Assessing Magnetic Particle Content in Algae Using Compact Time Domain Nuclear Magnetic Resonance

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ABSTRACT

The characterization of algae biomass is essential for ensuring the health of an aquatic ecosystem. Algae overgrowth can be detrimental to the chemical composition of a habitat and affect the availability of safe drinking water. In-situ sensors are commonplace in ocean and water quality monitoring scenarios where the collection of field data using readily deployable, cost-effective sensors is required. For this purpose, the use of compact time domain nuclear magnetic resonance (TD-NMR) is proposed for the assessment of magnetic particle (MP) content in algae. A custom NMR system capable of rapidly acquiring relaxometric data is introduced, and the T_2 relaxation curves of algae samples sourced from Lake Wateree in South Carolina are analyzed. A clear correlation between the relaxation rate and MP concentration of the samples is observed, and the viability of the proposed scheme for MP-based estimations concerning algae is discussed.

Keywords: ocean monitoring, in-situ sensors, algae, TD-NMR, magnetic particles

1. INTRODUCTION

Ocean monitoring is a far-reaching discipline concerned with the collection and analysis of aquatic data. The field is integral to many applications, including but not limited to conservation initiatives, disaster prevention, and both industrial and maritime enterprises alike. While ocean monitoring systems encompass remote sensing techniques[1] and even community knowledge,[2] the primary source of oceanographic data are in-situ sensors.[3] Such sensors are cost-effective and can be deployed in relatively straightforward manners. Further, application-specific sensors can be integrated as part of a larger sensor network, allowing for the interpolation of local and regional measurements to a global scale.[4]

The health of aquatic ecosystems is intimately related with the presence of microorganisms such as algae. Because algae form the base of aquatic food webs and are sensitive to numerous undesirable pollutants,[5] algae biomass is a common metric for ecosystem wellness. An excess of algae, however, can negatively impact aquatic ecosystems by chemically altering habitats and affecting the quality of drinking water.[6] The characterization and monitoring of algae biomass is therefore of paramount importance for environmental management. In particular, the iron uptake mechanisms of different algae have been the subject of much research,[7–9] being especially pertinent in commercial applications requiring the growth of microalgae.[10]

While various nuclear magnetic resonance (NMR) techniques have been employed for algae characterization,[11–13] to the knowledge of the authors, no studies report the use of T_2 relaxometry for the determination of

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magnetic particle content (MP) in algae. T_2 relaxometry is a subset of time domain nuclear magnetic resonance (TD-NMR) that allows for the acquisition of a sample's T_2 relaxation curve, a signal that quantifies the decay of nuclear magnetization following excitation by external, pulsed radiation. Despite the comparative low resolution of relaxometric data, select properties of a sample can be derived from the analysis of its T_2 curve, with sample hydrogen density and MP concentration known to correlate with the initial strength[14] and relaxation rate[15] of a T_2 curve, respectively.

This work proposes the use of compact TD-NMR for the measurement of MP content in algae. Specifically, a desktop NMR system is used to acquire the T_2 relaxation curves of algae samples sourced from Lake Wateree in South Carolina. Ensuing analysis reveals a clear correlation between the relaxation rate and MP concentration of the samples. The contribution of this work is demonstrating the viability of compact TD-NMR for MP-based estimations concerning algae.

2. MATERIALS AND METHODS

The compact TD-NMR system used for experiments is pictured in Fig. 1. This design is open source.[16] The system is under the control of a LabVIEW program running on the pictured laptop. The laptop interfaces with an NI-PXI chassis that houses an arbitrary waveform generator (PXI-5421), a pulse train generator (PXIe-5413), and a 16-bit digitizer (PXI-5922). Barring the first-stage low-noise amplifier and high-power amplifier, all electronics are included on a single printed circuit board (PCB).

The permanent magnet array consists of two grade N42 cylindrical dipole magnets that are axially magnetized and enclosed by a steel yolk.[17] To further enhance both field strength and homogeneity, 1018 carbon steel caps are appended to magnet surfaces. The resulting magnetic field achieves a peak flux density of 0.645 T, a value that corresponds to a Larmor frequency of approximately 27.5 MHz. The magnet array is designed for analytes to be in 5 mm test tubes.

