

QUALIFYING CLASSES OF ORGANIC
COMPOUNDS WITHIN UNPROCESSED PRODUCED
WATER USING ^1H -NMR ANALYSIS

By

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Title of Study: QUALIFYING CLASSES OF ORGANIC COMPOUNDS WITHIN
UNPROCESSED PRODUCED WATER USING ^1H -NMR ANALYSIS

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Abstract: Produced water (PW) is defined as any ground- or flowback water recovered during the process of petroleum extraction. This water is highly heterogenous, containing many different organic compounds associated with petroleum reservoirs. It is typically more saline than marine waters as well. Studies of produced water tend to examine specific fractions of organic compounds present; in this study, we examined unprocessed samples of produced water using ^1H -NMR, to create a qualitative profile of organic molecular functional groups present. Thirty samples of produced water were analyzed using a PE-ES-WATERGATE water suppression NMR experiment using an 800MHz NMR. Resulting spectra were then divided into discrete regions, broadly representative of the types of functional groups present. The conclusions of this research support this methodology's usage for produced water – while challenging, unprocessed PW can be successfully analyzed using NMR and meaningfully interpreted through spectral binning. Additionally, this methodology may be able to approximate the location of samples with unknown provenance, as Anadarko Basin PW samples with known and unknown origins displayed numerous similar spectral characteristics. However, certain classes of organic functional groups, namely those indicative of alkenes, were almost entirely absent from analysis. This absence must be fully investigated to determine whether there is a methodological bias against them or not.

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CHAPTER I

INTRODUCTION

Produced water (PW) is generally defined as any water that is generated and captured during the course of petroleum extraction. This can include both in-situ groundwater from reservoirs, and flowback water created during the course of well drilling and completion. Produced water makes up a significant portion of the output volume of petroleum wells. For example, global production can range from three to seven times the petroleum output per well (Wagner et al. 2016; Al-Ghouti et al. 2019). Industry water production has been approximately 70 billion barrels per annum (Veil et al. 2004). It is likely that this number is an underestimation, as global reporting is not uniform from region to region (Neff et al. 2011). Compositionally, produced water typically is as-or-more saline than ocean water and has a highly heterogeneous composition of organic and inorganic compounds. This composition also varies on a per-region to per-well basis (Collins 1975; Neff et al. 2011). However, despite this heterogeneity, produced water can almost always be considered a pollutant. Numerous compounds known to be toxic to life such as BTEX's, phenols, and phosphoric compounds have been consistently measured in produced water (Danforth et al. 2020). Developing a standardized treatment procedure is ultimately a costly affair, and consequently the majority of PW is simply disposed of.

Unfortunately, current disposal methods create issues of their own, as dumping into the ocean or evaporation pits risks polluting the local environment, and reinjection into the subsurface can trigger damaging earthquakes (Pollyea et al. 2019). This thesis intends to investigate ^1H Nuclear Magnetic Resonance (NMR) analysis as an ideal tool for expedient and novel characterization of organic compounds found within produced water. Specifically, unaltered, “whole-water” samples are examined, with the intention of creating as complete a profile of organic compound content as possible. It also will establish a method of characterizing different classes of organic compounds, via the grouping of compounds into discrete regions. This will provide a useful qualitative assessment of the types of organic compounds present, without needing to identify each compound present in a sample. This study will examine thirty samples of produced water from the Black Warrior Basin, AL and Anadarko Basin, OK to determine the efficacy of ^1H NMR analysis of unfractionated produced water. This study asserts that ^1H NMR is capable of analyzing near-totally unaltered specimens of produced water, and that with proper experimental design, a more-comprehensive profile of classes of organic functional groups can be acquired.

CHAPTER II

BACKGROUND

NMR is an established chemical analysis technique used by biologists, chemists, and geochemists. The primary use of this technique is to assist with determining the physical molecular structure of compounds, without that structure necessarily being known beforehand. This elucidation is achieved by subjecting a target compound to a high-powered magnetic field in order to excite specific atoms, most commonly protons in $^1\text{H-NMR}$, within that compound to generate their own magnetic field. The resulting atomic magnetic field is then recorded by the NMR and results are shown as a graphic spectrum made up of peaks representing the presence of specific hydrogens in a specific chemical environment, and their relationship to other hydrogens in that environment. This phenomenon is referred to as chemical shift. Briefly, chemical shift is a measure of a compounds' magnetic resonant frequency in relation to the instruments magnetic field. Generally, the more electronegative a compounds' component atoms, the further downfield, or away from the 0.0ppm mark, its signal peaks will appear. Specific chemical shifts for compounds can vary based on the minute variances between magnets as well as the solvent containing the target compound. Still, compound structure can still reliably be identified if the aforementioned impacts on chemical shift are known.

Additionally, the use of an internal standard, a separate compound with a narrowly defined chemical shift, can aid with correcting a target compounds' chemical shift.

Salinity

Samples like produced water which are generally highly heterogenous, have low organic carbon concentrations, or are highly saline, pose challenges for this type of analysis which must be overcome. For example, a significant impediment to NMR analysis are paramagnetic ions, namely salt. Accurate assessment of a compound's hydrogen quantity is heavily reliant on the instrument's magnetic field remaining undisturbed. However, this external magnetic field causes paramagnetic contaminants to generate fields of their own, consequently obfuscating analytical results and potentially rendering them useless (Pell et al. 2019). Unfortunately, many salt compounds are considered paramagnetic, and produced water tends to contain significant volumes of dissolved salts. High salinity in an NMR sample can have various deleterious effects, and in general it is preferable to remove salts before testing. There are a few ways which salinity/paramagnetism affects NMR analysis: paramagnetism impacts the chemical shift of compounds being analyzed by moving signal peaks beyond the ranges they would be expected. In one instance, the presence of salt at sample saturation changed the peak positions of carbohydrate molecules by as much as 0.5ppm from where they would be found in a desalinated solution (Zhu et al. 2019). Additionally, salinity may make the operation of the NMR instrument itself more difficult, either by pushing locking, shimming, and tuning values beyond the operational ranges of the instrument, or by altering acquisition parameters unexpectedly. The poorer the instrumental setup parameters, the less sensitive the NMR experiment will be. Coupled with low compound

concentration, there is the risk that signals will go undetected amongst the background noise. Graphically, peaks on resulting spectra will appear to widen and reduce in intensity, as hydrogen atom counts become inaccurate (Kirkland 2021). In addition, should a sample's salinity be too high, the NMR experiment can simply fail to execute. Samples like this are effectively unusable in NMR analysis without some sort of treatment beforehand.

While the effects of salinity are difficult to determine, they are not completely unpredictable. NaCl, one of the most common forms of salt found, is in fact diamagnetic, and prior study has shown that while organic compound peaks display reduced intensity, they are not shifted significantly in one direction or another (Kirkland 2021). Iron(III) however is highly paramagnetic, and in addition to reducing peak hydrogen peak intensity also shifts peaks downfield (Kirkland 2021). Functionally, it takes trial-and-error to establish the best instrument settings as acquisition parameters for a given sample. An example of this would be transverse relaxation time (T₂), which generally decreases as salinity increases (Deng et al. 2006). If not compensated for in some manner, this would make it appear as though compound signals are decreasing in intensity, to the point where peaks may not even be detected (Zhu et al. 2019). Such workarounds do exist, the inclusion of a reference standard with a known chemical shift for example, can help shift peaks in a spectrum back to their correct positions. In situations where instrument sensitivity is low, increasing the number of scans a sample is subjected to can build up signals to where accurate integrated hydrogen counts may be acquired. This is a somewhat brute-force way of getting around the problem of insensitivity as increasing the number of scans can dramatically increase the experiment

time duration. It may not be feasible in all circumstances. That said, it is technically possible, and scan durations may not have to be increased blindly. It has been shown previously that as long as the ratio between dissolved organic matter (DOM) and total dissolved solids (TDS) is greater than 0.002, the hydrogen count of a saline sample would be as accurate as a sample with no salt or other paramagnetic ions (Kirkland 2021).

Heterogeneity

Well-designed NMR methodology can address challenges raised by low sample concentrations, and to some degree, high salinity. However, the heterogeneity of organic compounds found in produced water presents a problem which must be addressed through other means. In many cases, the organic compounds found in PW present as a “smear” of ill-defined peaks, conceptually similar to an unresolved complex mixture (UCM) more commonly known in gas chromatography studies. UCM is the result of hundreds to thousands of different organic compound signatures blending together, making the resolution of any one compound a difficult process (Killops and Al-Juboori 1990). It is most often seen in degraded petroleum reservoirs, and is loosely composed of varying percentages of branched alkanes, alkylaromatics, or polycyclic aromatic hydrocarbons (PAHs) (Booth et al. 2007; Ventura et al. 2008; Melbye et al. 2009). Even in cases where the number of organic compounds is relatively limited, the signatures for each compound may be very similar to one another and overlap (DeVience et al. 2013). This obfuscates individual compound identification, although more qualitative assessments can still be made regarding classes of organic compounds.

While the presence of unresolved complex mixtures (UCM), limits identification of most individual organic compounds, NMR is still effective at identifying the

functional groups present. This is of specific importance, as the complete profile of organic compounds is not normally known beforehand; separation methods can make it easier to characterize fractions of the organic compounds present, but without a complete profile it is difficult to contextualize them. Establishing an NMR methodology which permits expedient and interpretable analysis of organic compounds in produced water is of paramount importance.

Experimental Design and Limitations

NMR analysis is capable of describing classes of organic compounds in samples of unaltered marine and lacustrine water, as well as prepared produced water samples. However, because organic compounds are normally present in low concentrations, it can be time-consuming to resolve them. Numerous individual scans are necessary in order to build up signals to the point where they are detectable from the background noise. Depending on the particular design of the equipment and experiment, the number of scans needed can range from a few hundred to tens of thousands (Lam and Simpson 2008). Consequently, the test time for a sample can be days-long, which can make its usage for large sample sets impractical and expensive. Additionally, water molecules are polar, and the magnet-based detection method of NMR will also register water on a spectrum. In this context, because water is so much more abundant than other compounds in PW, its' signal will become pronounced to where it potentially overwhelms the signals of other compounds. Fortunately, techniques and technology exist which can ameliorate these issues. High-powered NMR devices capable of operating at 600MHz and greater can more efficiently build-up signals, reducing the number of scans and time needed to generate interpretable spectra. Additionally, new experimental designs such as

WATERGATE enable more complete water suppression while preserving other signals (Lam and Simpson 2008; Adams et al. 2012). While these alone are not enough to resolve individual compounds, they do expedite NMR analysis while improving the signals of any functional groups present. At a minimum, it expedites the accurate, qualitative assessment of organic compound classes.

NMR instrumentation is traditionally most effective at determining the structure of one or two compounds in a sample at a time, as peaks will generally not overlap with one another, multiplets will be apparent and the composition of the sample will be constrained. For studies of natural and produced waters, the number of different compounds make that type of analysis impossible. Instead, in order to extract useful information from NMR spectra of these types of samples, signals are instead integrated together in broad groupings, which are representative of the rough amount of non-exchangeable protons associated with a class of organic compounds (Hertkorn et al. 2013). On its own, this technique cannot provide a quantitative result of exactly how much of a particular compound exists, or even the identity of said compound. However, this does enable a more qualitative assessment of the concentration and types of compounds present, which can be cross-checked with other analytical methods. Additionally, it can be performed quickly once the NMR spectrum has been generated, meaning at-a-glance evaluations of water can be acquired.

Separation Techniques

There are numerous established methods which can separate fractions of organic compounds and make characterization more feasible. One popular method commonly employed in produced water studies is solid-phase extraction (SPE). Briefly, SPE works

by introducing a solid sorbent to a target solution. This sorbent can be composed of a variety of different materials, each specializing in a set of compounds it can extract (Wagner et al. 2016). For example, XAD-4 and XAD-8 polymer sorbents are shown to be effective at capturing non-volatile aliphatic compounds (Zhang et al. 2021). However, it is difficult to efficiently capture all of a target compound contained within an initial sample, as capture rates vary between 20% to 90%, depending on the techniques used (Zhang et al. 2021). Additionally, sorbents which specialize in specific types of compounds invariably exclude others. Heterogeneous solutions can therefore make a complete organic compound characterization a time-consuming endeavor. Finally, the utility of this method can be limited by salinity, as salt can potentially bind to the sorbents as well.

Another method of sample concentration is lyophilization, or freeze-drying (Lam and Simpson 2008). As a way of removing water while preserving the original characteristics of a samples DOM, lyophilization is potentially one of the least destructive ways to concentrate complete profiles of DOM. However, it has also been shown that while low molecular weight DOM can be concentrated, certain volatile or heavily-oxygenated compounds such as carbonyls and carbohydrates can still be lost (Whitty et al. 2021). Additionally, salt is concentrated as well, which limits lyophilization's usefulness to more freshwater samples (Lam and Simpson 2008).

Liquid-liquid extraction (LLE) is a common, well-established method for extracting organic compounds from an aqueous solution. However, this technique has a number of weaknesses, each of which can skew the profile of organic compounds detected in a sample. For example, the method relies heavily on organic solvents to

separate and concentrate compounds for further analysis. More polar molecules, which prefer to stay in an aqueous phase, may not be effectively captured and could go undetected. Additionally, compared to other analogous methods of organic compound fractionation LLE appears to have lower recovery rates for DOM. For example, compared to atmospheric pressure photoionization (APPI), LLE recovers roughly one-third to one-half of the number of compounds (Yi et al. 2017). LLE performs even worse against solid-phase extraction (SPE) techniques. In a study of the recovery efficiency between SPE and LLE, LLE consistently recovered under 40% of test standards and organic compounds (Ostermann et al. 2015). Even for more targeted studies, there are preferable alternatives to LLE. Stir bar sorptive extraction (SBSE) has a similar recovery rate of PAH's to LLE (Krüger et al. 2011). However, that method uses significantly less organic solvent to extract the desired fraction, leading to decreased odds of false signals or loss of material due to volatilization. Strictly speaking, completely unaltered samples of water could yield the most accurate results for organic compounds present. However, raw water samples are rarely analysis-ready – colloids, particulate matter and high volumes of total dissolved solids (TDS) make some sort of sample preparation or methodological compensation a necessity.

Sampling Locations

Black Warrior Basin, AL

The Black Warrior Basin is a coalbed methane play located in northwest Alabama, straddling the border with Mississippi (Figure 1). It generates about 100 billion ft³/yr of natural gas, primarily methane. It also generates produced water at about 69 million bbl/yr (Pashin et al. 2014). Total dissolved solids (TDS) range approximately

between 2,000 and 50,000 mg/L throughout the basin, varying significantly due to the intrusion of freshwater from the southeast (Figure 1). There at the basin margin, bedding planes are uplifted and exposed, allowing meteoric water to enter deeper formations and move generally to the northwest (Pashin 2007). This freshwater reduces the salinity of the groundwater within its' zone of influence, though there are exceptions to this. Regardless of concentration, the specific salt ions that are found in the basin are overwhelmingly sodium chloride and to a lesser degree sodium bicarbonate, both of which are considered diamagnetic (Pashin et al. 2014; Kirkland 2021). Prior study of the basins' organic compounds concluded that they mainly comprised of aromatics, polycyclic aromatic hydrocarbons and phenols, with some lesser input from various aliphatics (Table 1)(Orem et al. 2014; Pashin et al. 2014). However, those studies used LLE to prepare their samples for analysis. As discussed earlier, LLE has significant drawbacks and inaccuracies when used in studies of organic compounds in ground or produced water. As it pertains to the Black Warrior Basin, a significant proportion of the total organic carbon (TOC) was not accounted for, with the unidentified portion consisting of approximately 98.9% to 99.9% of the overall TOC across the studies' sample set (Pashin et al. 2014). It can be reasonably said that a complete profile of present organic compounds, and their relative quantities, may not have been acquired.

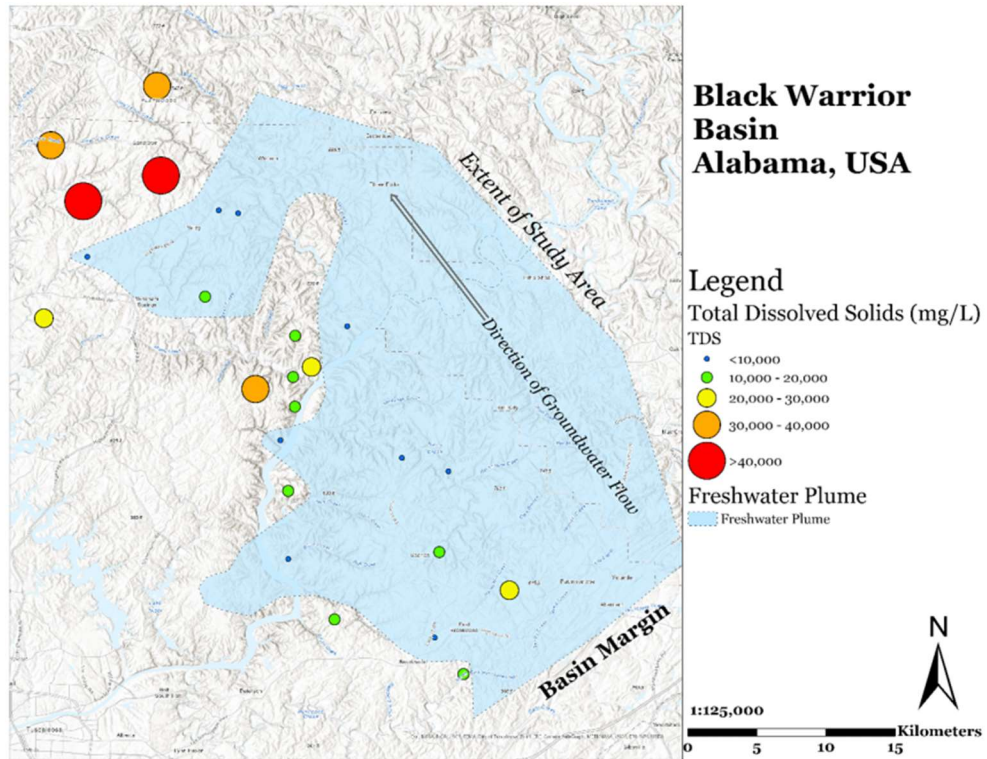
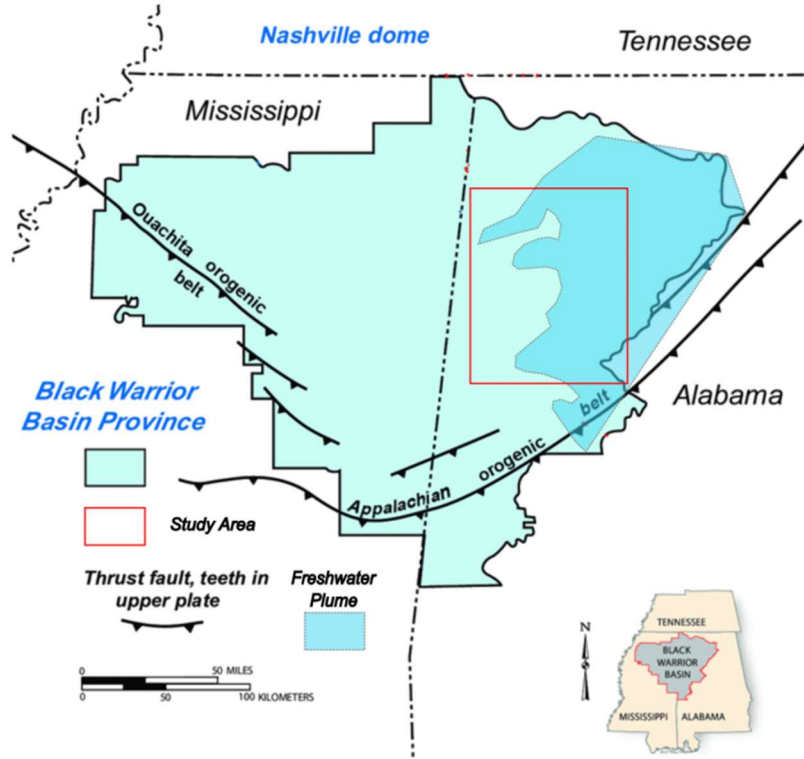


Figure 1. (Left) Map of the Black Warrior Basin (Modified from Pawlewicz and Hatch 2022). The full extent of the basin covers Alabama and Mississippi. Due to uplift from the Appalachian orogenic belt, meteoric water can easily enter the subsurface, flowing generally to the northwest. (Right) Map of the study area for the Black Warrior Basin in Alabama. Location of each sampled well along with its salinity (represented by TDS) is shown. Blue polygon indicates estimated extent of freshwater intrusion into the sampling area (recreated from Pashin et al. 2014).

Table 1. Compiled list of specific organic compounds present in produced water samples from the Black Warrior Basin, AL (Orem et al. 2014; Pashin et al. 2014). Additionally, broad compound types for each compound class are shown as well.

COMPOUND TYPE	COMPOUND CLASS	IDENTIFIED COMPOUNDS
<i>Aliphatics (Unsubstituted, Substituted)</i>	<i>Fatty Acids</i>	Acetate (Volatile)
		Dodecanoic Acid
		Tetradecanoic Acid
		Hexadecanoic Acid
		Octadecanoic Acid
		Hexadecenoic Acid Octadecenoic Acid
<i>Carbohydrates Alkyl-groups Other Non-Aromatic Compounds</i>	<i>Non-aromatic Compounds</i>	Triphenyl-phosphate
		Tributyl-phosphate
		Alkyl-phosphates
<i>PAH's Phenols Amides Heterocyclic Compounds Other aromatics</i>	<i>Polycyclic Aromatic Hydrocarbons (PAHs)</i>	Naphthalene
		Methyl-naphthalene
		Dimethyl-naphthalene
		Trimethyl-naphthalene
		Dimethyl-phenol
	<i>Phenols</i>	4-(1,1,3,3-tetramethylbutyl)-phenol
		2,4-bis(1,1-dimethylethyl)-phenol
	<i>Phthalates</i>	Dioctyl phthalate
		Dibutyl phthalate
	<i>Other Aromatics</i>	Acetophenone
		biphenyl
		Methylbiphenyl
		<i>Heterocyclic Compounds</i>
Methyl-quinoline		
Iso-quinoline		
Benzothiazole		
Di-benzothiophene		
Caprolactam		

Anadarko Basin, OK

The Anadarko Basin is a large, northwest-southeast trending hydrocarbon play, stretching across much of western Oklahoma, as well as parts of Kansas and Texas (Figure 2). Hydrocarbons of every kind have been found and extracted from the basin,

though natural gas is the dominant petroleum product (Higley et al. 2011). Much of the deep groundwater originates in the Morrow Fm, which due to the Wichita Uplift was trapped by the rapid sedimentation of new strata (Dickey and Soto 1974). Combined with the relatively small elevation changes throughout much of the basin, there is relatively little interaction between the deep groundwater reservoirs, from which produced water originates, and other sources of freshwater or fluid flow (Dickey and Soto 1974). Consequently, produced water generated from oil extraction in the basin is highly saline to briny, with reported chloride values ranging from 7,500 to 182,000 mg/L (Collins 1969). This salt, particularly in the Sooner Trend, Anadarko (basin), Canadian and Kingfisher (counties) (STACK) portion of the basin is primarily diamagnetic combinations of chloride, bromide and iodide-based salts. However, paramagnetic ions of strontium and barium have been recorded as being present as well (Collins 1969).

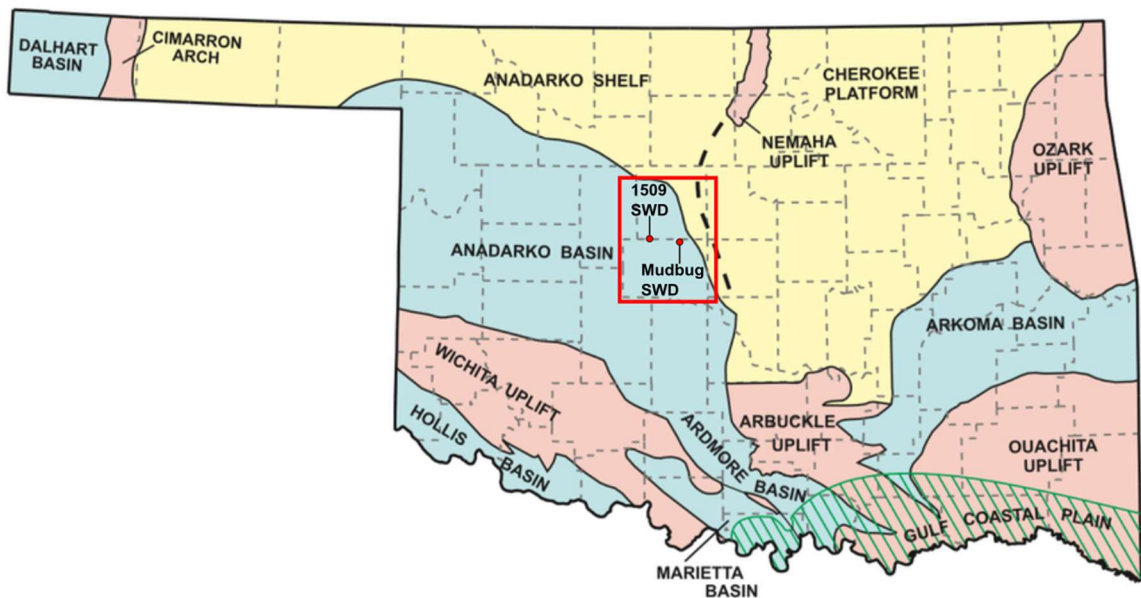


Figure 2. Map of the Anadarko Basin, OK. Exact locations for samples most samples in this set are unknown; two were collected from saltwater disposal (SWD) sites located near Okarche, OK (see red box)(Modified from Villalba 2016).

CHAPTER III

METHODOLOGY

General Procedures

Due to the low concentrations of organic compounds within the PW samples, and the fact that their composition was unknown, the possibility of accidental contamination was a concern. To minimize this risk, all produced water samples, solvents, and experimental solutions were handled and stored exclusively using glass carbonized at 450°C for 6 hours, along with Teflon-lined caps washed in a 10% HCl solution. Apart from the NMR sample tubes, all glassware was disposed of or recarbonized after use. To clean the NMR tubes, a 3:1 solution of concentrated HCl:HNO₃ was mixed to create aqua regia. This solution was inserted into the tubes and allowed to sit for approximately 24 hours, to ensure that the tubes were completely clean of organic compounds before reuse. After this, NMR tubes were rinsed thoroughly with milli-Q water and dried in an oven at 50°C for approximately 3 hours. When not in use, cleaned NMR tubes were wrapped in aluminum foil and kept in a dry storage cabinet.

