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Applications of Solid-state NMR Spectroscopy to Environmental Science

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Highlights

- Solid-state NMR probes the interactions between pollutants and minerals/organic matter on environmental interfaces
- Solid-state NMR provides atomic-level speciation in environmental samples
- Application of solid-state NMR in contemporary environmental topics
- Future perspectives are provided

Abstract

Environmental science is an interdisciplinary field, which integrates chemical, physical, and biological sciences to study environmental problems and human impact on the environment. This article highlights the use of solid-state NMR spectroscopy (SSNMR) in studies of environmental processes and remediation with examples from both laboratory studies and samples collected in the field. The contemporary topics presented include soil chemistry, environmental remediation (e.g., heavy metals and radionuclides removal, carbon dioxide mineralization), and phosphorus recovery. SSNMR is a powerful technique, which provides atomic-level information about speciation in complex environmental samples and interactions between pollutants as well as minerals/organic matter on different environmental interfaces. The challenges in the application of SSNMR in
environmental science (e.g., measurement of paramagnetic nuclei) are also discussed, and perspectives are provided for the future research efforts.

*Keywords*: Solid-state NMR, soil, environmental remediation, CO₂ mineralization, P recovery, pollutant-mineral interaction

**Graphical abstract**
1. Introduction

Environmental science is an interdisciplinary field spanning chemistry, geoscience, biology, and engineering which studies environmental problems and the human impact on nature. The rapid industrialization and urbanization have resulted in global environmental challenges including pollution, climate change, resource crisis, food security, etc. Increasingly, research activities are driven to understand these environmental issues, and mitigation measures such as environmental remediation, carbon dioxide (CO$_2$) sequestration, and resource recovery for a “Circular Economy” have become the focus of environmental studies. Environmental samples such as soil, sludge, and sediment are among the most complex and heterogeneous [1]. Furthermore, their analyses are often complicated due to the presence of multiple phases (e.g., liquids, solids, and gases) with components of both organic and inorganic origin. In addition, many environmental chemical processes proceed on interfaces, e.g., the binding of aqueous pollutants on mineral surfaces (a solid-water interface) [1]. Thus, several characterization techniques, often in combination with analytical or computational models, is needed to fully understand these complex samples and processes, which usually cover multiple length scales from Ångstrøm (Å) to centimeter [2].