A single 24 V power supply and linear regulators are used to power the entire system. For sample excitation, radio frequency (RF) pulses are generated by switching the output of the waveform generator following the Carr-Purcell-Meiboom-Gill (CPMG) pulse train. Tuning and matching capacitors are placed both in series with and across the probe to match its impedance with that of the system's 50 Ω cables. Following excitation, the NMR signal picked up by the probe is amplified and further mixed with the original sinusoid used for excitation. The resulting signal is again amplified before being passed through an active band-pass filter with lower and upper cutoff frequencies of 5 kHz and 15 kHz, respectively. The output of this filter is the final NMR signal.

Each scan of a sample consists of 3955 individual pulses, with a pulse of 7 μs corresponding to a 90° rotation of the sample's magnetization vector; the time between 90° and 180° pulses ("tau" value) is 0.625 ms. A typical NMR signal takes the form of that depicted in Fig. 2(a) showing three spin echos following the excitation of a

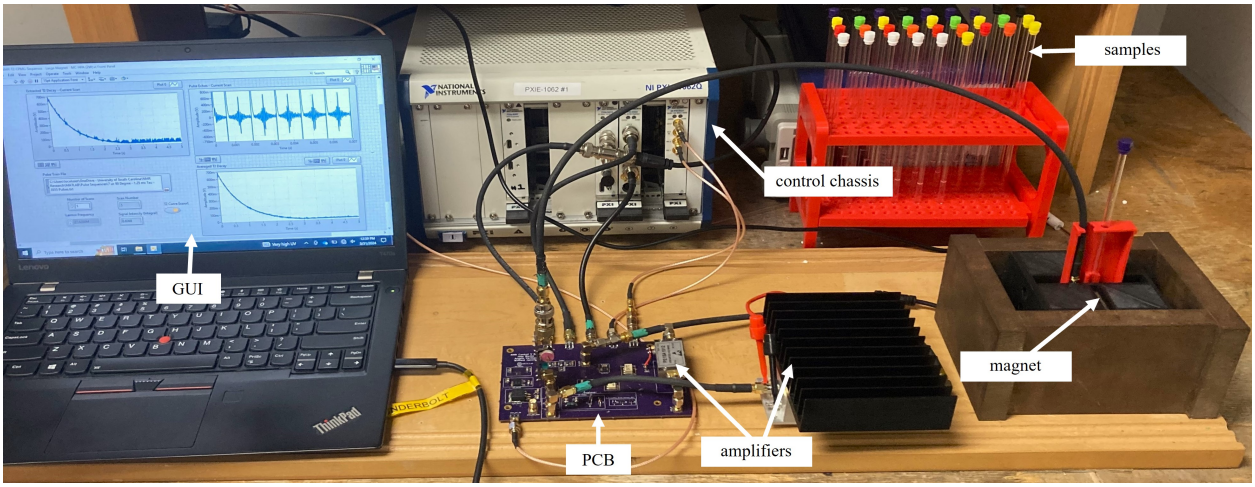


Figure 1. The compact TD-NMR system used in this work with key components and subsystems annotated.