Sample Collection, Handling and NMR Preparation

Prior to this thesis, produced water (PW) samples were collected from Blue Creek and Brookwood fields of the Black Warrior Basin (BWB) from 16 unique wellheads (Figure 1). PW samples were filtered on-site using Whatman Polyethersulfone (PES) 0.2 μm syringe filters (Quan Personal Communication). This sampling methodology is in line with similar produced water studies of the Black Warrior Basin (Orem et al. 2014). Additional samples of PW from Oklahoma were also acquired. These included a PW blend from different wellheads, a set of ten Oklahoma-based PW samples (exact origins are unknown), and two PW samples collected from saltwater injection sites located near Okarche, OK (Table 2). Prior to any analysis, samples were passed through a Whatman GF/F glass fiber filter using vacuum filtration, to remove particulate and colloidal matter which could interfere with NMR analysis. In the event the filters would be needed in the future, they were wrapped in aluminum foil and stored in a freezer. While not in use, produced water samples were kept frozen and dethawed only when used for experimentation.

For NMR experiments, 1mL samples were prepared using a mixture of produced water (H_2O) and D_2O , at a ratio of 9:1, with an additional 10.36 to 11.75 mg of sodium trimethylsilylpropanesulfonate (DSS) at a concentration of 1.42mM. This was used as a reference standard to provide an at-a-glance assessment of peak heights and to help normalize spectra, as well as enable accurate comparisons of different sample spectra. DSS is a variation of trimethylsilylpropanesulfonic acid (TMS). The addition of the sodium salt enables that compound to be dissolved in water, without fundamentally altering its properties as a reference.

Table 2. List of produced water samples analyzed. Three separate sample sets were used, in descending order they are: a set from the Black Warrior Basin in Alabama, collected directly from gas wellheads; a set from the Anadarko Basin, OK, shared by Dr. Prem Bikkina of the OSU Dept of Engineering; a set collected from a pair of saltwater disposal wells near Okarche, OK, also from the Anadarko Basin. Location and/or basic water chemistry data is incomplete for some sample sets.

SAMPLE SET	SAMPLE ID	REGION/ FIELD	LATITUDE	LONGITUDE	TDS (mg/L)	TOC (mg/L)	DOC (mg/L)
BLACK WARRIOR BASIN	13175	Blue Creek	33.62651	-87.48241	38235		
	12860	Blue Creek	33.55244	-87.52991	45431	10.3	2.22
	11991	Blue Creek	33.56906	-87.47993	46210	1.69	1.89
	12006	Blue Creek	33.54673	-87.4428	6810	6.84	0.79
	11987	Blue Creek	33.5448	-87.43034	4356		
	11664	Blue Creek	33.4913	-87.45152	15801	5.95	1.48
	6764	Blue Creek	33.47227	-87.36022	2216		
	6279	Blue Creek	33.42059	-87.39386	11824		
	11238	Brookwood	33.36657	-87.39807	11140		0.87
	11398	Brookwood	33.38768	-87.3251	5243	77.8	1.73
	11496	Brookwood	33.37906	-87.29517	3485		
	15421	Brookwood	33.27233	-87.30387	2248	3.18	1.33
	15089	Brookwood	33.30269	-87.25598	23119		1.64
	6189	Blue Creek	33.4319	-87.41919	32955	7.01	3.91
	13744	Blue Creek	33.44606	-87.38318	20440	38.2	30.36
	14091	Blue Creek	33.47739	-87.55519	26984	5.67	4.17
	5682	Blue Creek	33.43963	-87.39493	15506	6.13	0.83
ANADARKO OSU	Vecta	Oklahoma					
	LDC	Oklahoma					
	23/26						
	2202	Oklahoma					
	Apache 1102	Oklahoma					
	Apache PW #3	Oklahoma	n.d.	n.d.	n.d.	n.d.	n.d.
ANADARKO LAGOON	2201	Oklahoma					
	5210- 5211	Oklahoma					
	Wilkerson 1-20-H	Oklahoma					
	5207	Oklahoma					
1509 SWD	Anadarko/ STACK	35.725839	-98.151264				
Mudbug SWD	Anadarko/ STACK	35.717681	-97.888385	n.d.	n.d.	n.d.	

Control Sample – Synthetic Produced Water

To aid with validation of methods and results, a synthetic produced water sample was additionally created. To simulate the profile of organic compounds found in naturally occurring produced water, an over-the-counter brand of engine fuel was used (CAS# 8006-61-9: Natural Gasoline) (Figure 3). This fuel is purported to contain no ethanol and have an octane rating of 92. In other words, it contained no other compounds other than fuel gas. Natural gasoline, as defined by the EPA, is itself a blend of approximately 150 different specific hydrocarbons; while those compounds are difficult to determine, overall it consistently contains majority saturated aliphatics (ChemicalBook 2017; US Environmental Protection Agency 2022). Specifically, it generally contains 60-70% alkanes, 6-9% alkenes, and 25-30% aromatic compounds (ChemicalBook 2017).



Figure 3. Product information of the fuel used to create the synthetic produced water sample. This product purportedly contains only Natural Gasoline (CAS#: 8006-61-9), at an octane rating of 92. It specifically does not contain ethanol.

A solution of 1-part natural gasoline to 9-parts Milli-Q water was created and kept in a 60mL amber vial. To capture those compounds which would prefer the water phase, the solution was mixed using a FisherScientific Vortex Mixer for 1 hour every 24 hours, for a total mixing time of 4 hours. Following this, the oil and water phases were separated and placed in new amber vials. The oil portion was placed in a freezer and kept for potential future study – the water portion was used to create an NMR testing sample in

the same manner as the natural produced water samples and was subjected to the same experimental regimen.

NMR Analysis

The Black Warrior Basin sample set was initially collected in 2015, and consequently it was deemed necessary to reexamine those samples to verify that there had not been any degradation or chemical alteration since initial collection and analysis. To this end, ¹H-NMR analysis was performed using a Bruker Avance400MHz NMR operating at 400.152MHz, and a preset water-suppression experiment (noesygppr1d) (Table 3). This served a secondary purpose in determining whether this testing regimen would be sufficient in regards to experimental run times and effective solvent suppression, or if a different experimental design would be needed.

Table 3. NMR acquisition parameters used with A400/noesy- experimental design. Default settings were used, with the exception of the acquisition delay (D1), changed from 2 sec to 1 sec, and the total number of scans (NS), increased from 8 to 4096.

F2 - Acquisition Parameters		F2 - Acquisition Parameters (cont.)	
Time	3.26 h	ZGOPTNS	-DFLAG_BLK
INSTRUM	spect	SFO1	400.1518817 MHz
PROBHD	Z116098_0222 (NUC1	1H
PULPROG	noesygppr1d	P0	10.00 μsec
TD	32768	P1	10.00 μsec
SOLVENT	H2O+D2O	PLW1	13.89000034 W
NS	4096	PLW9	0.00005556 W
DS	2	GPNAM[1]	SMSQ10.100
SWH	8417.509 Hz	GPZ1	50.00 %
FIDRES	0.513764 Hz	GPNAM[2]	SMSQ10.100
AQ	1.9464192 sec	GPZ2	-10.00 %
RG	15.75	P16	1000.00 μsec
DW	59.400 μsec	F2 - Processing Parameters	
DE	6.50 μsec	SI	16384
TE	298.0 K	SF	400.15 MHz
D1	1.0 sec	WDW	EM
D8	0.01 sec	SSB	0
D12	0.00002 sec	LB	0.30 Hz
D16	0.0002 sec	GB	0
TD0	1	PC	1.00

Ultimately, all produced water samples were analyzed using a Bruker Neo800MHz NMR operating at 800.334MHz, with a cryoprobe attachment for improved signal-to-noise ratio of result spectra. In lieu of a noesy-style water suppression experiment, another water suppression method termed PE-ES-WATERGATE (zgesgpe) was utilized (Adams et al. 2012). This method has been shown to improve water signal suppression in NMR spectra where the volume of water greatly outweighs the sample compound concentration. Additionally, it better preserves those compound signals located near to the water signal, or those which may have functional groups that can exchange protons with water and get unintentionally suppressed (Adams et al. 2012). NMR signal locking, tuning, and shimming were performed manually, and specific values for these steps inevitably varied between samples. Default acquisition parameters were used, with the exception the acquisition delay (D1), decreased from 2 sec to 1 sec, and number of scans (NS), increased from 8 to 1536, with a total runtime of approximately 1.5 hours per sample (Table 4).

Table 4. Partial list of NMR acquisition parameters used with N800/zgesgppe experimental design. Default settings were used, with the exception of the acquisition delay (D1), changed from 2 sec to 1 sec, and the total number of scans (NS), increased from 8 to 1536. This also increased the testing time for each sample to approximately 1.5 hours.

F2 - Acquisition Parameters		F2 - Acquisition Parameters (cont.)	
Time	1.26 h	ZGOPTNS	
INSTRUM		SFO1	800.334 MHz
PROBHD		NUC1	1H
PULPROG	zgesgppe	P0	
TD		P1	
SOLVENT	H2O+D2O+salt	PLW1	
NS	1536	PLW9	
DS	4	GPNAM[1]	SMSQ10.100
SWH		GPZ1	50.00 %
FIDRES		GPNAM[2]	SMSQ10.100
AQ		GPZ2	-10.00 %
RG		P16	
DW		F2 - Processing Parameters	
DE		SI	
TE	298.0 K	SF	800.33 MHz
D1	1.0 sec	WDW	
D8	0.01 sec	SSB	
D12	0.00002 sec	LB	
D16	0.0002 sec	GB	
TD0	1	PC	

Spectra Processing

NMR spectra processing was performed using MestReNova v14.2. All spectra were subject to a sequential workflow including apodization, phase correction, baseline correction, normalization, and peak selection/integration (Figure 4). Particular care was taken to ensure the overall form of each spectrum was preserved, in order to minimize risks of unintentionally altering data and results. Each step is detailed as follows:

Exponential and Gaussian apodization functions were applied to each spectrum, using the default values of 0.3 Hz and 1.0 Hz respectively. Phase correction consisted of first inverting spectra to ensure that compound signals were positive values, as needed. Due to the nature of the samples, many of the spectra peaks were “out-of-phase” or showed non-

symmetrical peak shapes independent of the compounds present. To correct this, PH0 and PH1 values were adjusted to fix these errors in the spectra. Because of the largely unknown composition of samples, this correction was deemed completed and satisfactory based on the reference standard peak shape. In other words, if the reference peak was phased correctly, it was assumed the rest of the spectra was as well. Baseline correction applied a multipoint baseline correction using a smooth segment algorithm. Correction points were exclusively selected using MNova's automated selection tool, to avoid any manual selection bias. Following this, spectra intensity values were normalized by setting the reference peak intensity at 100. This permitted more accurate cross-comparison of different sample spectra, as the reference standard quantity is known. Finally, compound peaks and peak integrals were identified, again using strictly automated processes to avoid subjective biasing as much as possible.

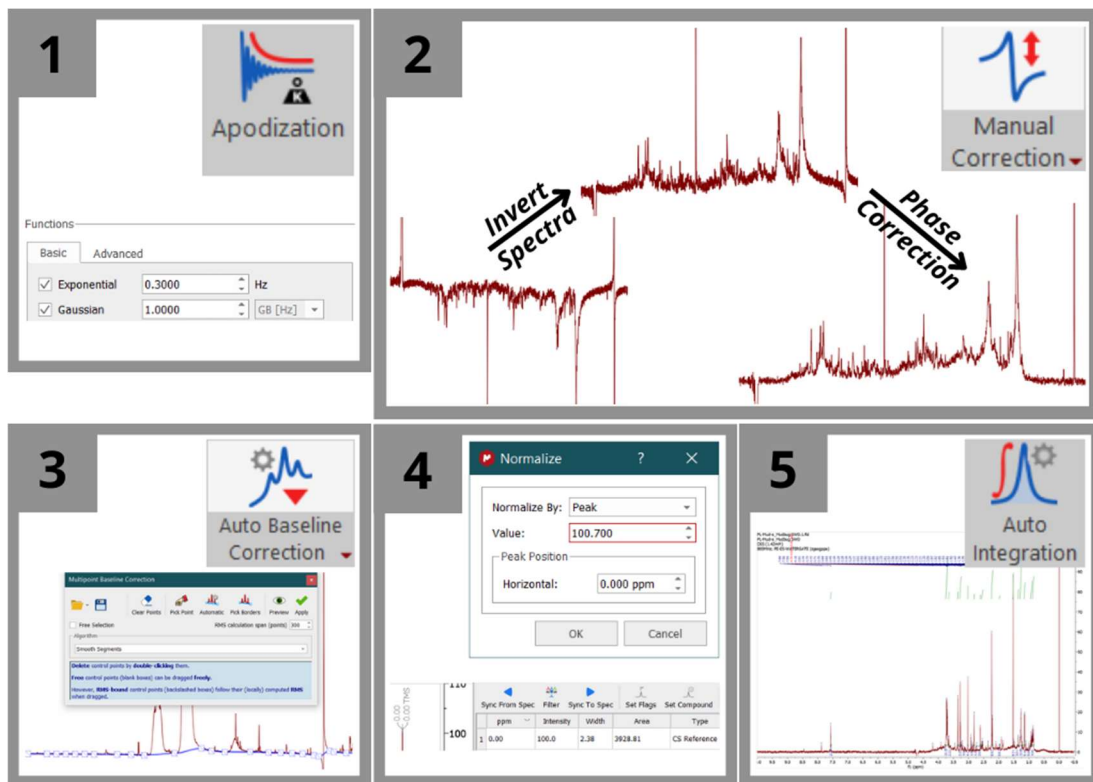


Figure 4. Diagram of each step taken to process and refine NMR spectra for further analysis. All results were processed using MestReNova v14.2.

Compound Classification

Post-processing, the spectra were divided in to 5 discrete regions along the x-axis, each broadly indicative of the types of functional groups present. These regions have been previously established by prior DOM/produced water work conducted by Guéguen et al. 2012, Hertkorn et al. 2013, and Zhang et al. 2021, and are described as they are used in this study in Figure 5 (below). Three additional callouts in the spectra were also recorded: At **0.0ppm** was the reference standard peak (DSS). Between **2.08 – 2.25ppm** was acetate/acetone (Wishart et al. 2009; Babij et al. 2016). This compound in particular was important to keep track of, as a clear and out-sized signal relative to other peaks could be indicative of either a contamination during sample preparation or suggest the presence of biological influence on PW samples and spectra. Additionally, while the chemical shift for acetone in deuterated water is nominally 2.22ppm, the presence of salt could shift this peak outside its' expected value. Finally, between **4.5 – 4.8ppm** was the solvent water signal. This was never included in quantification, as the PE-ES-WATERGATE NMR experiment was designed to suppress it specifically. Upon classification, the peak count in each region (P_{reg}) was divided by the total number of detected peaks in a spectrum (P_{tot}) to determine each region's share of peaks (R_{reg}) ($100 \times \frac{P_{reg}}{P_{tot}} = R_{reg}$). Averages of each region percentage across groups of spectra were also calculated, to help determine whether larger trends in the data existed.

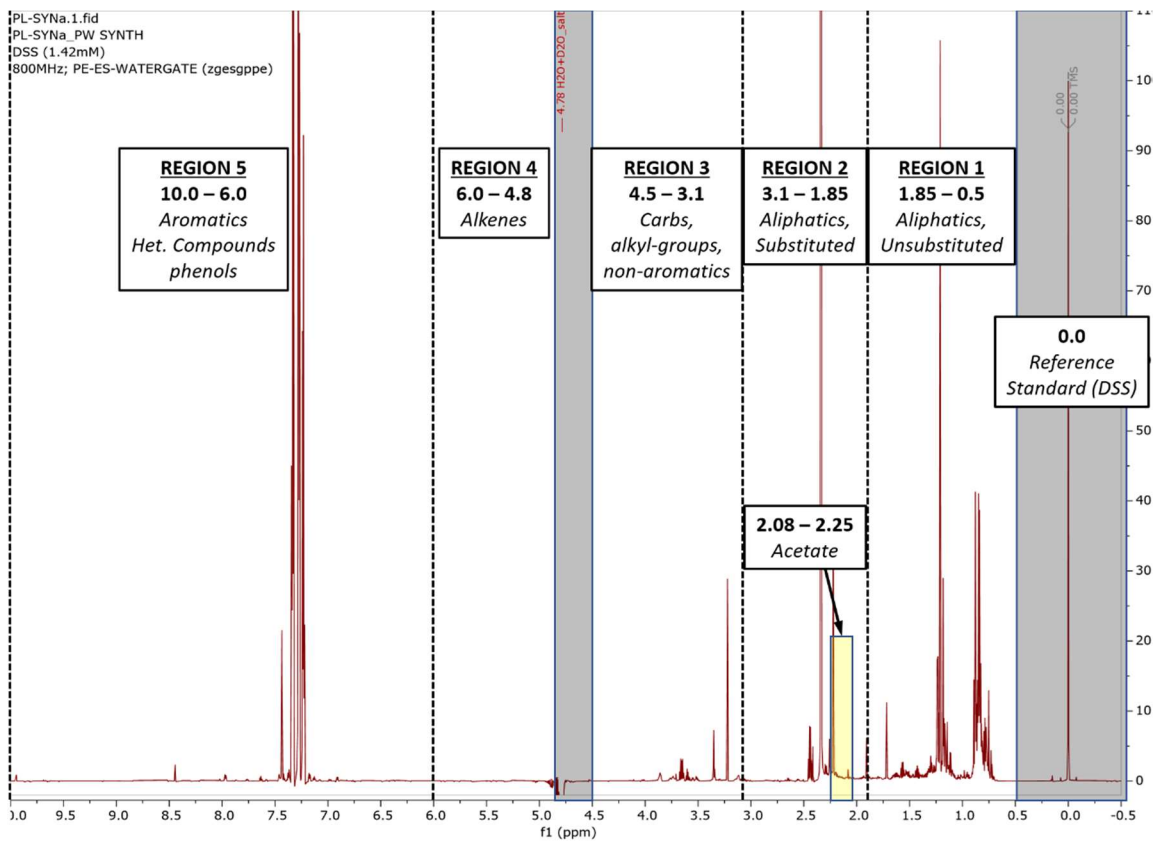


Figure 5. NMR spectrum of the synthetic produced water sample. X-axis spectral bins are shown and identified based on what types of organic compounds they generally represent. Additional callouts for the DSS standard and acetate signals are shown. Areas highlighted in red were not considered for any type of organic compound quantification.

CHAPTER IV

RESULTS

Synthetic Produced Water

The spectrum of the synthetic sample identified 92 distinct peaks (Figure 6). 56% of detected peaks were found within Regions 1 and 2 (43% and 13% respectively). 13% of peaks were detected in Region 3 (non-aromatic compounds), and the remaining 30% of peaks were found in Region 5 (aromatics). No peaks were found in Region 4 (alkenes). The percentage of each region largely falls within the expected ranges for Natural Gasoline, though Region 4 alkenes are the exception. Officially, natural Gasoline should contain approximately 6-9% alkenes by composition.

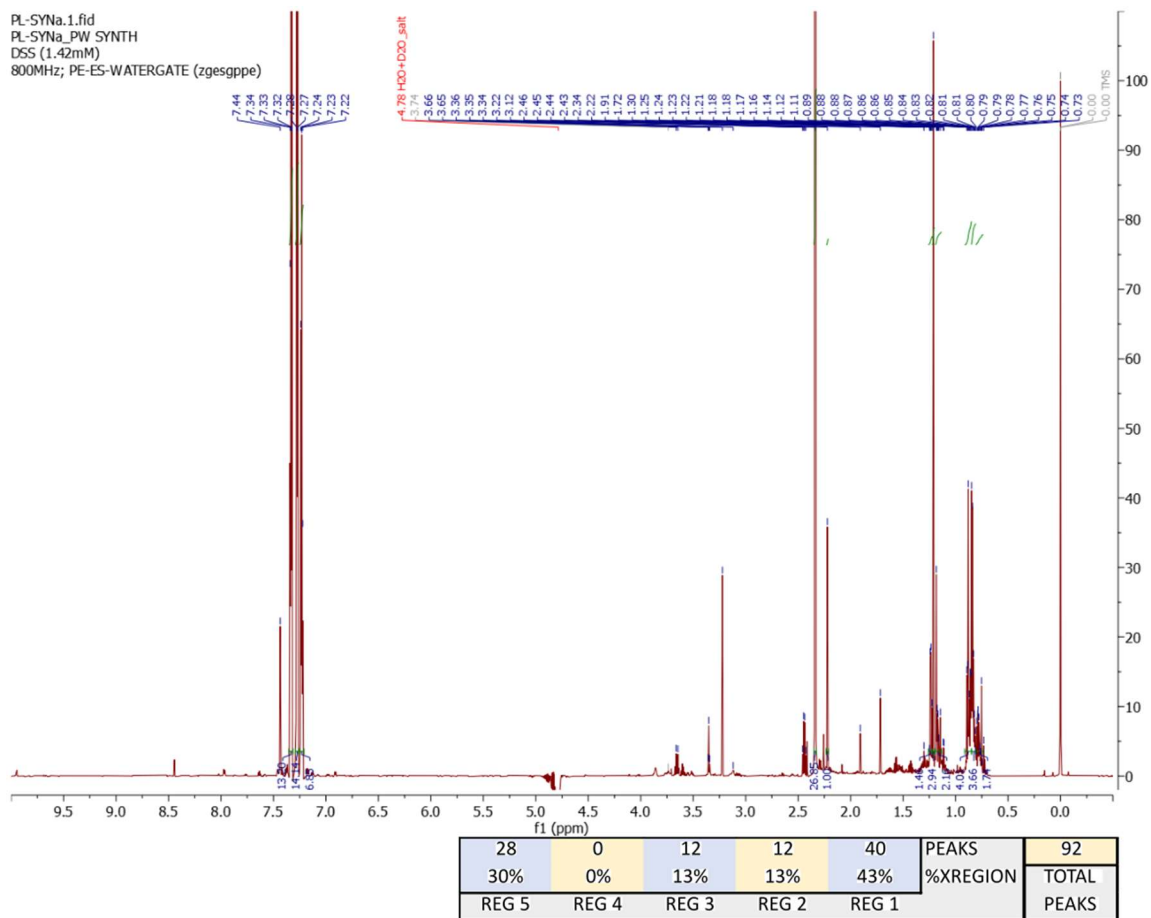


Figure 6. NMR spectrum of the synthetic produced water sample (PW SYNTH) along with raw peak counts and percentages for each binning region. Result was generated using the N800/WATERGATE NMR experimental regimen.

Black Warrior Basin – Initial Analysis

NMR spectra collected using the A400/noesy- experiment indicated that the produced water samples from the Black Warrior Basin had not decomposed or been altered in any significant way, since their initial collection and analysis in 2016 (Figure 7). Any observed differences were concluded to have come from changes in spectra processing or variations in experimental parameters. While this was encouraging, several drawbacks came to light regarding the methodology. Due to the low concentration of organic compounds relative to water volume, it took approximately three and a half hours of test time to build up interpretable compound signals. Because water also produces a

signal in NMR analysis, the long experiment time greatly amplified its signal, to the point where it could obscure signals from nearby organic compounds. Finally, it was discovered that this experiment had suppressed certain compound signals, specifically peaks located in Region 5 (6.0-10.0ppm). It is suspected that the pre-saturation portion of the noesy- experiment inadvertently suppressed certain functional groups present in these compounds. Specifically, these functional groups could exchange their ^1H -protons with ^2H -protons, which would not be detected on a ^1H -NMR experiment.

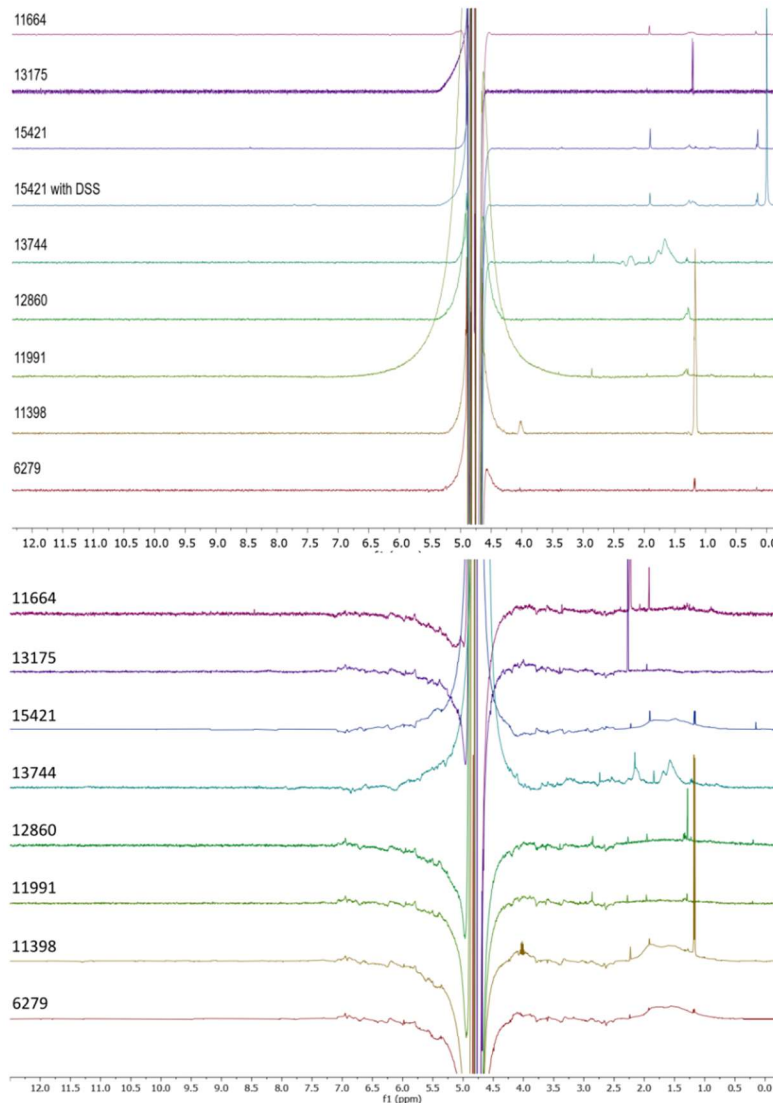


Figure 7. NMR spectra of Black Warrior Basin produced water samples, from initial analysis in 2016 (top) and most recent testing (bottom). There appears to be no significant differences between the two sets of results – any observed differences in spectra were concluded to have come from variations in testing parameters. Spectra were obtained using an A400 NMR running a noesygppr1d water suppression experiment. Of note is that the water signal, centered at approximately 4.75ppm, is significantly larger than the organic compound signals, and potentially obscures them. Suspected phenol compound signatures found between 6.5 and 8.5ppm also appear suppressed. One additional observation is that there appears to be a large region (~2.6 – 7.3ppm) on either side of the water peak where the baseline on either side distinctly mirrors one another. This may be an artifact of the water suppression, in which case the noesy- suppression experiment would be a suboptimal NMR experiment, as it introduces false peaks and obscures real ones.