To obtain atomic-level information (i.e., $\approx$ Å) in an environmental sample or process, NMR spectroscopy is a powerful technique, as it is isotope (element) selective and can provide detailed insight into the chemical speciation (via the isotropic chemical shift, $\delta_{iso}$) as well as allow for quantification of the different species in complex, multiphase environmental samples. Furthermore, NMR spectroscopy can probe the intermolecular interaction between pollutants and minerals/organic matter via correlation experiments, and provide insight into the transport and transformation of these substances in the environment [3, 4]. More than a decade ago, the application of NMR spectroscopy in environmental science was reviewed with focus on the characterization of soil organic matter and sorption by soils as well as environmental contaminants and their transformation [5]. The reader is
referred to the excellent reviews by Simpson et al. [1, 2], in which the different NMR techniques applicable for structural characterization of natural organic matter (NOM) and its interaction with contaminants are discussed in detail. Liquid-state NMR spectroscopy provides high-resolution spectra, from which structural information of the targeted nucleus can be obtained. However, only the soluble fractions in the samples can be probed [1]. For environmental samples like soil, sediments, and sludge, which are mainly insoluble, extraction with solvents can alter the intermolecular interactions and the chemical composition of the targeted molecules/ions inside, thereby providing an incomplete insight into the actual sample composition and the relevant environmental processes. Solid-state NMR (SSNMR) can provide an overview of a bulk sample in a noninvasive manner with less sample handling. It is generally applied for the characterization of solid samples with emphasis on chemical speciation such as identification of mineral phases [6]. Moreover, SSNMR studies of minerals have been central for the benchmarking of density functional theory (DFT)-calculations of NMR parameters for inorganic materials [7]. It is also extensively used to probe the interactions between pollutants and solids (e.g., to identify binding sites) on the atomic level [4, 8]. Local structural information such as the oxidation state and coordination number of a particular element can also be obtained from X-ray absorption spectroscopy (XAS) which covers both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS) [9]. However, it is very difficult to employ XAS on light elements such as H, C, and N (i.e., the first two rows of the periodic table of the elements), which are generally accessible by SSNMR. Thus, SSNMR and XAS are complementary techniques and represent a powerful combination in environmental studies. Moreover, the use of XAS relies on the access to a synchrotron, where several beamlines at international synchrotron facilities are optimized for environmental science studies. However, instrument time is generally granted via peer-reviewed proposals with three to nine months from proposal submission to beam time. In contrast, SSNMR can often be performed in-house at moderate
magnetic fields on routine NMR spectrometers equipped with a double resonance $^1$HX (H is proton and X denotes any other NMR nucleus) magic angle spinning (MAS) NMR probe and standard-size rotors (3.2-7.0 mm). Although SSNMR is less sensitive than liquid-state NMR and is limited to isotopes present in reasonable quantities (i.e., the major components present), isotope enrichment may alleviate this issue in laboratory studies [10]. Table 1 summarizes the properties of selected NMR isotopes of relevance in environmental science [11], and nuclei with high natural abundance (e.g., $^{27}$Al, $^{31}$P, and $^{19}$F) in environmental samples are usually easily approachable by SSNMR. A second challenge is the presence of elements like iron, manganese, lanthanides, and actinides, which often contain unpaired electrons, can lead to substantially broadened and “invisible” NMR signals due to the paramagnetic properties, as will be discussed in Section 6.1.

This review focuses on the applications of SSNMR on several contemporary topics in environmental science. First, recent SSNMR studies on soil, whose characteristics are significantly related to many environmental processes given its interfaces with the lithosphere, biosphere, hydrosphere, and atmosphere, are reviewed and discussed. Second, the applications of SSNMR in environmental remediation, including sequestration of contaminants (e.g., heavy metals and radionuclides) and carbon dioxide (CO$_2$) mineralization for mitigating climate change, are reviewed. Third, recent SSNMR studies on resource recovery, e.g., removal and recovery of phosphorus from wastewater to achieve “Circular Economy” [12], are summarized. Finally, the challenges in SSNMR studies of environmental samples and processes are discussed, and future perspectives are provided.

2. Practical and theoretical aspects of SSNMR studies in environmental science

Detailed knowledge about quantum mechanics beyond the basic undergraduate chemistry and physics courses is needed for a detailed understanding of NMR theory especially analyses of advanced pulse sequences and spin systems, but not needed for application of SSNMR as an analytical method. This render SSNMR a valuable characterization technique in environmental
science. Below are some key aspects of SSNMR theory summarized with emphasis on application for non-NMR experts with limited knowledge of quantum mechanics. A general introduction to SSNMR with the use of only basic quantum mechanics can be found in Ref. [13], and the some older references on SSNMR studies of clays, zeolites, and aluminum containing minerals were written for non-NMR specialists [14, 15]. More detailed references, which cover the fundamentals of SSNMR of inorganic materials [16, 17] and paramagnetic NMR spectroscopy (pNMR) [18, 19] are available. Here the information that can be obtained from analyses of SSNMR spectra of environmental samples is briefly summarized.

