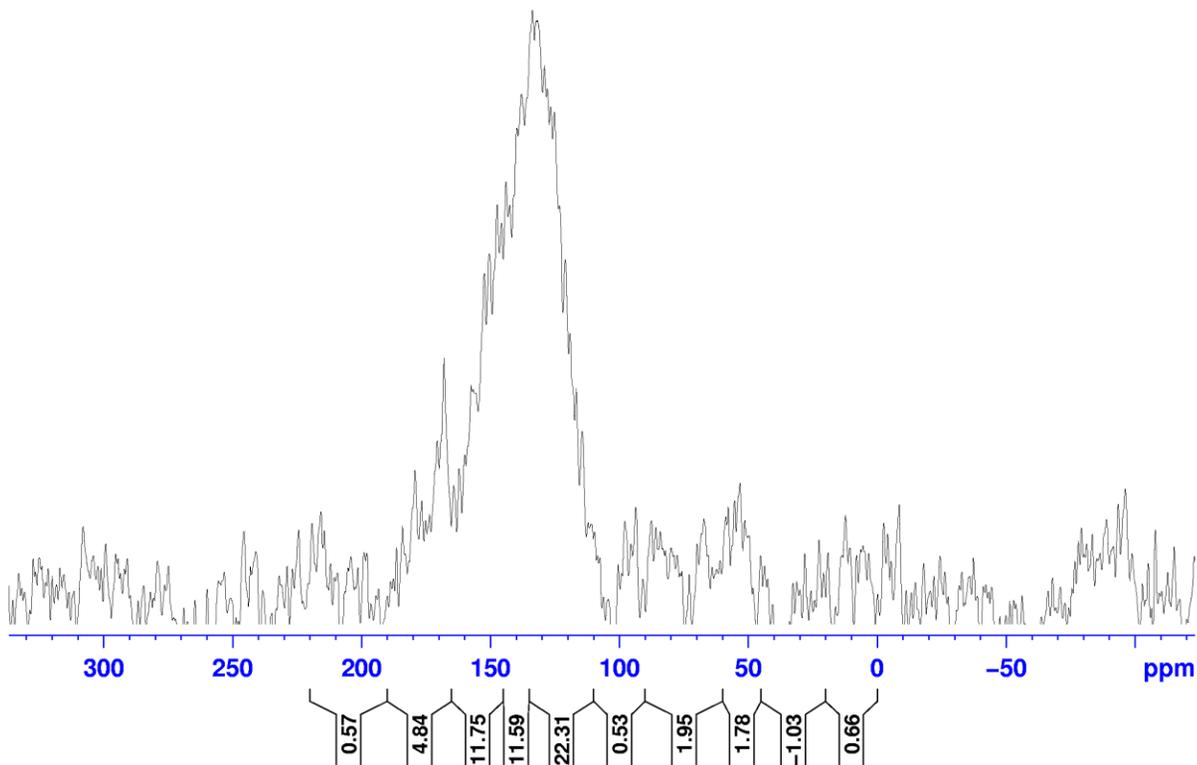
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
```



Waco Wetland Fire charcoal sample site 6
 162.3mg
 Direct polarization with dipolar dsephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

125



```

Current Data Parameters
NAME      VonBargen_WWF6Char_060712
EXPNO    4
PROCNO   3

F2 - Acquisition Parameters
Date_    20120608
Time     17.40
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nqs
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGPTINS

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

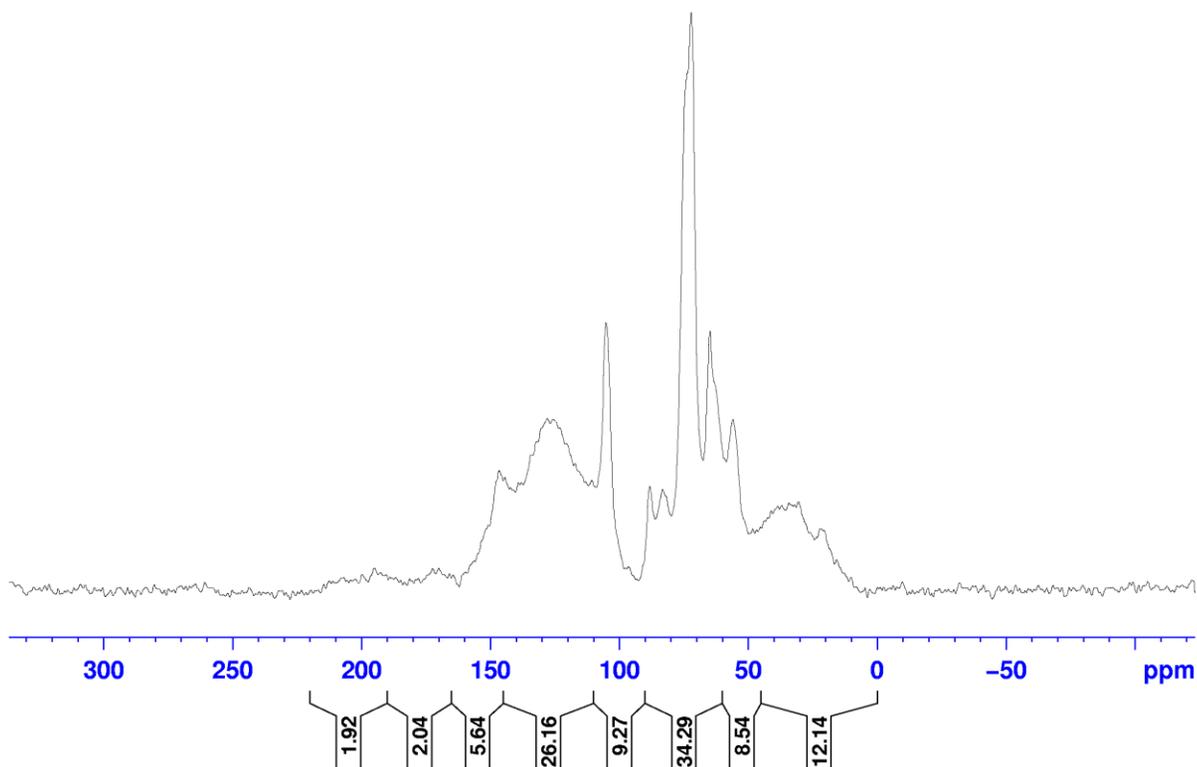
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4679928 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 7
 169.2mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

126



```

Current Data Parameters
NAME      VonBargen_WWF7Char_101212
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20121129
Time      17.29
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_WCH
TD         1024
SOLVENT   CDCl3
NS         1
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.0000000
D1         3.00000000 sec
D31        0.00020000 sec
TD0        4
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

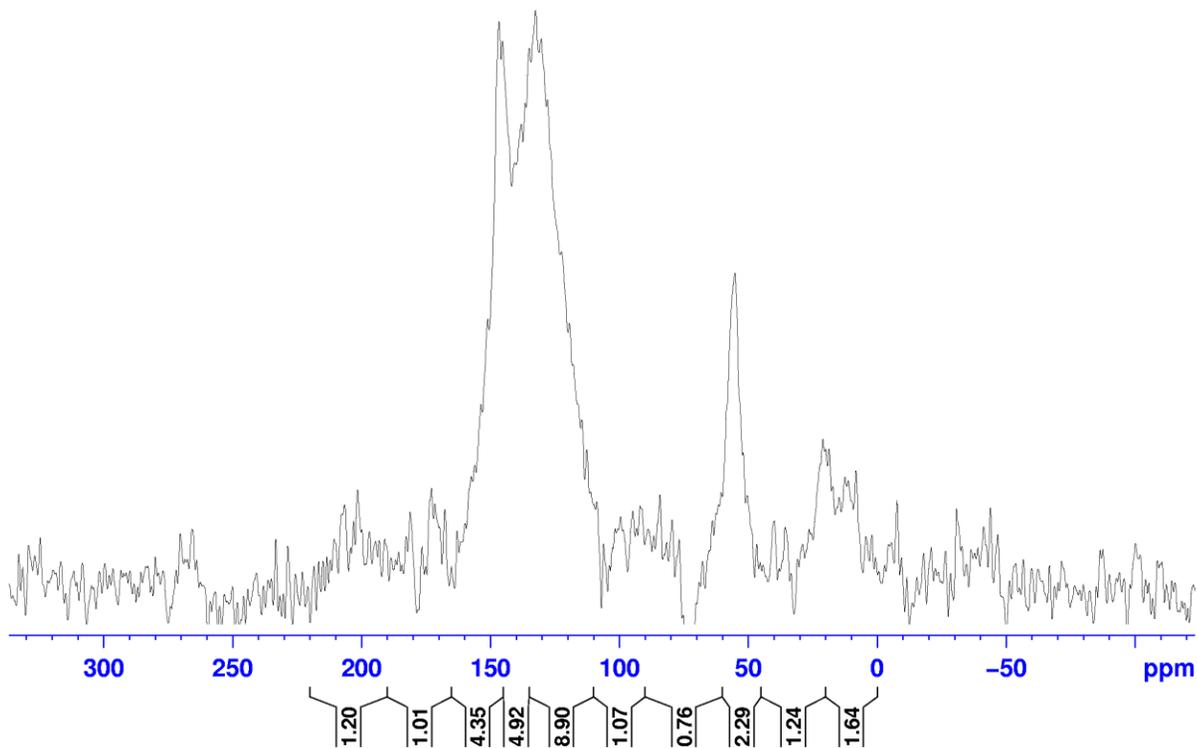
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2      5.50 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squa100.1000
SFOAL0     0.500
SPOFFS0    0 Hz
SEW0       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 7
 169.2mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

127



```

Current Data Parameters
NAME      VonBargen_WWF7Char_101212
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20121013
Time      15.17
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqs_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D2         0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2        7.90 usec
P15       2000.00 usec
PLW1      110.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

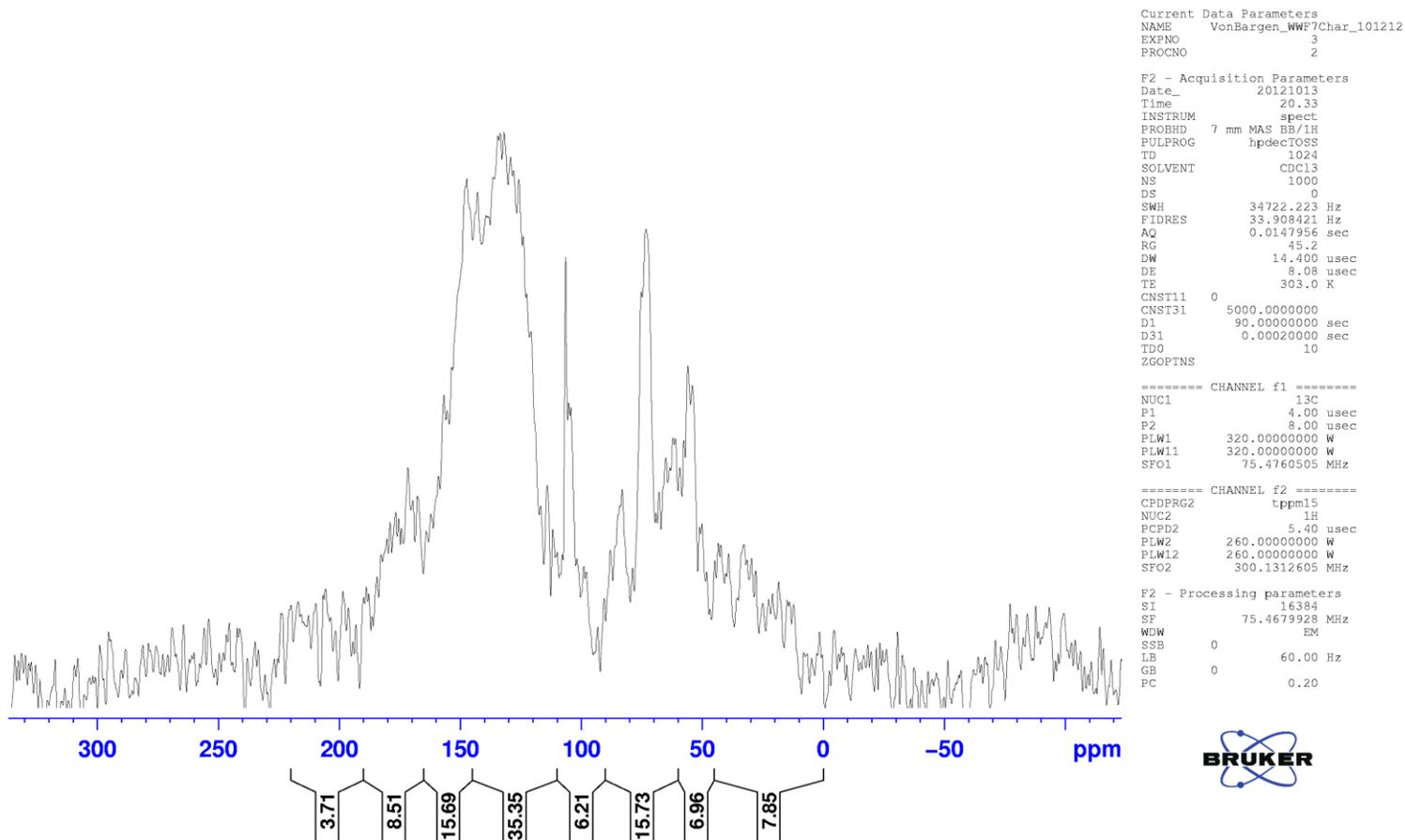
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
P3        2.85 usec
PCPD2     5.50 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SPNAM0    Squa100.1000
SFOALO    0.500
SPOFFS0   0 Hz
SEW0      85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



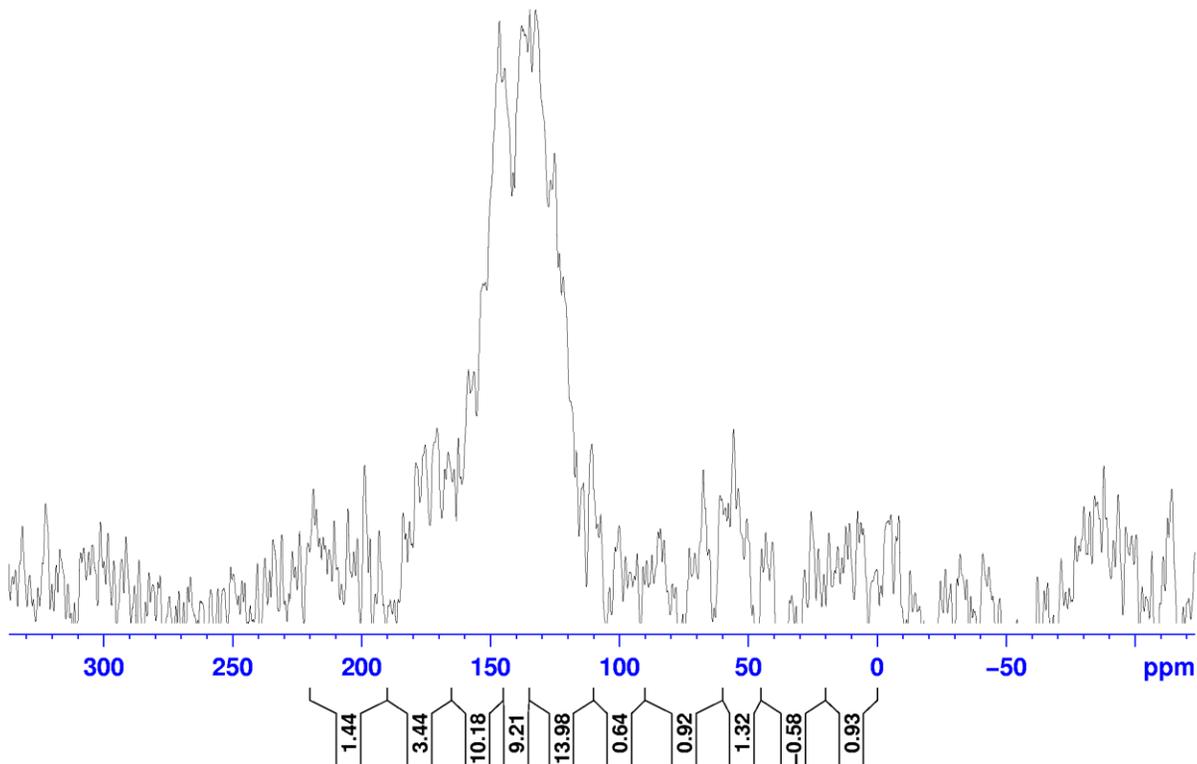
Waco Wetland Fire charcoal sample site 7
 169.2mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

128



Waco Wetland Fire charcoal sample site 7
 169.2mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