Black Warrior Basin – Primary Analysis

Examination of Black Warrior Basin samples with the N800/WATERGATE experiment regimen corroborated the conclusion of the initial testing, that there did not

appear to be an appreciable change in organic composition despite the samples' age. Compared to the initial analysis, the solvent peak was effectively suppressed without accidentally suppressing aromatic functional group signals (Figure 8). The suppressed solvent peak had a midpoint at approximately 4.7ppm, though the exact location varied slightly by +/-0.2ppm. Median peak count across the sample set was 17 with an average count of 20; the overall range varied between 7 and 44 recorded peaks (Table 5). The majority of signals are located in Regions 1 and 2 (0.5 – 1.85ppm; 1.85 – 3.1ppm), which makes up approximately 57% to 87% of all detected peaks in the sample set (Table 5). Signals were detected in Region 3 (3.1 – 4.5ppm) and comprised the majority of the remaining peaks in each sample, up to 50% of all detected peaks in one case. Three samples had additional minor signals in Region 5 (6.0 – 10.0ppm). No peaks were ever detected in Region 4 (4.8-6.0ppm). The peaks in Regions 1 and 2 are interpreted as likely belonging to hydrogens of alkanes, allylic alkenes and other aliphatic compound classes. Smaller peaks observed between 7.5-8.5ppm are interpreted to be phenolic hydrogens, based on previous work characterizing the Black Warrior Basin (Pashin et al. 2014). In Regions 1 and 2 there frequently was a low but consistent “hump” in the baseline. This was interpreted as being conceptually similar to an unresolved complex mixture (UCM), frequently described in GC/MS studies of organic compound mixtures. As results pertain to acetate, no clear signals were detected in sample spectra, indicating that it was not uniquely enriched in the basin.

Table 5. Spectral classification results for the Black Warrior Basin produced water sample set. Region averages of spectra are also shown, based on the TDS of the respective samples. The synthetic produced water sample is also included as a point of reference to a defined composition of organic compound types. It is NOT included in any region average calculations.

SAMPLE SET	WELL ID	TDS (mg/L)	TOTAL PEAKS	REGION 1%	REGION 2%	REGION 3%	REGION 4%	REGION 5%
SYNTH	Tru-Fuel	n.d.	92	43%	13%	13%	0%	30%
	6764	2216	44	52%	30%	18%	0%	0%
	15421	2248	30	47%	13%	40%	0%	0%
	11496	3485	22	55%	9%	36%	0%	0%
	11987	4356	17	41%	41%	18%	0%	0%
	11398	5243	21	48%	10%	43%	0%	0%
	12006	6810	22	27%	41%	32%	0%	0%
	11238	11140	14	50%	7%	43%	0%	0%
	6279	11824	9	44%	11%	44%	0%	0%
	5682	15506	11	27%	18%	45%	0%	9%
	11664	15801	18	50%	33%	17%	0%	0%
	13744	20440	29	48%	24%	21%	0%	7%
	15089	23119	10	40%	40%	20%	0%	0%
	14091	26984	16	38%	13%	50%	0%	0%
	6189	32955	47	45%	23%	21%	0%	11%
	13175	38235	7	43%	29%	29%	0%	0%
	12860	45431	15	60%	27%	13%	0%	0%
	11991	46210	15	40%	47%	13%	0%	0%
TDS<10000 Averages		4060	26	45%	24%	31%	0%	0%
TDS>=10000 Averages		26150	17	44%	25%	29%	0%	2%
Total Averages		18353	20	44%	24%	30%	0%	2%

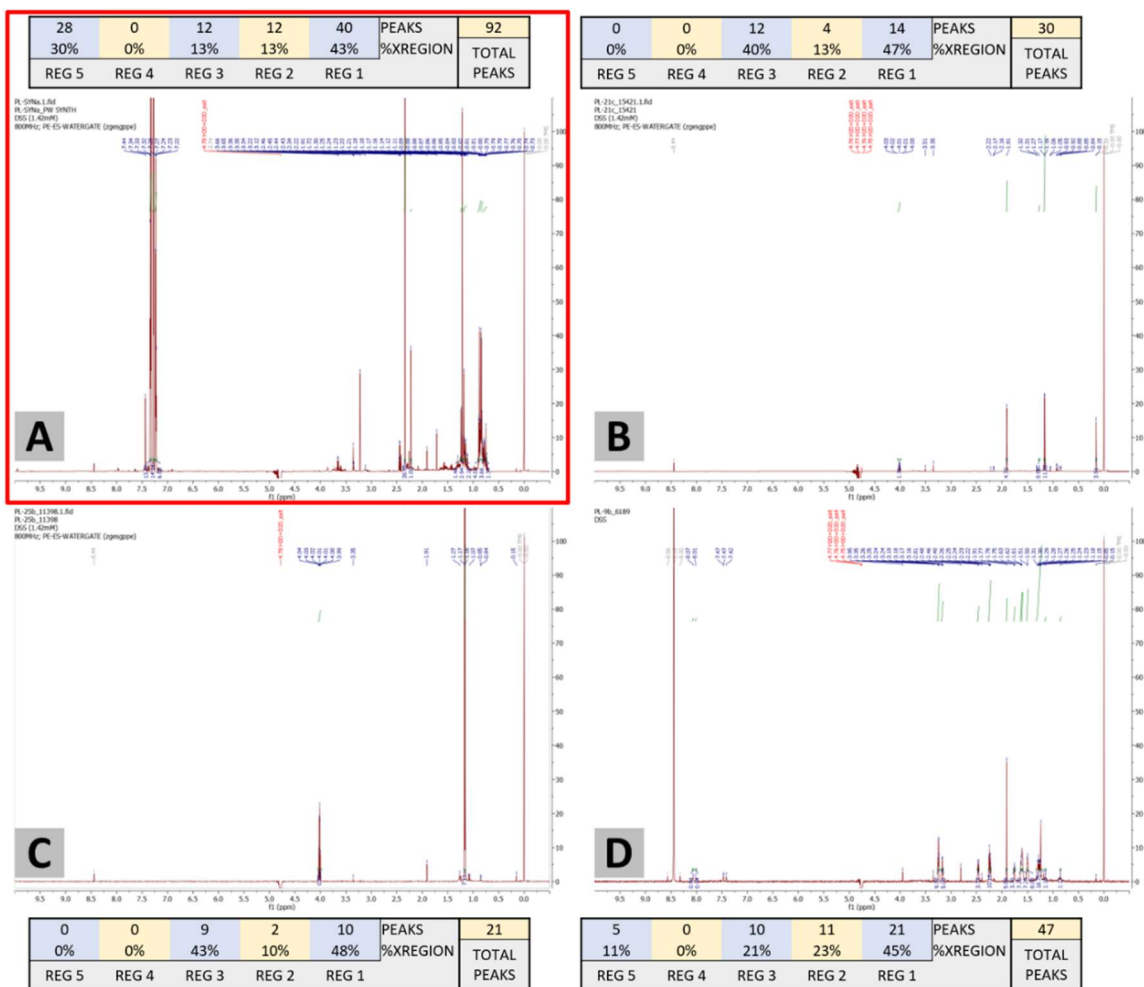


Figure 8. NMR spectra of produced water from wells in the Black Warrior Basin as well as the synthetic produced water sample A, highlighted in the red box. Spectra was obtained using the PE-ES-WATERGATE NMR experiment run on a Bruker N800 NMR. Compound signals present are broadly representative of the full range of organic compounds present within the BWB sample set. The three other spectra are representative of the samples in the set which have TDS below 10,000mg/L (B, C, Well ID 15421 and 11398 respectively), and above 10,000mg/L (D, Well ID 6189), and highlight the broad morphological differences between samples in the set.

Anadarko Basin

Twelve samples of produced water from the Anadarko Basin in Oklahoma were analyzed using the N800/PE-ES-WATERGATE NMR methodology. Compared to the Black Warrior Basin sample set, there were generally more detected compound peaks, with a median peak count of 66, averaging 98 peaks per spectrum across the sample set. The range of peak counts was more extreme than the Black Warrior Basin, with a minimum peak count of 19 and a maximum of 291 (Table 6). On average, peaks were

distributed slightly more evenly across the entire spectrum, and peak intensities were generally higher than the BWB sample set, based on comparison to the reference standard (Figure 9). However, a summed average of 91% of all detected signals still fell within Regions 1, 2 and 3 (Table 6). Region 1 aliphatic compound signals comprised between 21% and 47% of organic compound peaks within a sample. Region 2 ranged from 19% and 37% of signals. Within Region 3, carbohydrate and other non-aromatic compound signals ranged between 20% and 42% of total detected peaks, with one sample (5207) having a particularly low percentage of 8%. By comparison, few alkene compounds displayed peaks in Region 4, with at most 4% of total signals presenting in that region. Finally, Region 5 aromatics made up anywhere from 0% to 24% of all compound signals within a sample. As results pertain to acetate, no clear and out-sized signals were detected in sample spectra, indicating that it was not uniquely enriched in the basin.

Table 6. Spectral classification results for the Anadarko Basin produced water sample set. Region averages of spectra are also shown and are divided into two groupings based on their subset. The third grouping is the total region averages across the entire Anadarko sample set. The synthetic produced water sample is also included as a point of reference to a defined composition of organic compound types. It is NOT included in any region average calculations. Also note that TDS information was not included for this sample set as it was not collected.

SAMPLE SET	WELL ID	TOTAL PEAKS	REGION 1%	REGION 2%	REGION 3%	REGION 4%	REGION 5%
SYNTHETIC	Tru-Fuel	92	43%	13%	13%	0%	30%
ANADARKO	1509 SWD	47	21%	36%	38%	0%	4%
LAGOON	Mudbug SWD	73	44%	30%	22%	0%	4%
	Vecta	291	43%	26%	20%	1%	10%
	LDC 23/26	59	29%	31%	36%	0%	5%
	2202	202	27%	18%	42%	4%	10%
ANADARKO OSU	Apache 1102	79	23%	37%	23%	3%	15%
	Apache	29	41%	34%	21%	0%	3%
	2201	19	53%	21%	26%	0%	0%
	PW #3	118	47%	19%	29%	0%	4%
	5210-5211	33	36%	24%	33%	0%	3%
	Wilkerson 1-20-H	195	29%	23%	29%	4%	15%
	5207	37	38%	27%	8%	0%	24%
AVERAGES	Lagoon Averages	60	33%	33%	30%	0%	4%
	OSU Averages	106	37%	26%	27%	1%	9%
	Total Averages	98	36%	27%	27%	1%	8%

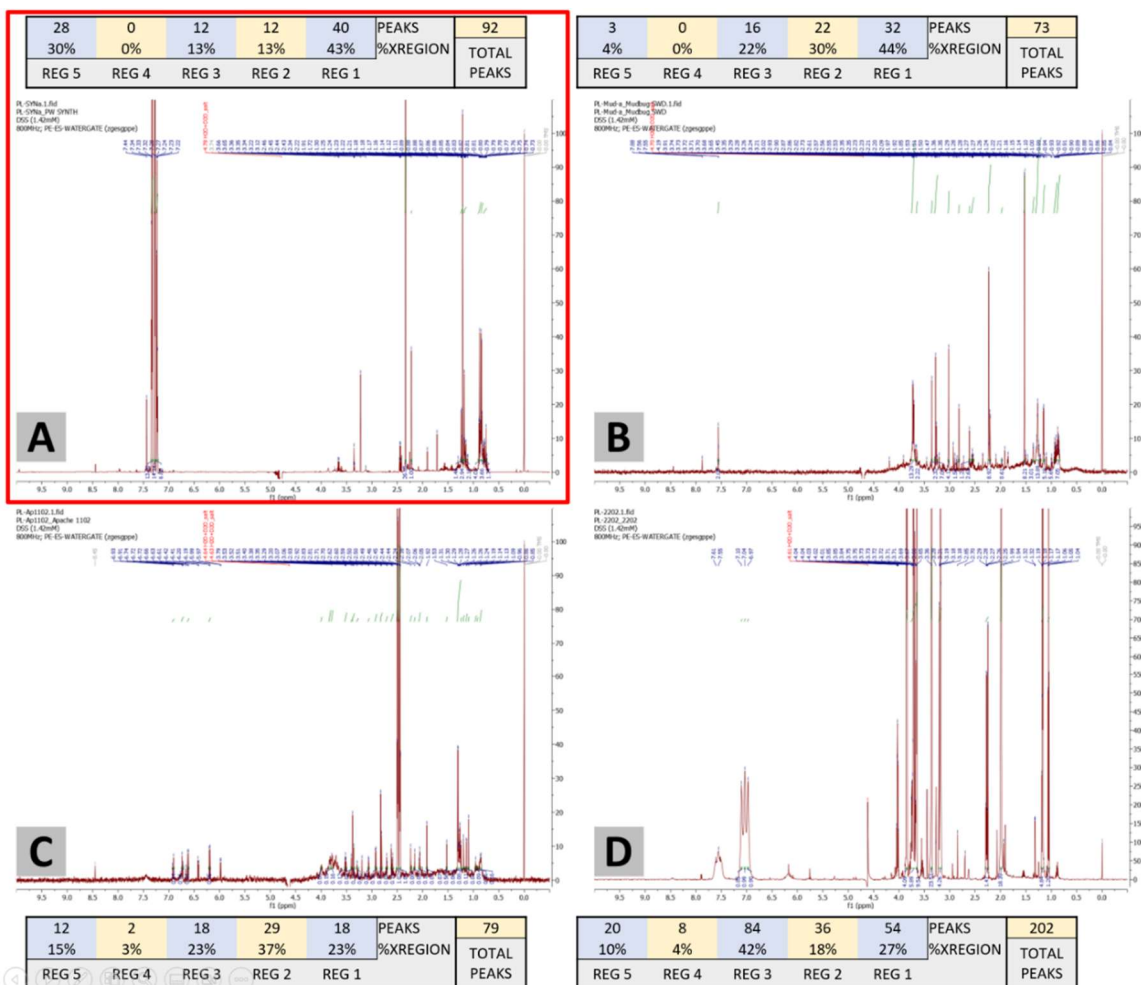


Figure 9. NMR spectra of produced water collected from the Anadarko Basin ,OK, as well as the synthetic produced water sample A, highlighted in the red box. B (Mudbug SWD) and C (Apache 1102) are PW sample from the two different sample subsets, Lagoon subset and OSU Engineering subset respectively. These subsets were collected at different locations, times and circumstances. Nevertheless, both show a morphologically similar UCM and positioning of peak clusters. Signal intensities are also comparable. D (2202) is from the same subset as C but shows a significantly different spectral profile. Peak clusters are still located in roughly the same spots along the x-axis, though in C, Region 2 holds a smaller percentage of identified peaks than Region 2 in D. The inverse is the case for Region 3 between the two. Peak intensities are much higher than the reference standard for D. In every case however, the majority of identified peaks were found in Regions 1-3 (0.5 to 4.5ppm), with occasional signals in Region 5 (6.0 to 10.0ppm).

CHAPTER V

DISCUSSION

NMR Analysis for Produced Water

NMR is capable of reliably analyzing samples of produced water that have not been pre-processed, beyond filtration of colloidal material. Many analysis techniques usually alter the sample in some way, whether during analysis itself or as a sample preparation requirement. The methodology utilized throughout this research indicates that a more complete profile of organic compounds within PW can be acquired. It would be necessary to understand the exact compound composition beforehand to make assertions as to whether it is capturing a full profile of organic compounds. However, we can say with some confidence that fractions of DOM are being detected that would otherwise be overlooked. Oftentimes, the presence of salt can seriously impede an instrument's operation, sometimes to the point of failure. Even if it can operate, results can be skewed/obfuscated to varying and unpredictable degrees, limiting a results' usefulness. NMR is no different in this respect. However, it is shown here that with proper methodological planning, the challenges salt pose can be overcome. As it pertains to NMR, salt makes it increasingly difficult to acquire ideal locking, shimming, and tuning of the instrument on a sample.

It also will shift the location of compound peaks beyond the ranges they would be found in normally. However, even with relatively high salt content NMR can still successfully analyze produced water samples and generate a useable result. The raw spectrum will not be “ideal” and will require more attention during processing than less saline samples. However, spectra can still be corrected, particularly through the use of a reference standard. It’s known quantity and peak shape can be used as a guide to determine how much correcting a particular sample spectrum needs. Using a reference compound can also mitigate the effect of chemical shift due to saline interference. The compound used in this study for example, DSS, has a defined position on a spectrum at 0.0ppm. Salt shifts every peak in a spectrum, so it is a simple matter of processing to shift compound peaks to their true locations, using the reference standard. Additionally, previous work has demonstrated that the chemical shift from salinity can be predicted. Between this and the known position of a reference, NMR spectra can be effectively corrected to ensure that compound peaks are being accurately represented (Kirkland 2021).

X-Axis Binning Validation

For direct studies of produced water, the binning technique implemented by Zhang et al. 2021 for SPE-treated produced water samples also works studies using unprocessed samples. The binning concept itself was derived from studies of fluvial and marine dissolved organic matter (DOM) (Guéguen et al. 2012; Hertkorn et al. 2013). This suggests that the concepts and analysis methods in those kinds of studies are valid in PW studies as well. For the synthetic produced water sample derived from Natural Gasoline, each binning regions’ peak percentages fell largely within the expected ranges outlined by the CAS registry and EPA. This suggests that our analysis methodology of unaltered

produced water can create accurate profiles of the organic compounds that might be found dissolved therein, regardless of compound size, polarity, or phase preference. There is one major exception to this that needs to be investigated first, before this binning technique might be considered fully vetted. As a group, alkenes were virtually non-existent in any produced water sample, whether it originated from the Anadarko Basin, Black Warrior Basin, or was created synthetically. Natural Gasoline officially contains 6-9% alkenes (ChemicalBook 2017). However, the NMR spectra of the synthetic sample showed no signals of any kind in that region. As a rule-of-thumb, alkenes are not typically water-soluble. As a group they are non-polar which makes it difficult to extract them into that phase. Regarding the reference sample, organic compounds were moved to the water phase using only physical agitation. While it's possible this mixing was not enough to capture alkene compounds, it did appear to be enough to capture at least some alkanes and aromatics. These compound types are also typically non-polar. It remains unclear whether the supposed 6-9% alkene content of Natural Gasoline is in fact present at all, or if the alkene fraction is particularly resistant to entering the water phase. The latter is certainly possible, as alkenes are more typically found as long-chained compounds, which can be extremely water-insoluble (Zhang et al. 2021). Ultimately, additional testing would need to be performed to determine the exact cause for alkenes' absence.

Fortunately, as this absence applies to the produced water samples, there is a bit more clarity. As natural systems go, long-chained alkenes are not normally associated with petroleum, natural gas, or coalbed fields, and at least in the case of the Black Warrior basin, no specific alkene compounds were ever recorded (Pashin 2007; Orem et

al. 2014). Where they do exist, they are a by-product of pyrolysis (Zhang et al. 2021). Alkenes are more common in surface water systems, where comparatively fresh organic matter dominates, and the breakdown of such matter generates alkenes in the form of fulvic acid (Guéguen et al. 2012). NMR as a technique has previously been shown to detect alkenes as well as any other type of compound, so it is unlikely that their absence is a consequence of methodological deficiencies (Hertkorn et al. 2013). It may be that there are simply no alkenes to detect in the produced water samples, or that they are in such low concentration that their signals were obscured by the spectra baselines. It would be prudent to verify the results of the NMR with another method, to confirm if this is the case.

Black Warrior Basin

It was posited earlier in this report that the prior analyses of Orem et al. 2014 and Pashin et al. 2014 only captured a partial profile of the various types of organic compounds present throughout the basin. In those studies, aromatic compounds were found to comprise the bulk of recorded organics. The numerical results of this study are in contradiction to those ones. Only 3 of the 17 samples in the set (5682, 13744, 6189) showed any evidence of aromatics (as represented by the percent of total peaks detected contained within Region 5). The share of aromatic peaks was very small for these samples, with Region 5 percentages of 7%, 9% and 11%. When compared to the synthetic sample, individual aromatic signals were both fewer in number as well as intensity. Region 3 had a higher average share of peaks, ranging from 13% to 50% of the total peak count for a given sample. This is despite the region peak count being low throughout the set as well. Therefore, this higher Region 3 percentage is likely not a

result of more signals being detected there; rather, it is a calculation artifact caused by the of signals in Region 5.

As previously discussed, there is an inverse relationship between the concentration of salts and the overall intensity of NMR signal peaks (Kirkland 2021). The NMR spectra of the Black Warrior Basin produced water would seem to follow this trend. 6 of the 17 samples in the set (6764, 15421, 11496, 11987, 11398, 12006) had TDS values under 10,000 mg/L, and in these six, numerous, low-intensity peaks were detected throughout all spectra regions and comprised a significant proportion of the overall peak count in each sample. However, there is a major obfuscating factor. The reason TDS was low in these six was due to fresh surface water entering the deeper basin strata and entraining the older groundwater (Pashin 2007). This entrainment would likely reduce the DOM of any produced water in this part of the basin or alter its chemical profile. Flushing the groundwater could reduce the presence of colloids and by extension, aromatic compounds (Orem et al. 2007; Pashin et al. 2014). In the six samples with TDS <10,000 mg/L, no peaks were ever identified in Region 5. However, the rest of the samples, presumably not greatly affected by freshwater flushing, also lacked significant aromatic signatures – only three samples had any sort of Region 5 signal, and no consistent trend could be established between them. It may not be only natural freshwater flow that could reduce organics signals. Orem et al. 2014 postulated that the reduction in signal quantity year over year was indicative of the produced water near organics-rich coalbeds being pumped away during the course of natural gas extraction. The groundwater which replaced it in those pores would not have as much time to dissolve

the organic compounds in the rock matrix, and consequently when that water was pumped out, it would appear less contaminated.

Anadarko Basin

Supplemental information pertaining to individual produced water samples, such as location, TOC or DOC, was not collected, so unfortunately specific trends between TDS, DOM and organic compound class cannot be interpreted like they could be with the Black Warrior Basin sample set. However, more general assessments can still be made regarding the produced water in the set. TDS is generally much higher in the Anadarko Basin, up to 185,000 mg/L in places (Collins 1969). There is evidence to suggest that this influenced the result NMR spectra – 5 of the 12 samples in the set – Vecta, PW#3, 2202, Wilkerson 1-20-H and 5207 – had numerous peak intensities much greater than in the reference standard, while the rest had intensities below or equivalent to the reference. Additionally, those five sample spectra generally had a greater number of peaks in a wider range of positions, morphologically speaking. As for the others, they can be divided into two additional groups. Four of the remaining 7 samples displayed numerous low-intensity peaks, most of which were riding atop a distinct UCM found between 0.5ppm and 4.5ppm (Regions 1-3) (Figure 10). The remaining three samples – 2201, 5210-5211 and Apache – had the lowest peak counts of the sample set, with 19, 32 and 29 recorded peaks respectively. They also had an indistinct UCM presence. However, the peaks that were present were pronounced and easily identifiable from the baseline or each other. The four spectra which had similar spectra are of particular note due to the fact that only two of them had known collection locations, collected from disposal sites west of Okarche, OK in the heart of the STACK. That the other two with unknown locations had

very similar spectra could be an indication that they originated from the same area. At the very least, their respective produced waters could be coming from the same hydrologic body. Further investigation would be prudent to determine this relationship.

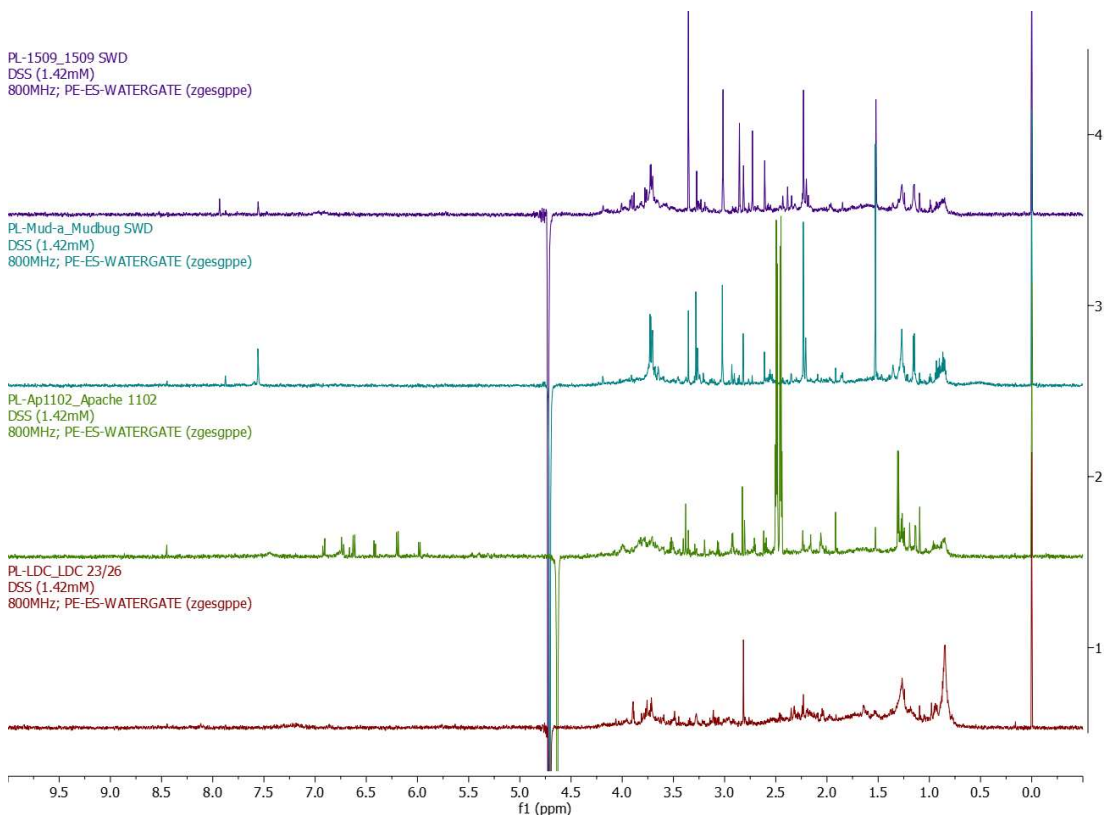


Figure 10. Stacked $^1\text{H-NMR}$ spectra of four samples from the Anadarko Basin, OK. All four showed similar morphology: numerous identified peaks, peak intensities around or below reference standard intensity, and a distinct UCM which most of the peaks in each spectra ride atop. To note, the spatial collection locations are known for 1509 SWD and Mudbug SWD, while they are not for Apache 1102 and LDC 23/26. It may be then that the two unknowns originated from the same area as the two knowns, or at least they are related hydrogeologically. Additional information will be needed to say for sure, however.