2.1. Interpretation of SSNMR spectra

The majority of environmental SSNMR studies focus on the determination of the isotropic chemical shift ($\delta_{\text{iso}}$, ppm), i.e., the position of the NMR resonance, which is modified by shielding of the nucleus by the surrounding electron distribution and therefore depends on the atoms/ions in the nearest coordination spheres as well as the bonding geometry. Hence, $\delta_{\text{iso}}$ is a fingerprint of the species present and their local environment. For example, $\delta_{\text{iso}}(^{13}\text{C})$ is extensively used for identification of functional groups in organic soil matter [20] and $\delta_{\text{iso}}(^{29}\text{Si})$ reflects the degree of condensation of the silicate tetrahedra as well as the number of four-coordinate aluminum units in the second coordination sphere in (aluminum)silicates such as clays, zeolite, and silicate minerals [14]. The most common assignment strategy in environmental science is to compare the observed $\delta_{\text{iso}}$ with those of chemically well-defined model compounds such as minerals and molecular species. This approach is illustrated for the interpretation of $^{31}\text{P}$ MAS NMR spectra of a struvite specimen and a wastewater precipitate in Fig.1. Computational methods, especially based on Density Functional Theory (DFT; “NMR crystallography”), are often used for assignment and interpretation of SSNMR spectra [17]. However, the approach is sparingly used in environmental science due to the complexity of the systems and the fact that many environmental processes take place on the surface or in poorly
crystalline materials [7, 21, 22]. Quadrupolar nuclei, which have a nuclear spin, $I$, larger than $\frac{1}{2}$, constitute about two thirds of the NMR active nuclei. In addition to the chemical shift interaction, the quadrupole interaction, which reflects the interaction of the nuclear quadrupole moment (eQ) with the electric field gradient tensor (V), is generally present except in the rare cases of local cubic symmetry, e.g., for $^{23}\text{Na}$ and $^{35}\text{Cl}$ in halite, and for highly mobile species (liquids) [13, 16]. Most studies of quadrupole nuclei focus on the so-called central transition ($\pm \frac{1}{2} \leftrightarrow -\frac{1}{2}$), which is only affected by the quadrupolar interaction as described by second-order perturbation theory [23]. It may give rise to a characteristic line shape from which $\delta_{\text{iso}}$, as well as the quadrupole coupling constant ($C_Q$) and asymmetry parameter ($\eta_Q$) can be determined using NMR simulation software (vide infra). Most importantly, the center of gravity of the isotropic resonance for a quadrupolar nucleus does not correspond to $\delta_{\text{iso}}$ (unlike $I = \frac{1}{2}$ nuclei) due to the so-called second-order quadrupole shift, which depends on the magnetic field strength and size of the quadrupolar interaction [13-15]. For samples with weak and moderate quadrupole interactions (resonance line width is comparable or smaller than the MAS frequency), the two dimensional (2D) multiple quantum MAS (MQ-MAS) and satellite transition MAS (ST-MAS) NMR spectra can be used to remove the second order line broadening and thereby increase the spectral resolution [13, 16, 23]. When the signal width is significantly larger, static NMR spectra should be recorded using echo sequences and the use of sensitivity enhancement by, e.g., cross-polarization (CP), dynamic frequency sweep (DFS), and/or Carr-Purcell-Meibom-Gill sequences should be considered [24]. For NMR spectra acquired using MAS, care should be taken to precisely set the magic-angle, and single-pulse (SP) NMR spectra should be acquired using a short flip angle ($< 15^\circ$) to ensure uniform excitation [13, 15, 23].

For environmental samples, the NMR nucleus of interest is often present at a low concentration, thereby the frequently observed background signals from the NMR rotor and probe should be corrected by, e.g., subtraction of NMR spectra of the background signal or the use of an
echo-sequence. We have observed significant background signals for $^1$H (rotor), $^{13}$C (polymers used for e.g., rotor endcaps, spacers and drive tips, and certain stators), $^{19}$F (polymers used for e.g., rotor endcaps, spacers and drive tips, and certain stators), $^{25}$Mg (MgO in zirconia rotors), $^{27}$Al (rotor sleeve), and $^{29}$Si (rotor sleeve). For example, $^{27}$Al background signals vary significantly between different rotor sleeve batches and manufacturers, but with less variation within the same batch.