129



```

Current Data Parameters
NAME      VonBargen_WWF7Char_101212
EXPNO     4
PROCNO    2

F2 - Acquisition Parameters
Date_     20121015
Time      20.04
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_nqs
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOP1NS

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

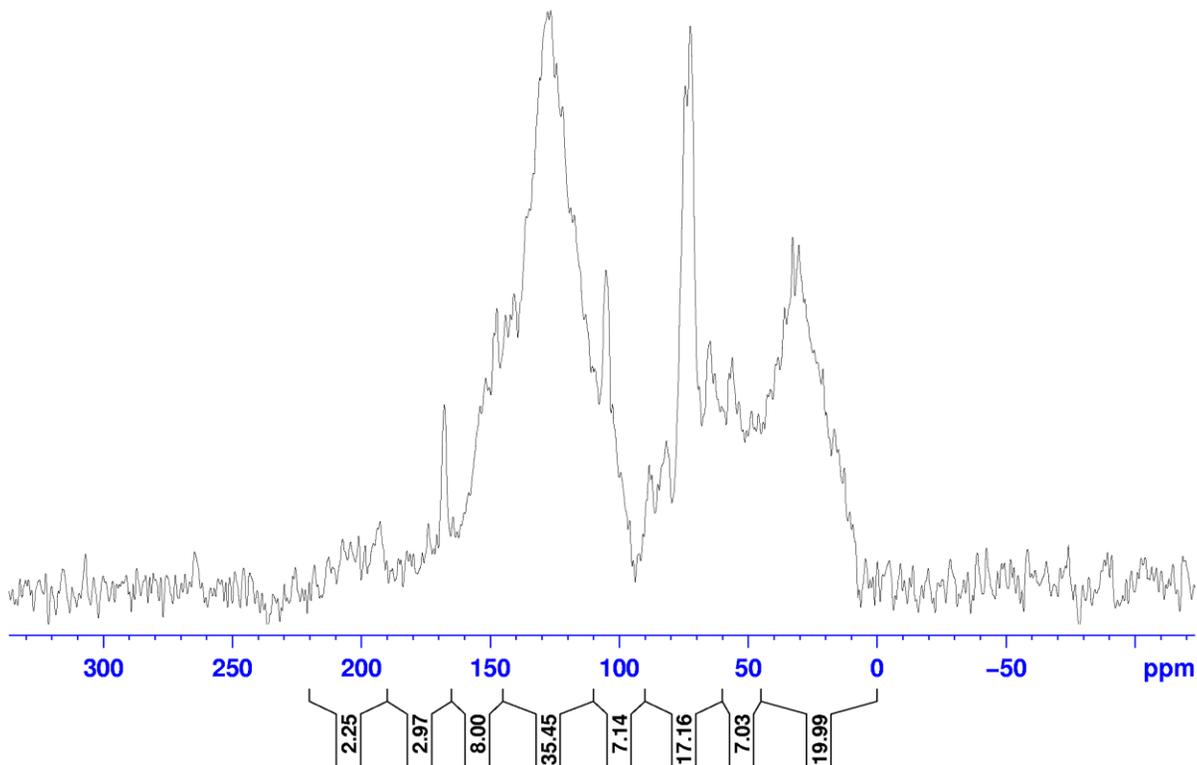
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 8
 163.5mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

130



Current Data Parameters
 NAME VonBargen_WWFBChar_50512
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120505
 Time 10.24
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG cptoss_WCH
 TD 1024
 SOLVENT CDCl3
 NS 4000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 3.00000000 sec
 D31 0.00020000 sec
 ZGPTNS -DTOSSB

===== CHANNEL f1 =====
 NUC1 13C
 P2 8.00 usec
 P15 2000.00 usec
 PLW1 110.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

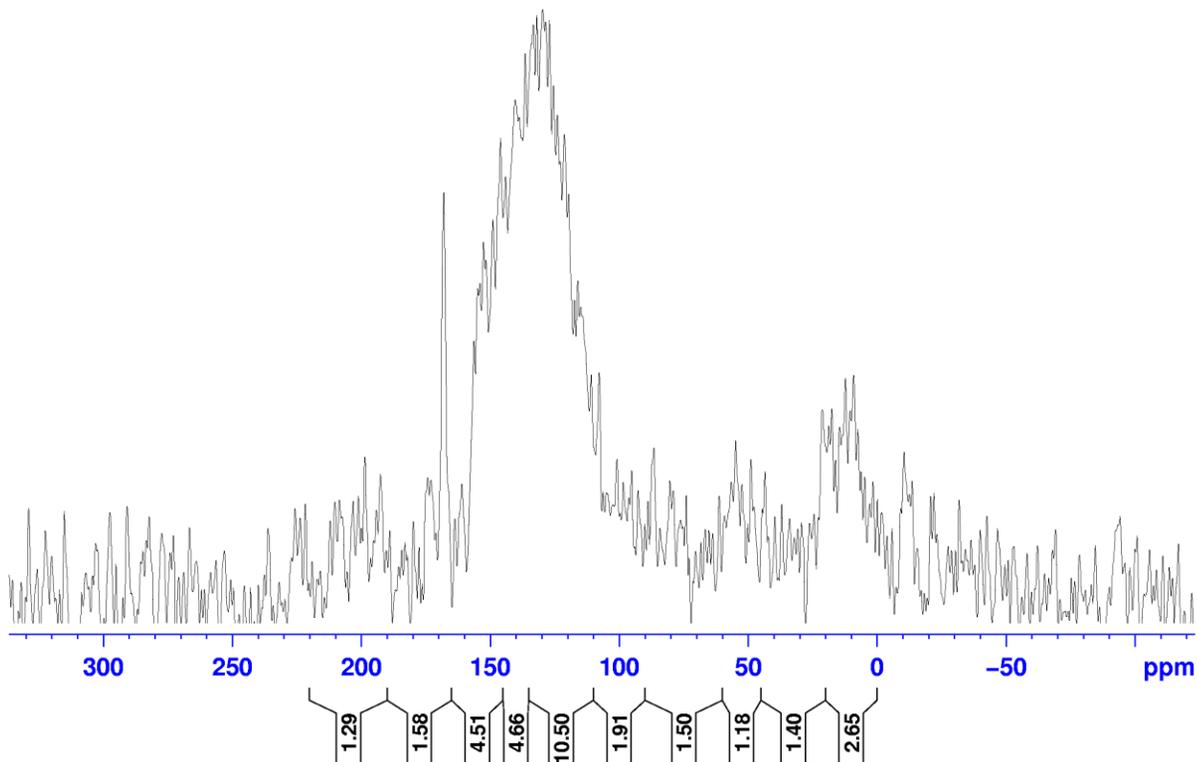
===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 P3 2.85 usec
 PCPD2 5.50 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz
 SFOA0 Squal00.1000
 SFOAL0 0.500
 SPOFFS0 0 Hz
 SPW0 85.00000000 W

F2 - Processing parameters
 SI 16384
 SF 75.4680013 MHz
 WDW EM
 SSB 0
 LB 50.00 Hz
 GB 0
 PC 0.20



Waco Wetland Fire charcoal sample site 8
 163.5mg
 CPMAS square100 with dipolar dephasing, tppm15 decoupling, and Total Suppression of Sidebands (TOSS)
 NOTE: this acquisition was run with -DROSSB option
 Probe: 7 mm, 5kHz MAS

131



```

Current Data Parameters
NAME      VonBargen_WWFSChar_50512
EXPNO    2
PROCNO    1

F2 - Acquisition Parameters
Date_    20120505
Time     17.07
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_nqs_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOPTNS  -DROSSB

===== CHANNEL f1 =====
NUC1     13C
P2       8.00 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4680028 MHz
WDW      EM
SSB      0
LB       50.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 8
 163.5mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 ZG OPTION: -DtossB.
 Probe: 7 mm MAS 5kHz MAS
 AFTER EMPTY ROTOR BACKGROUND SUBTRACTION

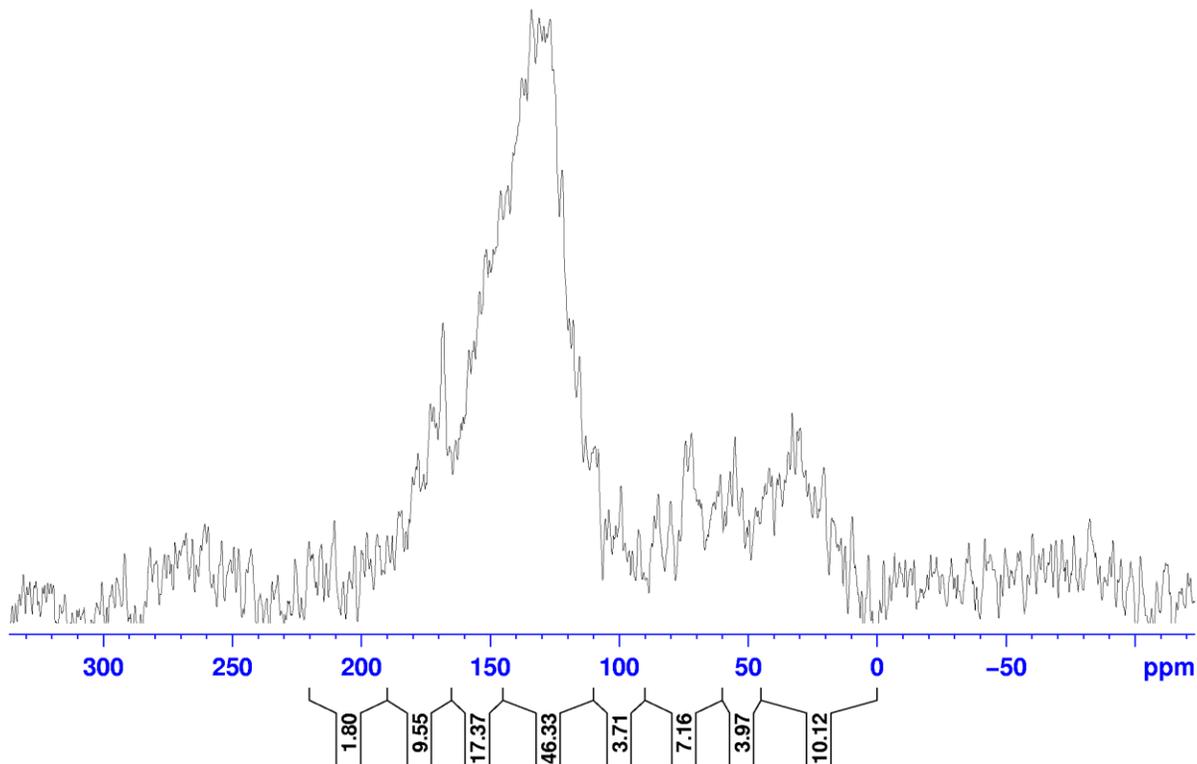
Current Data Parameters
 NAME VonBargen_WWF8Char_50512
 EXFNO 3
 PROCNO 2

F2 - Acquisition Parameters
 Date_ 20120506
 Time 18.07
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG hpdecToss
 TD 2048
 SOLVENT CDCl3
 NS 1000
 DS 0
 SWH 34722.223 Hz
 FIDRES 16.954210 Hz
 AQ 0.0295412 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 90.00000000 sec
 D31 0.00020000 sec
 ZGOPTNS -DTOSSB

===== CHANNEL f1 =====
 NUC1 13C
 P1 4.00 usec
 P2 8.00 usec
 PLW1 320.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

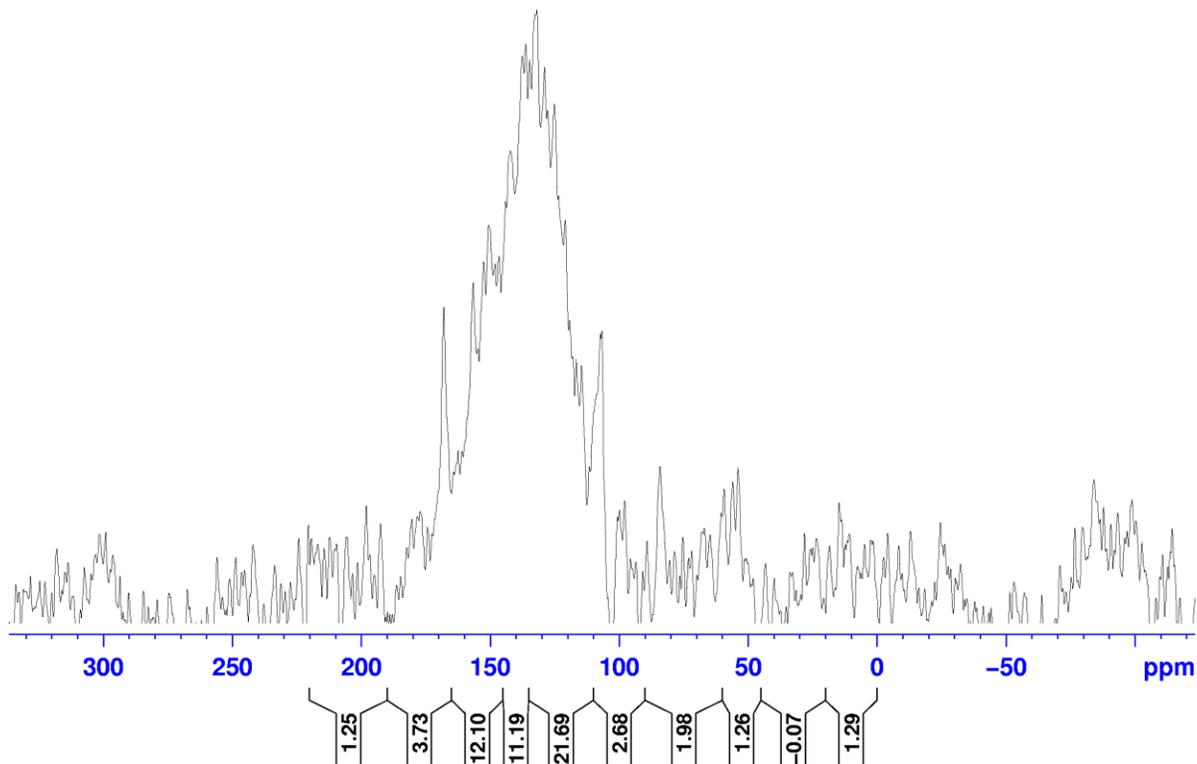
===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 PCPD2 5.40 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz

F2 - Processing parameters
 SI 16384
 SF 75.4680013 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Waco Wetland Fire Charcoal site 8
 163.5mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 ZG OPTION: -DtossB.
 Probe: 7 mm , 5kHz MAS