As with the Black Warrior Basin, Region 5 aromatics were depleted relative to the synthetic sample. Region 5 percentages ranged between 0% to 24%, with an overall average of 8%. This sample set was also filtered of colloids prior to analysis, so the possible reasons for this depletion are likely the same as the Black Warrior Basin (removal of colloids may have removed aromatic compounds)(Orem et al. 2007). Interestingly, Region 3 peak percentages were also higher than in the synthetic sample,

with percent values ranging between 21% to 42% (with one low outlier at 8%), averaging to 27% across the sample set. This is in spite of Region 5 generally having a greater proportion of recorded peaks in a given sample. The conclusion here is that both basin sample sets have Region 3 composing a higher proportion of peaks in a sample than the synthetic baseline; however, the pathways by which this occurs are different. In the Black Warrior Basin, Region 3 is “enriched” due to a calculation artifact consequent of Region 5 being essentially devoid of any peaks whatsoever. In the Anadarko Basin, it appears that produced water is genuinely enriched with Region 3 compound types.

Anadarko Basin Region 2 also appears to hold a higher percent of identified peaks. Compared to the synthetic sample Region 2 value of 13%, the Anadarko Basin sample set values ranged from 18% to 37%, averaging at 27%. As with Region 3, region peak counts were higher, so these percentages are not a side-effect of some other thing. Regarding the types of compounds present, this suggests that aliphatic compounds make up the bulk of the DOM present in the Anadarko Basin produced water, with specific enrichment of unsaturated alkanes, possibly containing carbon substitutions in their structure.

Improvements to Sample Collection, Preparation

The core methodology pertaining to sample collection and preparation is sound and has been used in numerous studies of marine water, and a few of produced water. However, more extensive investigations of this kind may wish to consider accounting for the following:

Impact of Colloids and Particulates

The only preparatory action performed on the PW samples was to filter out colloidal material, as they could potentially negatively impact NMR analysis. However, it suggested that this material may serve as a natural fractionating mechanism for organic compounds (Orem et al. 2007). Therefore, its removal could impact the composition of organic compounds in a sample. PAHs are particularly vulnerable to this, as they are a class of volatile compounds which generally do not prefer aqueous phases. They may preferentially adsorb to colloids as a consequence (Orem et al. 2007). The benefit of this is that PAHs are stabilized when in an aqueous solution, and less likely to volatilize. However, by filtering out colloidal material this fraction may be lost (Krüger et al. 2011). Therefore, it may be worth investigating the influence colloids have on the detection of organic material, PAHs specifically. Given the importance paramagnetic effects have on NMR analysis, exploring colloids impact here may also be prudent, particularly since produced water nearly always comes in contact iron or other paramagnetic ions at some point during its recovery (Kirkland 2021).

Change in Compound Composition over Time

Larger studies of produced water should consider analyzing the change in compound composition over time. Prior investigation of Black Warrior basin PW indicated that the overall composition of samples, taken from the same locations but on different dates, changed over the span of a year (Orem et al. 2007). In that study, the change was attributed to groundwater recharge from younger, freshwater sources. This effectively “flushed out” the groundwater and its containing aquifers, reducing the DOM volume in produced water (Orem et al. 2007). Colloids were particularly affected by this.

Given the proposed relationship between colloids and PAHs, certain classes of organic compounds might be more affected than others. Each basin has its own unique sources of hydrocarbons, organic compounds in general, and hydrogeology. Establishing produced water trends over time could be beneficial to long-term management of produced water.

Ultrafiltration of Produced Water

Ultrafiltration is one of the numerous methods for separating a solution into distinct fractions. However, instead of concentrating compounds by chemically selecting them or removing water, UF separates samples based on molecular size. Essentially, a solution is forced through a membrane filter whose pores are of a specific size. Molecules smaller than the pores will tend to pass through the filter, while molecules larger will be retained. With the prudent choice of filter material and pore size for example, salts can be removed from a solution while other compounds are retained (Wandera et al. 2011). UF is commonly used to isolate proteins, or to characterize dissolved organic matter (DOM) in ocean water. However, there are very few publications which describe its use as part of a produced water study. One such study has indicated that UF can successfully separate polar aliphatic functional groups such as carboxyls, hydroxyls and phenols with molecular weights greater than 100kDa (Sun et al. 2021). Additional research describing the advantages and limitations of using UF for produced water characterization could be a beneficial path for future investigation. It is posited that UF may be an effective method for “picking apart” UCM, and isolating compounds or groups of compounds which can adversely affect human health. Specific compounds of interest would include phenol compounds, tributyl phosphate, dodecanoic acid and naphthalene. These compounds have previously been identified as toxic to humans (Danforth et al. 2020), and have also

previously been identified in available PW samples (Pashin et al. 2014). Additionally, each of these compounds have molar masses greater than common salts such as sodium chloride or sodium bicarbonate. With proper experimental design, it is hypothesized that these compounds, and other low molecular-weight UCM compounds could be retained and described, while simultaneously removing the salts which make analysis more difficult across the board.

Spectra Quantification using the Y-axis

In $^1\text{H-NMR}$, the y-axis technically does not exist – the y-axis values present in spectra are considered arbitrary and unitless. On their own, they are useful only in internal comparisons of hydrogen quantities. While imperfect, the presence of a compound with known quantity (reference standard) opens avenues for improving whole-water NMR analysis of produced water. With an expanded analysis methodology, it may be possible to meaningfully quantify organic compound concentrations, at least on a class basis. Depending on the desired goal, compound quantification using $^1\text{H-NMR}$ spectra could take a few approaches. One possible method would be “Y-Axis Thresholding”. Conceptually, this is a straightforward assessment of organic compound quantity which utilizes the same sort of binning methodology used to qualify organic compound classes along the x-axis. A hypothetical quantification design could create certain thresholds along the y-axis of an NMR spectrum, determined as some percentage of the DSS peak (setting the DSS peak to an intensity value of 100 simplifies this process) (Figure 11). Peaks could then be tallied in the same manner as the x-axis binning. Combining both x- and y-axis binning could allow for a sort of “heat map” to be created, which could provide an at-a-glance fingerprint of a produced waters’ organic compound types and

quantities. While this process might be easy to do, a potential drawback would be that this method would not be able to discriminate between PW samples from the same source but at different concentrations. If a raw quantity assessment is all that is required, then this may be less of an issue, but past that different quantification strategies would need to be explored.

WELL ID	FIELD	LATITUDE	LONGITUDE	TDS	TOC	DOC
Tru-Fuel	N/A	N/A	N/A	n.d.	n.d.	n.d.
0	0	0	1	0	1	Y>=500
1	0	0	0	0	1	Y>=200
3	0	0	0	1	4	Y>=100
5	0	2	6	22	35	Y>=5
1	0	3	2	9	15	Y>=2
16	0	6	3	8	33	Y>=0.5
2	0	1	0	0	3	Y<0.5
28	0	12	12	40	92	TOTAL
XREG5	XREG4	XREG3	XREG2	XREG1		PEAKS
0%	0%	0%	1%	0%	1%	Y>=500%
1%	0%	0%	0%	0%	1%	Y>=200%
3%	0%	0%	0%	1%	4%	Y>=100%
5%	0%	2%	7%	24%	38%	Y>=5%
1%	0%	3%	2%	10%	16%	Y>=2%
17%	0%	7%	3%	9%	36%	Y>=0.5%
2%	0%	1%	0%	0%	3%	Y<0.5%
30%	0%	13%	13%	43%		
%XREG5	%XREG4	%XREG3	%XREG2	%XREG1		

Figure 11. Theoretical design of a y-axis quantification scheme, created from spectrum information of the synthetic sample. Each identified peak is placed in a bin according to its' position (ppm) and intensity values (left). This is converted into a heatmap (right) which can provide an at-a-glance assessment of both types of organic compounds present, as well as their quantities. A drawback of this method is that it may not be able to differentiate between two different concentrations of the same sample without that knowledge being available prior.

Another possible way to quantify NMR spectra would be a Peak Ratio Assessment. In most NMR spectra of produced water, there are at least a few signal peaks which are clearly defined and have much greater intensity than the rest. It is also not uncommon for specific peaks to present in identical positions in spectra across a sample set. Hypothetically, the peak intensity values could be used as the basis for creating spectral ratios, that could serve as a unique “fingerprint” for a sample. Such a technique to produced water would likely be challenging, given that the extreme heterogeneity of produced water samples makes it difficult to identify specific single peak positions. However, if successfully implemented this method could be a more nuanced assessment of organic functional groups and could determine the ratios between various peaks in a spectrum as opposed to simply tallying peak intensities. This quantification technique would work best with large sample sets, particularly from the same basin. That way, a complete x/y spectra analysis would create a map of what sorts of organic compounds are present, how much there is, and where it came from.

Conclusion

This study investigated NMR’s capability to efficiently analyze unaltered samples of produced water, as well as qualify the types of organic compounds contained in solution. Thirty samples of produced water, 17 from the Black Warrior Basin, AL and 12 from the Anadarko Basin, OK, along with a synthetic sample derived from pure Natural Gasoline were examined using a PE-ES-WATERGATE NMR experiment. These samples were unaltered in any way, except for an initial vacuum filtration to remove particulate and colloidal material. Each result NMR spectrum were then divided into five “regions” based on position along the x-axis, representing broad classes of organic

compounds. The number of identified peaks in each region were tallied and peak percentages for each region were tabulated, which in turn were used to assess broader, basin-scale trends. The x-axis binning schema was shown to work with unprocessed produced water samples, as the region percentages in the synthetic sample were in line with prior information regarding Natural Gasoline. Future improvements to this line of research should focus on some type of y-axis assessment of compound peaks, with the intent of providing a more nuanced analysis of compound classes and their variation over time and space. Improvements to the sampling regime may also be warranted, specifically to include colloidal material which may impact the detected presence of aromatic compounds. Finally, while it has been shown that high salt content does not disable NMR analysis, techniques for removing this salt without greatly altering the organic compound content should be investigated as well. At the very least, some assessment of the error introduced by salt should be examined and quantified.

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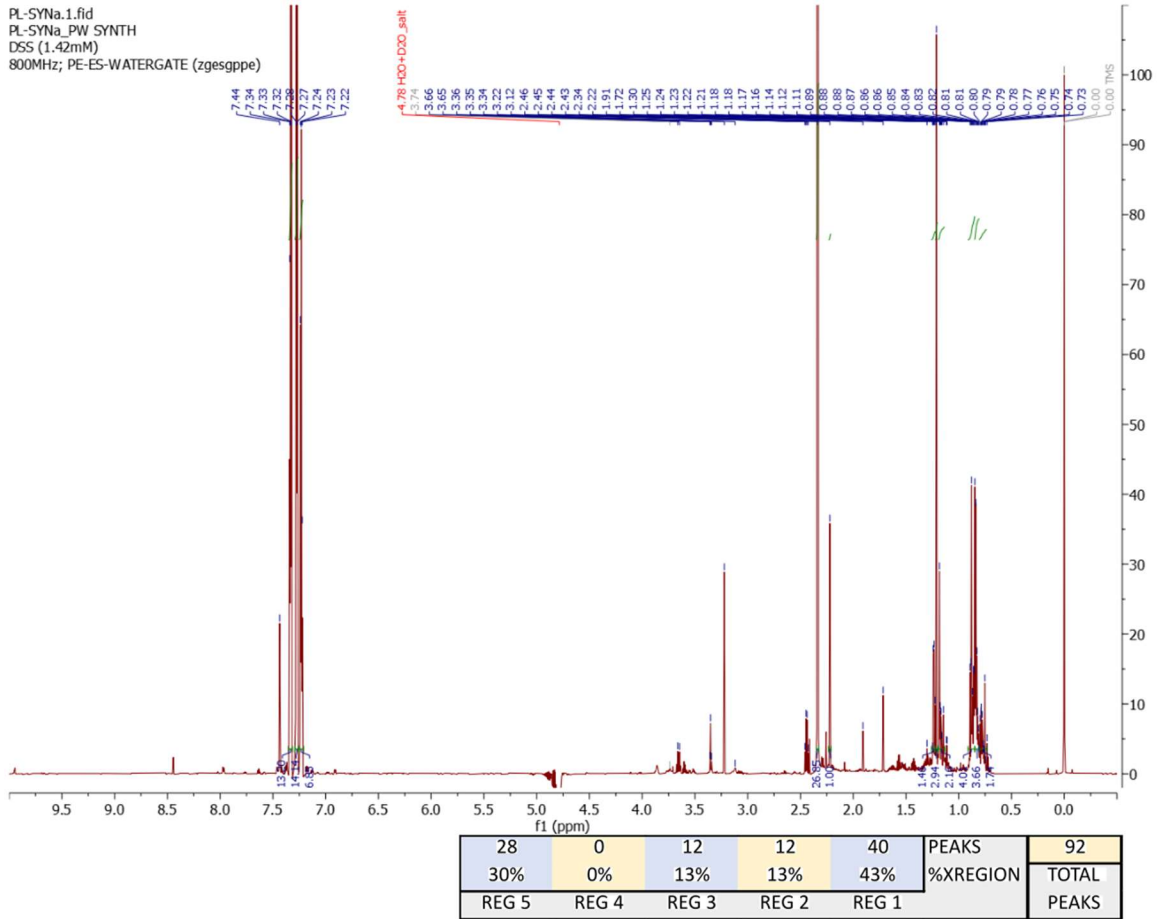
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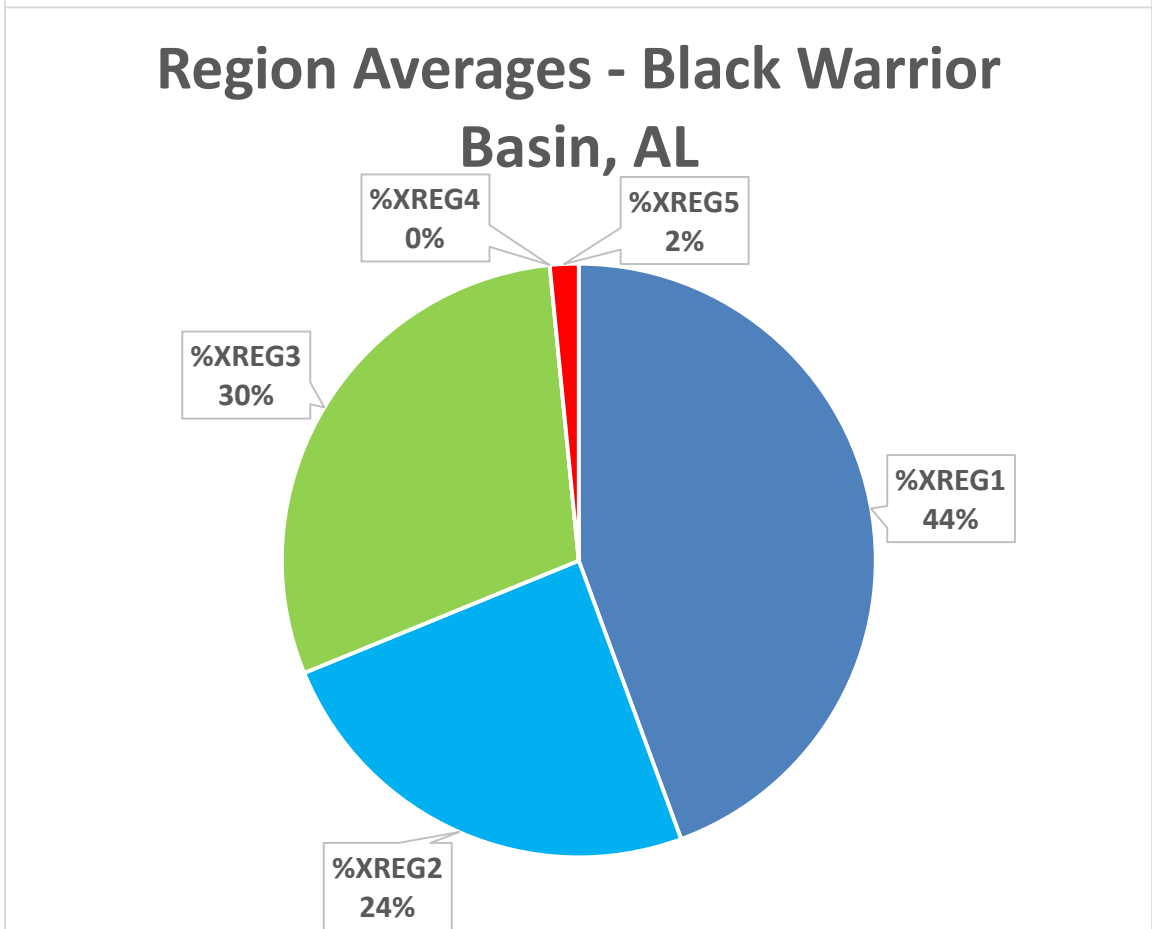
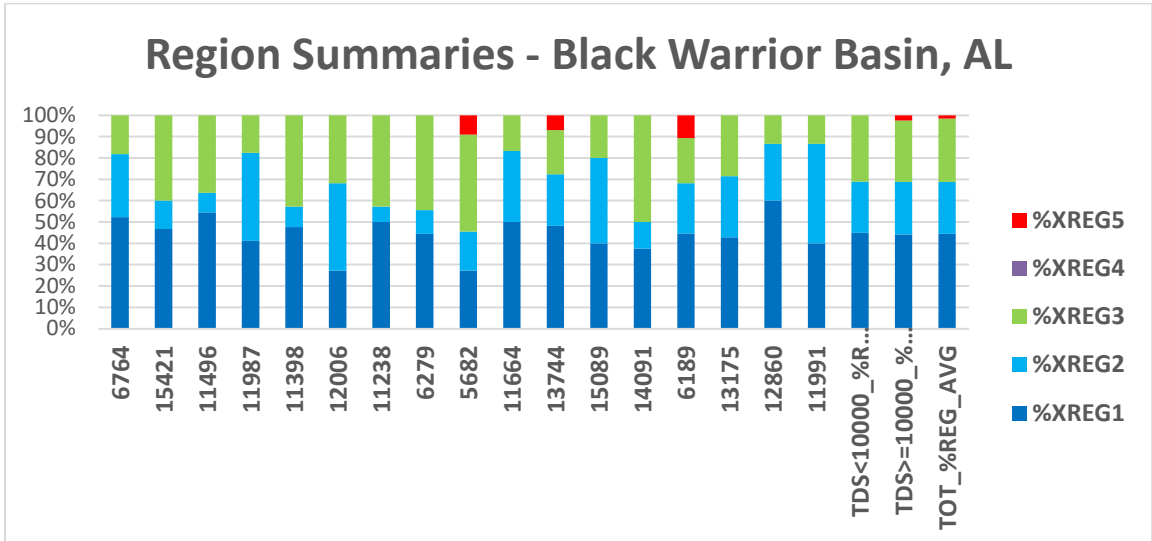
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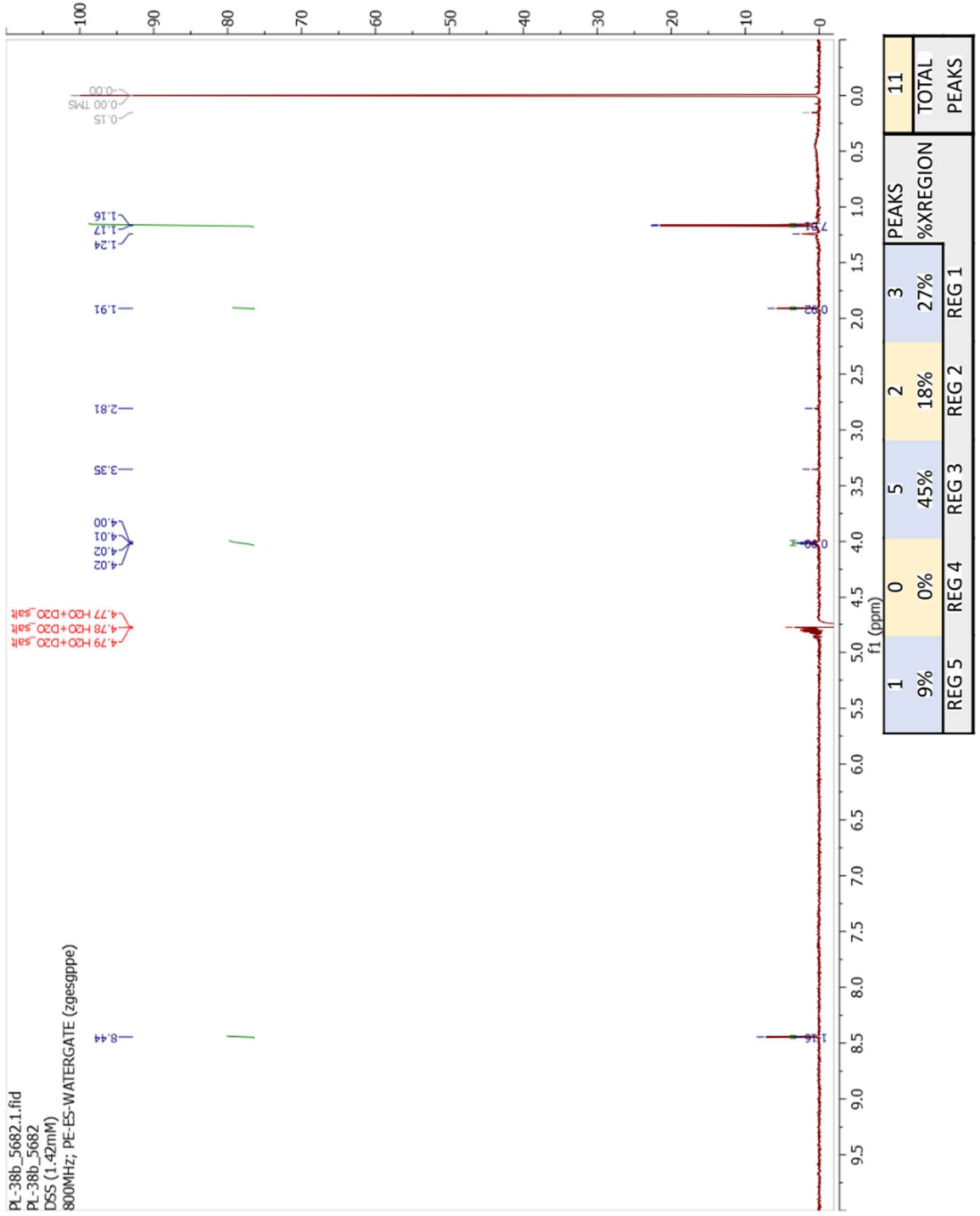
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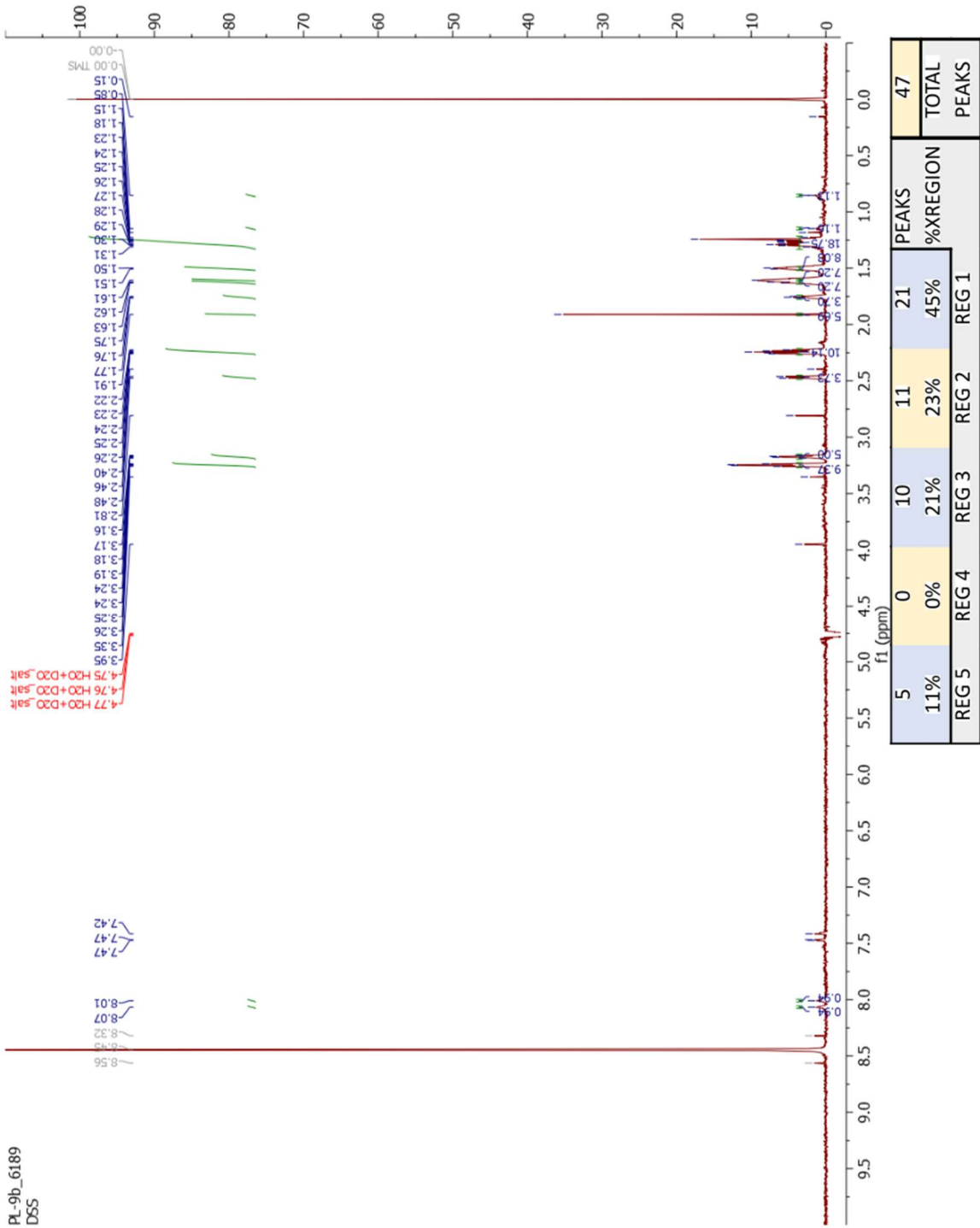
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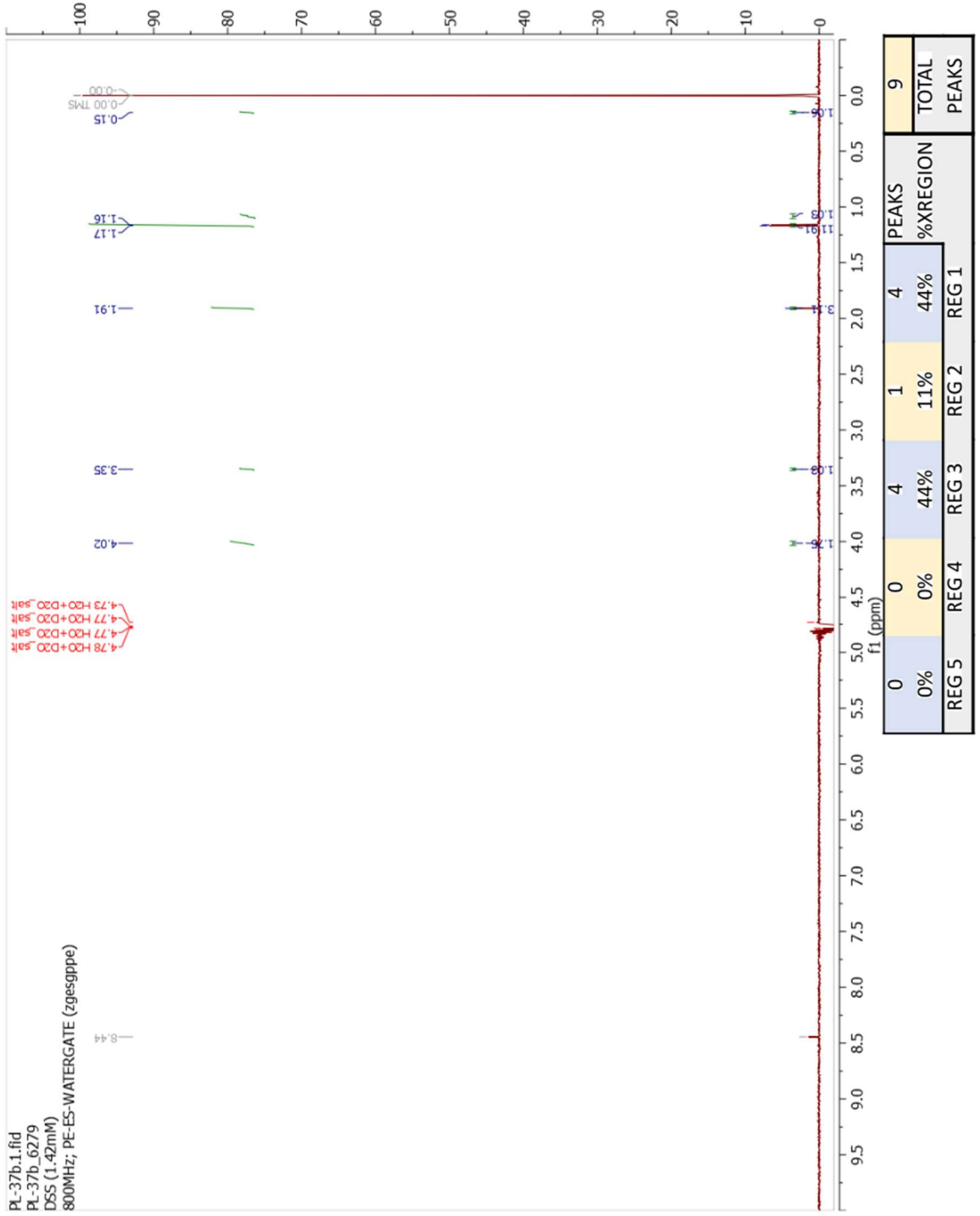


