Vol. 1(1), November 2024, pp. 53-57 Radiance NEWSLETTER

Nuclear Magnetic Resonance Spectroscopy in Environmental Research

Nihita Linson[1], Jissy Jacob[2,3], Sunny Kuriakose[4]

[1]Research and Postgraduate Department of Chemistry, St. George's College Aruvithura Mahatma Gandhi University, Kottayam, Kerala, India-686122.nihitaresearch@gmail.com

[2] International and Inter University Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kottayam, Kerala-686560, India. Jissyjacob990@gmail.com

[3]Professor and Research Guide, St. Thomas College, Palai. sunnykuriakose30@gmail.com

Nihita Linson Jissy Jacob Sunny Kuriakose

Nuclear Magnetic Resonance (NMR) spectroscopy is a highly effective analytical technique used in various scientific disciplines, including environmental chemistry. It provides detailed insights into molecular structures, interactions, and dynamics, crucial for analyzing complex environmental systems. One-dimensional (1D) NMR determines the types of nuclei and their quantities, while multidimensional NMR reveals correlations between nuclei, showing how they are connected to form a complete structure [1]. NMR is also capable of resolving overlapping signals in complex structures or environmental matrices such as soil, sediment, water, or airborne particles. Ecosystems are constantly evolving and impacted by various biological, chemical, and physical processes, including climate change, urbanization, agriculture, and industrial activity [1, 2]. Understanding molecular-level processes within ecosystems is crucial and NMR is essential for research on clean energy, biofuels, wastewater treatment, and metabolic reactions. It also reveals the toxicity of contaminants and their method of action, even at sublethal levels. Combining current NMR approaches improves our understanding of carbon cycling, sustainable agriculture, pollutant fate, bioavailability, toxicity, sequestration, and remediation [3].

NMR spectroscopy can be used for studying environmental matrices, utilizing various techniques at different scales to understand molecular complexities in different environmental samples. The different types of NMR spectroscopy commonly used in environmental research are a) solution-state NMR spectroscopy, b) solid-state NMR spectroscopy, c) gel-phase NMR spectroscopy, d) comprehensive multiphase NMR spectroscopy, e) low field and portable NMR, f) hyphenated techniques, and g) magnetic resonance imaging. These techniques assess spatial interactions, diffusion, relaxation, line shape, and chemical shift changes in solid, gel, and solution states, particularly in the context of environmental samples [1, 2]. Some of the key applications of NMR spectroscopy in environmental research are summarized in Figure 1 and discussed in detail.