133



```

Current Data Parameters
NAME      VonBargen_WWF8Char_50512
EXPNO    4
PROCNO   3

F2 - Acquisition Parameters
Date_    20120507
Time     8.54
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_Rqs
TD       2048
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   16.954210 Hz
AQ       0.0295412 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOPTNS  -DTOSSB

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

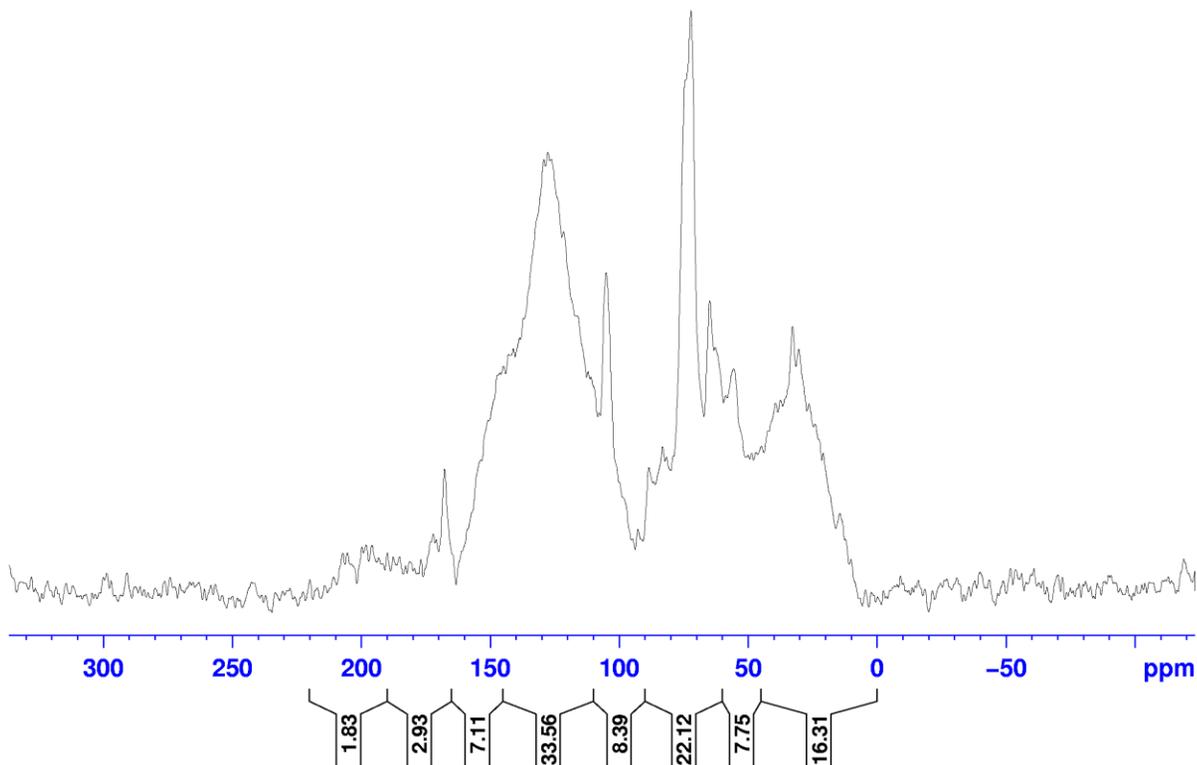
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4680013 MHz
WDW      EM
SSB      0
LB       70.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 9
 187.1mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

134



Current Data Parameters
 NAME VonBargen_WWF9Char_092412
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120924
 Time 9.09
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG cptoss_WCH
 TD 1024
 SOLVENT CDCl3
 NS 4000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 3.00000000 sec
 D31 0.00020000 sec
 TD0 1
 ZGOPTNS

===== CHANNEL f1 =====
 NUC1 13C
 P2 7.90 usec
 P15 2000.00 usec
 PLW1 110.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

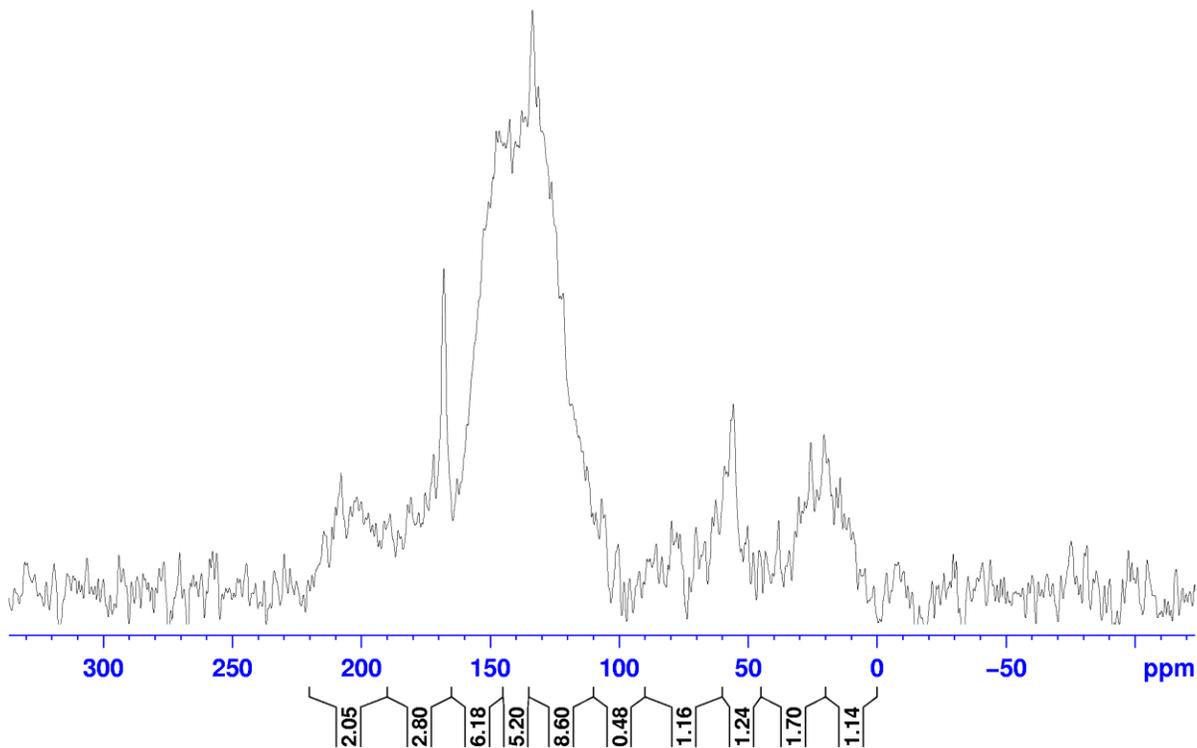
===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 P3 2.85 usec
 PCPD2 5.50 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz
 SPNAME Squal00.1000
 SFOAL0 0.500
 SPOFFS0 0 Hz
 SEW0 85.00000000 W

F2 - Processing parameters
 SI 16384
 SF 75.4679911 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Waco Wetland Fire charcoal sample site 9
 187.1mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

135



```

Current Data Parameters
NAME      VonBargen_WWF9Char_092412
EXPNO    2
PROCNO    1

F2 - Acquisition Parameters
Date_    20120924
Time     15.52
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_nqs_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.0000000
D1       3.00000000 sec
D20      0.00007000 sec
D31      0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

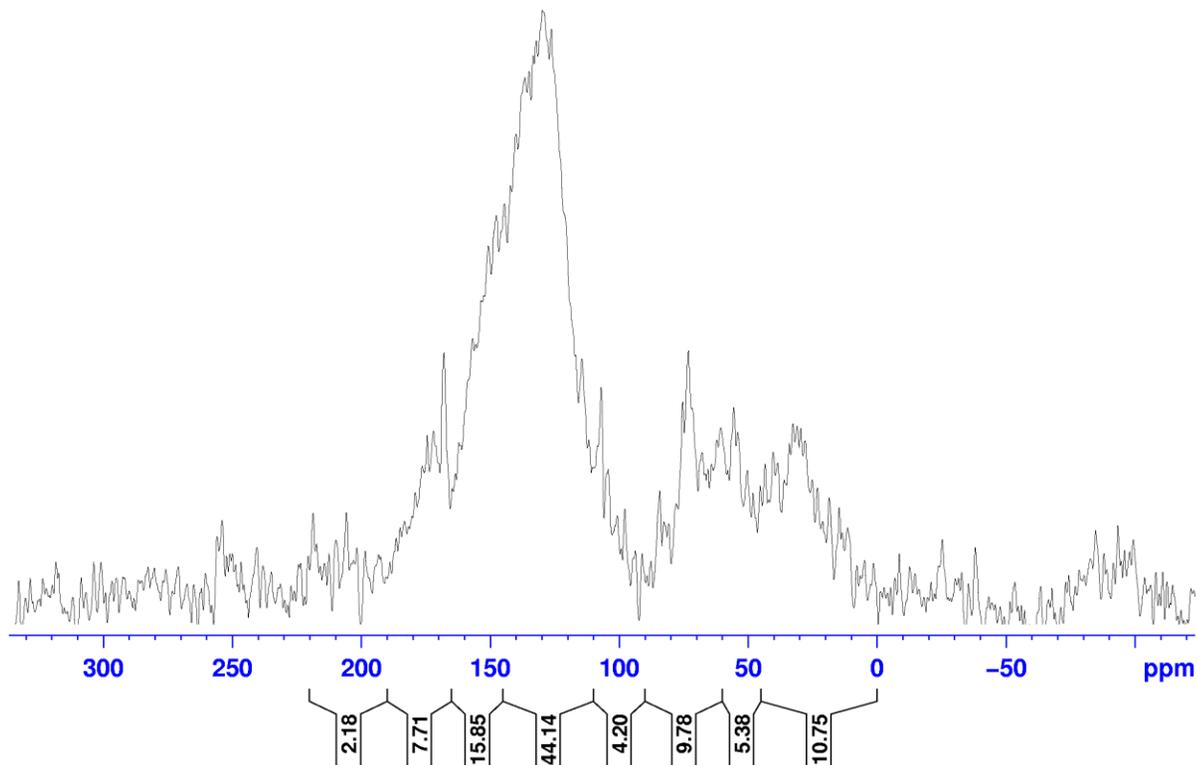
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 9
 187.1mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

136



```

Current Data Parameters
NAME      VonBargen_WWF9Char_092412
EXPNO     3
PROCNO    2

F2 - Acquisition Parameters
Date_     20120929
Time      19.10
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
TD0        1
ZGPTINS

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

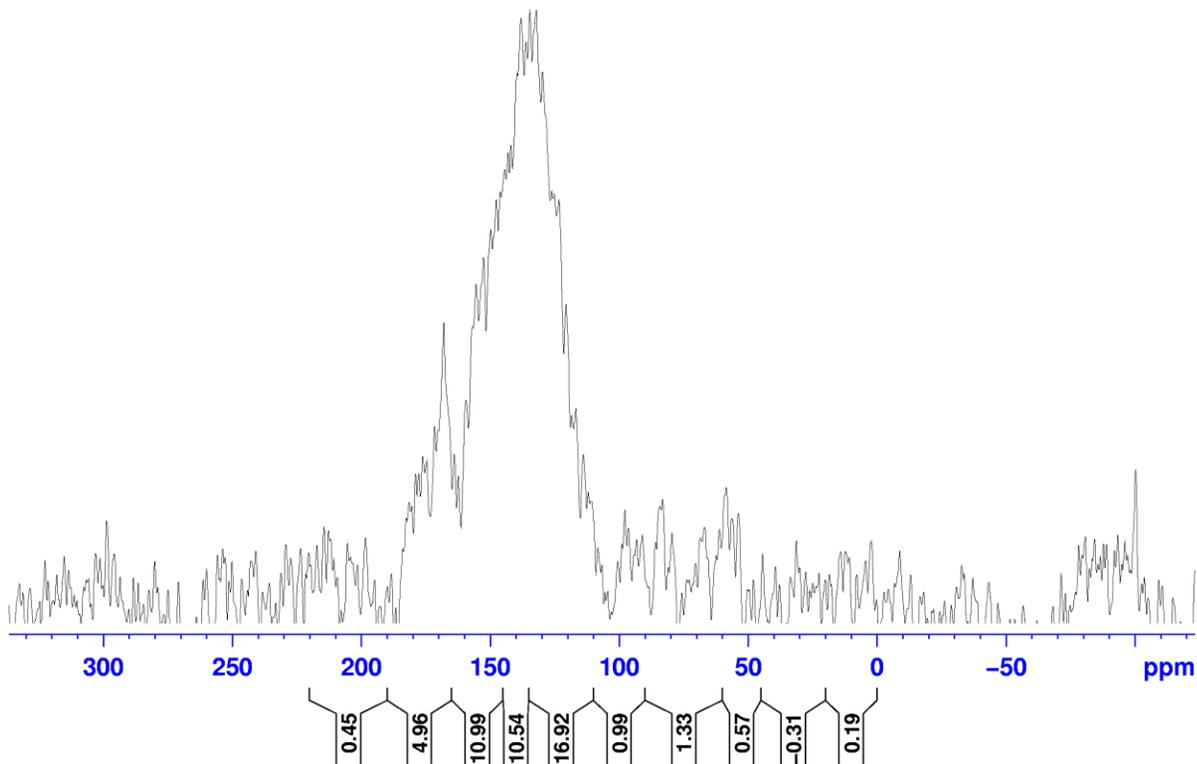
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2     5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 9
 187.1mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

137



```

Current Data Parameters
NAME      VonBargen_WWF9Char_092412
EXPNO    4
PROCNO   2

F2 - Acquisition Parameters
Date_    20120930
Time     20.11
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nqs
TD        1024
SOLVENT  CDCl3
NS        1000
DS        0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ        0.0147956 sec
RG        45.2
DW        14.400 usec
DE        8.08 usec
TE        303.0 K
CNST11   0
CNST31   5000.000000
D1        90.00000000 sec
D20       0.00007000 sec
D31       0.00020000 sec
ZGOP1NS

===== CHANNEL f1 =====
NUC1      13C
P1        4.00 usec
P2        8.00 usec
PLW1      320.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

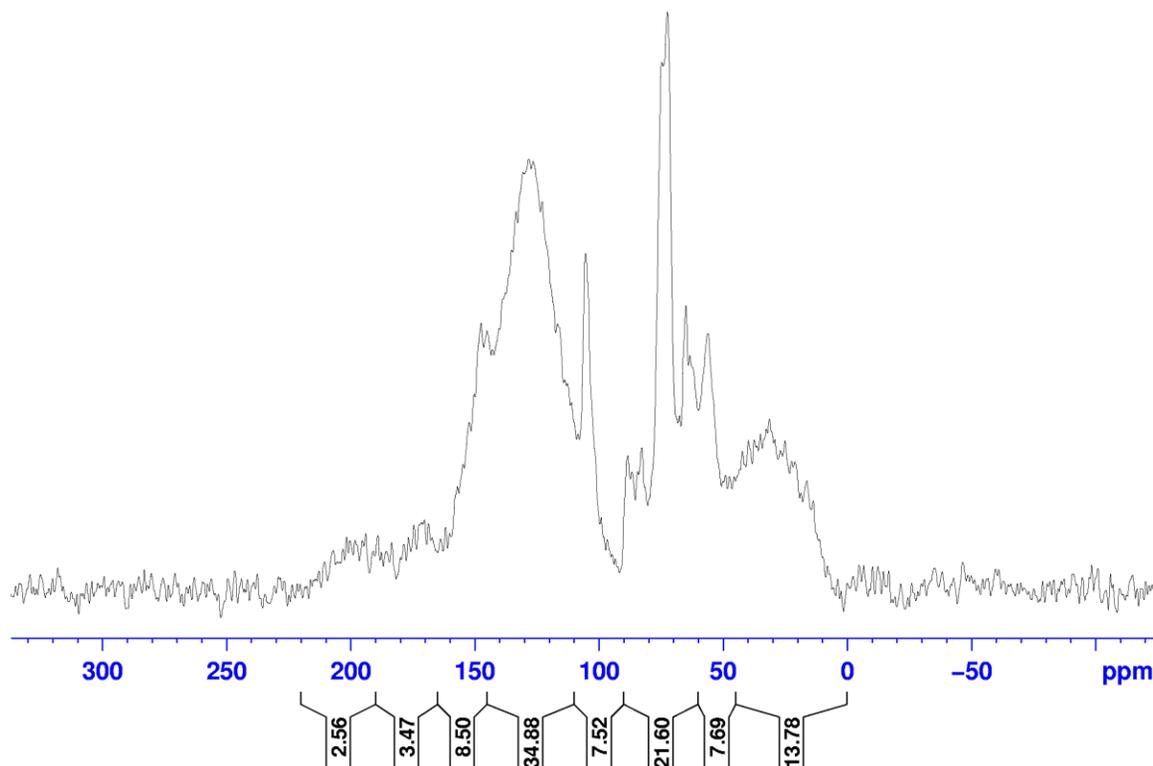
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
PCPD2     5.40 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz

F2 - Processing parameters
SI        16384
SF        75.4679928 MHz
WDW       EM
SSB       0
LB        60.00 Hz
GB        0
PC        0.20
  
```



Waco Wetland Fire Charcoal sample site 10
 149.6mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

138



Current Data Parameters
 NAME VonBargen_WWF10Char_42712
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20120427
 Time 15.09
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG cptoss_WCH
 TD 1024
 SOLVENT CDC13
 NS 4000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 3.0000000 sec
 D31 0.00020000 sec
 ZGPTNS -DTOSSB

===== CHANNEL f1 =====
 NUC1 13C
 P2 8.00 usec
 P15 2000.00 usec
 PLW1 110.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 P3 2.85 usec
 PCPD2 5.50 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz
 SPNAM0 Squa100.1000
 SPOAL0 0.500
 SPOFFS0 0 Hz
 SPW0 85.00000000 W

F2 - Processing parameters
 SI 16384
 SF 75.4680013 MHz
 WDW EM
 SSB 0
 LB 50.00 Hz
 GB 0
 PC 0.20



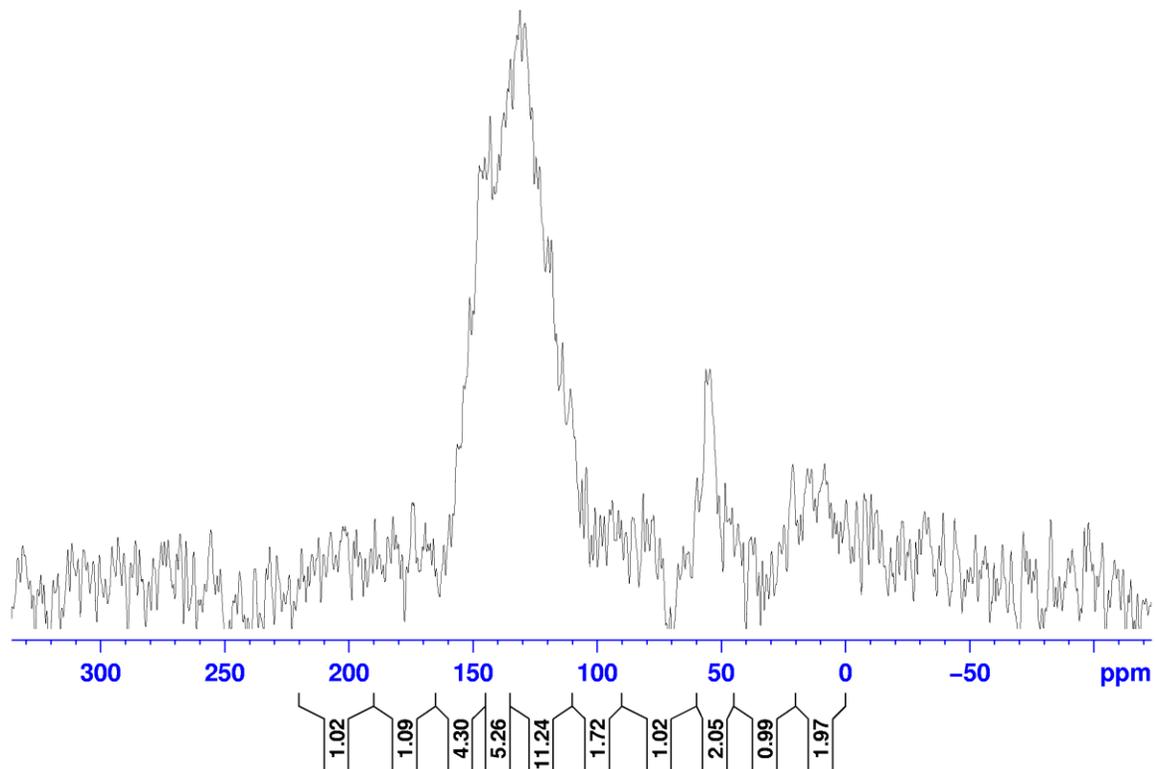
Waco Wetland Fire Charcoal sample site 10

149.6mg

CPMAS square100 with dipolar dephasing, tppm15 decoupling, and Total Suppression of Sidebands (TOSS)

Probe: 7 mm 5kHz MAS

139



Current Data Parameters
NAME VonBargen_WWF10Char_42712
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120427
Time 21.52
INSTRUM spect
PROBHD 7 mm MAS BB/1H
PULPROG cptoss_nqs_WCH
TD 1024
SOLVENT CDCl3
NS 4000
DS 0
SWH 34722.223 Hz
FIDRES 33.908421 Hz
AQ 0.0147956 sec
RG 45.2
DW 14.400 usec
DE 8.08 usec
TE 303.0 K
CNST11 0
CNST31 5000.000000
D1 3.00000000 sec
D20 0.00007000 sec
D31 0.00020000 sec
ZGPTNS -DTOSSB

===== CHANNEL f1 =====
NUC1 13C
P2 8.00 usec
P15 2000.00 usec
PLW1 110.00000000 W
PLW11 320.00000000 W
SFO1 75.4760505 MHz

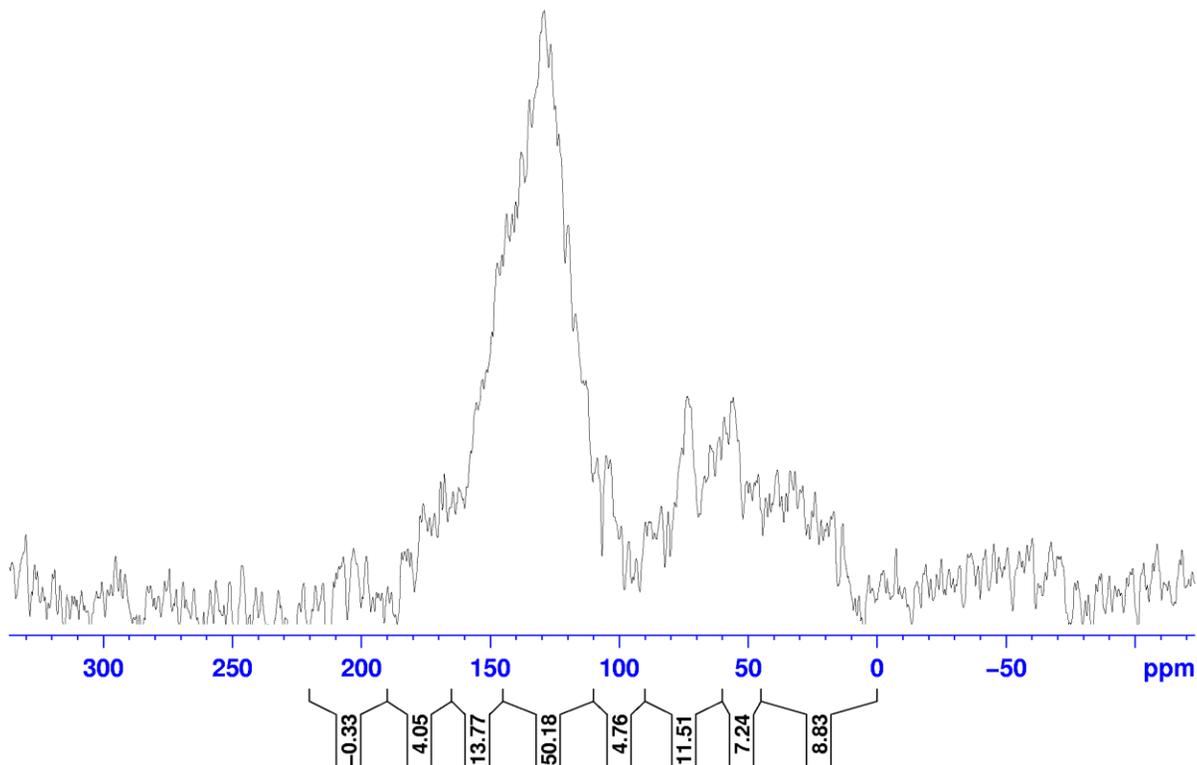
===== CHANNEL f2 =====
CPDPRG2 tppm15
NUC2 1H
P3 2.85 usec
PCPD2 5.40 usec
PLW2 260.00000000 W
PLW12 260.00000000 W
SFO2 300.1312605 MHz
SPNAM0 Squa100.1000
SFOAL0 0.500
SPOFFS0 0 Hz
SPW0 85.00000000 W

F2 - Processing parameters
SI 16384
SF 75.4680028 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20



Waco Wetland Fire Charcoal sample site 10
 149.6mg
 hpdec with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

140



```

Current Data Parameters
NAME      VonBargen_WWF10Char_42712
EXPNO    3
PROCNO   2

F2 - Acquisition Parameters
Date_    20120428
Time     17.53
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdecTOSS
TD       2048
SOLVENT  CDCl3
NS       1200
DS       0
SWH      34722.223 Hz
FIDRES   16.954210 Hz
AQ       0.0295412 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       60.00000000 sec
D31      0.00020000 sec
ZGOPINS  -DToSSB

===== CHANNEL f1 =====
NUC1      13C
P1        4.00 usec
P2        8.00 usec
PLW1      320.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2      1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI        16384
SF        75.4680013 MHz
WDW       EM
SSB       0
LB        70.00 Hz
GB        0
PC        0.20
  
```



Waco Wetland Fire Charcoal sample site 10

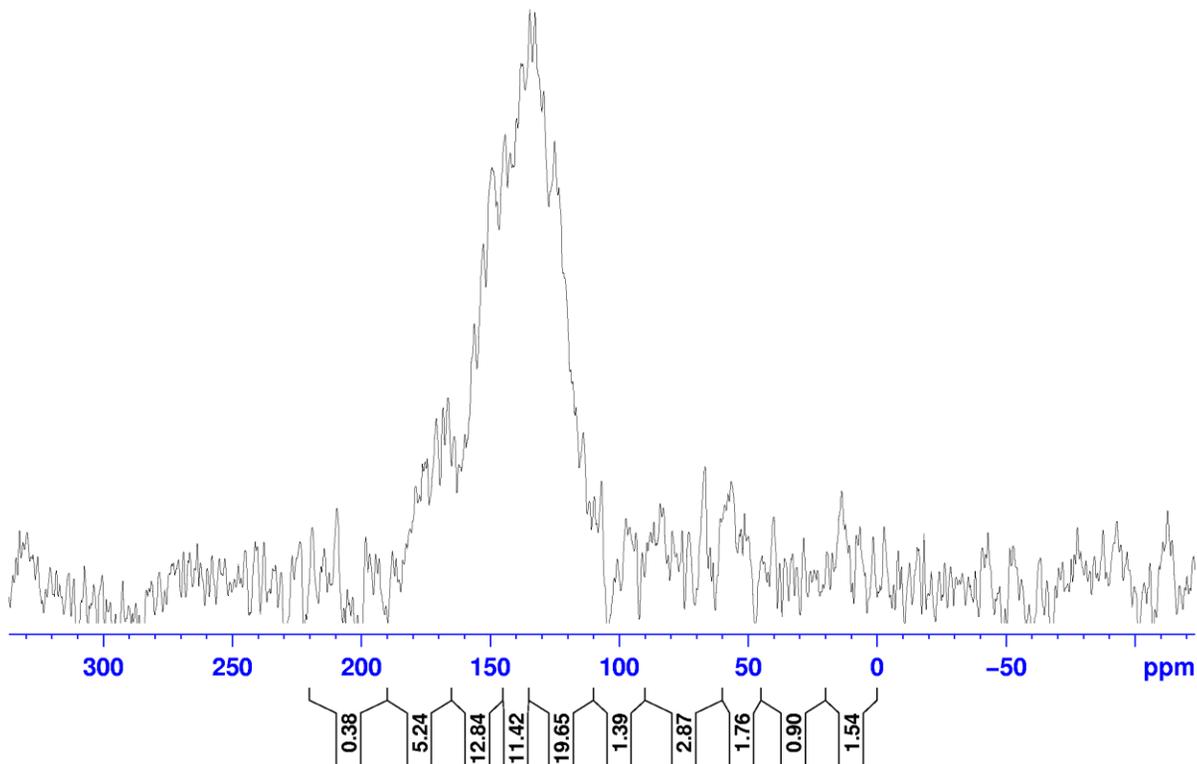
149.6mg

hpdec (direct polarization) with dipolar dephasing, Total Sideband Suppression (TOSS), and TPPM15 decoupling

ZG OPTION: -DtossB.

Probe: 7 mm , 5kHz MAS

141



```
Current Data Parameters
NAME      VonBargen_WWF10Char_42712
EXPNO    4
PROCNO    2

F2 - Acquisition Parameters
Date_     20120428
Time      20.43
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_nqs
TD         2048
SOLVENT   CDCl3
NS         1200
DS         0
SWH        34722.223 Hz
FIDRES     16.954210 Hz
AQ         0.0295412 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         60.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS   -DTOSSB

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

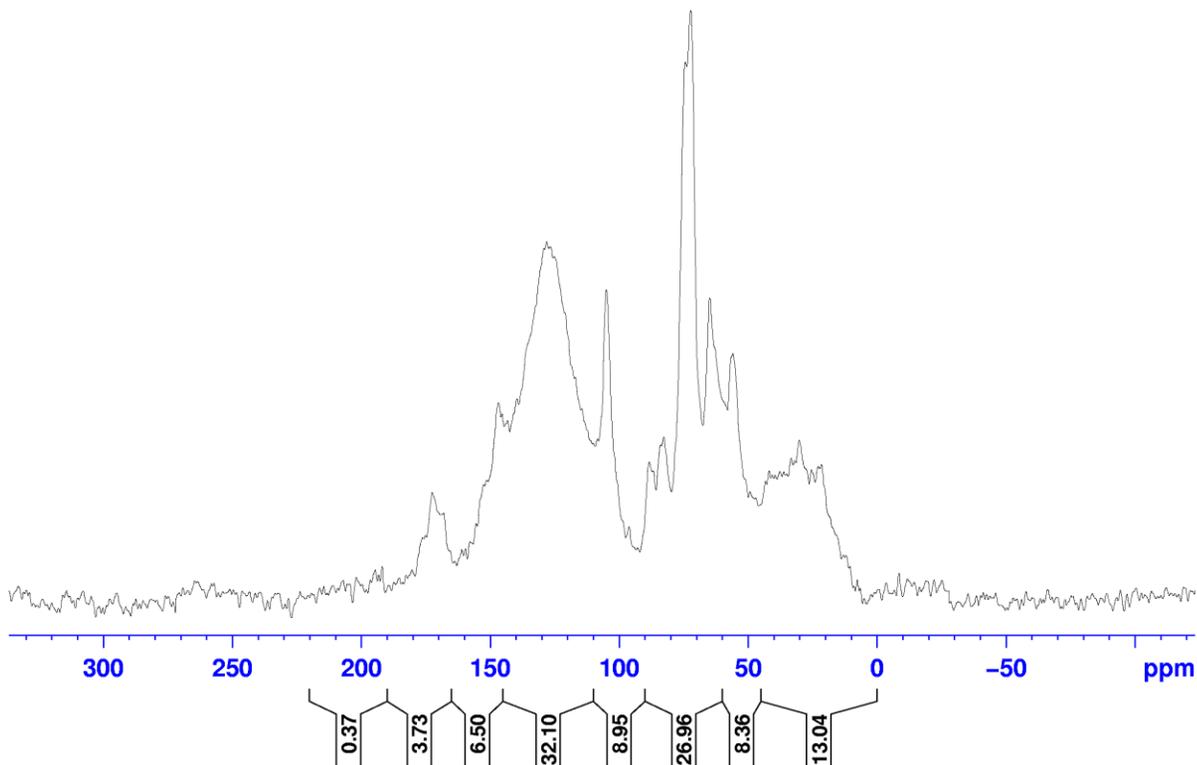
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2     5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4680013 MHz
WDW        EM
SSB        0
LB         70.00 Hz
GB         0
PC         0.20
```



Waco Wetland Fire charcoal sample site 11
 171.0mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

142



```

Current Data Parameters
NAME      VonBargen_WW11Char_091412
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120914
Time     15.20
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D31      0.00020000 sec
TD0      1
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

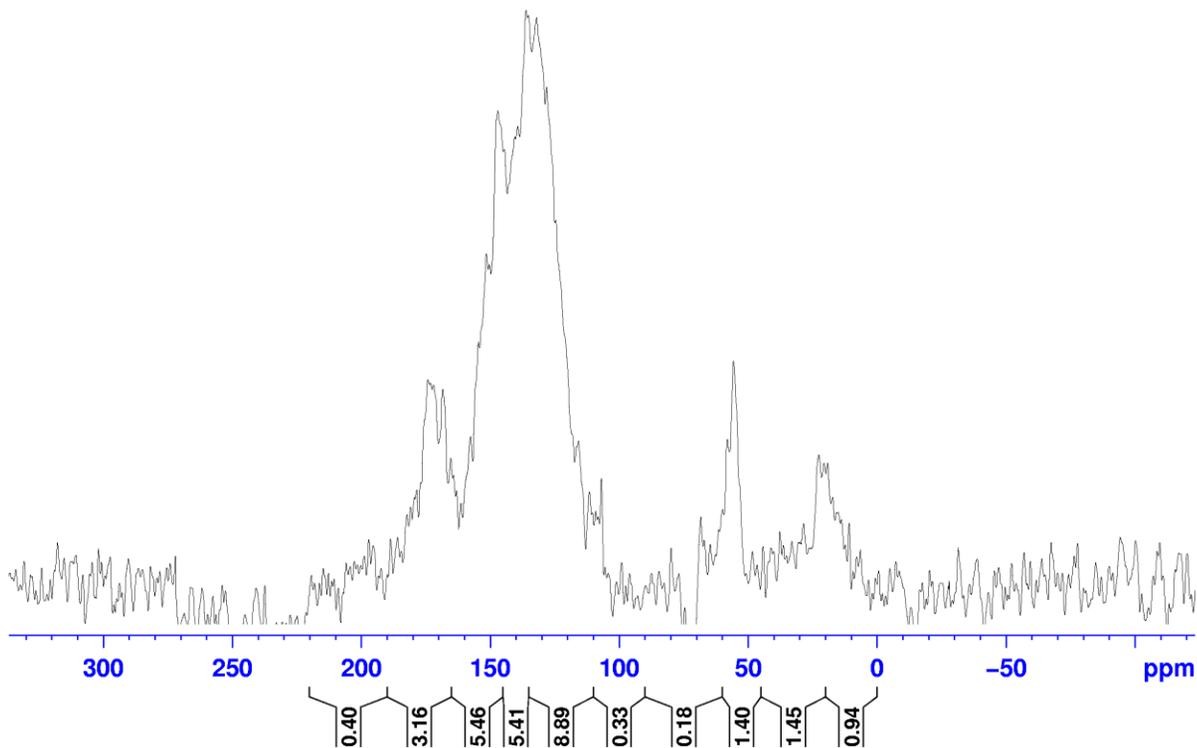
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOALO   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire Charcoal sample site 11
 171.0mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