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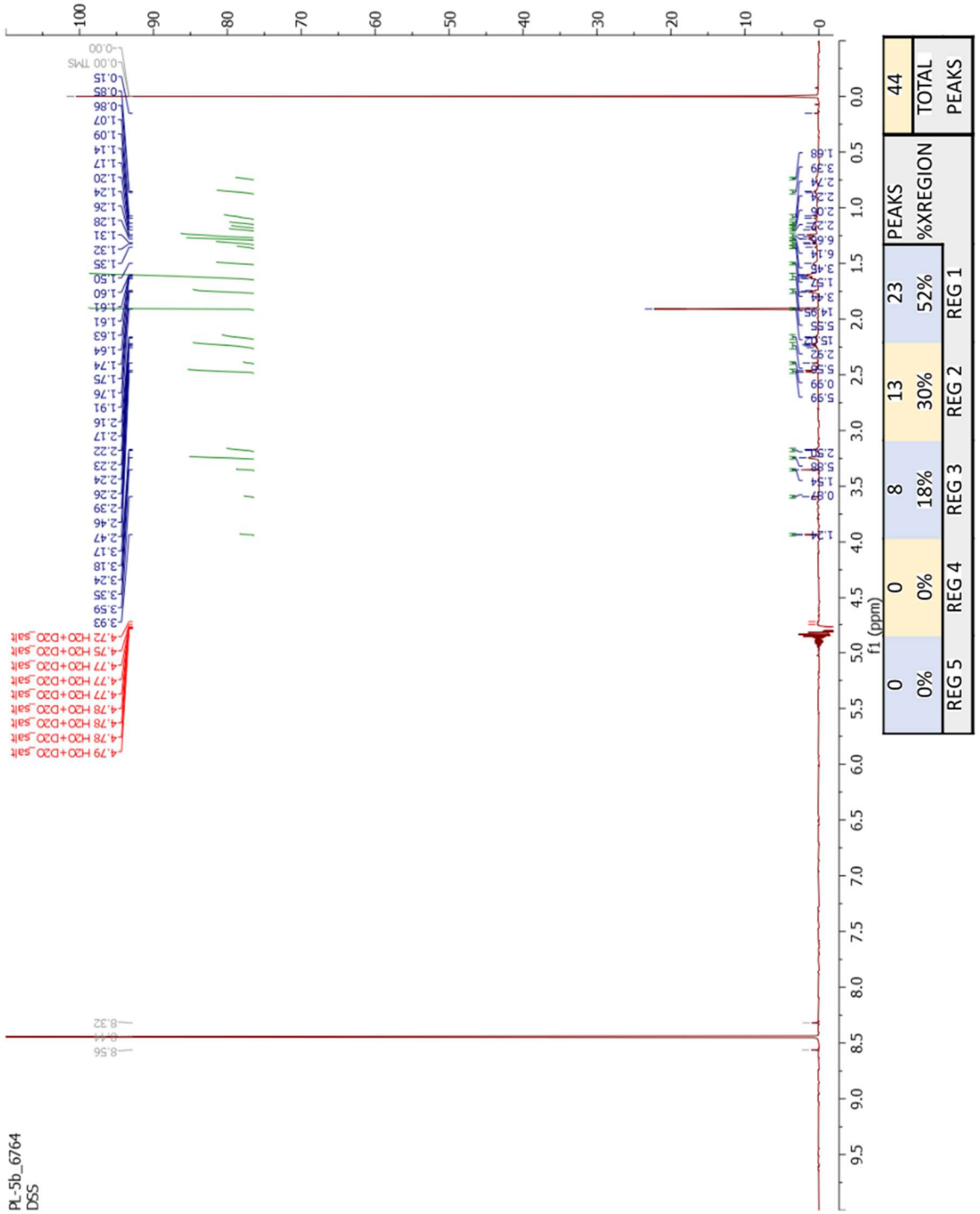
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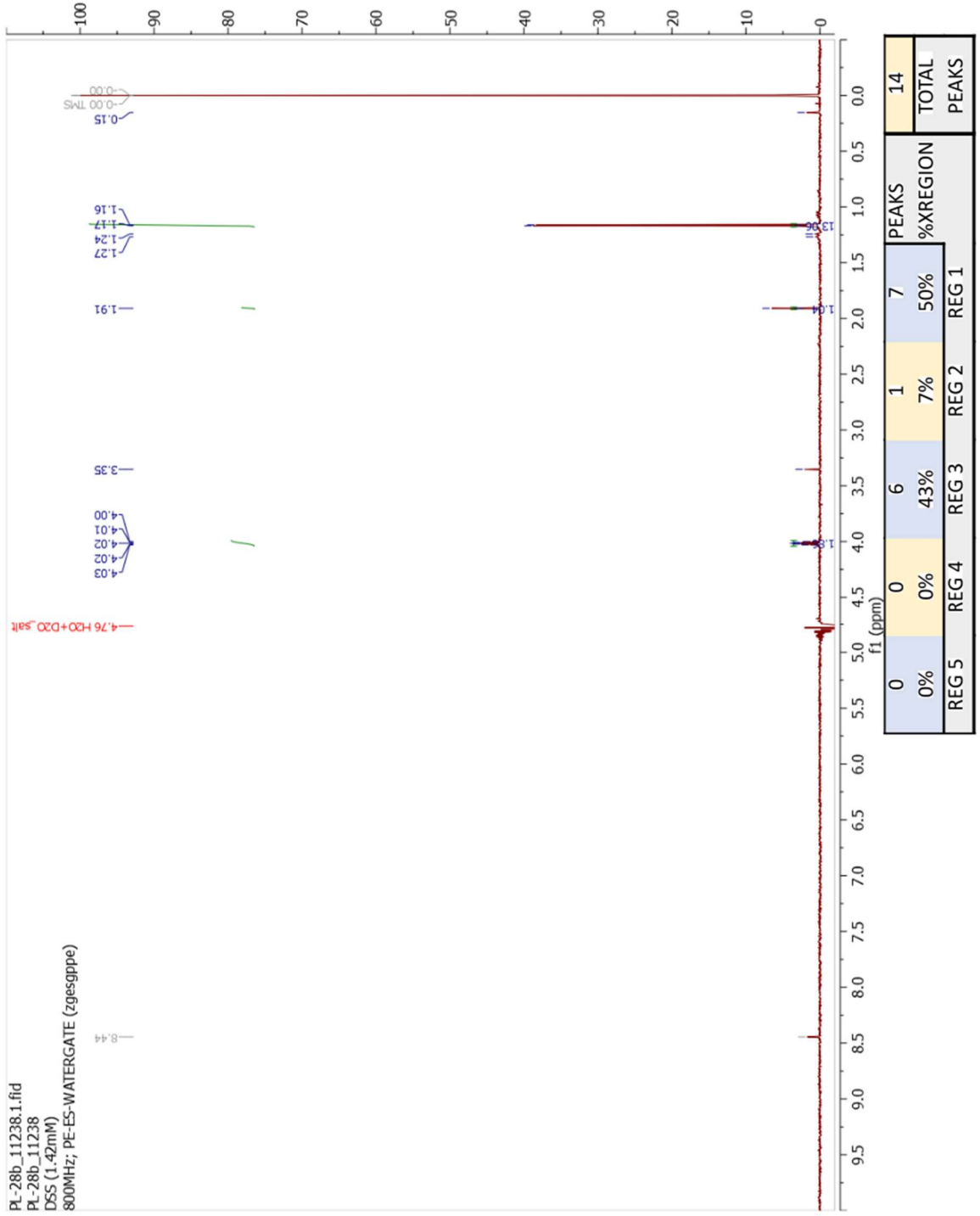
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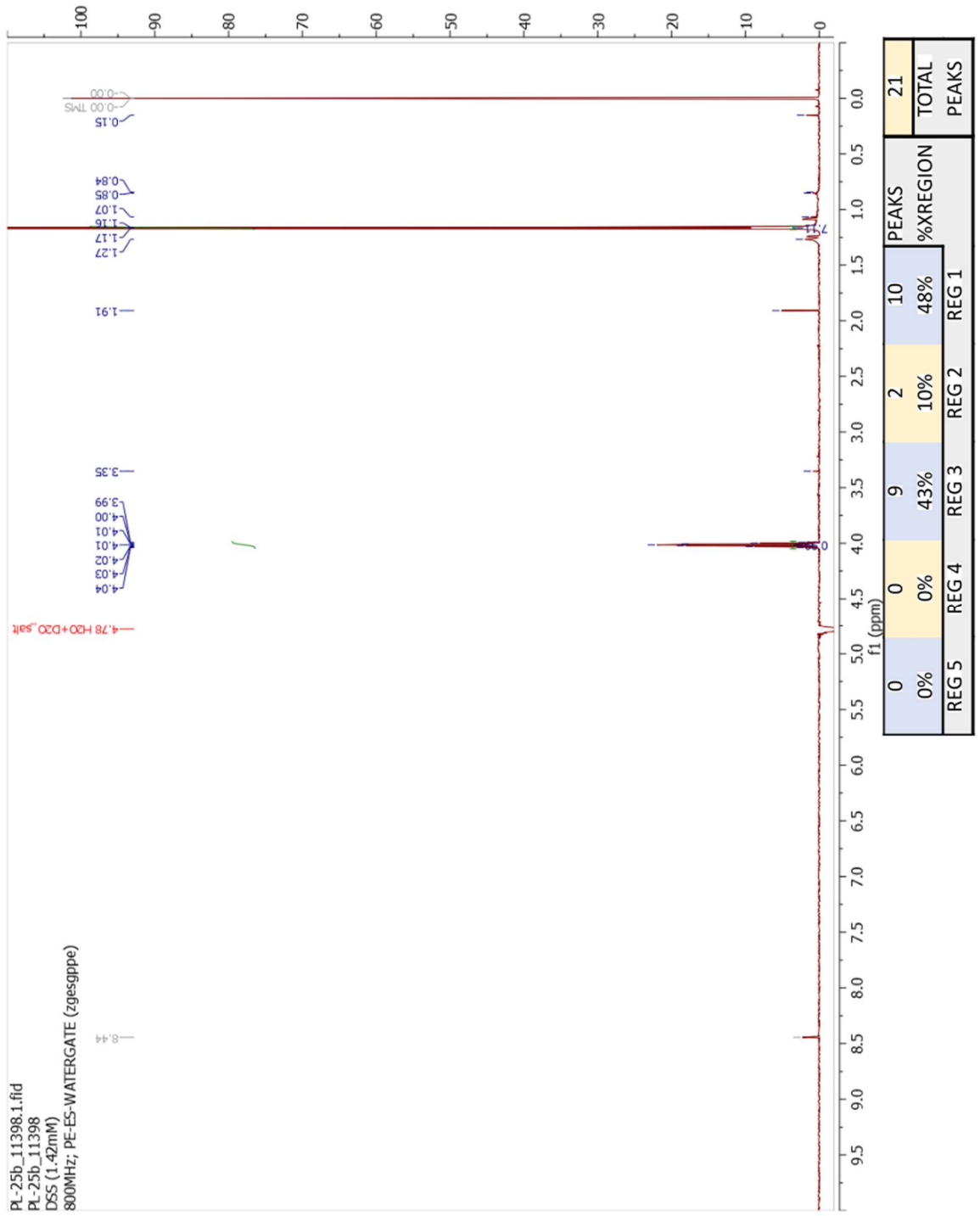
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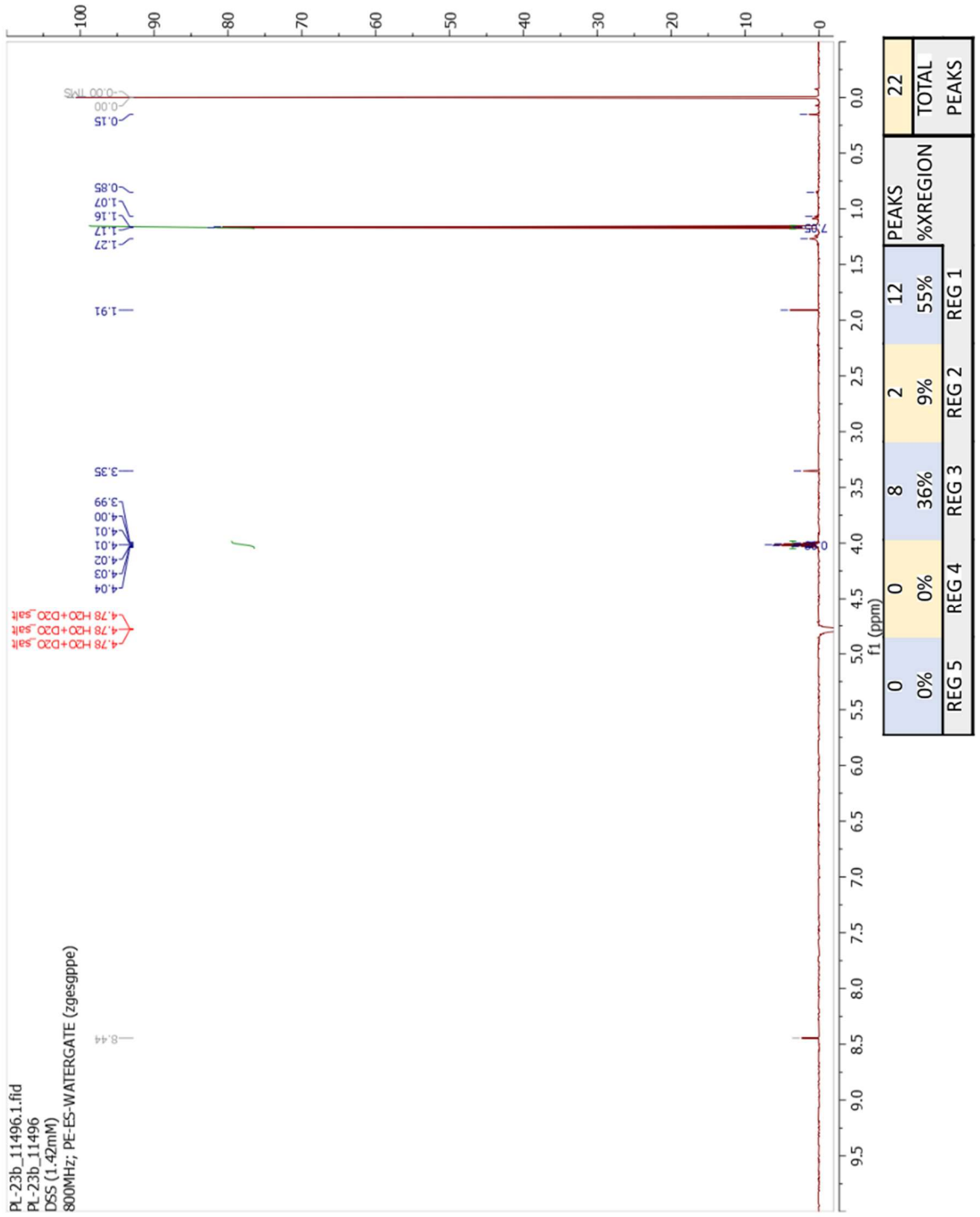
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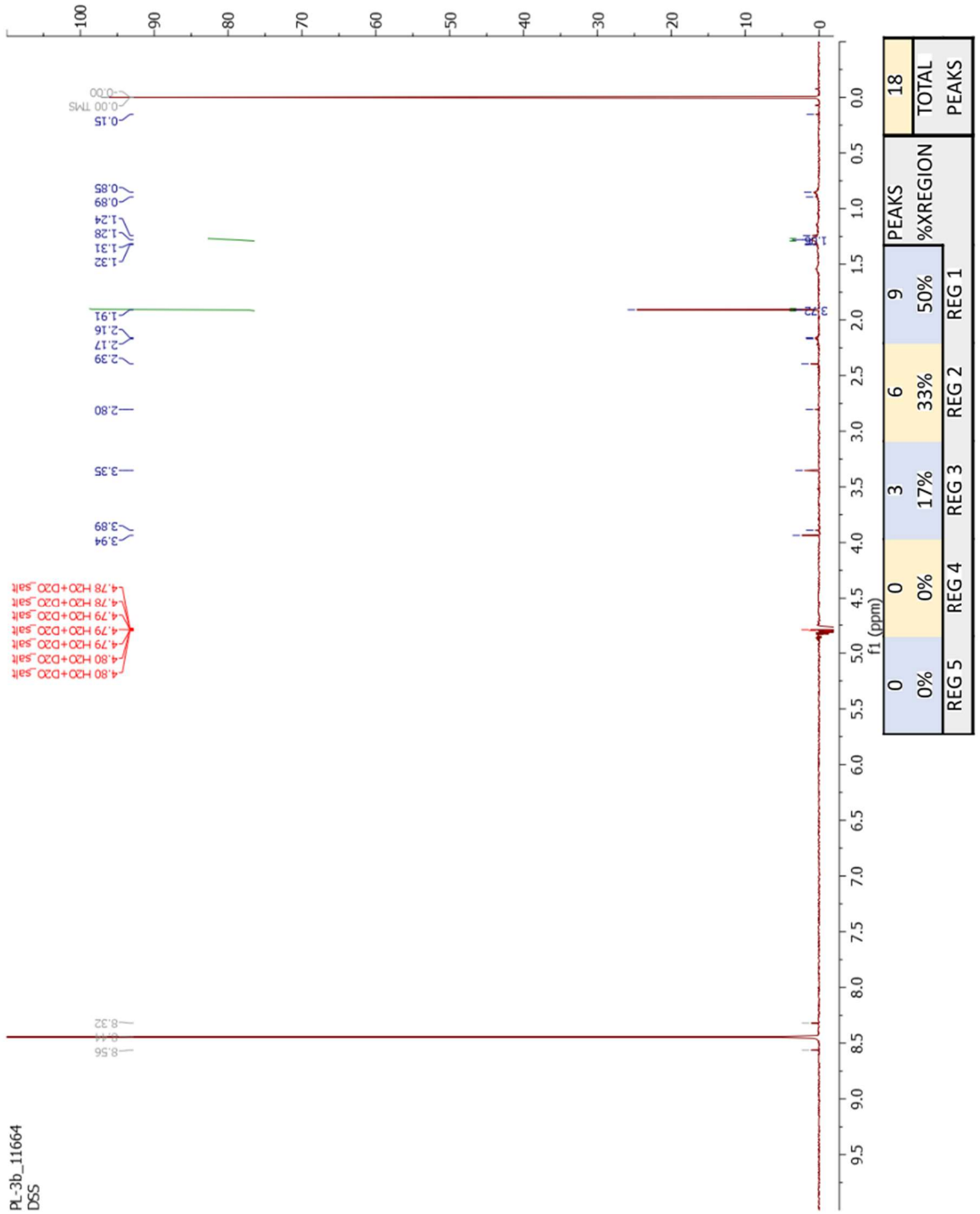
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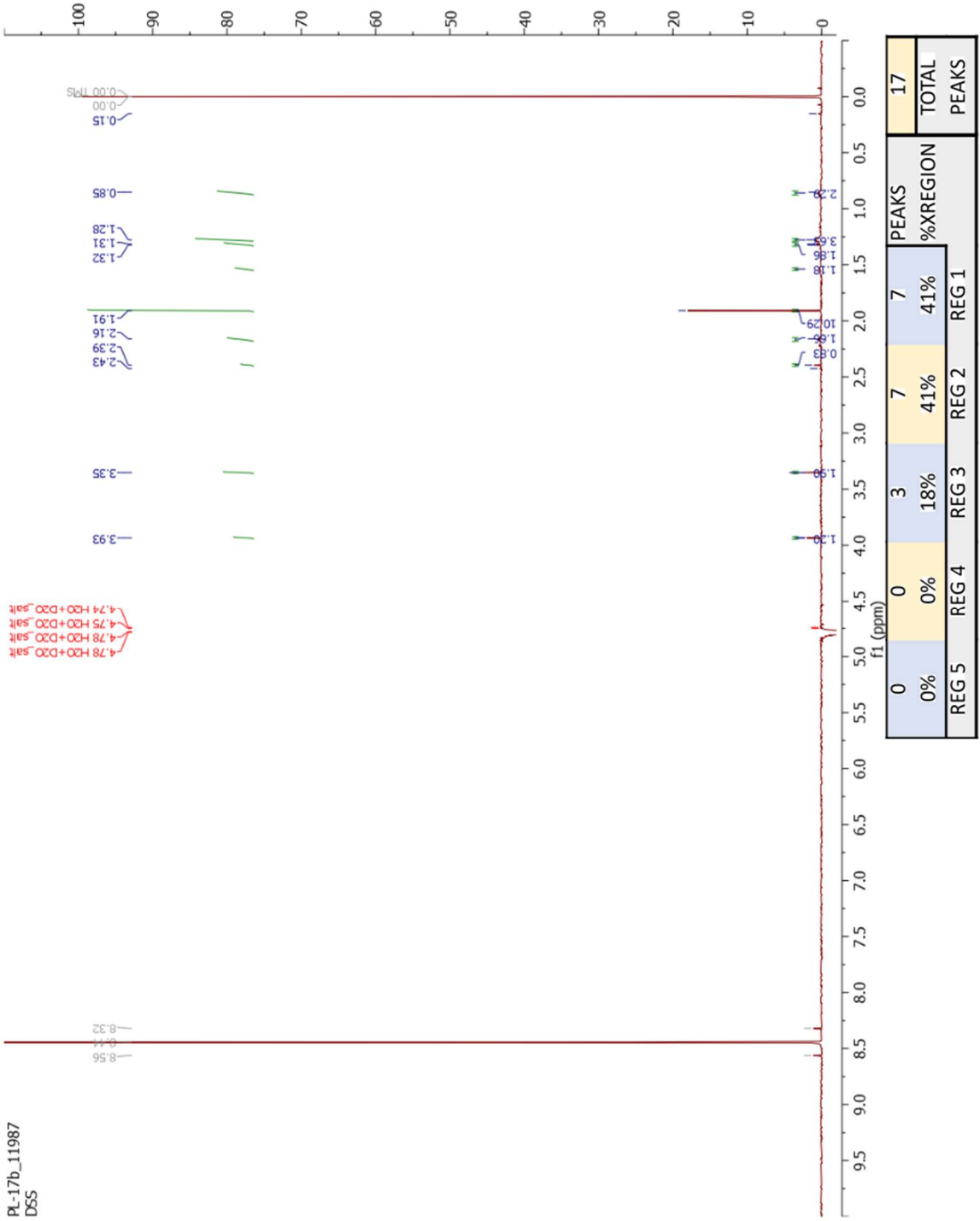