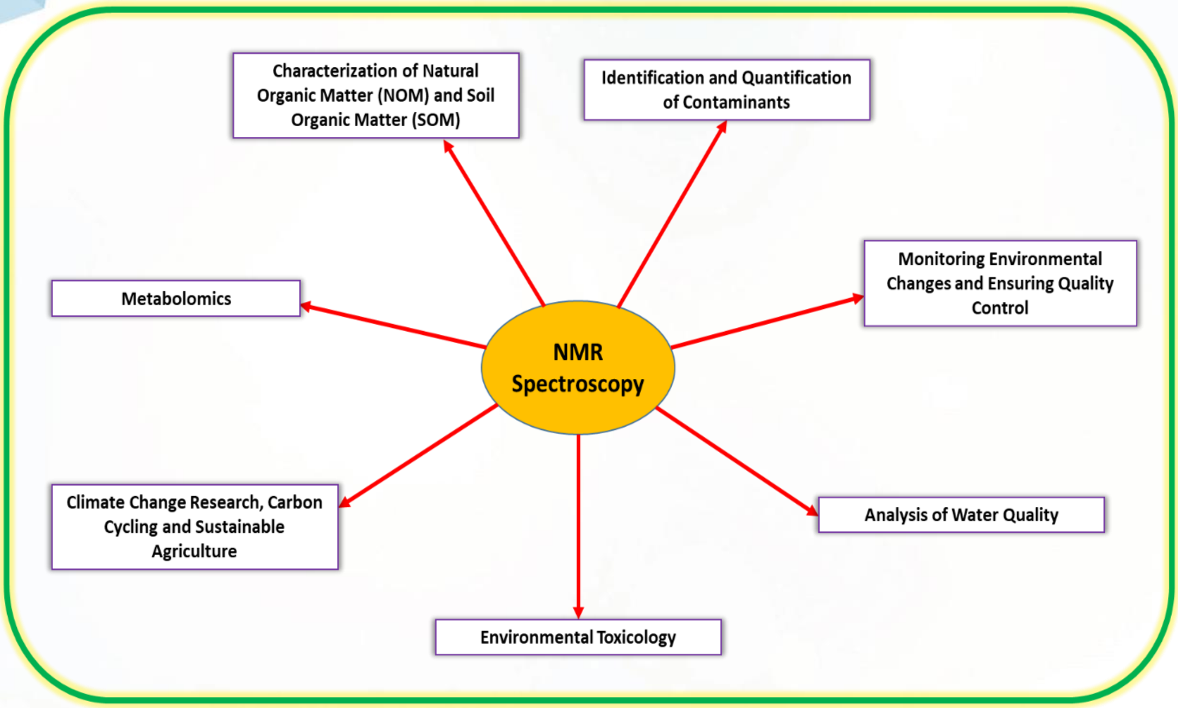

Figure 1: Key applications of NMR spectroscopy in environmental research

1. **Identification and Quantification of Contaminants**: NMR spectroscopy is a powerful tool for identifying and quantifying environmental contaminants, including pollutants in water, soil, and air. It accurately distinguishes between different chemical species and determines their concentrations. Studies have explored noncovalent pollutant interactions with soil using ^{13}C or ^{19}F solid-state NMR and ^{1}H HR-MAS NMR, as well as covalent binding using ^{15}N NMR. These studies provide insights into the molecular environment of the pollutant, elucidating binding mechanisms and soil components. However, most pollutant-soil studies use indirect methods, such as measuring binding coefficients, which do not provide molecular-level information about binding mechanisms [4].

2. **Characterization of Natural Organic Matter (NOM) and Soil Organic Matter (SOM)**: Natural Organic Matter (NOM) is a complex mixture of organic compounds found in soil, water, and sediments. NMR spectroscopy helps characterize NOM by elucidating its composition and interaction with contaminants. Solid-state NMR, particularly ^{13}C and ^{15}N NMR, is crucial for identifying functional groups and structural components. Techniques like CP/MAS and spectral-editing are used for this purpose. Advanced NMR techniques can identify nitrogen forms and study segmental dynamics, providing a comprehensive understanding of NOM's structural heterogeneity. Combining NMR with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) allows molecular-level characterization, providing insights into NOM's composition and structure. Soil organic matter (SOM) is also studied using NMR spectroscopy. It helps assess soil quality and understand carbon sequestration processes, particularly in vulnerable ecosystems like the Arctic and peatlands. SOM can bind with metals, organic pollutants, and soil minerals. NMR, particularly solid-state NMR (SSNMR), is used to study soil chemistry and environmental remediation processes, such as heavy metal and

radionuclide removal, carbon dioxide mineralization, and phosphorus recovery. Later, techniques such as cross-polarization-magic angle spinning (CP-MAS), solid-state ^{13}C NMR were employed in SOM studies. Advanced NMR studies can better understand SOM as a complex blend of microbial and plant residues, enabling predictions of soil aggregate structure, humification processes, fertility, and stability, and its response to climate change, intensive agriculture, and land-use change [1, 2].

3. **Monitoring Environmental Changes and Ensuring Quality Control**: NMR can track changes in environmental samples over time or due to different treatments. It provides atomic-level information on pollutants and interactions, aiding in real-time monitoring of environmental photochemical processes. Solid-state NMR spectroscopy is used for environmental processes and remediation, while in-vivo NMR spectroscopy offers a unique view of the living metabolome. NMR spectroscopy is also used in quality control processes for environmental monitoring instruments and methods, ensuring accurate data collection. SSNMR provides atomic-level information on speciation in complex samples, aiding in soil chemistry studies, remediation, and phosphorus recovery [5]. Combining ^{1}H and ^{13}C NMR spectroscopy with chemometric methods allows for comprehensive quality control of fats and oils, including the analysis of fatty acid distribution, cis/trans composition, free fatty acids, peroxides, and aldehydes, enhancing authenticity control [2].

4. **Analysis of Water Quality**: NMR spectroscopy is used for analyzing water quality parameters like dissolved organic matter, nutrients, and pollutants, providing insights into contaminants' sources and fates. It's also increasingly used to analyze wastewater, providing insights into its composition, treatment processes, and potential impacts. Techniques like solvent suppression and multidimensional NMR help overcome challenges posed by the complex and dilute nature of wastewater. Borehole NMR is an emerging geophysical method used in hydrogeology investigations for in situ assessments of porosity, water content, mobile and immobile water fraction, and estimates of permeability [3].

5. **Environmental Toxicology**: NMR spectroscopy can be applied in toxicological studies to understand the interactions between contaminants and biological systems, helping to assess the environmental impact of pollutants. In-vivo NMR is a powerful tool for understanding environmental toxicity. It allows for the monitoring of dissolved metabolites and the detection of all components (solutions, gels, and solids) in organisms, providing a unique window into the living metabolome [1, 2].

6. **Climate Change Research, Carbon Cycling and Sustainable Agriculture:** NMR spectroscopy aids in studying carbon cycling and storage in ecosystems, which is essential for understanding climate change impacts and developing mitigation strategies. Advanced stable isotope and NMR techniques can enhance our understanding of carbon and nutrient cycling in forest ecosystems, aiding in climate change response and local management practices. Nuclear magnetic resonance technology can accurately predict CO_2 migration and changes in underground reservoirs, aiding in selecting project sites, estimating storage capacity, and ensuring storage security [1-3].