143



```

Current Data Parameters
NAME      VonBargen_WW11Char_091412
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20120914
Time      23.02
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqs_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2         7.90 usec
P15        2000.00 usec
PLW1      110.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

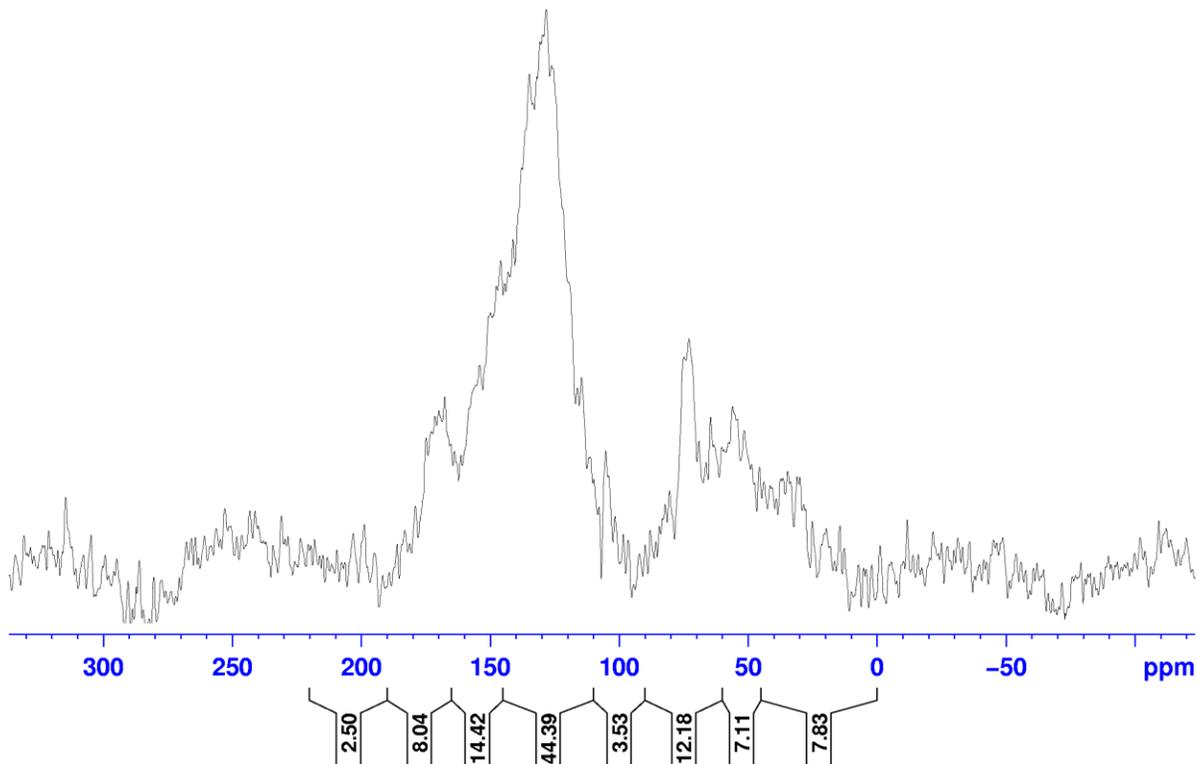
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2      5.50 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SPNAM0     Squa100.1000
SFOAL0      0.500
SPOFFS0    0 Hz
SEW0       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire Charcoal sample site 11
 171.0mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

144



```

Current Data Parameters
NAME      VonBargen_WWF11Char_091412
EXPNO     3
PROCNO    2

F2 - Acquisition Parameters
Date_     20120916
Time      0.03
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.0000000 sec
D31        0.0002000 sec
TD0        1
ZGOP1NS

===== CHANNEL f1 =====
NUC1       13c
P1         4.00 usec
P2         8.00 usec
PLW1       320.0000000 W
PLW11      320.0000000 W
SFO1       75.4760505 MHz

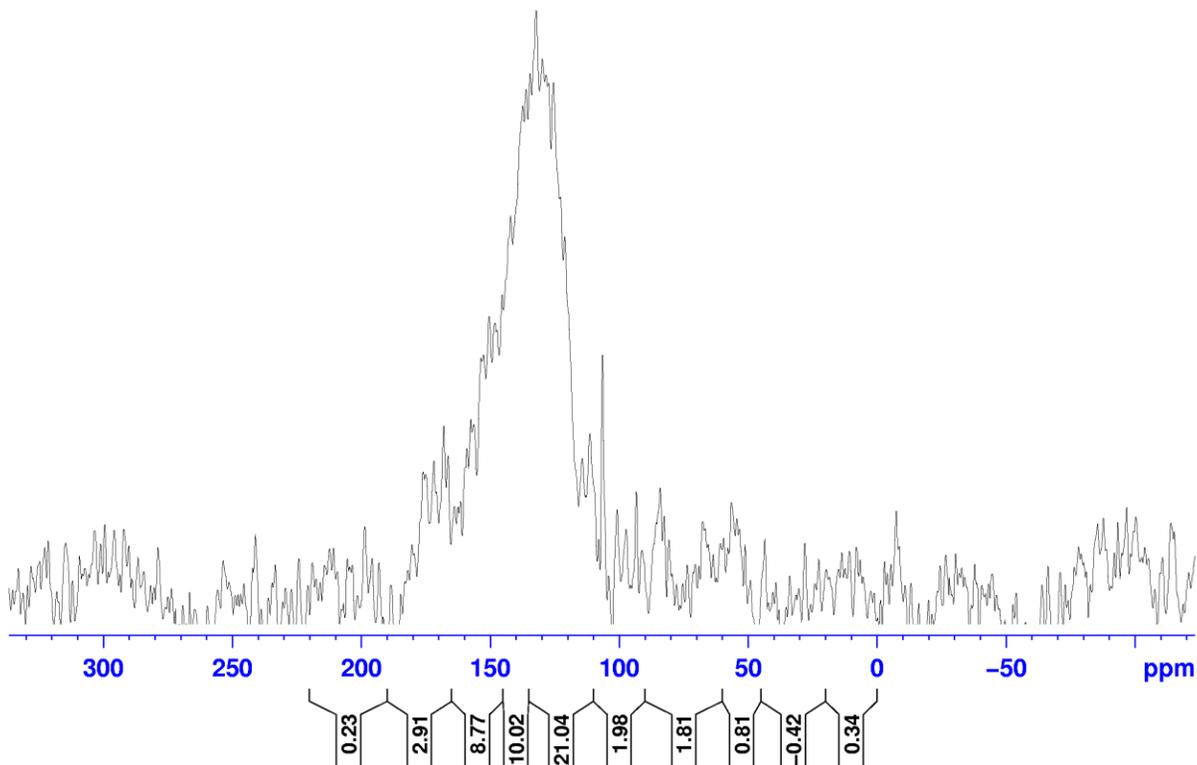
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.0000000 W
PLW12      260.0000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 11
 171.0mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

145



```

Current Data Parameters
NAME      VonBargen_WWF11Char_091412
EXPNO    4
PROCNO   2

F2 - Acquisition Parameters
Date_    20120917
Time     1.03
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdec_toss_nqs
TD        1024
SOLVENT  CDCl3
NS        1000
DS        0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ        0.0147956 sec
RG        45.2
DW        14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11   0
CNST31   5000.000000
D1        90.0000000 sec
D20       0.00007000 sec
D31       0.00020000 sec
ZGPGTNS

===== CHANNEL f1 =====
NUC1      13c
P1         4.00 usec
P2         8.00 usec
PLW1      320.0000000 W
PLW11     320.0000000 W
SFO1      75.4760505 MHz

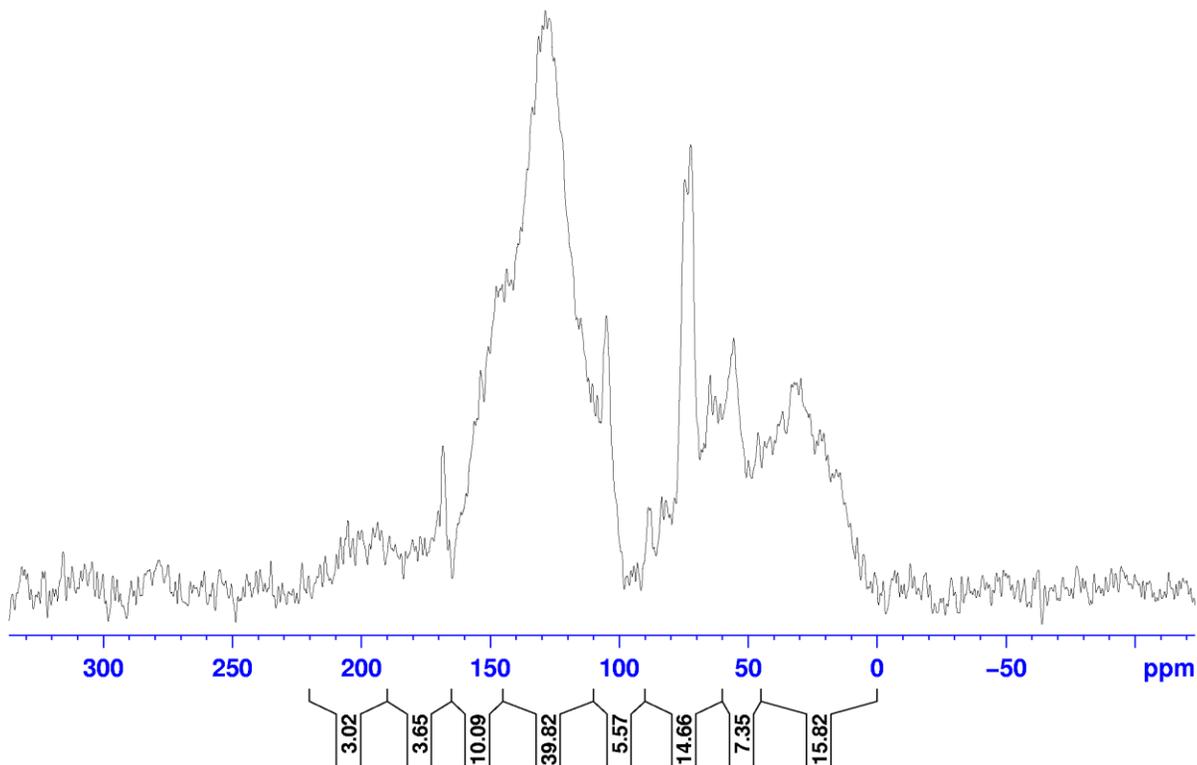
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2       1H
PCPD2     5.40 usec
PLW2      260.0000000 W
PLW12     260.0000000 W
SFO2      300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire Charcoal sample site 12
 172.3mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

146



```

Current Data Parameters
NAME      VonBargen_WWF12Char_51112
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120511
Time     16.38
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DM       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D31      0.00020000 sec
ZGPTNS   -DTOSSB

===== CHANNEL f1 =====
NUC1     13C
P2       8.00 usec
P15     2000.00 usec
PLW1    110.00000000 W
PLW11   320.00000000 W
SFO1    75.4760505 MHz

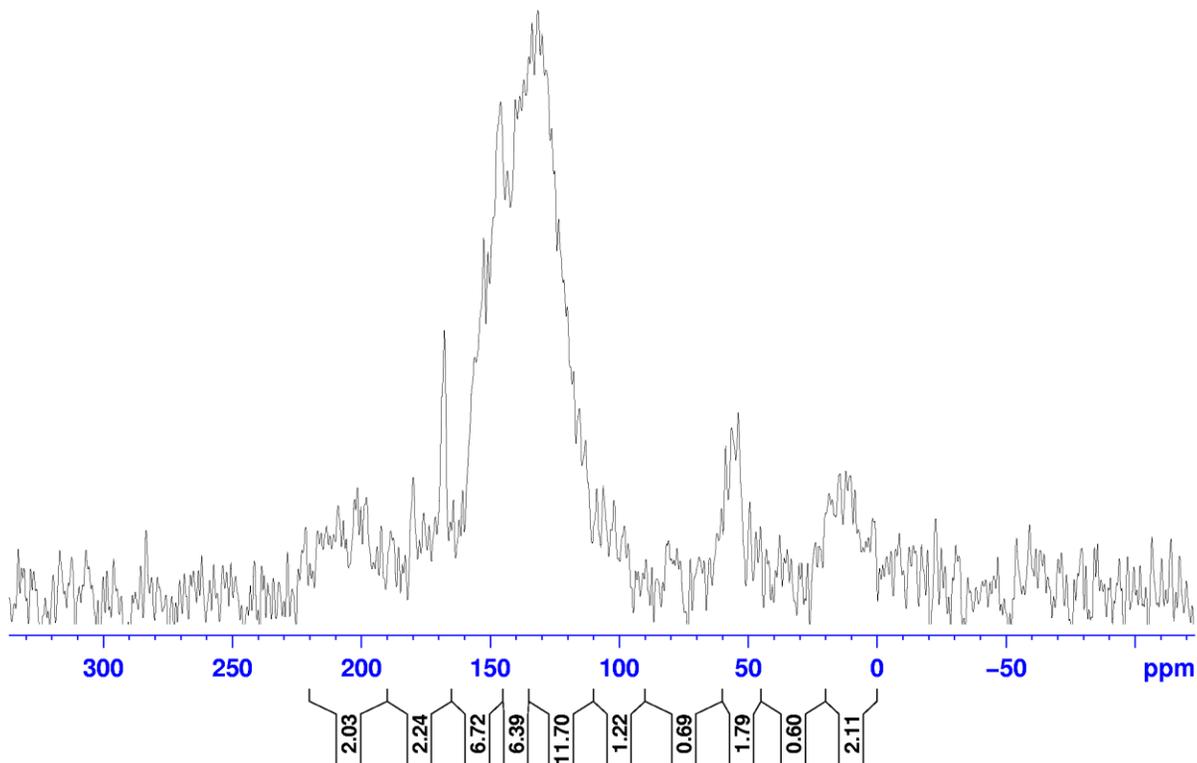
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2    260.00000000 W
PLW12   260.00000000 W
SFO2    300.1312605 MHz
SFXAM0   Squal00.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SPW0    85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4680013 MHz
WDW      EM
SSB      0
LB       50.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire Charcoal sample site 12
 172.3mg
 CPMAS square100 with dipolar dephasing, tppm15 decoupling, and Total Suppression of Sidebands (TOSS)
 NOTE: this acquisition was run with -DROSSB option
 Probe: 7 mm, 5kHz MAS

147



```

Current Data Parameters
NAME      VonBargen_WWF12Char_51112
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20120511
Time      23.19
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqs_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.0000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS   -DROSSB

===== CHANNEL f1 =====
NUC1      13C
P2         8.00 usec
P15        2000.00 usec
PLW1      110.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

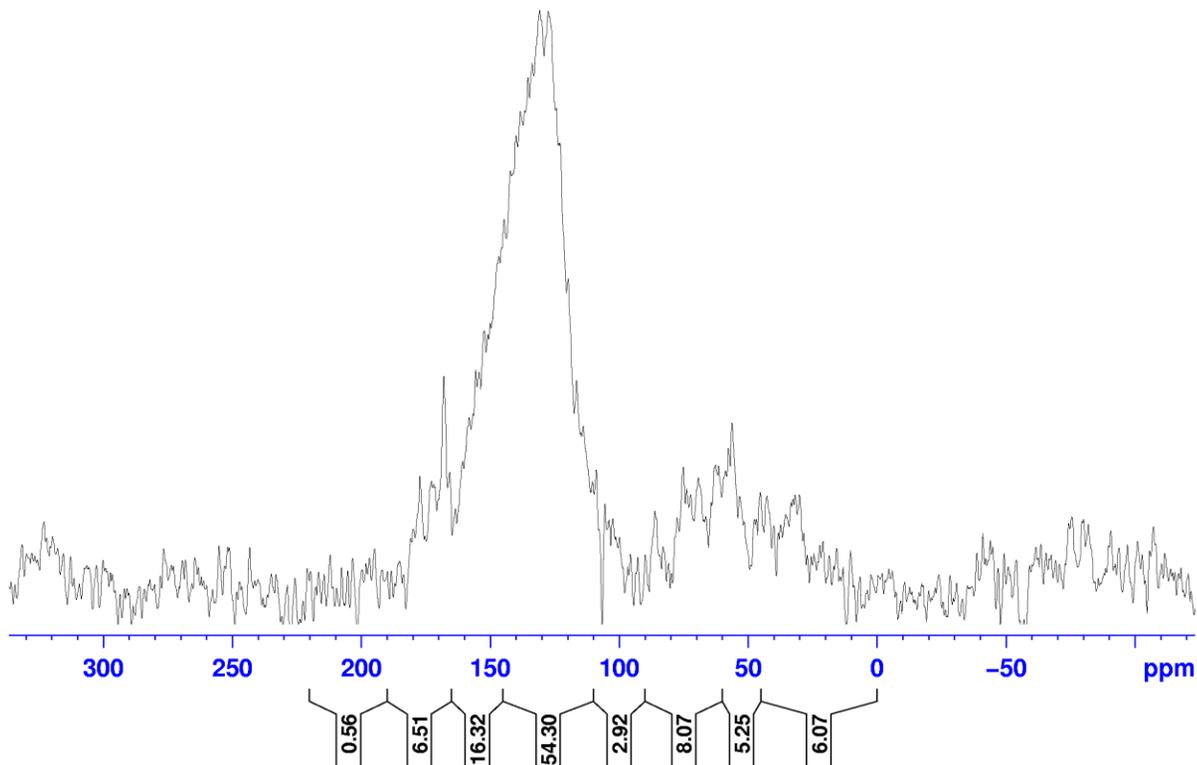
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2       1H
P3         2.05 usec
PCPD2      5.40 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz
SPNAM0     Squa100.1000
SFOAL0     0.500
SPOFFS0    0 Hz
SEW0       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4680028 MHz
WDW        EM
SSB        0
LB         50.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire Charcoal sample site 12
 172.3mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 ZG OPTION: -DtossB.
 Probe: 7 mm MAS 5kHz MAS
 AFTER BACKGROUND SUBTRACTION

148



```

Current Data Parameters
NAME      VonBargen_WWF12Char_51112
EXPNO     3
PROCNO    2

F2 - Acquisition Parameters
Date_     20120513
Time      0.20
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD         2048
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     16.954210 Hz
AQ         0.0295412 sec
RG         45.2
DW         14.400 usec
DE         17.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D31        0.00020000 sec
ZGOPINS   -DTOSSB

===== CHANNEL f1 =====
NUC1       13C
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