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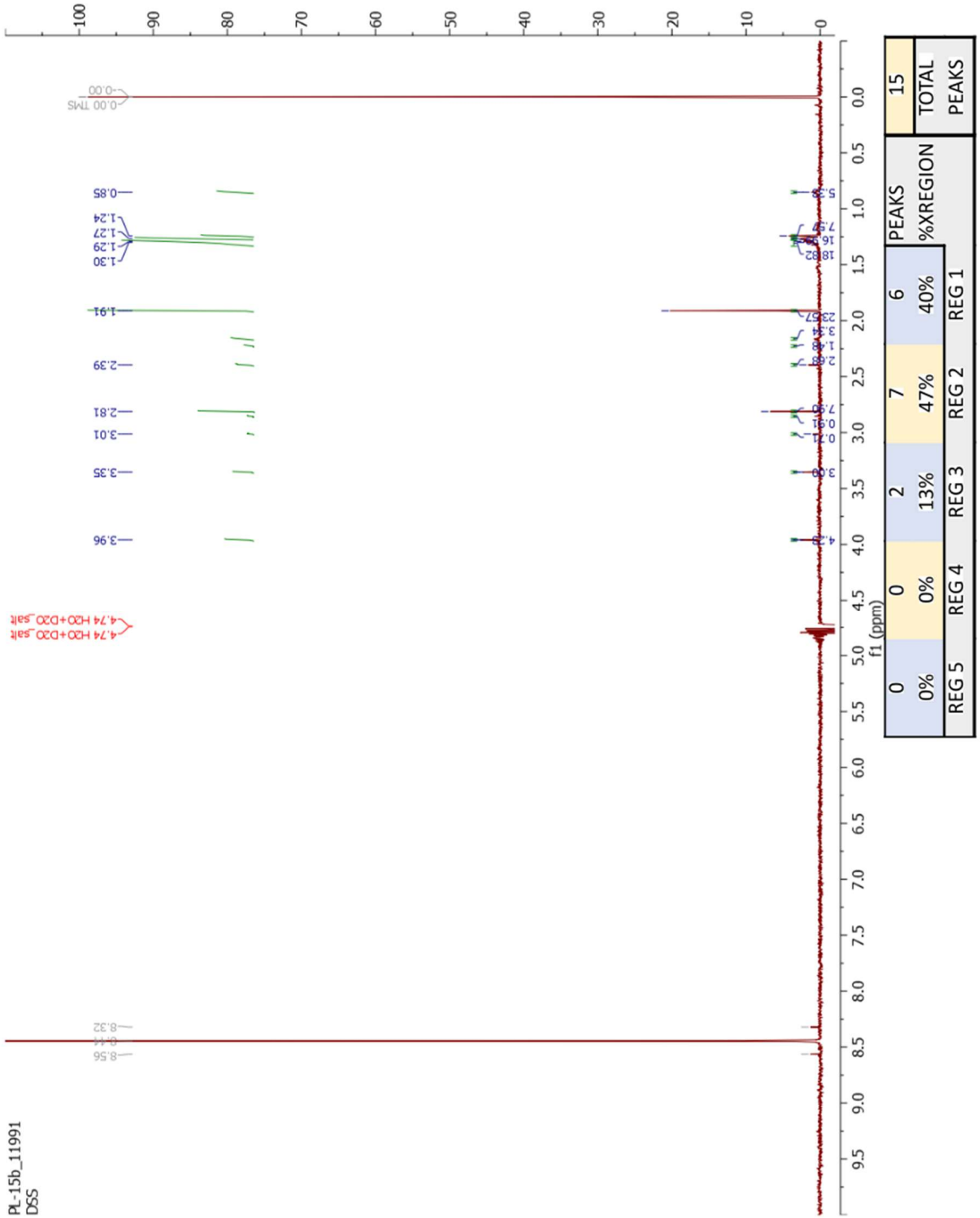
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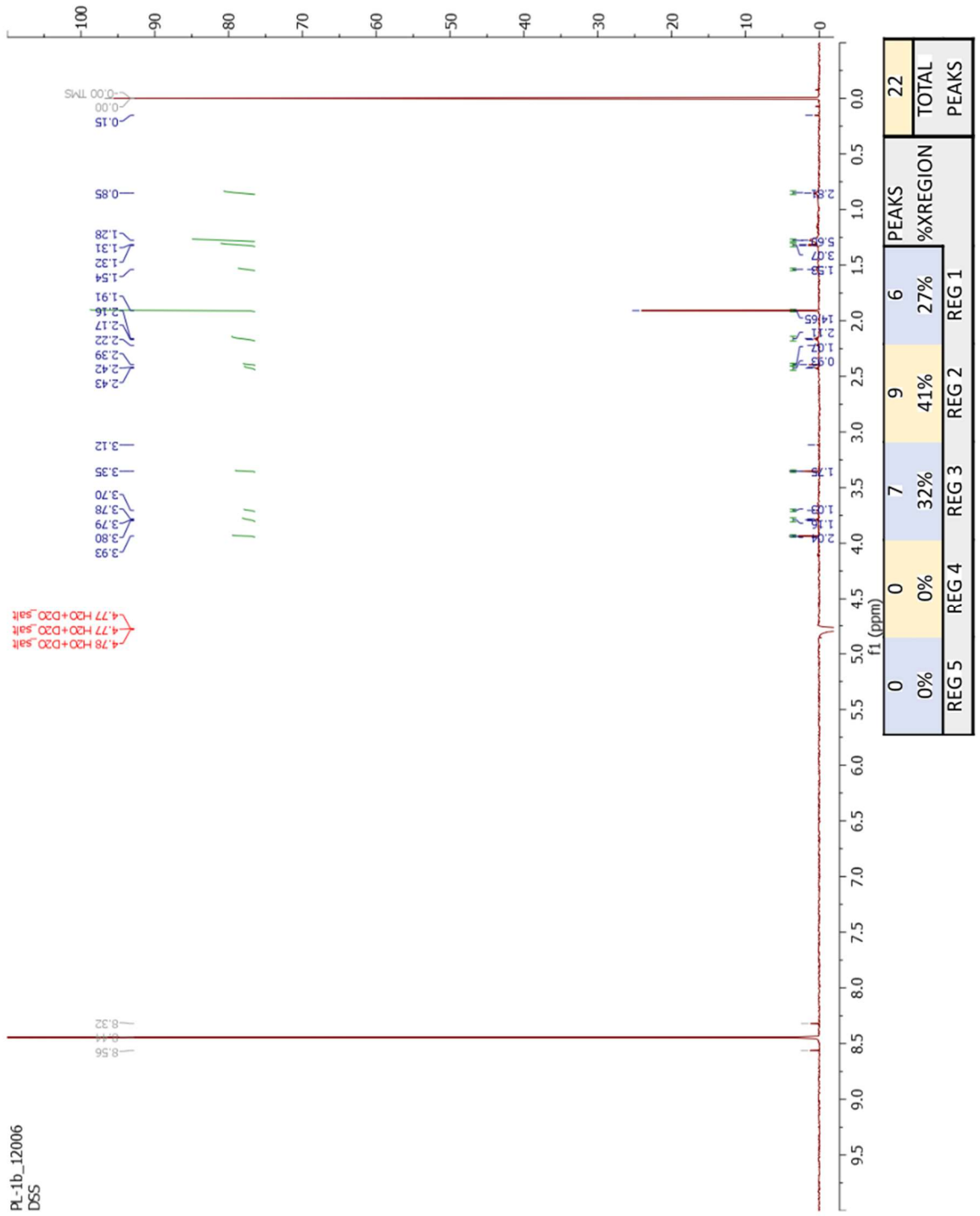


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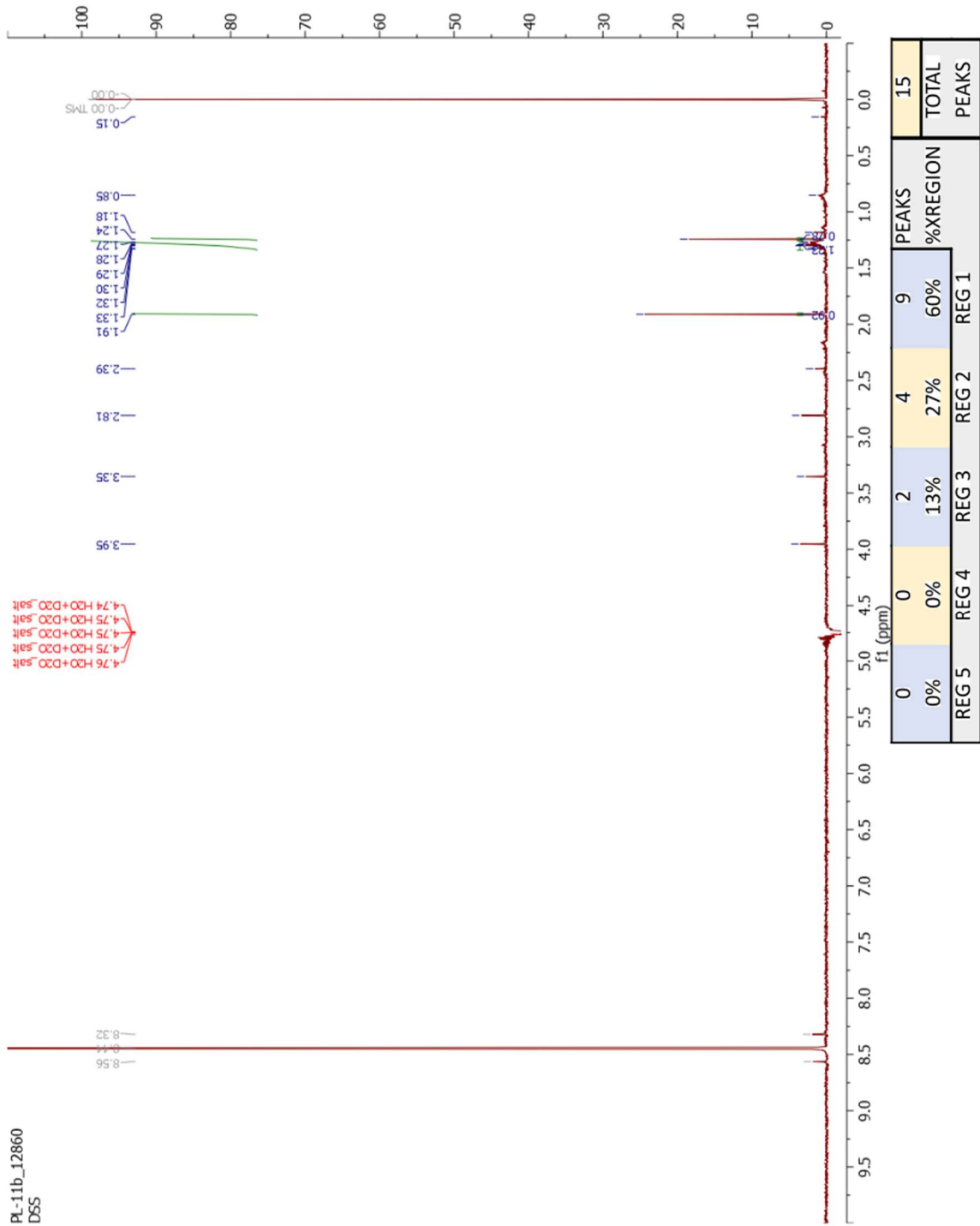
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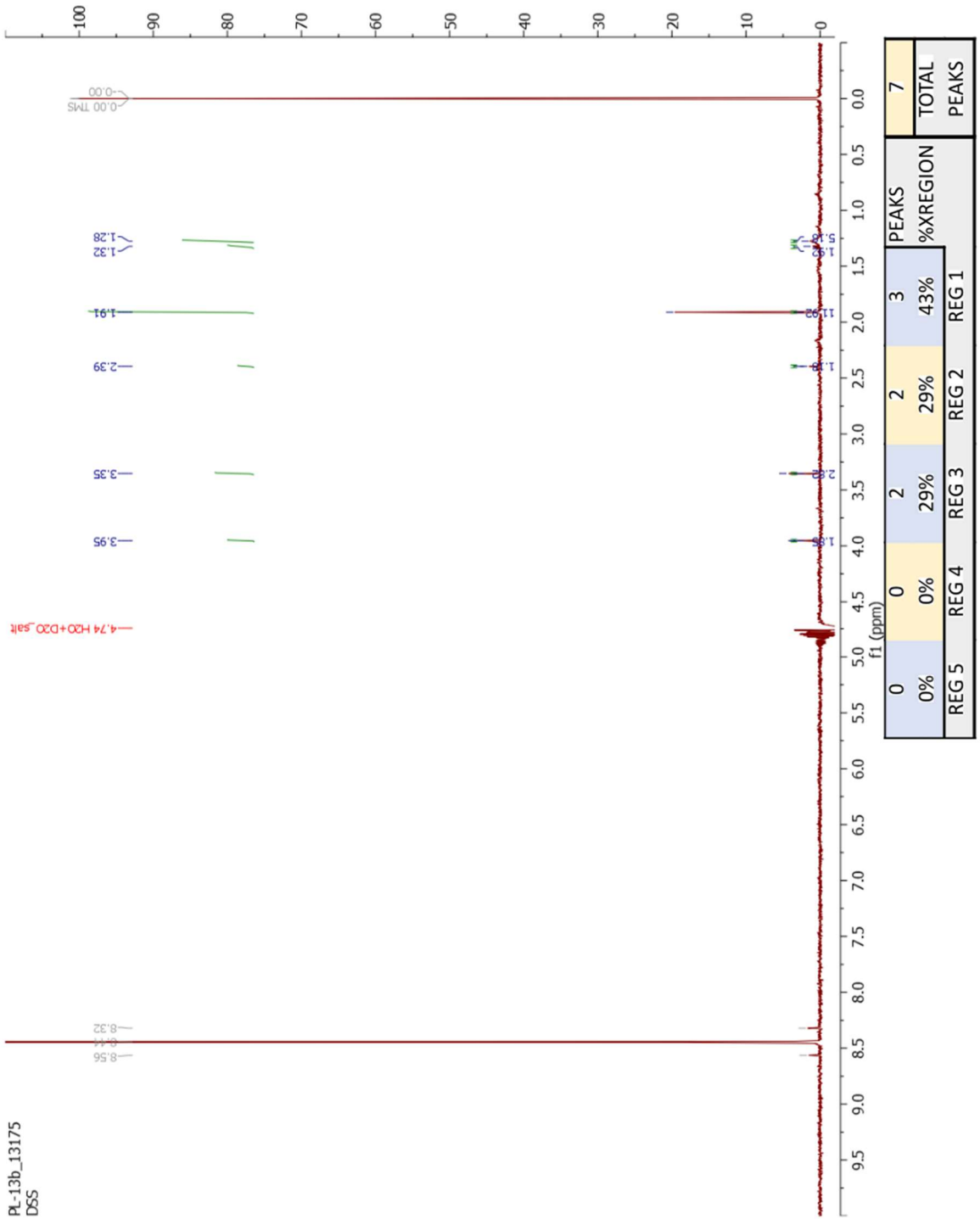
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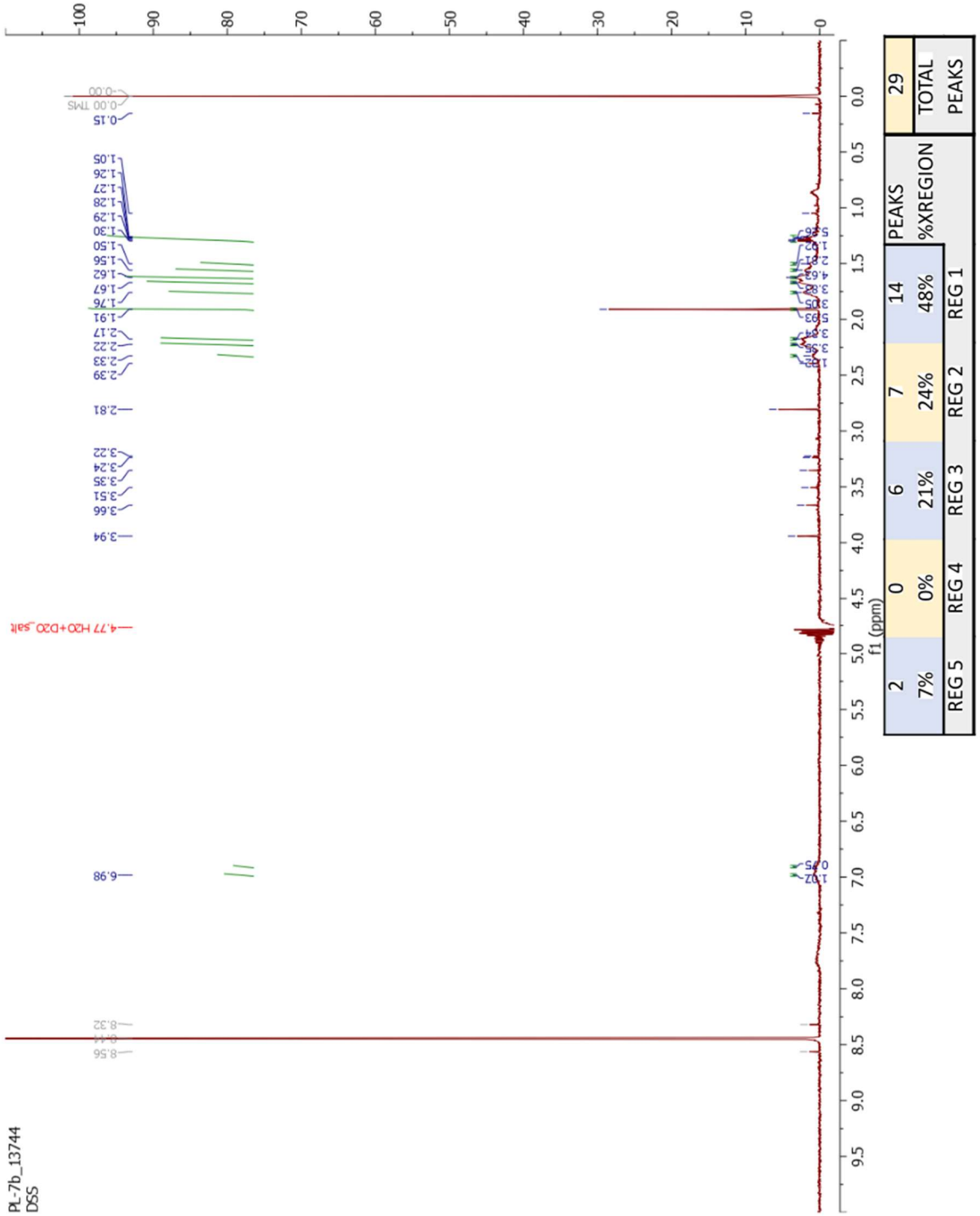


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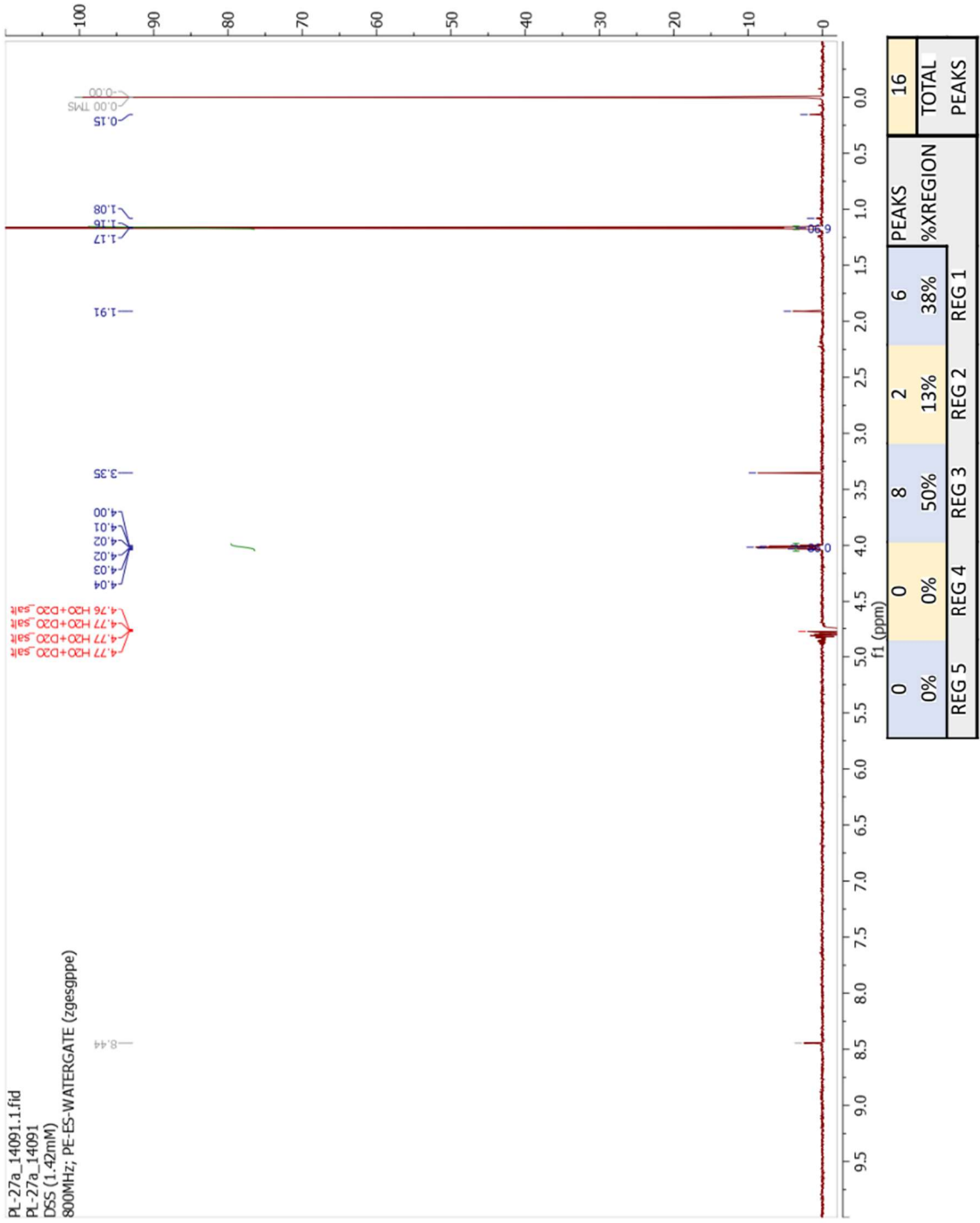


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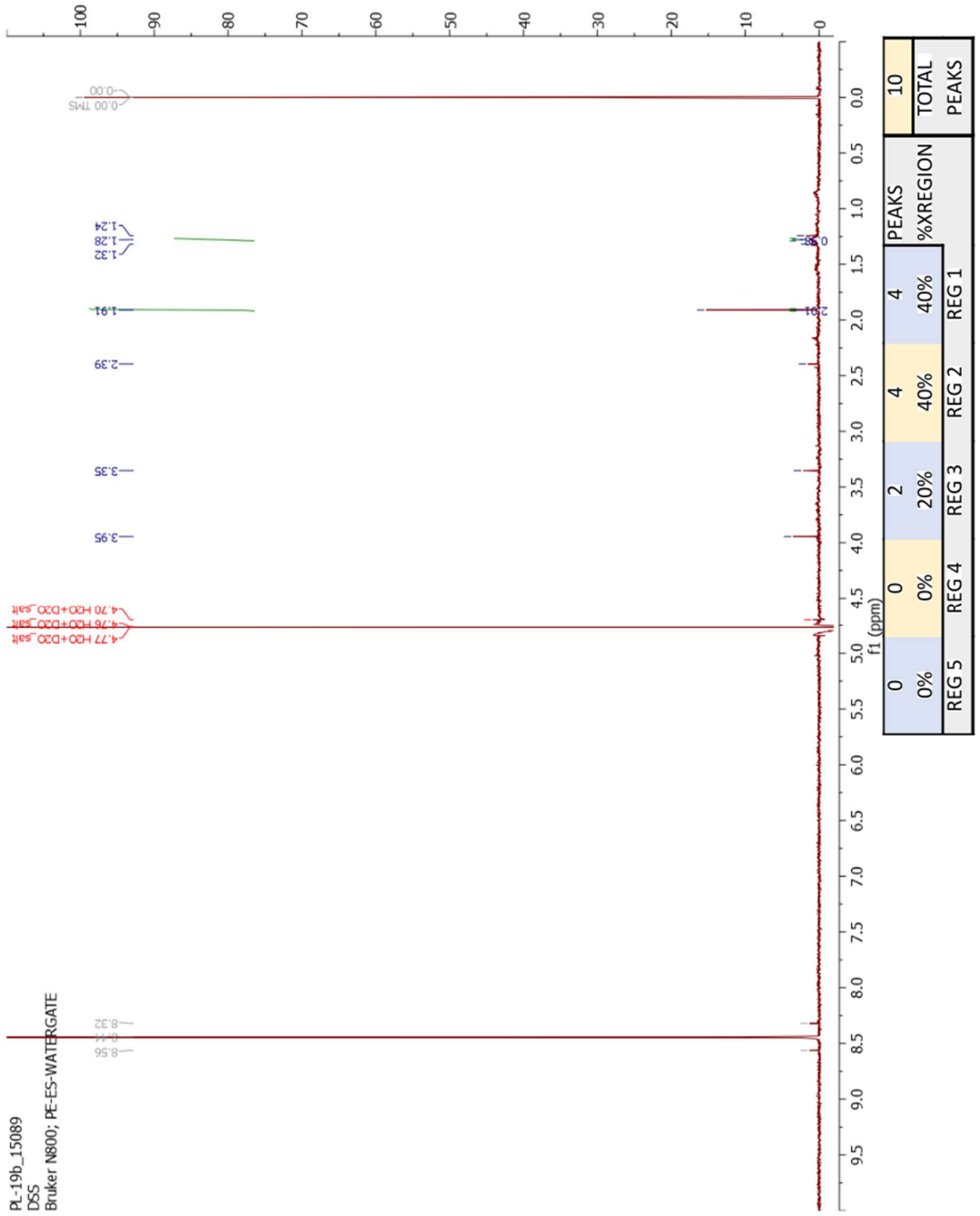