Further structural information can be obtained using the J (indirect spin-spin) and dipolar coupling, which are interactions between two different NMR nuclei a few chemical bonds away (J-coupling) and less than 5-10 Å (dipolar coupling), respectively [13]. These two interactions are the foundation of numerous 1D and 2D NMR experiments used for structural assignment, e.g., COSY, HETCOR, REDOR, TRAPDOR, and HSQC. These experiments are designed to correlate two NMR resonances, i.e., structural assignment either heteronuclear (resonances from two different elements, e.g., $^1$H and $^{29}$Si) and homonuclear (two different resonances of one element, e.g., two different $^{27}$Al) [13]. Moreover, the dipolar interaction is also extensively used to increase the signal intensity from insensitive nuclei (I) with low abundance and/or low gyromagnetic moment using CP transfer from a sensitive nuclei (S) generally $^1$H or alternatively $^{19}$F and $^{31}$P, which have high abundance and gyromagnetic ratio. It is emphasized that CP-MAS NMR spectra should be interpreted with care, as they are not quantitative due to non-uniform polarization transfer and some parts of the sample may be invisible [13].

2.2. Analyses of SSNMR Spectra

The NMR spectrometer software allows for processing and basic analyses of NMR spectra, e.g., deconvolution to determine the isotropic chemical shifts and spectral integration to calculate the relative concentrations of different species. More detailed data analyses such as simulations and extraction of NMR parameters, e.g., quadrupole coupling parameters ($C_0, \eta_0$), can be performed using
3. Soil

The solid phase of soil is divided into the organic and the inorganic fractions, whose relative concentrations are quite variable as they depend on the geological and chemical conditions. The organic fraction, i.e., soil organic matter, consists of about 15% living organisms and 85% of dead biomass [31]. Humic substances are generated as an important organic component in soil by the decay of plants and animals debris at the soil surface by microbes and other detritus feeders [32]. The inorganic fraction, i.e., soil minerals, consists of primary minerals from parent rocks and secondary minerals generated by weathering [31], including a wide range of minerals like silicates (e.g., quartz and clays), (oxy)hydroxides, and carbonates, of which many serve as binding sites for pollutants.

3.1. Soil organic matter

Soil organic matter, the largest continental carbon (C) stock [31], is highly correlated to the physical, chemical, and biological processes in soil. The characterization of soil organic matter can provide important insight into the soil fertility, soil contamination, global climate change (C sequestration) etc. [2, 33]. However, it is not easily achievable as soil is the most complicated biomaterial on the planet [34]. Liquid-state NMR can characterize the extractable organic matter in a suite of different programs including ssNake [25], DMFit [26], QuadFit [27], WinSolids [28], and SpinWorks [29]. More complex NMR analyses of e.g., spin systems can be performed by SIMPSON [30], which requires a more detailed understanding of NMR theory. It should be emphasized that the SSNMR spectra of environmental samples often show significant variation in the chemical environment due to defects such as vacancies and impurities. This leads to a distribution (variation) in chemical shifts and quadrupole interaction parameters, which is reflected as broader lines and deviation from the ideal (theoretical) NMR line shape. Several of the NMR simulation programs mentioned above (e.g., QuadFit, DM-Fit, and ssNake) allow for a distribution in NMR parameters.
soil (e.g., humic acids), but most environmental studies on soil prefer to understand soil samples in their natural state given that pretreatment (e.g., extraction) may change the structure of organic matter and influence the properties of soil [1]. SSNMR spectroscopy has been employed to investigate organic matter in soil samples with minimum or no pretreatment. SSNMR was reported to be more accurate and precise than XANES spectroscopy for the quantification of the different organic C species in soil at organic C concentrations above 10 mg/g [35]. We will focus on some recent SSNMR studies of soil organic matter to illustrate the applications of environmental importance, e.g., effect of environmental factors on soil organic C stabilization, and contaminants transport in soil, as the application of SSNMR for analysis of soil organic matter has been extensively reviewed [1, 20, 36-39].