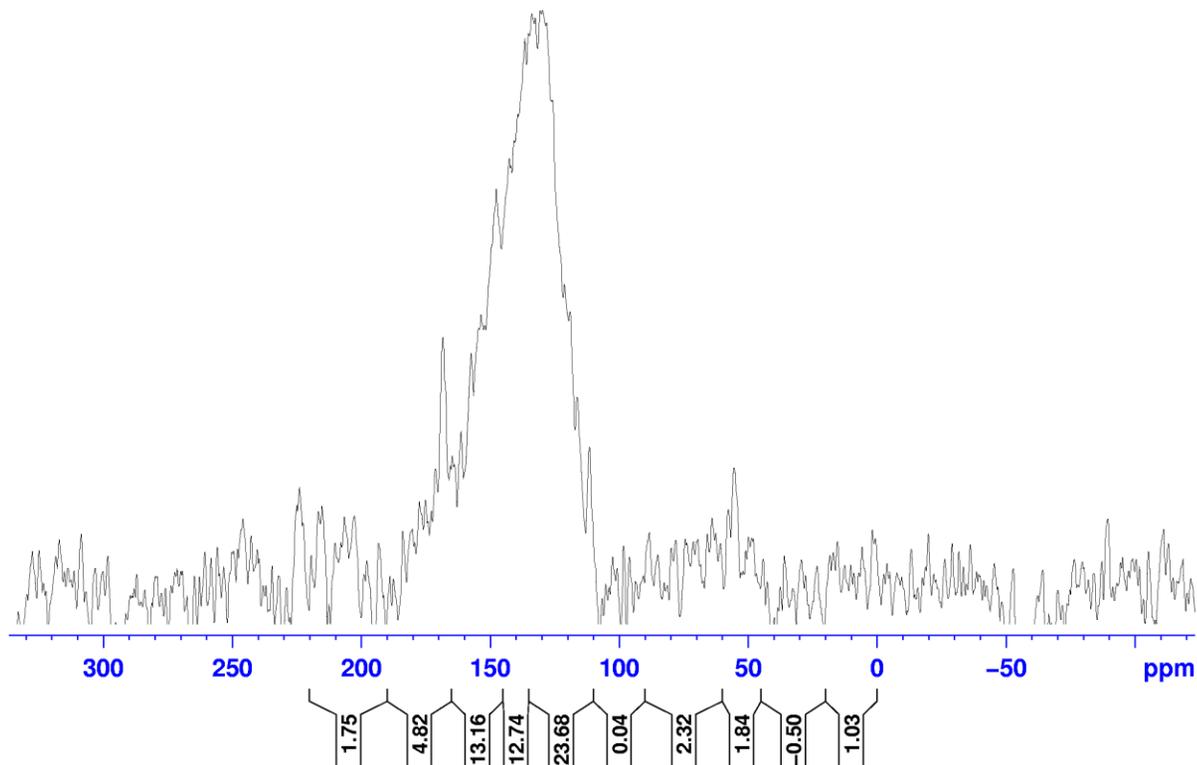
===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4680013 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire Charcoal sample site 12
 172.3mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 ZG OPTION: -DtossB.
 Probe: 7 mm , 5kHz MAS
 AFTER BACKGROUND SUBTRACTION

149



```
Current Data Parameters
NAME      VonBargen_WWF12Char_51112
EXPNO     4
PROCNO    2

F2 - Acquisition Parameters
Date_     20120514
Time      1.21
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_nqs
TD         2048
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     16.954210 Hz
AQ         0.0295412 sec
RG         45.2
DW         14.400 usec
DE         17.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS   -DTOSSB

===== CHANNEL f1 =====
NUC1      13C
P1         4.00 usec
P2         8.00 usec
PLW1      320.00000000 W
PLW11     320.00000000 W
SFO1      75.4760505 MHz

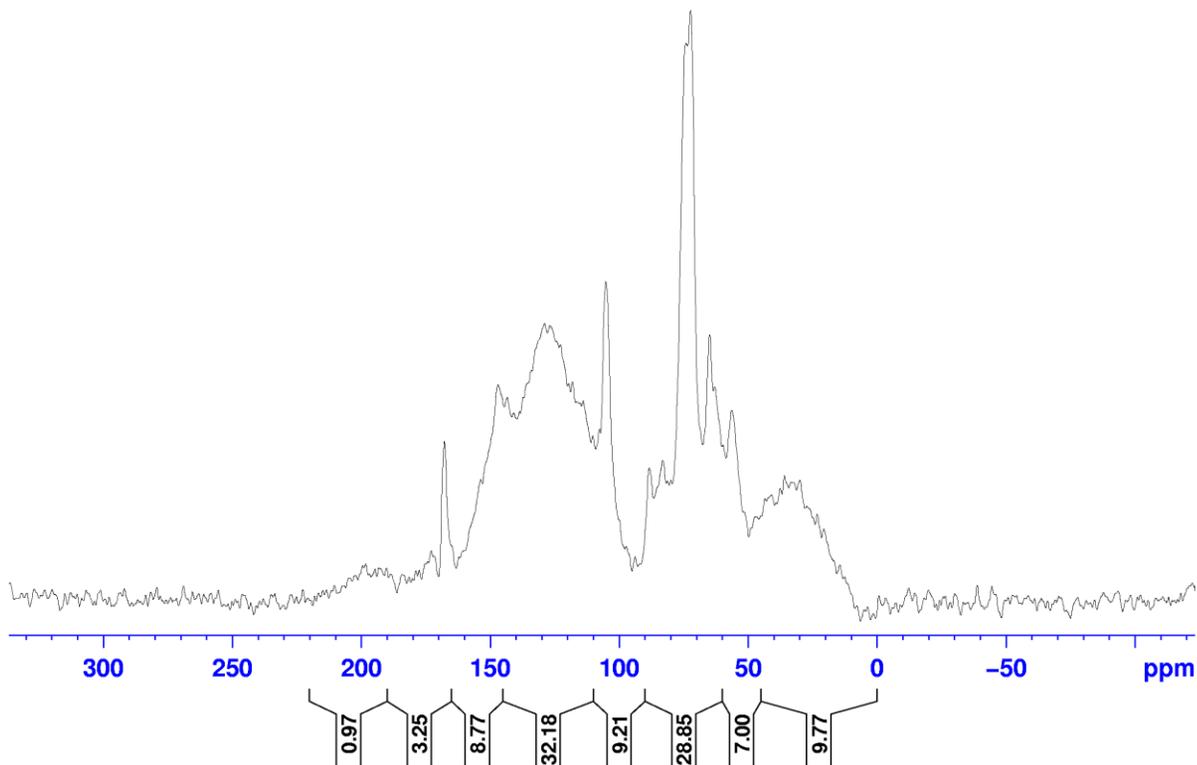
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
PCPD2     5.40 usec
PLW2      260.00000000 W
PLW12     260.00000000 W
SFO2      300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4680013 MHz
WDW        EM
SSB        0
LB         70.00 Hz
GB         0
PC         0.20
```



Waco Wetland Fire charcoal sample site 13
 185.0mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

150



```

Current Data Parameters
NAME      VonBargen_WW13Char_090712
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120907
Time     14.50
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.0000000
D1       3.00000000 sec
D31      0.00020000 sec
TD0      1
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

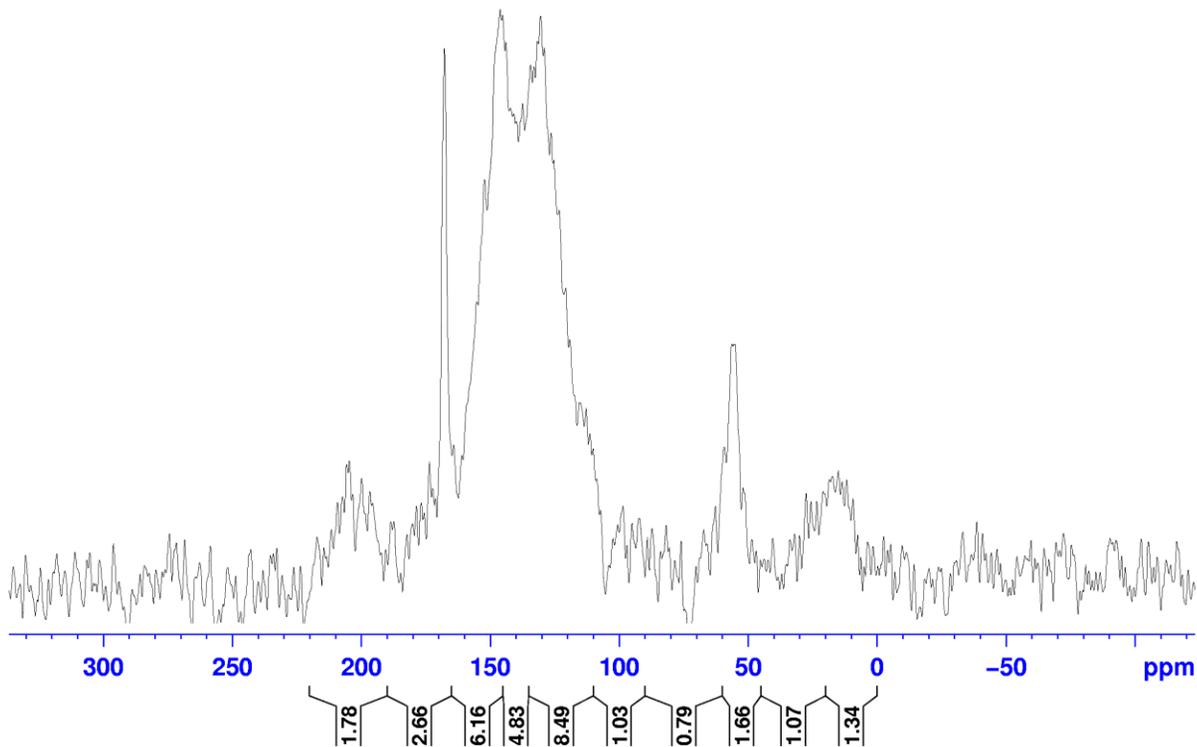
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire chacoal sample site 13
 185.0mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

151



```

Current Data Parameters
NAME      VonBargen_WW13Char_090712
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20120907
Time     21.32
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_nqs_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.0000000
D1       3.00000000 sec
D20     0.00007000 sec
D31     0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

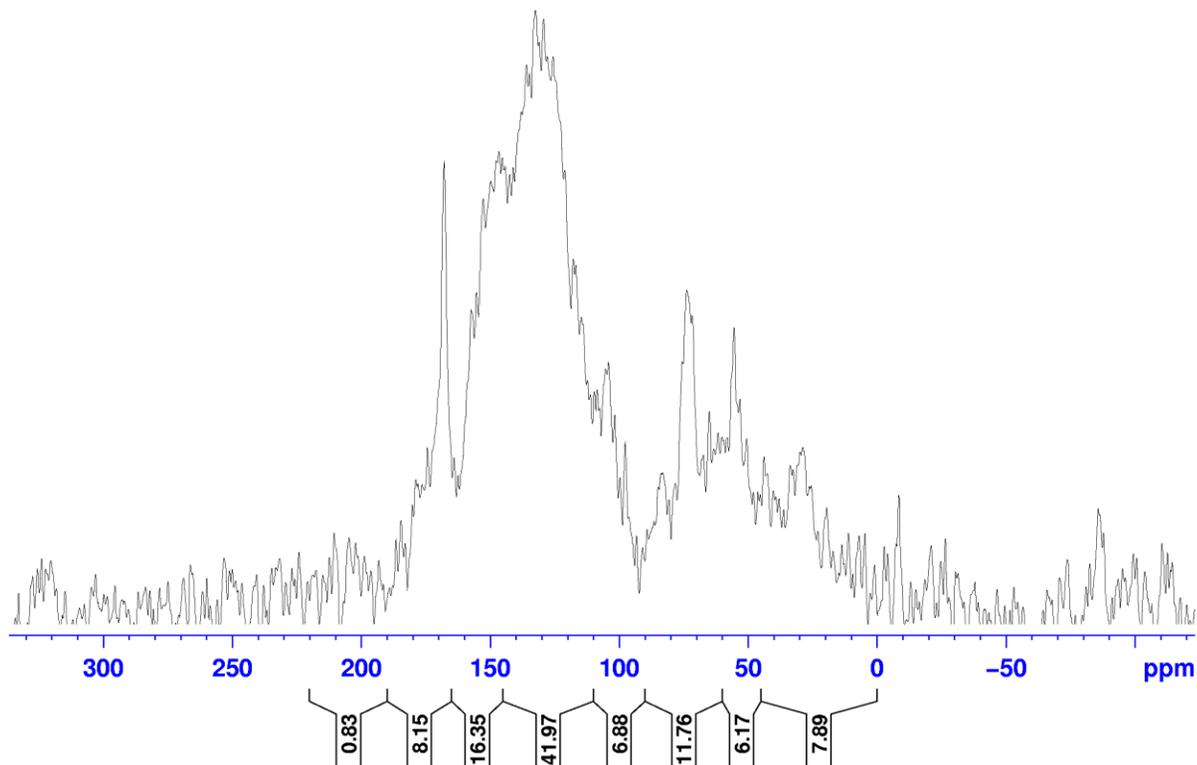
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOALO   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 13
 185.0mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

152



```

Current Data Parameters
NAME      VonBargen_WWF13Char_090712
EXPNO     3
PROCNO    3

F2 - Acquisition Parameters
Date_     20120908
Time      22.33
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdecTOSS
TD        1024
SOLVENT   CDCl3
NS        1000
DS        0
SWH       34722.223 Hz
FIDRES    33.908421 Hz
AQ        0.0147956 sec
RG        45.2
DW        14.400 usec
DE        8.08 usec
TE        303.0 K
CNST11    0
CNST31    5000.000000
D1        90.0000000 sec
D31       0.00020000 sec
TD0       1
ZGPTNS

===== CHANNEL f1 =====
NUC1      13c
P1        4.00 usec
P2        8.00 usec
PLW1     320.0000000 W
PLW11    320.0000000 W
SFO1     75.4760505 MHz

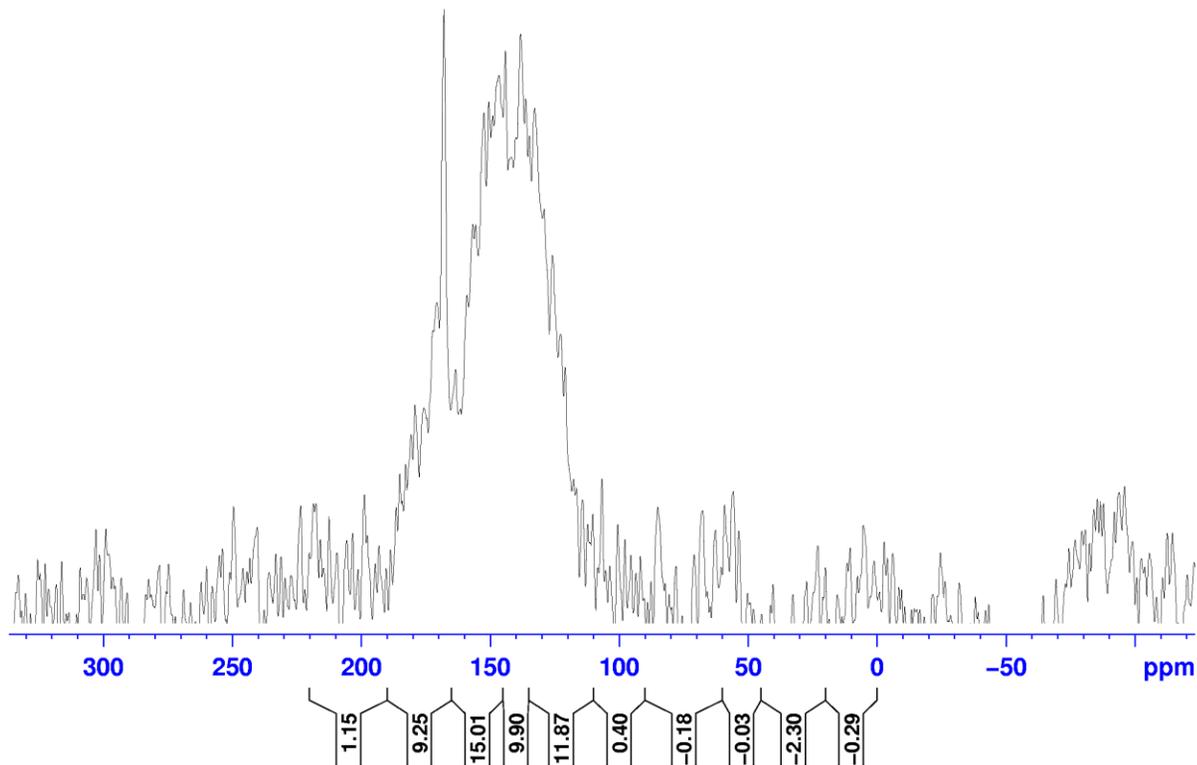
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2      1H
PCPD2     5.40 usec
PLW2     260.0000000 W
PLW12    260.0000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI        16384
SF        75.4679928 MHz
WDW       EM
SSB       0
LB        60.00 Hz
GB        0
PC        0.20
  
```



Waco Wetland Fire charcoal sample site 13
 185.0mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