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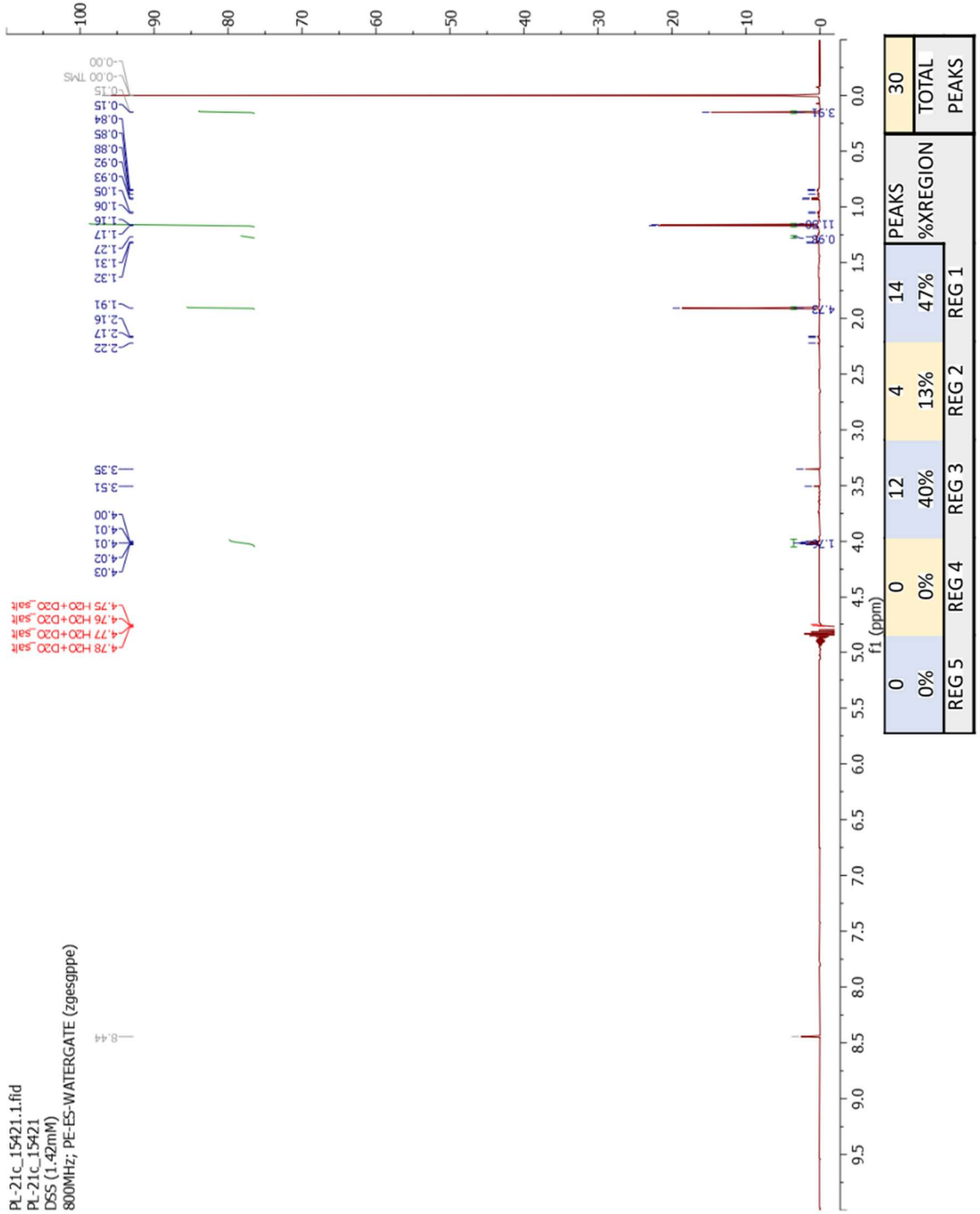


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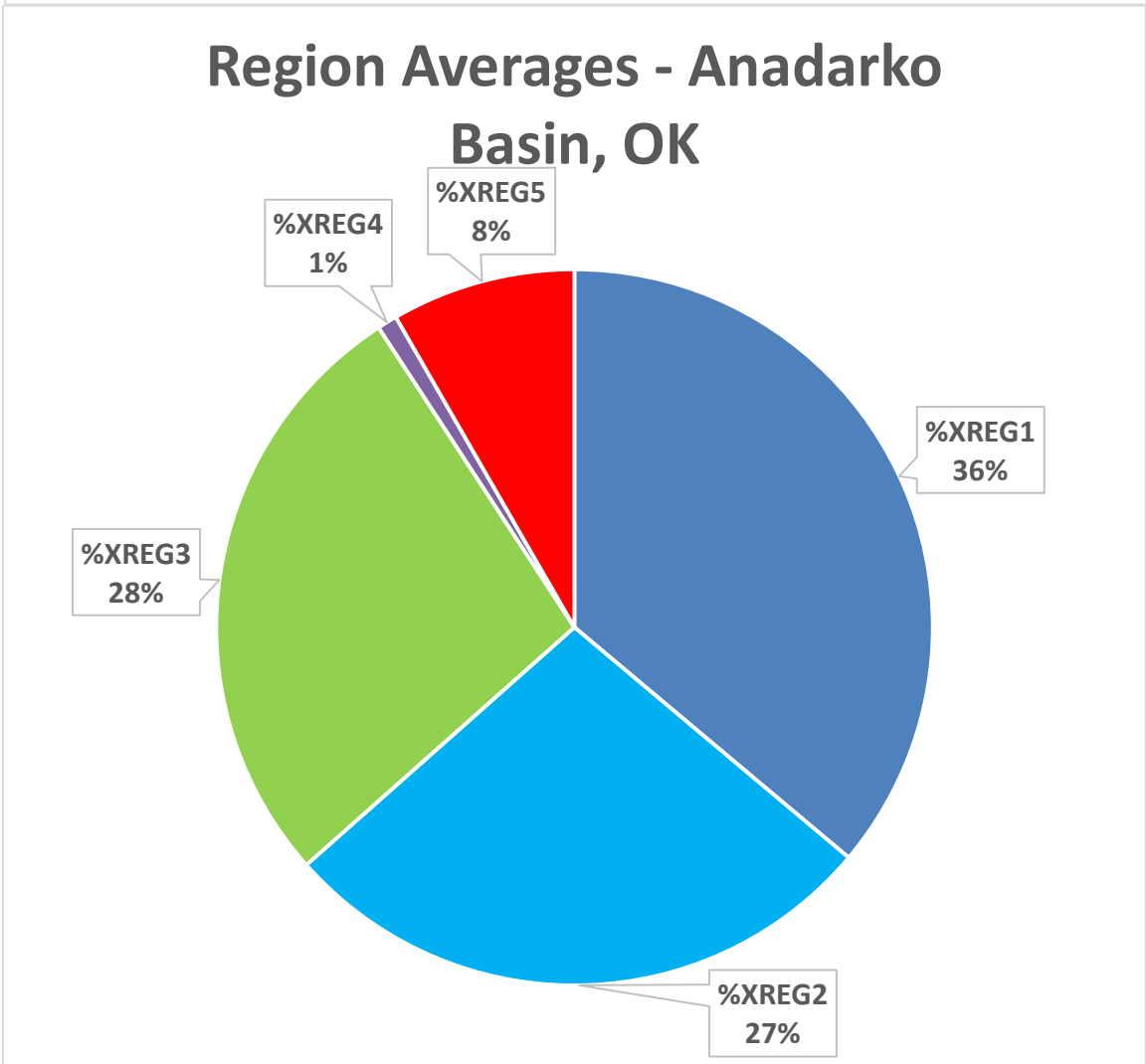
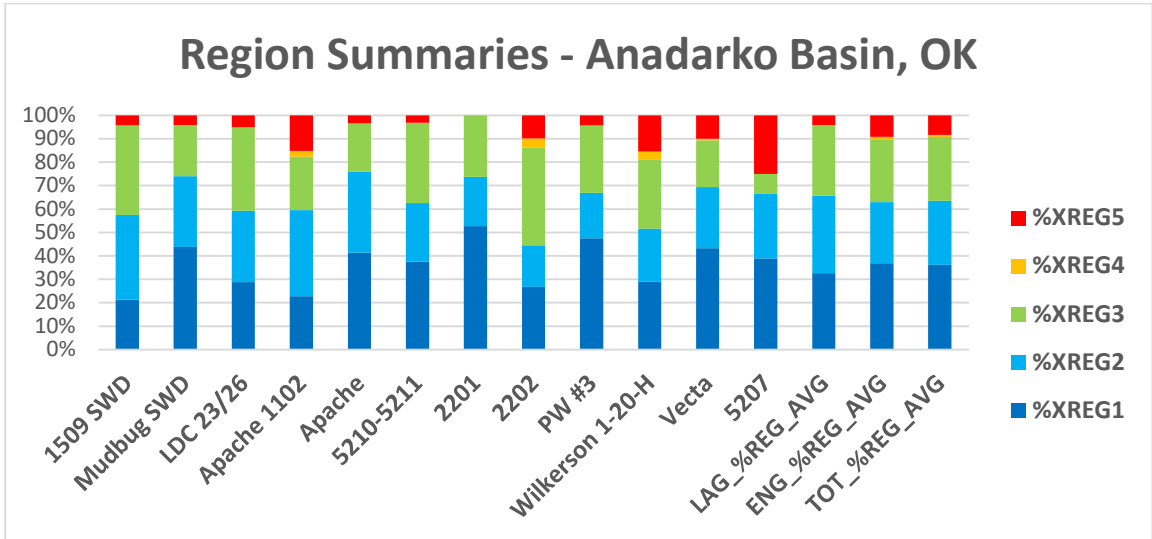
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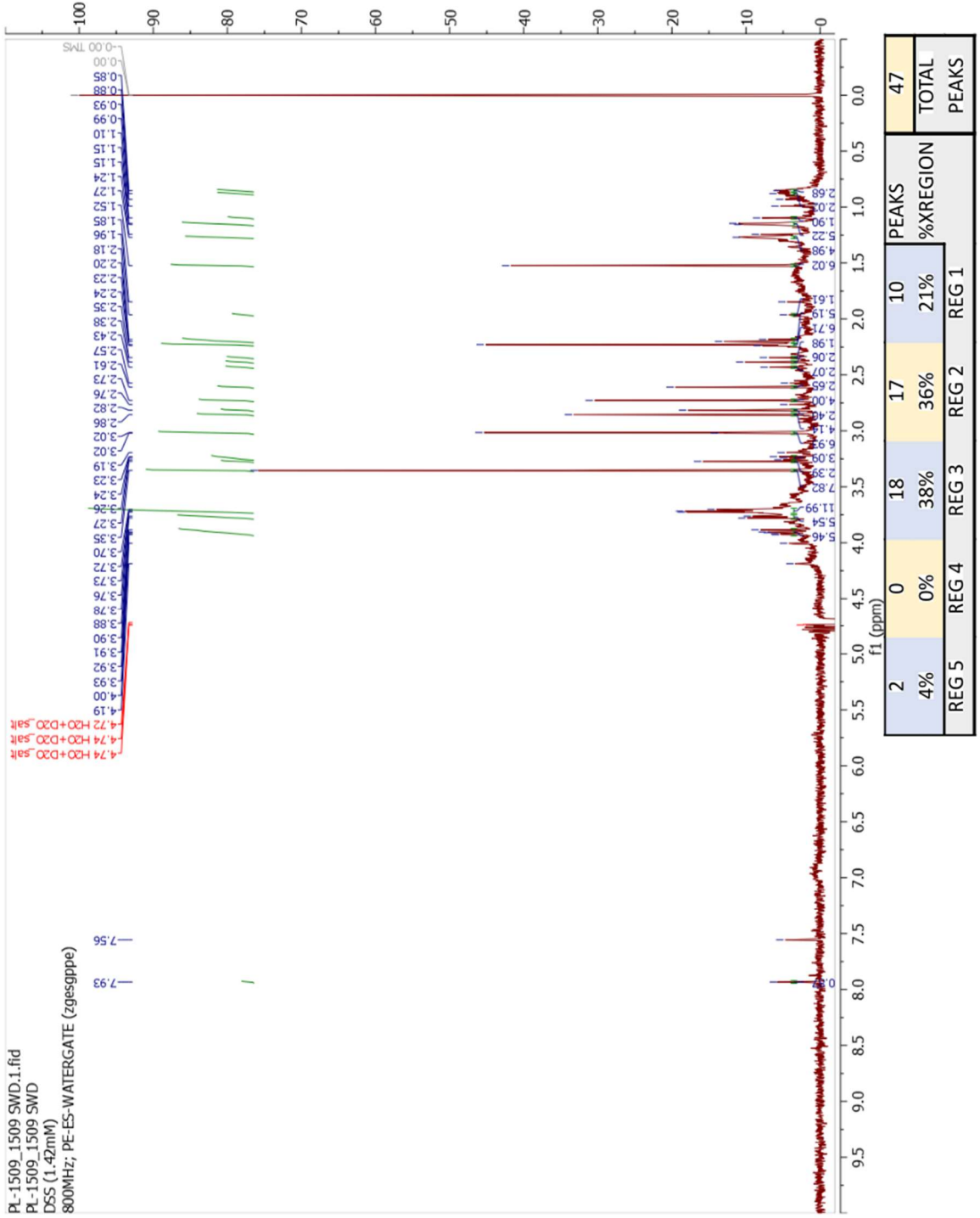
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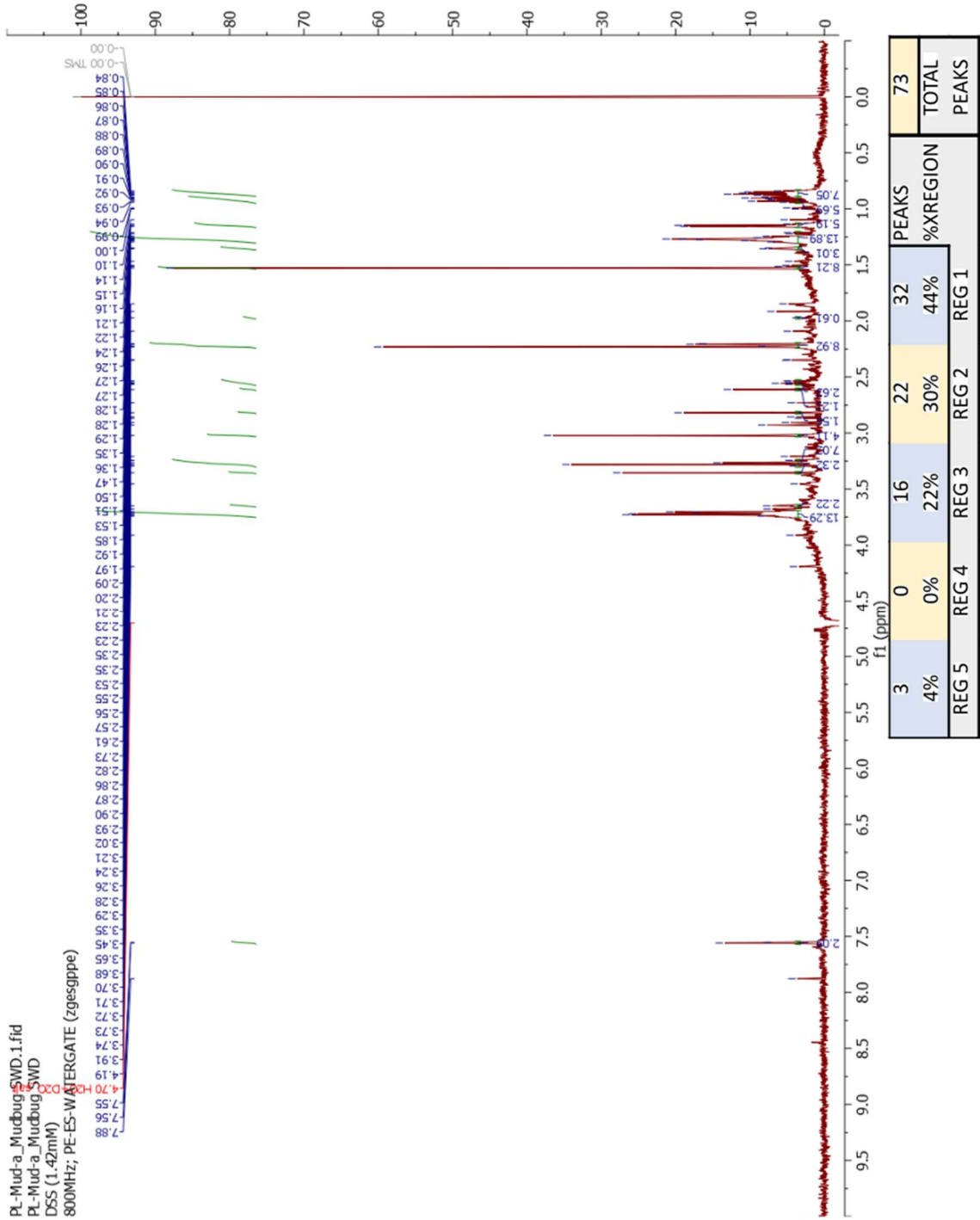
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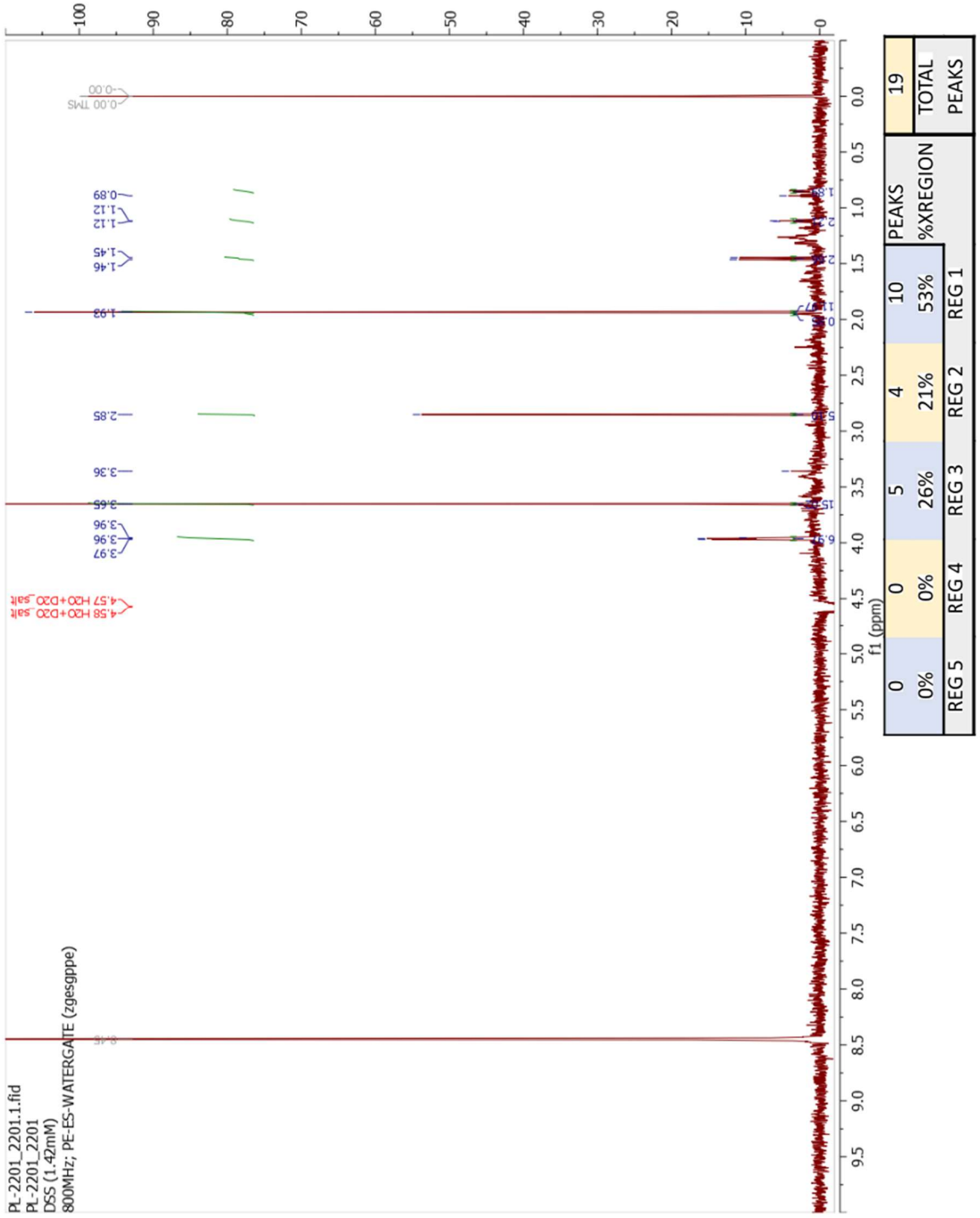