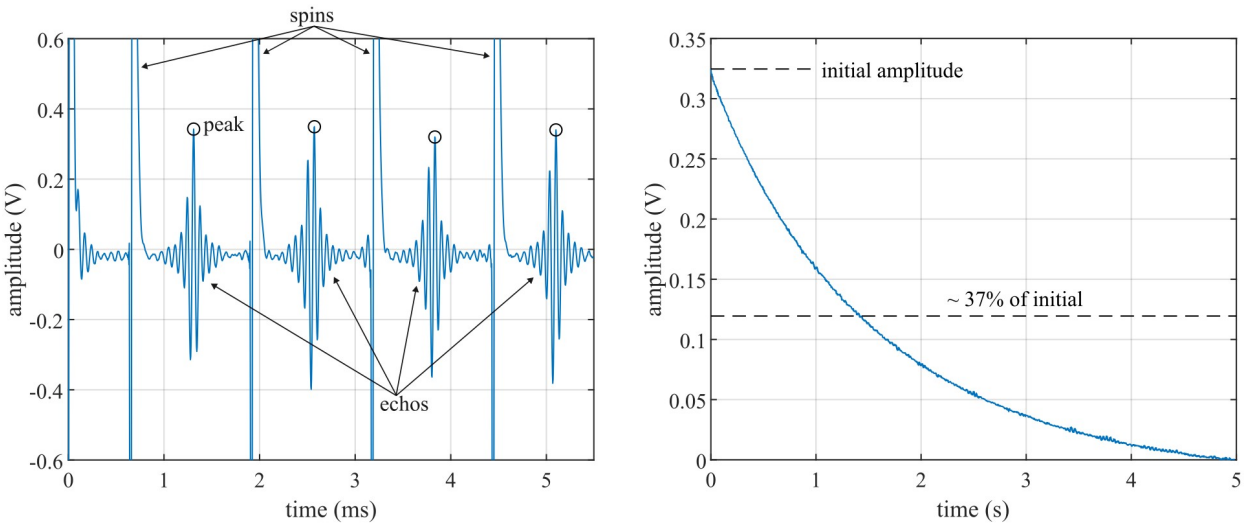


Figure 2. Example TD-NMR signals. (a) Three spin echos from a sample of tap water following one 90° and two 180° RF pulses. (b) The T_2 relaxation curve of tap water constructed from 3955 spin echos.

sample of tap water with one 90° and two 180° RF pulses. The implemented LabVIEW program automatically identifies and records the peak voltage associated with each spin echo. This sequence of voltages forms the T_2 relaxation curve of the sample, a decaying exponential that is described by

$$M_{xy}(t) = M_0 \exp\left(-\frac{t}{T_2}\right), \tag{1}$$

where $M_{xy}(t)$ is the bulk magnetization of the spins in the transverse plane, M_0 is the magnetization at thermal equilibrium, and T_2 is the primary relaxation time. Fig. 2(b) shows the T_2 curve of a sample of tap water constructed from the peak echos of Fig. 2(a). Note that after one T_2 time, a sample's relaxation curve will have decayed to 37% of its initial strength as $M_{xy}(T_2) \approx 0.37 M_0$.

For analysis, four algae samples were sourced from Lake Wateree in South Carolina. Three of the samples were collected from the same shoreline and flash frozen using liquid nitrogen; these samples are referenced as A-01, A-02, and A-03. A fourth algae sample, A-04, was collected from a different shoreline of Lake Wateree on a much later date. Also unlike the previous three samples, A-04 was not frozen using liquid nitrogen; rather,

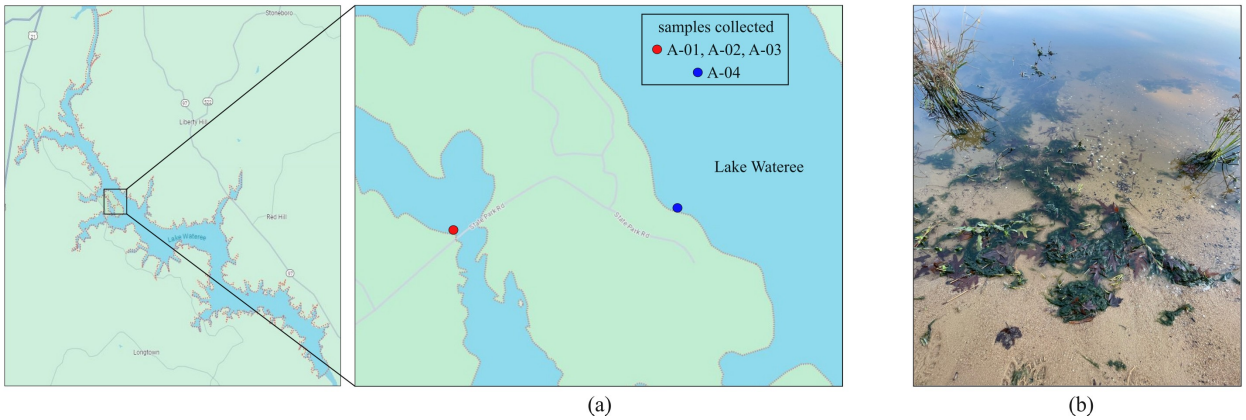
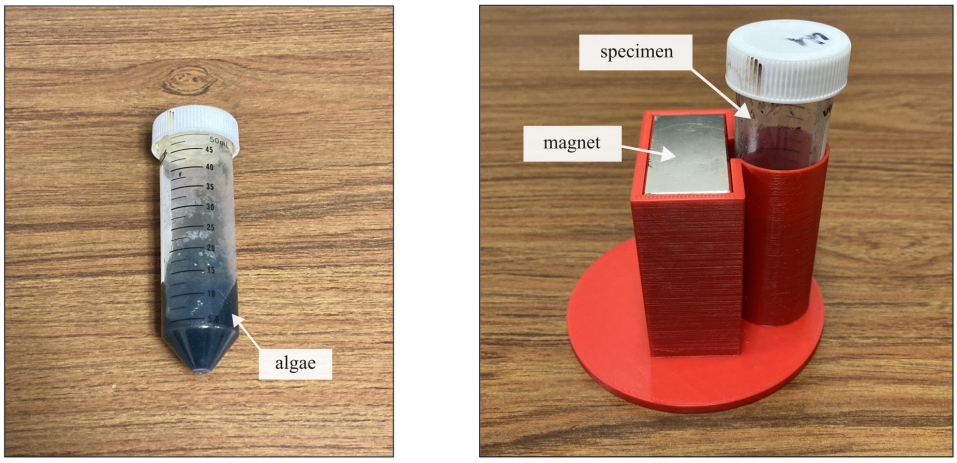