7. **Metabolomics:** Metabolomics is a discipline that examines metabolite fluxes resulting from alterations in metabolic functions caused by diseases or external stressors. This field has found considerable applications in ecology and ecotoxicology, concentrating on the interactions between organisms and their environments, such as exposure to pollutants, variations in nutrients or temperature, and changes in pH or salinity. Due to the diversity of organisms in soil and water, many keystone organisms lack a mapped genome or characterized proteome. The quick alterations in metabolites observed within hours of stress have spurred the extensive use of NMR in environmental metabolomics. This field has the potential to transform our understanding of how environmental changes affect ecosystem health and act as an environmental monitoring early warning system. NMR spectroscopy plays a crucial role in environmental metabolic applications by offering a detailed fingerprint of all the metabolites present. The minimal preparation of the samples allows high-throughput analysis, yielding many NMR spectra for multivariate statistical approaches like principal component analysis. Optimizing parameters for small molecule data acquisition has yielded a relative standard deviation of less than 1% for ^{1}H NMR spectra, demonstrating excellent analytical reproducibility. NMR-based metabolism is highly reproducible across different laboratories [1, 2, 6].

Overall, NMR spectroscopy is a valuable tool in environmental research, providing non-destructive, quantitative, and structurally informative analysis of environmental substances and procedures. It gives detailed insights into soil chemistry, wastewater analysis, environmental toxicity, carbon cycling, and element local environment. Its applications enhance our understanding of complex environmental systems and processes, aiding in effective environmental protection and remediation efforts. NMR is perfect for analyzing in vivo samples because it is non-destructive. However, issues including apparatus expense, cryogenic maintenance, perceived knowledge, technical obstacles, and low sensitivity limit its widespread usage in environmental research. The assignment of 100,000 molecular formulas produced by mass spectrometry (MS) to particular chemical structures is one of the biggest problems in environmental research. By revealing the relationships between these molecular formulas, NMR makes it possible to combine NMR and MS data to find difficult unknowns. NMR is used in both targeted and untargeted methods for identifying marker species, retrieving metabolic or microconstituent fingerprints, tracing contamination origins, studying heavy metal contaminants, and characterization of materials for environmental remediation applications. Advancements in instrumental technologies have greatly benefited NMR techniques, with the development of powerful cryomagnets, high-sensitivity multichannel probes, and cryoprobes leading to the widespread availability of high-resolution instruments [7]. The diffusion of solid-state probes and the development of sophisticated pulse sequences further enhance NMR's utility in environmental problems. Its applications continue to expand as new techniques and methodologies are developed.

References

1. Simpson, A. J.; Simpson, M. J.; Soong, R. Nuclear Magnetic Resonance Spectroscopy and Its Key Role in Environmental Research. *Environ. Sci. Technol.* **2012**, *46* (21), 11488–11496. https://doi.org/10.1021/es302154w.
2. Simpson, A. J.; Simpson, M. J.; Soong, R. Environmental Nuclear Magnetic Resonance Spectroscopy: An Overview and a Primer. *Anal. Chem.* **2018**, *90* (1), 628–639. https://doi.org/10.1021/acs.analchem.7b03241.
3. Anaraki, M. T.; Lysak, D. H.; Downey, K.; Kock, F. V. C.; You, X.; Majumdar, R. D.; Barison, A.; Lião, L. M.; Ferreira, A. G.; Decker, V.; Goerling, B.; Spraul, M.; Godejohann, M.; Helm, P. A.; Kleywegt, S.; Jobst, K.; Soong, R.; Simpson, M. J.; Simpson, A. J. NMR Spectroscopy of Wastewater: A Review, Case Study, and Future Potential. *Progress in Nuclear Magnetic Resonance Spectroscopy* **2021**, *126–127*, 121–180. https://doi.org/10.1016/j.pnmrs.2021.08.001.
4. Cardoza, L. A.; Korir, A. K.; Otto, W. H.; Wurrey, C. J.; Larive, C. K. Applications of NMR Spectroscopy in Environmental Science. *Progress in Nuclear Magnetic Resonance Spectroscopy* **2004**, *45* (3–4), 209–238. https://doi.org/10.1016/ j.pnmrs. 2004.06.002.
5. Wang, Q.; Nielsen, U. G. Applications of Solid-State NMR Spectroscopy in Environmental Science. *Solid State Nuclear Magnetic Resonance* **2020**, *110*, 101698. https://doi.org/10.1016/j.ssnmr.2020.101698.
6. Nagana Gowda, G. A.; Raftery, D. NMR-Based Metabolomics. In *Cancer Metabolomics*; Hu, S., Ed.; Springer International Publishing: Cham, 2021; Vol. 1280, pp 19–37. https://doi.org/10.1007/978-3-030-51652-9_2.
7. Conte, P.; Chillura Martino, D. F.; Lo Meo, P. The Meaning of Pollution and the Powerfulness of NMR Techniques. In *The Environment in a Magnet*; Conte, P., Chillura Martino, D. F., Meo, P. L., Eds.; Royal Society of Chemistry, 2024; pp 1–9. https://doi.org/10.1039/BK9781837671250-00001.