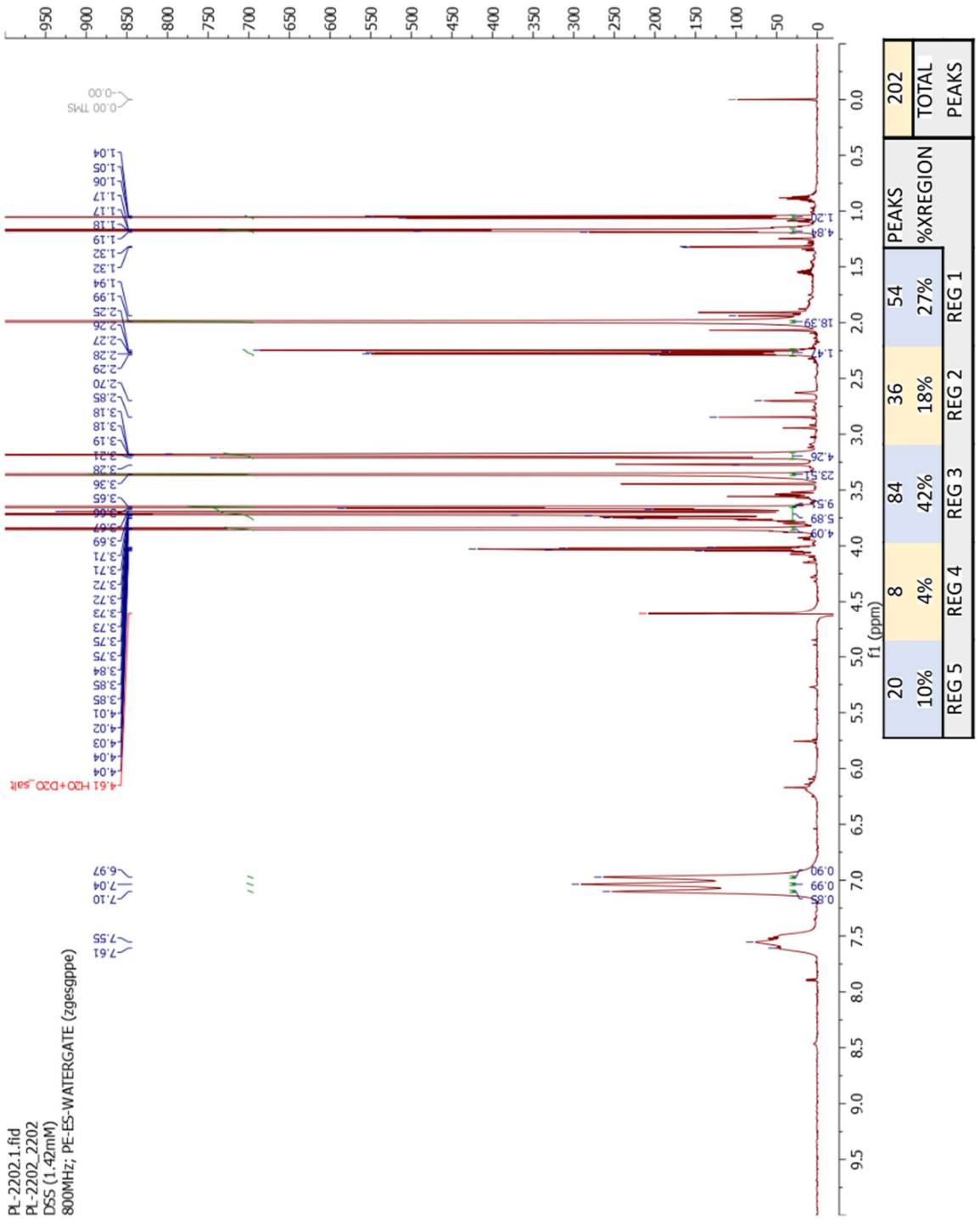
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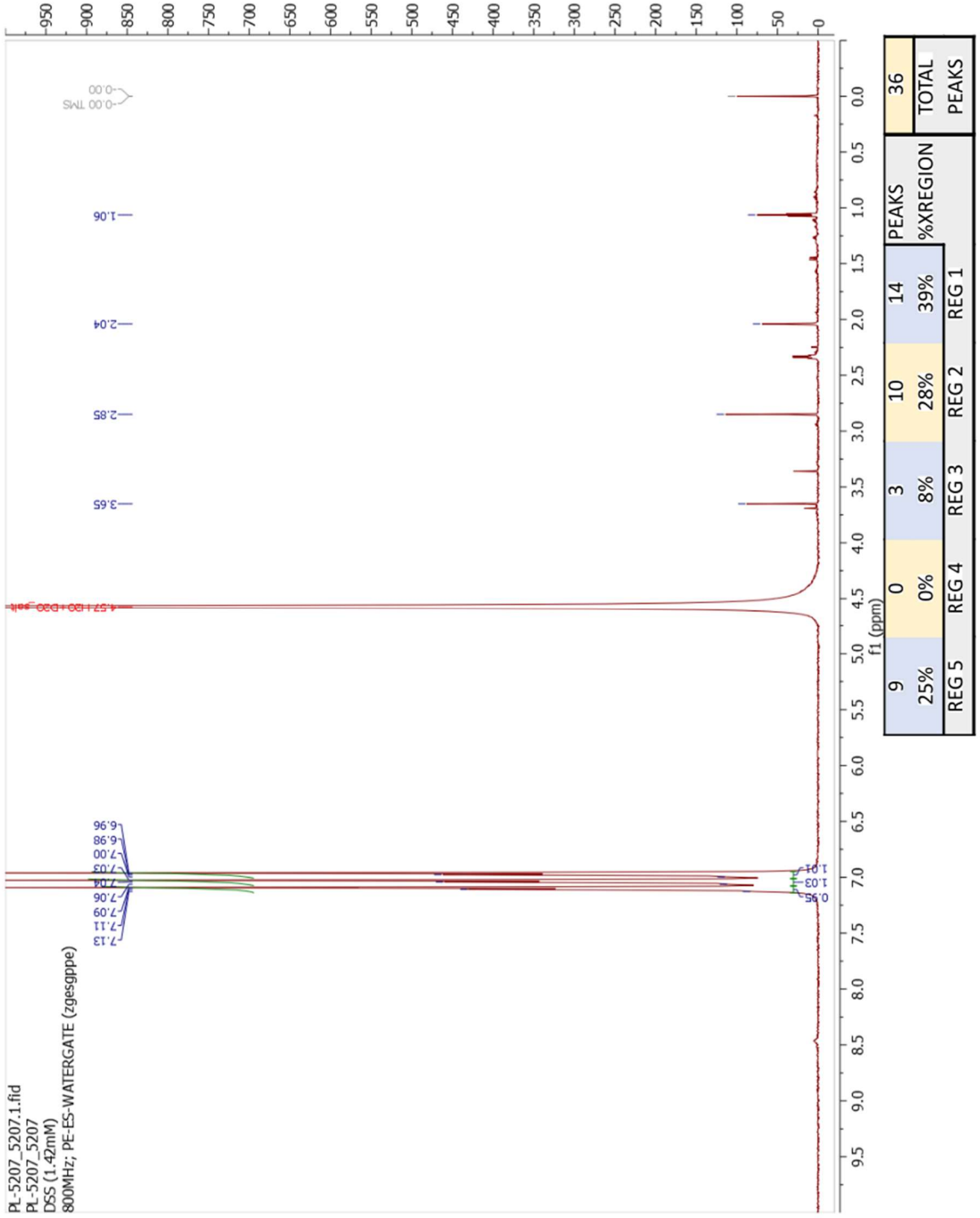
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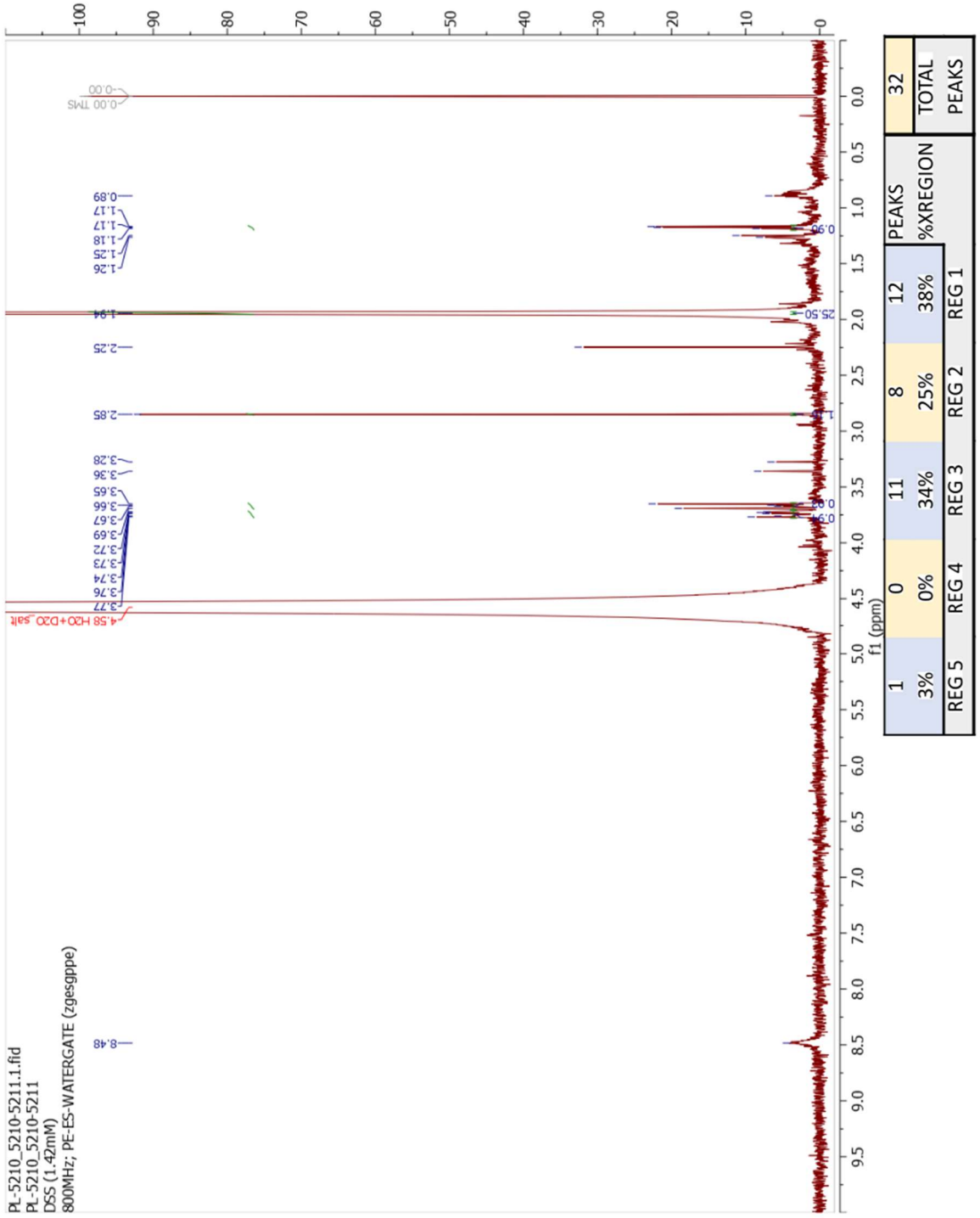
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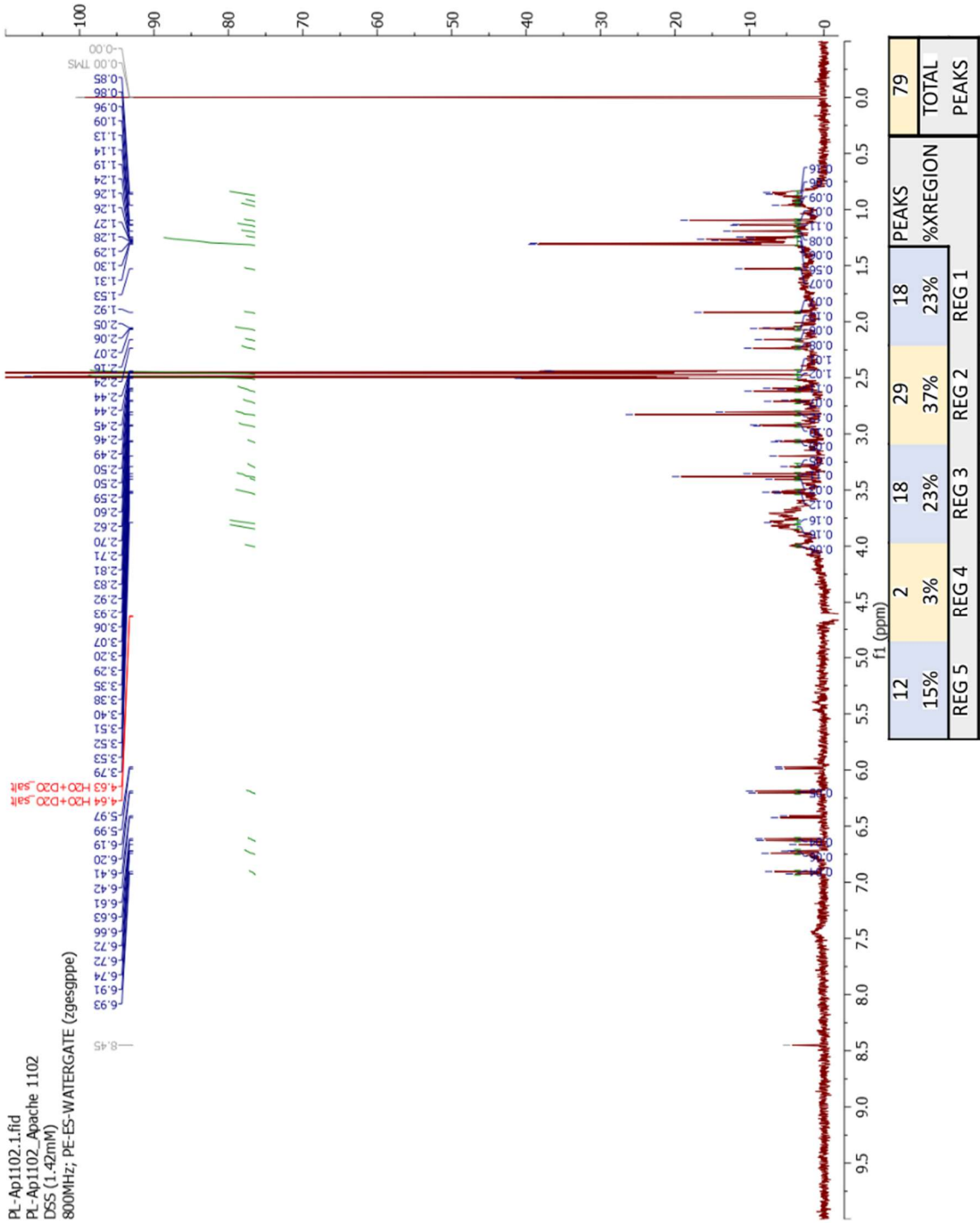
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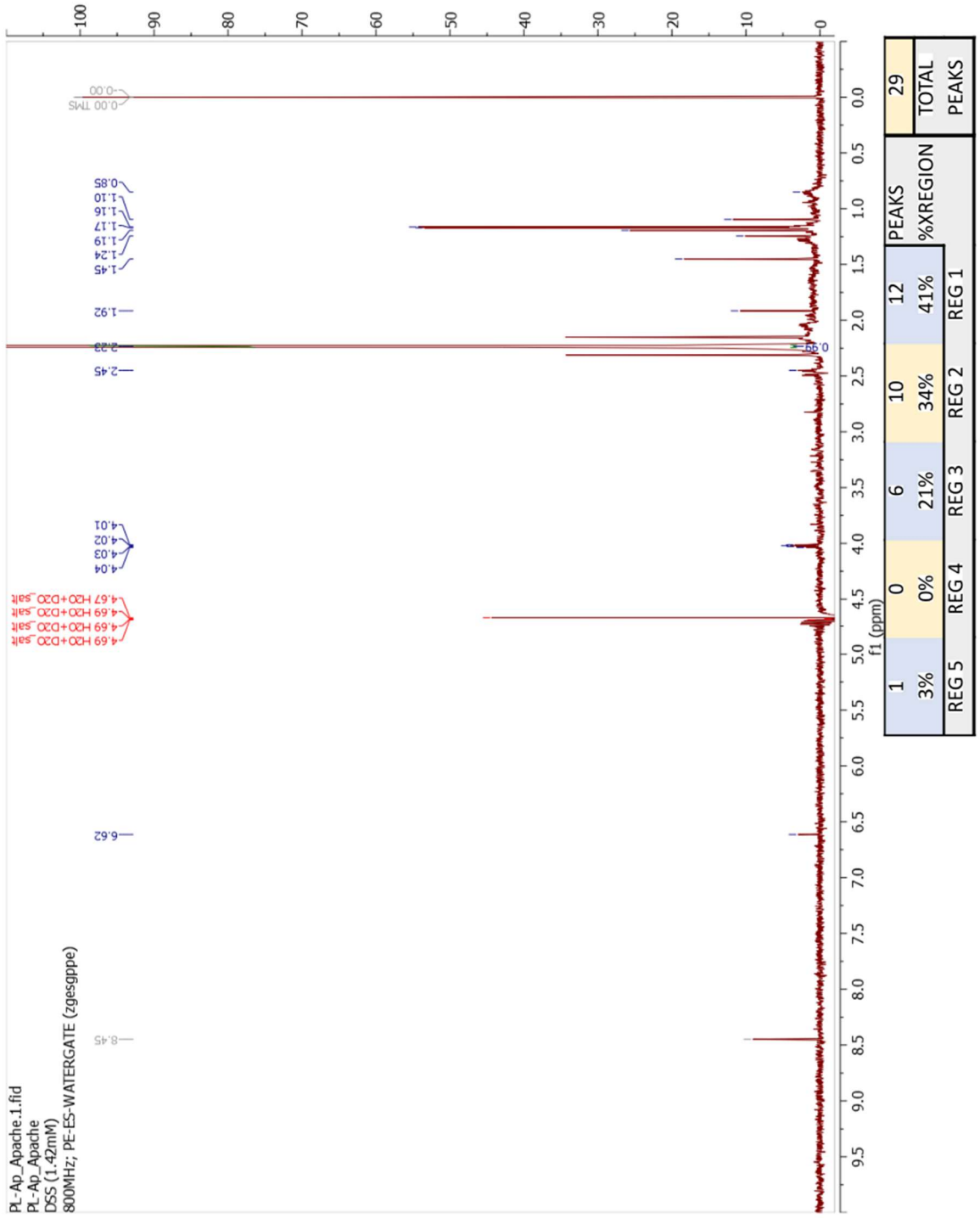
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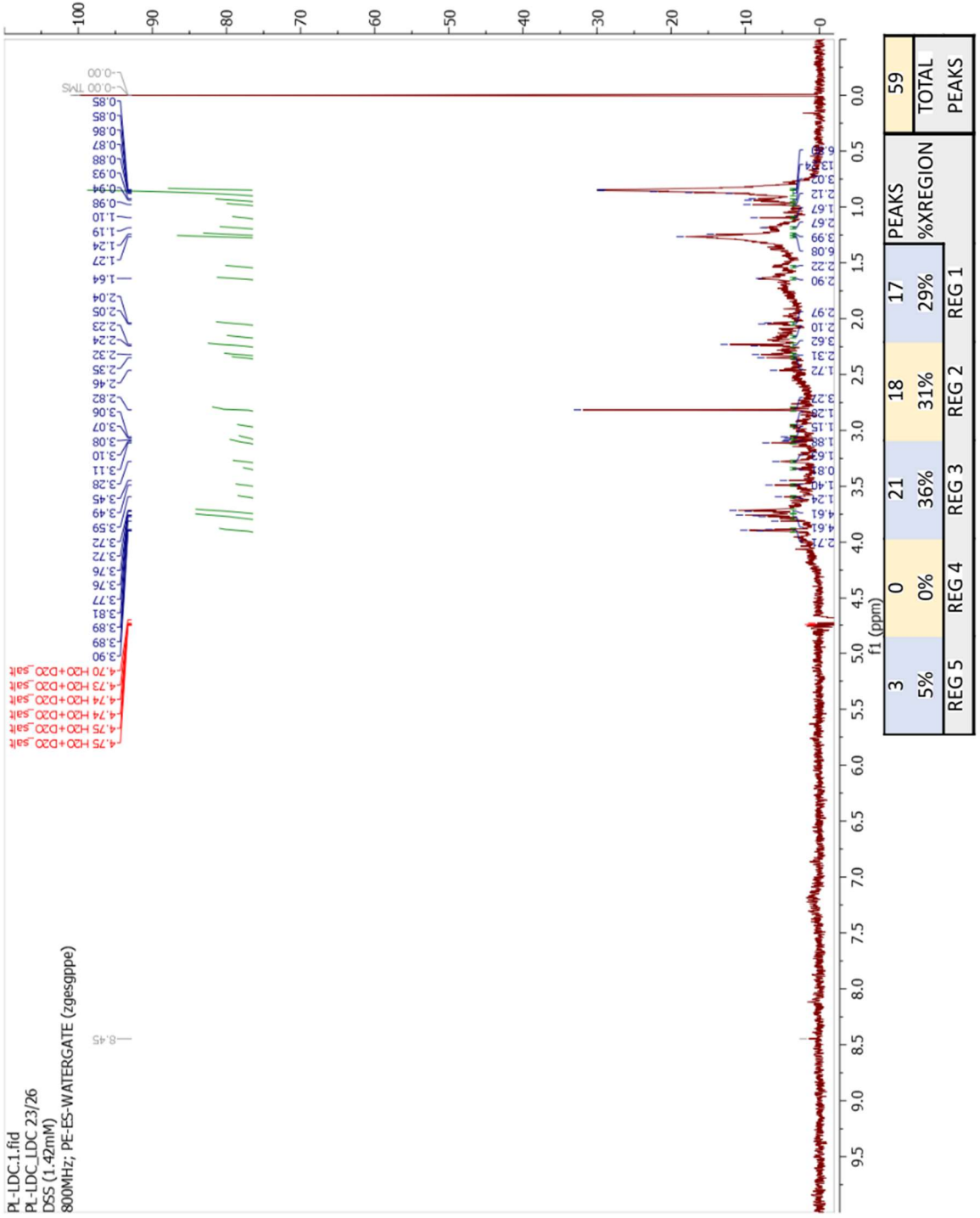
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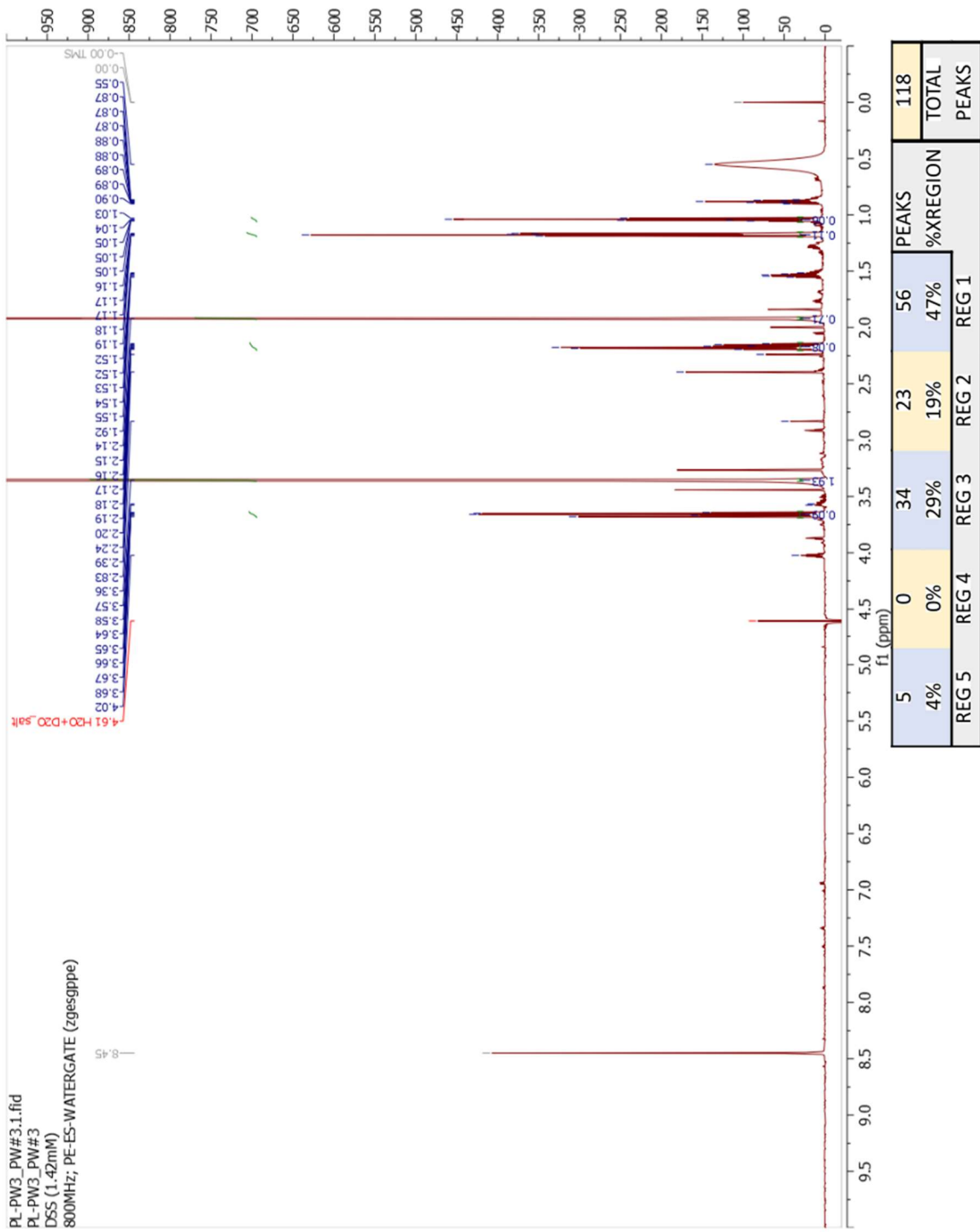
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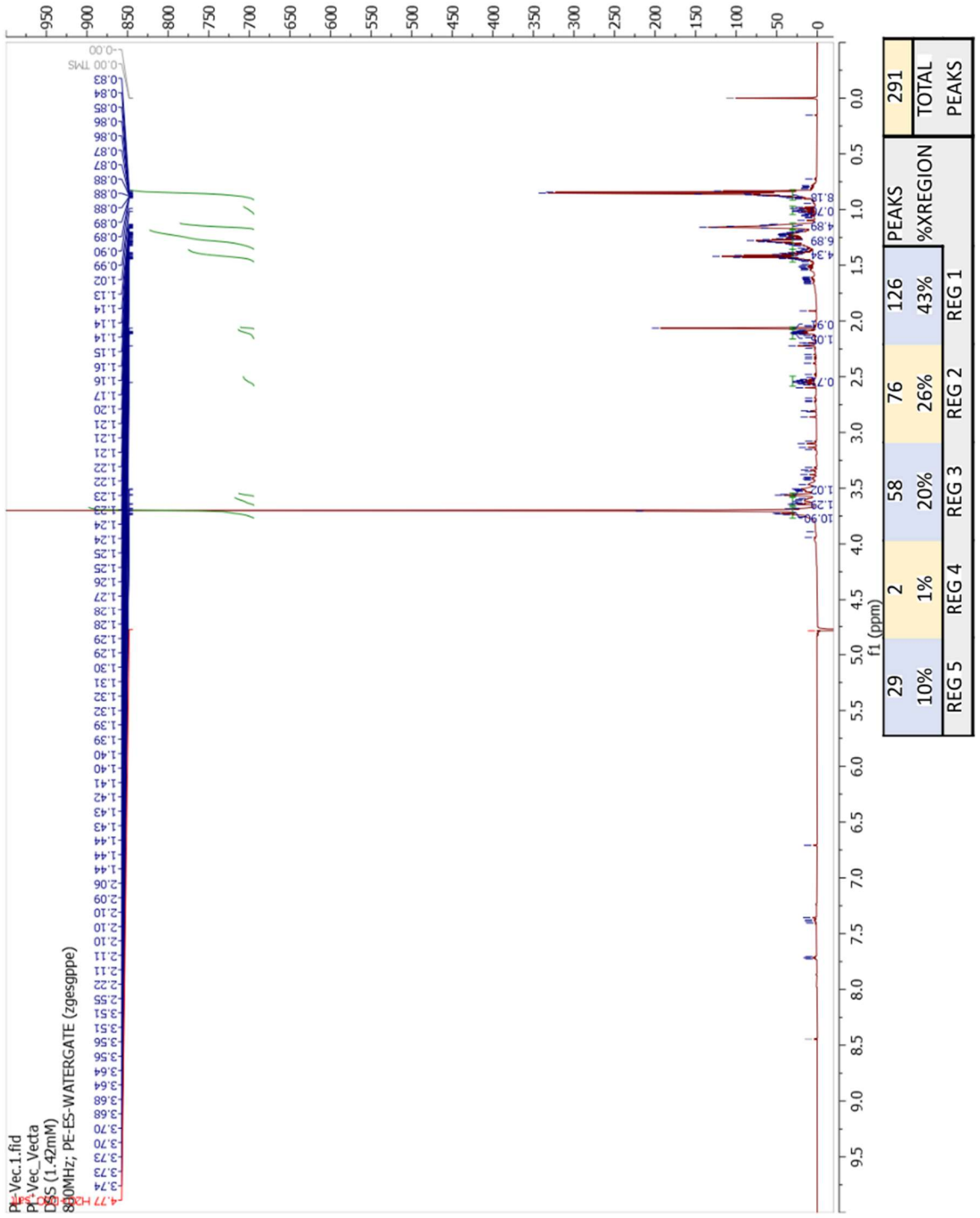
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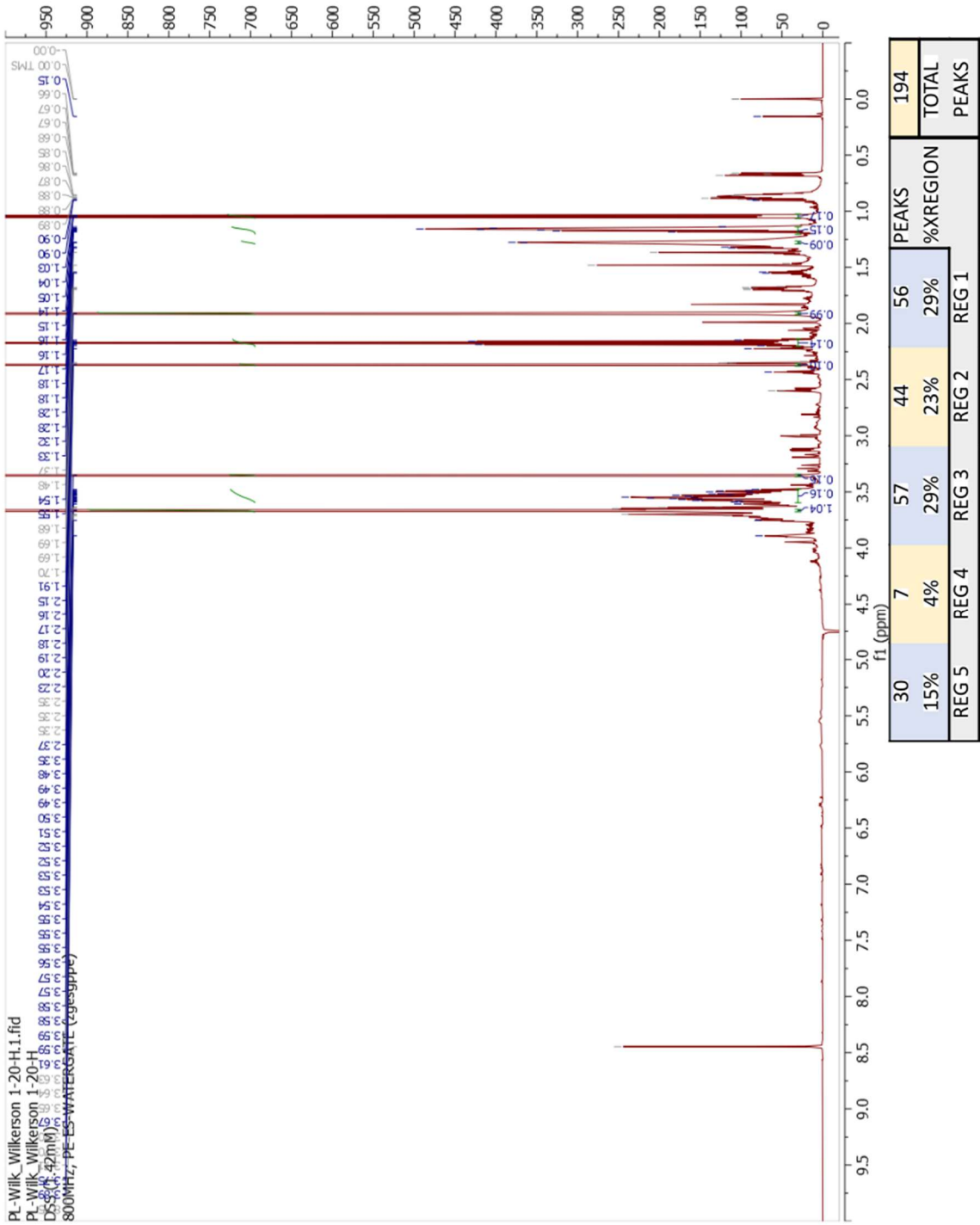
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WELL ID: PW#3



WELL ID: Vecta



WELL ID: Wilkerson 1-20-H

VITA

Peter E. Loree

Candidate for the Degree of

Master of Science

Thesis: QUALIFYING CLASSES OF ORGANIC COMPOUNDS WITHIN
UNPROCESSED PRODUCED WATER USING ¹H-NMR ANALYSIS

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