Figure 3. Algae sampling locations. (a) Map of Lake Wateree showing the location that each algae sample was collected. (b) The algae mat from which A-04 was collected.

the sample was directly mixed with MilliQ (MQ) water and sonicated. See Fig. 3 for a visualization of algae sampling locations.

To establish that the algae samples have relaxation rates distinguishable from surrounding water, A-01, A-02, and A-03 were submerged in MQ water and placed into 5 mm NMR tubes. The introduced TD-NMR system was then used to acquire the T_2 relaxation curves of the samples measured at four distinct locations along each NMR tube. Specifically, the test tubes were positioned into the NMR probe in increments of 25 mm (1 in), and at each depth the T_2 curves of the samples were obtained. Relaxation rates were identified by fitting first-order exponentials of the form present in Eq. (1). Note that the relaxation rate of a sample is simply the reciprocal of its T_2 time, i.e., $R_2 = 1/T_2$.

To verify that any differences in relaxation rate are due to the presence of MPs, a simple experiment was conducted using A-04 in Fig. 4(a) and the MP separator of Fig. 4(b). The MP separator comprises an N52 permanent magnet and 3D printed housing with adjacent slots for both the magnet and a centrifuge tube. The apparatus is designed such that when a specimen is loaded, MPs will be attracted to the wall of the container nearest the magnet. A sample extracted from the opposite side of the container will therefore contain a minimal concentration of MPs. Following the sonication of A-04, the TD-NMR system was first used to measure the relaxation curve of the sample without MP separation. The specimen was then loaded into the MP separator and left to sit for half an hour. The T_2 curve of a sample extracted following MP separation was subsequently acquired.



(a) (b)

Figure 4. MP separation experiment. (a) Sample A-04 before sonication. (b) Rudimentary MP separator consisting of a permanent magnet and 3D printed housing.

3. RESULTS AND DISCUSSION

Fig. 5 shows the relaxation rates acquired by probing along the NMR tubes housing A-01, A-02, and A-03. The measured relaxation rates are noticeably large, being comparable in magnitude to those obtained from pure magnetite samples.[15] Moreover, it can be seen that the relaxation rates increase as measurement locations approach algal material, indicating an association between algae and MPs. Indeed, while the measured relaxation rates are everywhere greater than that of MQ water, the highest relaxation rates are observed in algae-dense regions of the samples. Fig. 6 pictures the T_2 curves probed from A-04 both before and after undergoing MP separation. A clear decrease in relaxation rate is identified following MP separation, thus confirming that the large relaxation rates of the algae samples are due to the presence of MPs.