153



Current Data Parameters
 NAME VonBargen_WWF13Char_090712
 EXPNO 4
 PROCNO 3

F2 - Acquisition Parameters
 Date_ 20120909
 Time 23.33
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG hpdec_toss_nqs
 TD 1024
 SOLVENT CDCl3
 NS 1000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 90.0000000 sec
 D20 0.00007000 sec
 D31 0.00020000 sec
 ZGOPTNS

===== CHANNEL f1 =====
 NUC1 13c
 P1 4.00 usec
 P2 8.00 usec
 PLW1 320.0000000 W
 PLW11 320.0000000 W
 SFO1 75.4760505 MHz

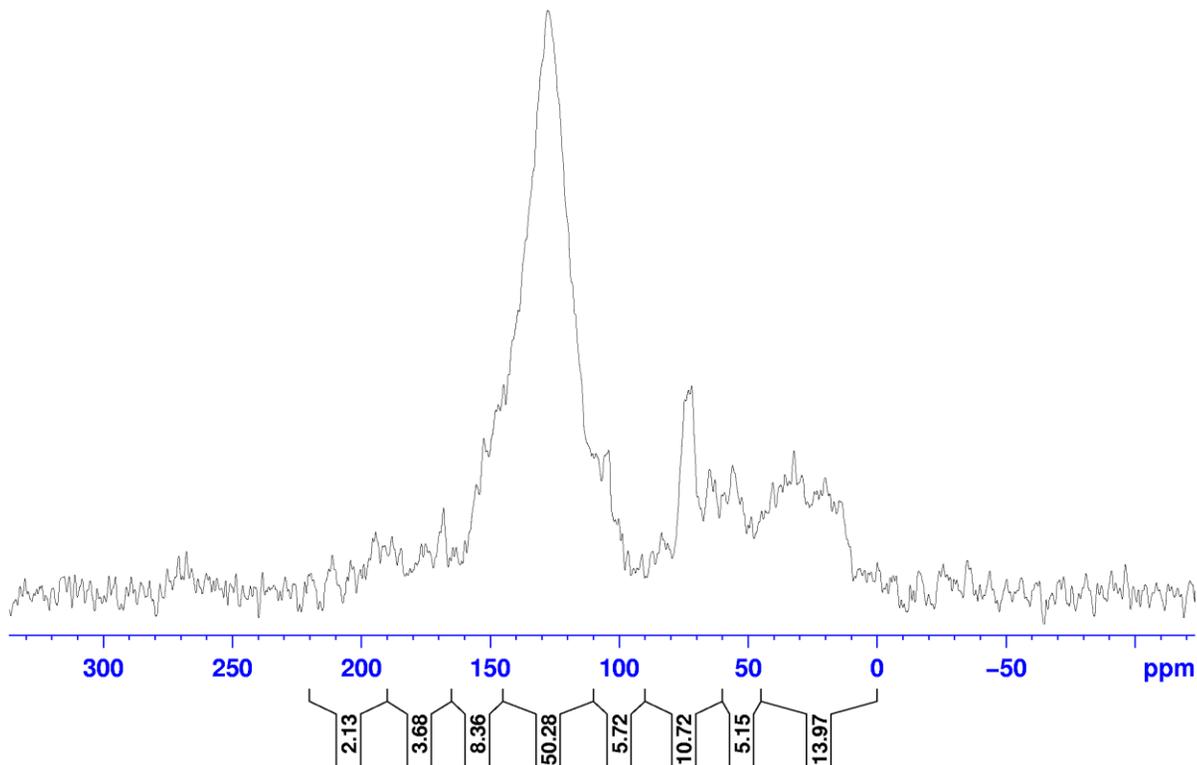
===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 PCPD2 5.40 usec
 PLW2 260.0000000 W
 PLW12 260.0000000 W
 SFO2 300.1312605 MHz

F2 - Processing parameters
 SI 16384
 SF 75.4679928 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Waco Wetland Fire charcoal sample site 14
 153.8mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

154



```

Current Data Parameters
NAME      VonBargen_WWF14Char_060412
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120604
Time     17.24
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.0000000 sec
D31      0.00020000 sec
ZGPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.0000000 W
PLW11    320.0000000 W
SFO1     75.4760505 MHz

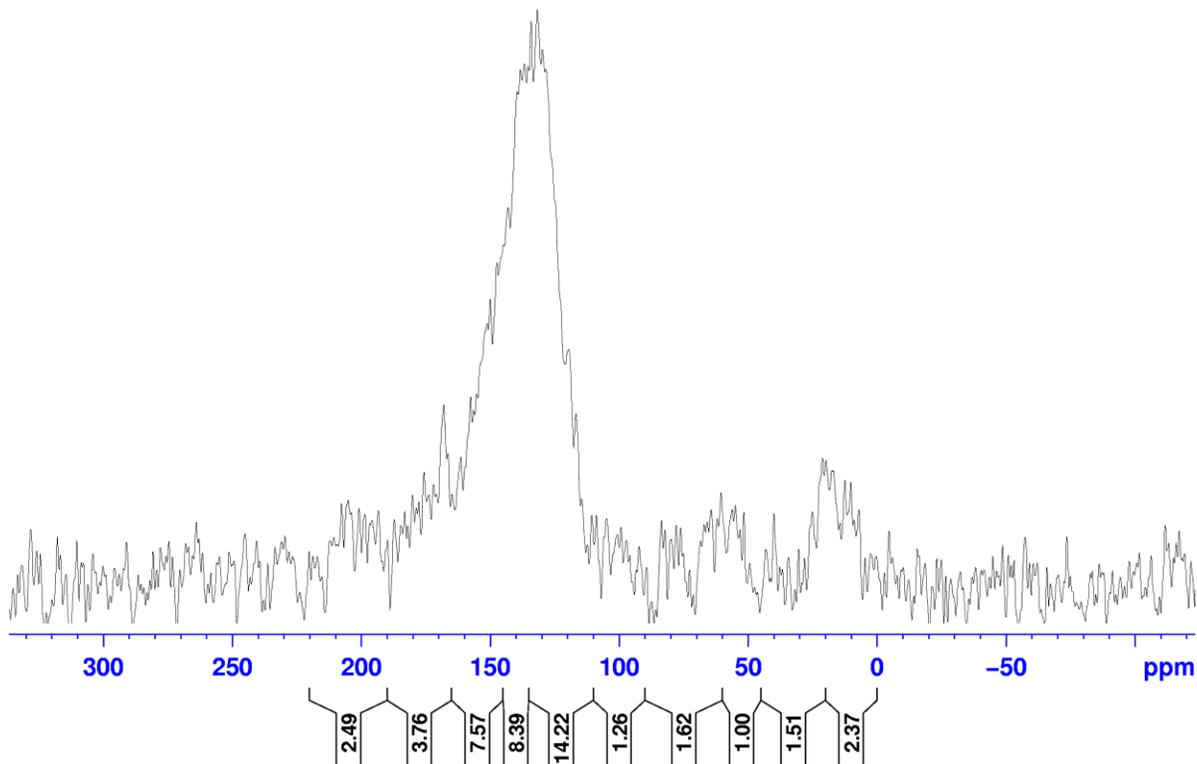
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.0000000 W
PLW12    260.0000000 W
SFO2     300.1312605 MHz
SFXAM0   Squal100.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SPW0     85.0000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 14
 153.8mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

155



```

Current Data Parameters
NAME      VonBargen_WWF14Char_060412
EXPNO    2
PROCNO    1

F2 - Acquisition Parameters
Date_    20120605
Time     0.07
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_nqs_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D20     0.00007000 sec
D31     0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

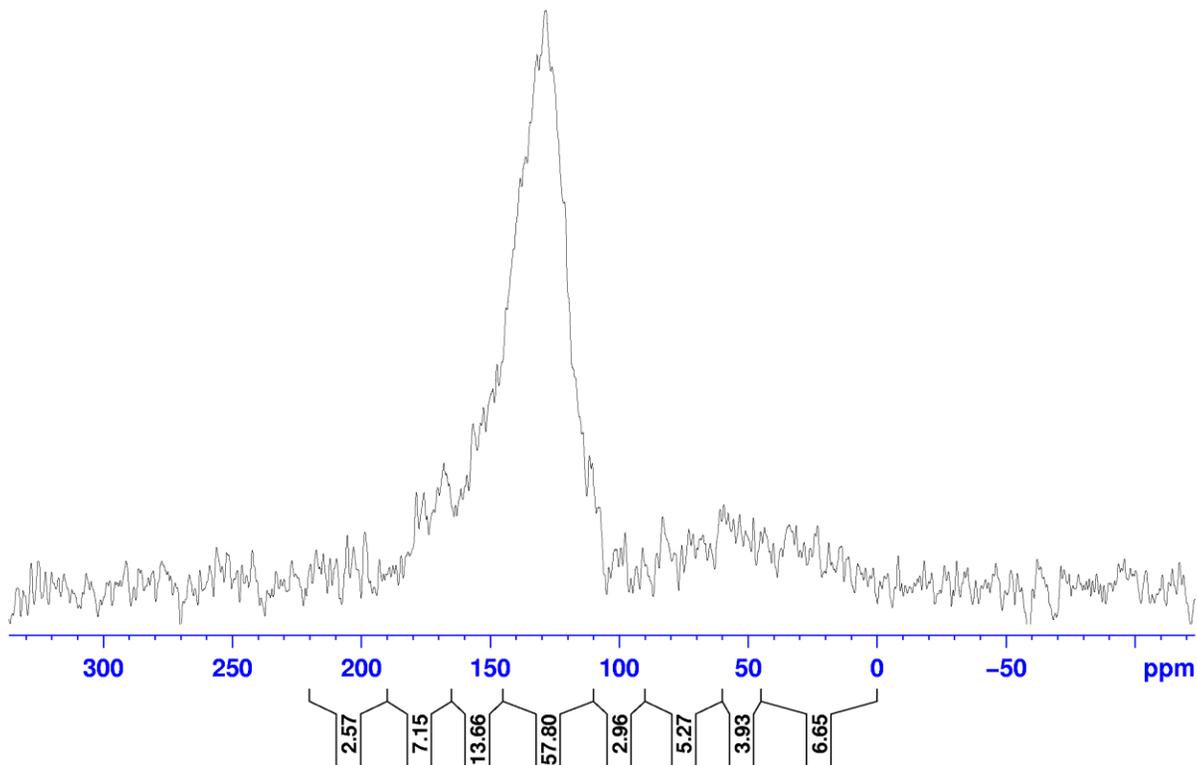
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 14
 153.8mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

156



```

Current Data Parameters
NAME      VonBargen_WWF14Char_060412
EXPNO    3
PROCNO   2

F2 - Acquisition Parameters
Date_    20120605
Time     9.07
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdecTOSS
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.0000000 sec
D31      0.00020000 sec
ZGPTNS

===== CHANNEL f1 =====
NUC1     13C
P1       4.00 usec
P2       8.00 usec
PLW1     320.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

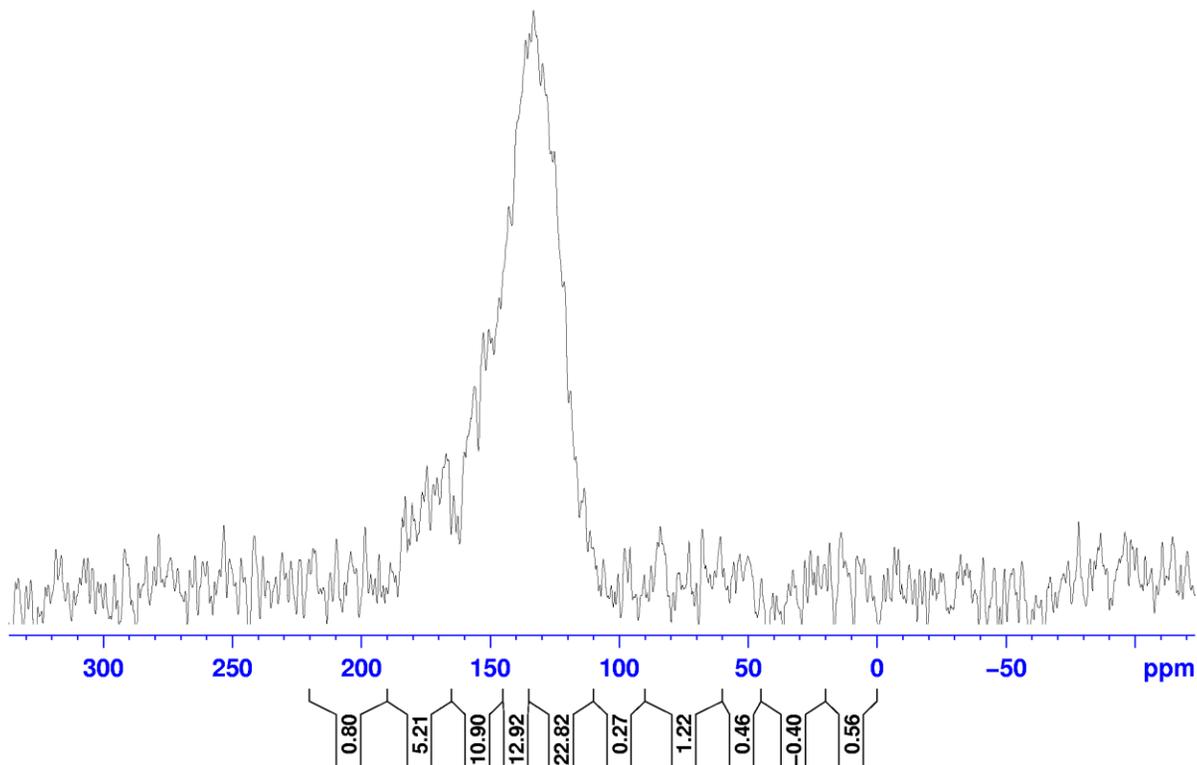
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4679928 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 14
 153.8mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

157



Current Data Parameters
 NAME VonBargen_WWF14Char_060412
 EXPNO 4
 PROCNO 2

F2 - Acquisition Parameters
 Date_ 20120606
 Time 10.15
 INSTRUM spect
 PROBHD 7 mm MAS BB/1H
 PULPROG hpdec_toss_nqs
 TD 1024
 SOLVENT CDCl3
 NS 1000
 DS 0
 SWH 34722.223 Hz
 FIDRES 33.908421 Hz
 AQ 0.0147956 sec
 RG 45.2
 DW 14.400 usec
 DE 8.08 usec
 TE 303.0 K
 CNST11 0
 CNST31 5000.000000
 D1 90.0000000 sec
 D20 0.00007000 sec
 D31 0.00020000 sec
 ZGPGTNS

===== CHANNEL f1 =====
 NUC1 13c
 P1 4.00 usec
 P2 8.00 usec
 PLW1 320.00000000 W
 PLW11 320.00000000 W
 SFO1 75.4760505 MHz

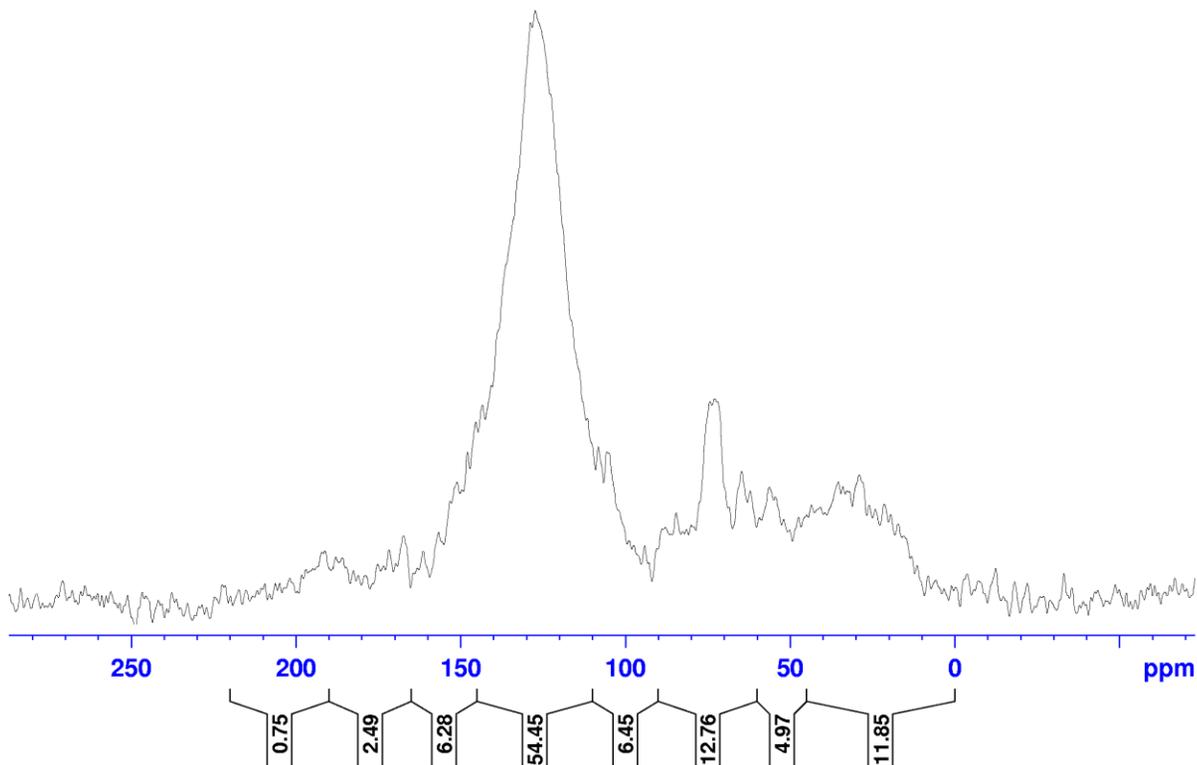
===== CHANNEL f2 =====
 CPDPRG2 tppm15
 NUC2 1H
 PCPD2 5.40 usec
 PLW2 260.00000000 W
 PLW12 260.00000000 W
 SFO2 300.1312605 MHz

F2 - Processing parameters
 SI 16384
 SF 75.4679928 MHz
 WDW EM
 SSB 0
 LB 60.00 Hz
 GB 0
 PC 0.20



Waco Wetland Fire charcoal sample site 15
 157.3mg
 CPMAS square100 with tppm15 decoupling and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

158



```

Current Data Parameters
NAME      VonBargen_WWF15Char_083112
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20120831
Time     15.36
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  cptoss_WCH
TD       1024
SOLVENT  CDCl3
NS       4000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       3.00000000 sec
D31      0.00020000 sec
TD0      1
ZGOPTNS

===== CHANNEL f1 =====
NUC1     13C
P2       7.90 usec
P15      2000.00 usec
PLW1     110.00000000 W
PLW11    320.00000000 W
SFO1     75.4760505 MHz

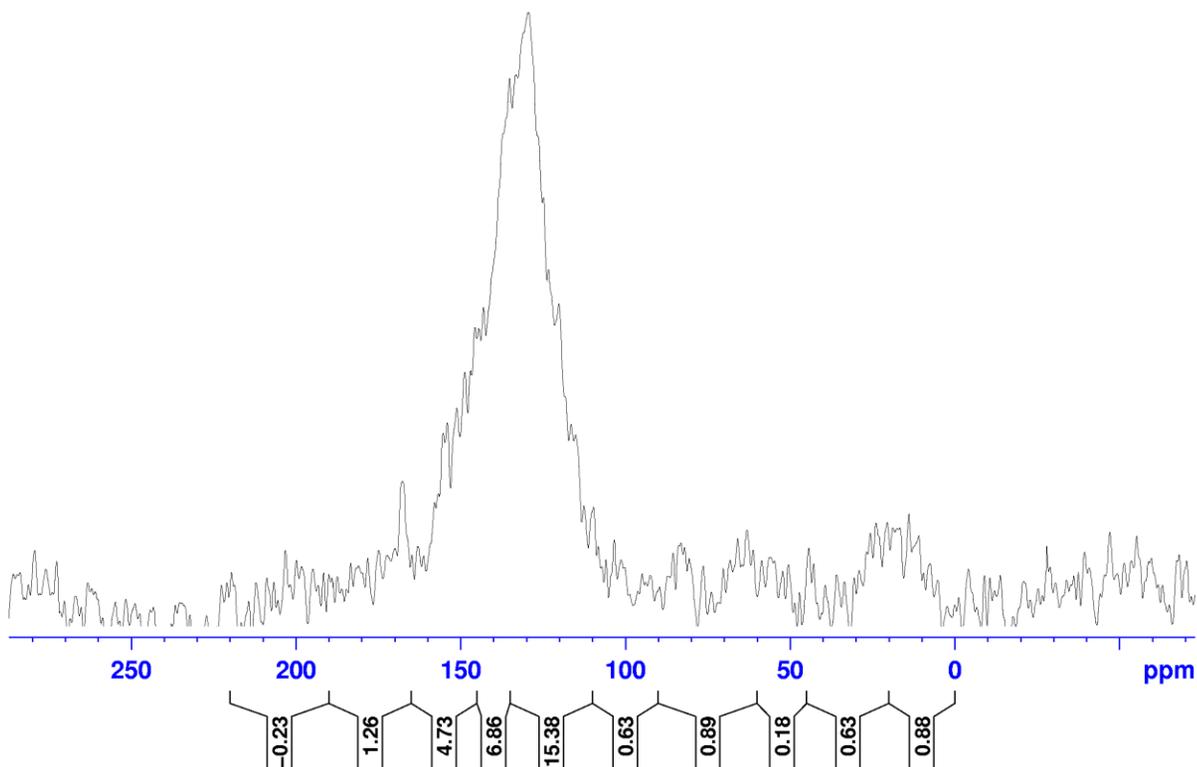
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
P3       2.85 usec
PCPD2    5.50 usec
PLW2     260.00000000 W
PLW12    260.00000000 W
SFO2     300.1312605 MHz
SPNAM0   Squa100.1000
SFOAL0   0.500
SPOFFS0  0 Hz
SEW0     85.00000000 W

F2 - Processing parameters
SI       16384
SF       75.4679911 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 15
 157.3mg
 CPMAS square100 with tppm15 decoupling, dipolar dephasing, and Total Suppression of Sidebands (TOSS)
 Probe: 7 mm 5kHz MAS

159



```

Current Data Parameters
NAME      VonBargen_WWF15Char_083112
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20120831
Time      22.17
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   cptoss_nqs_WCH
TD         1024
SOLVENT   CDCl3
NS         4000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         3.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1      13C
P2         7.90 usec
P15        2000.00 usec
PLW1       110.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

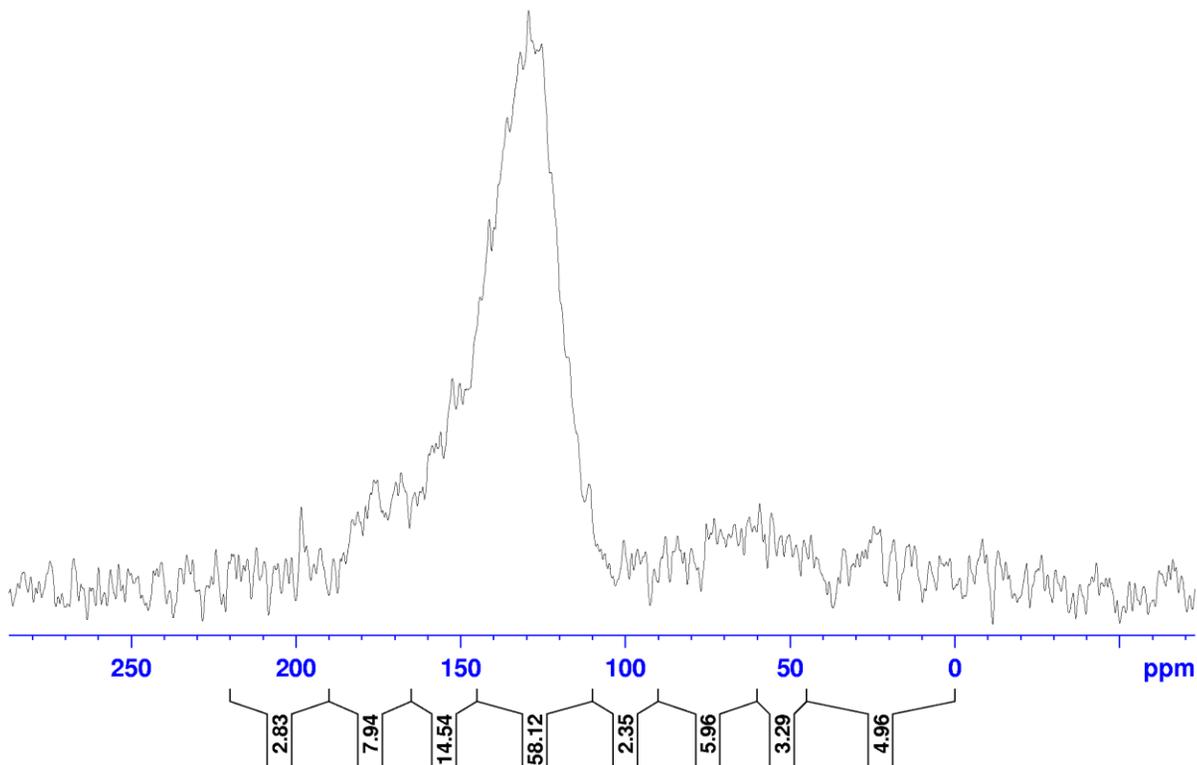
===== CHANNEL f2 =====
CPDPRG2   tppm15
NUC2       1H
P3         2.85 usec
PCPD2      5.50 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz
SPNAM0     Squa100.1000
SFOAL0     0.500
SPOFFS0    0 Hz
SEW0       85.00000000 W

F2 - Processing parameters
SI         16384
SF         75.4679911 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



Waco Wetland Fire charcoal sample site 15
 157.3mg
 hpdec (direct polarization) with Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

160



```

Current Data Parameters
NAME      VonBargen_WWF15Char_083112
EXPNO    3
PROCNO   3

F2 - Acquisition Parameters
Date_    20120901
Time     23.18
INSTRUM  spect
PROBHD   7 mm MAS BB/1H
PULPROG  hpdecTOSS
TD       1024
SOLVENT  CDCl3
NS       1000
DS       0
SWH      34722.223 Hz
FIDRES   33.908421 Hz
AQ       0.0147956 sec
RG       45.2
DW       14.400 usec
DE       8.08 usec
TE       303.0 K
CNST11   0
CNST31   5000.000000
D1       90.0000000 sec
D31      0.00020000 sec
TD0      1
ZGOP1NS

===== CHANNEL f1 =====
NUC1     13c
P1       4.00 usec
P2       8.00 usec
PLW1     320.0000000 W
PLW11    320.0000000 W
SFO1     75.4760505 MHz

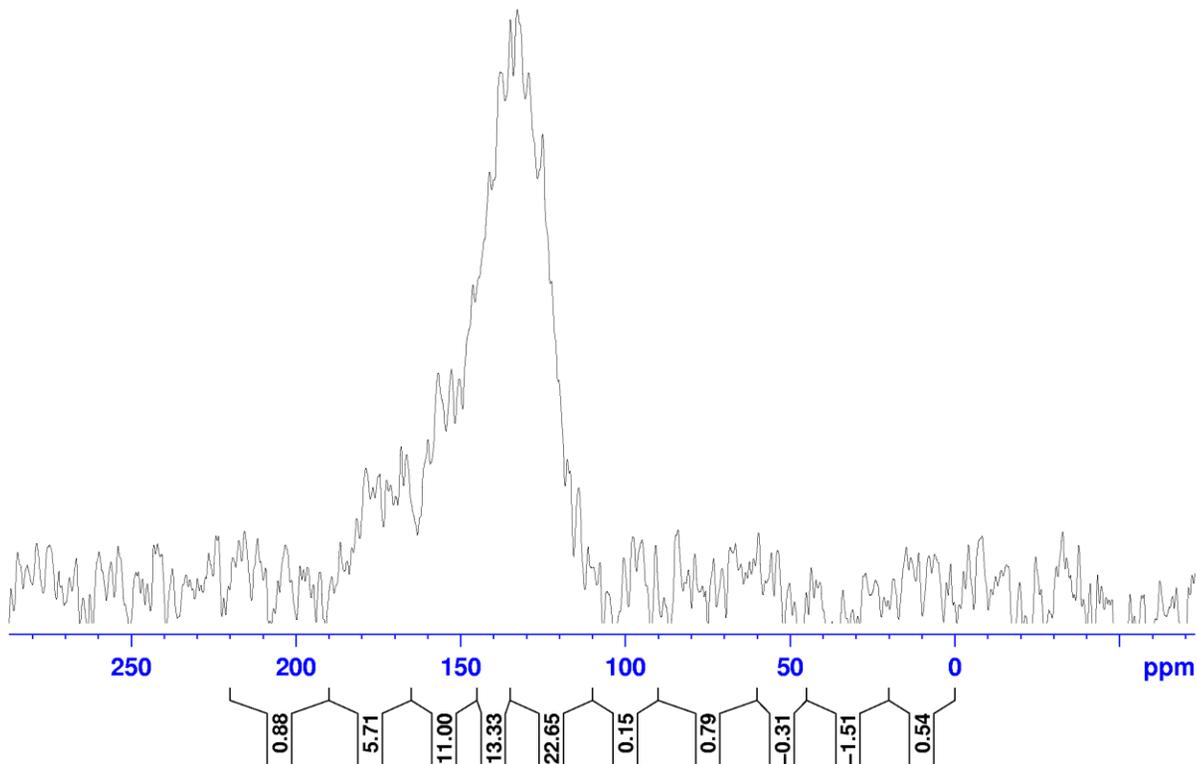
===== CHANNEL f2 =====
CPDPRG2  tppm15
NUC2     1H
PCPD2    5.40 usec
PLW2     260.0000000 W
PLW12    260.0000000 W
SFO2     300.1312605 MHz

F2 - Processing parameters
SI       16384
SF       75.4679928 MHz
WDW      EM
SSB      0
LB       60.00 Hz
GB       0
PC       0.20
  
```



Waco Wetland Fire charcoal sample site 15
 157.3mg
 Cross polarization with dipolar dephasing Total Sideband Suppression (TOSS) and TPPM15 decoupling
 Probe: 7 mm MAS 5kHz MAS

161



```

Current Data Parameters
NAME      VonBargen_WWF15Char_083112
EXPNO     4
PROCNO    2

F2 - Acquisition Parameters
Date_     20120903
Time      0.18
INSTRUM   spect
PROBHD    7 mm MAS BB/1H
PULPROG   hpdec_toss_nqs
TD         1024
SOLVENT   CDCl3
NS         1000
DS         0
SWH        34722.223 Hz
FIDRES     33.908421 Hz
AQ         0.0147956 sec
RG         45.2
DW         14.400 usec
DE         8.08 usec
TE         303.0 K
CNST11    0
CNST31    5000.000000
D1         90.00000000 sec
D20        0.00007000 sec
D31        0.00020000 sec
ZGPGTNS

===== CHANNEL f1 =====
NUC1       13c
P1         4.00 usec
P2         8.00 usec
PLW1       320.00000000 W
PLW11      320.00000000 W
SFO1       75.4760505 MHz

===== CHANNEL f2 =====
CPDPRG2    tppm15
NUC2       1H
PCPD2      5.40 usec
PLW2       260.00000000 W
PLW12      260.00000000 W
SFO2       300.1312605 MHz

F2 - Processing parameters
SI         16384
SF         75.4679928 MHz
WDW        EM
SSB        0
LB         60.00 Hz
GB         0
PC         0.20
  
```



APPENDIX D

Residual Analysis

Residual Analyses of Calibration Charcoals

Calibration Sample Type	Furnace Temp. (°C)	CP						DP					
		X _b			C/C			X _b			C/C		
		X _b	X _b '	Residual	C/C	C/C'	Residual	X _b	X _b '	Residual	C/C	C/C'	Residual
Cattail	300	0.18	0.18	0.00	-0.02	0.96	-0.98	0.22	0.23	-0.01	0.00	1.00	-1.00
	400	0.43	0.37	0.06	0.10	1.24	-1.14	0.59	0.45	0.14	0.19	1.33	-1.14
	500	0.48	0.56	-0.08	0.13	1.52	-1.39	0.84	0.67	0.17	0.37	1.66	-
Willow	250	0.13	0.08	0.04	-0.05	0.82	-0.86	0.23	0.12	0.11	0.00	0.83	-0.83
	350	0.24	0.27	-0.04	0.01	1.10	-1.09	0.38	0.34	0.04	0.08	1.16	-1.08
	450	0.59	0.46	0.12	0.19	1.38	-1.19	0.64	0.56	0.07	0.22	1.49	-1.27
Willow (reburn)	550	0.56	0.65	-0.09	0.17	1.66	-1.49	0.74	0.78	-0.05	0.29	1.82	-1.53
	550	0.72	0.65	0.07	0.28	1.66	-1.39	0.89	0.78	0.11	0.43	1.82	-
Pecan	225	0.08	0.04	0.04	-0.07	0.75	-0.82	0.06	0.07	-0.01	-0.08	0.75	-0.83
	350	0.30	0.27	0.02	0.04	1.10	-1.06	0.29	0.34	-0.06	0.03	1.16	-1.13
	400	0.35	0.37	-0.02	0.06	1.24	-1.18	0.30	0.45	-0.16	0.04	1.33	-1.29
Pine	450	0.64	0.46	0.18	0.22	1.38	-1.16	0.55	0.56	-0.01	0.17	1.49	-1.32
	500	0.58	0.56	0.03	0.19	1.52	-1.34	0.73	0.67	0.06	0.29	1.66	-1.37
	300	0.16	0.18	-0.02	-0.03	0.96	-0.99	0.16	0.23	-0.08	-0.03	1.00	-1.03
Magnolia	400	0.33	0.37	-0.04	0.05	1.24	-1.19	0.27	0.45	-0.19	0.02	1.33	-1.31
	450	0.49	0.46	0.03	0.13	1.38	-1.25	0.38	0.56	-0.18	0.08	1.49	-1.41
Magnolia	300	0.09	0.18	-0.09	-0.06	0.96	-1.02	-	0.23	-	-	1.00	-
	600	-	0.75	-	-	1.80	-	0.74	0.89	-0.15	0.29	1.99	-1.70

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