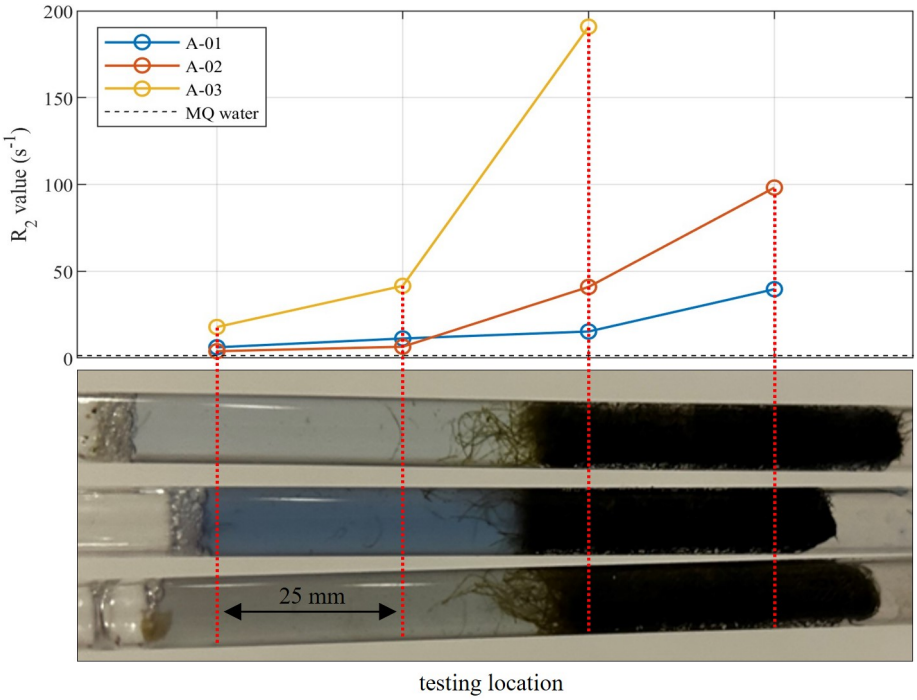


Figure 5. Relaxation rates measured along the NMR tubes housing A-01, A-02, and A-03. The relaxation rate of MQ water has been overlaid for reference.

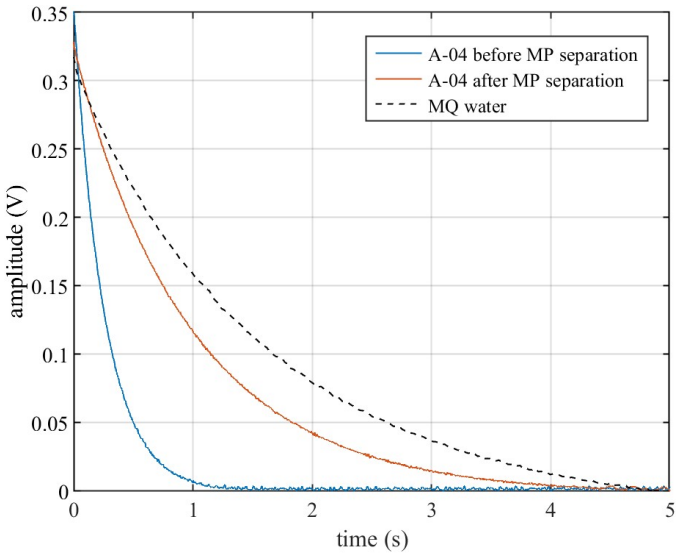


Figure 6. T_2 relaxation curves of the sonicated fourth algae sample both before and after MP separation. The T_2 curve of MQ water has been plotted for reference.

4. CONCLUSION

This work proposed the use of compact TD-NMR for the assessment of MP content in algae. A custom desktop NMR system consisting of a permanent magnet, an NI-PXI chassis, and a single PCB was used to measure the T_2 relaxation curves of four algae samples sourced from Lake Wateree in South Carolina. After probing along three NMR tubes housing algae samples, it was observed that relaxation rate was maximized in algae-dense regions. To demonstrate that the large relaxation rates of the samples were due to the presence of MPs, the T_2 curve of a fourth algae sample was acquired both before and after undergoing MP separation. A clear decrease in the

decay rate of the sample was recognized following MP separation, verifying that MP content within the algae was the source of measured differences in relaxation rate. The applications of this work are in ocean and water quality monitoring where research into novel in-situ sensing techniques is an ongoing effort. Future work will focus on the integration of a flow-through system, allowing for the development of a compact TD-NMR sensor with automatic probing capabilities.

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