Using the isotropic chemical shifts observed for soil organic matter composition (e.g., alkyl C at 0-45 ppm, O-alkyl C at 45-110 ppm, aromatic C at 110-160 ppm, and carboxylic C at 160-190 ppm, shown in Fig. 2) [39], $^{13}$C CP-MAS NMR has been widely applied to investigate the response of soil biochemistry to external factors such as wildfire [40], fertilization [41, 42], and straw amendments [43, 44]. For example, the C stabilization mechanism in mangroves and salt marshes, which have typically higher C sequestration rates and greater soil C stocks than other terrestrial ecosystems, was investigated by $^{13}$C CP-MAS NMR. The simpler molecular structure of C revealed greater decomposition of soil organic matter in soil with invasion of $S.$ alterniflora (exotic cordgrass) than that in mangrove forest [45]. The $^{13}$C CP-MAS NMR spectra also showed the major role of organo-mineral association and recalcitrant C in the stabilization of soil organic C in salt marsh and mangrove soil, respectively [45]. Furthermore, the CP total sideband suppression (TOSS) $^{13}$C NMR spectra of straw-amended soil under anaerobic and aerobic incubation were recorded (Fig. 2). The alkyl C/O-alkyl C ratio (A/O-A), which is the ratio of recalcitrant C/labile C (the larger the ratio, the more stable the C stock), was calculated based on the relative abundance of different C groups.
determined by spectral integration. It was observed that the A/O-A ratio of soil organic matter increased from 0.5 to 0.6 under anaerobic condition but decreased to 0.4 under aerobic condition after a 360-day incubation. This suggested enrichment of recalcitrant aliphatic components in anaerobic soil with more stable C stock [44]. Additionally, soil organic matter is found to be highly correlated with the retention of organic contaminants in soil due to its hydrophobic and aromatic character [46, 47].

To understand the fate of sulfonamides (antibiotics extensively used in animal husbandry) in soil, Berns et al. [4] incubated $^{15}$N-labeled sulfadiazines with a typical agricultural soil (Luvisol). $^{15}$N labelling was required for an observable $^{15}$N NMR signal due to the low natural abundance (0.37%) of $^{15}$N, c.f., Table 1. The humic acid fraction of the incubated soil was isolated and lyophilized prior to acquisition of $^{15}$N CP-MAS NMR spectra, which indicated the formation of amide bonds and Michael adducts during the transport of sulfadiazines in the soil based on a comparison with $^{15}$N SSNMR spectra of synthetic model compounds [4].

Although SSNMR provides an overview of the composition of soil organic matter, it usually lacks sufficient sensitivity for targeted compound analysis, due to the low signal-to-noise ratios of the NMR spectra caused by the combination of a low concentrations of NMR active elements (e.g., C and N) and the presence of paramagnetic ions [42]. A combination of SSNMR with target organic compound analysis by more sensitive techniques such as gas-chromatography-mass spectrometry (GC-MS) and/or XAS can be helpful [42]. For example, XANES spectroscopy can provide excellent spectra with high signal-to-noise ratios for organic C-poor subsoil samples, whereas this is not the case for $^{13}$C CP-MAS NMR spectroscopy even after sample treatment with HF [35]. Also, it is noteworthy that a rough comparison between signal intensities is allowed in solid-state CP-MAS NMR analysis by recording NMR spectra with similar amounts of samples and identical scan numbers [4, 45]. Moreover, the relative concentration of the different C functional groups can be estimated by signal intensity integration [44].
3.2. Soil minerals

The mineral particles in soil are mainly divided into three types by size: Sand (0.1-2.0 mm), silt (0.002-0.1 mm), and clays (less than 0.002 mm) [32]. With high surface area, ion exchange capability, and high negative surface charge, clays are regarded as the most reactive components of soil [48]. As the main mineral constituents in clays, clay minerals (e.g., hydrous Al phyllosilicates) and metal (e.g., Fe and Al) (hydr)oxides significantly regulate the mobility of potential pollutants in the environment. They have been extensively studied since the early days of SSNMR development due to the favorable NMR properties of the major elements inside, e.g., $^1$H, $^{27}$Al, and $^{29}$Si (Table 1) [49]. The reader is referred to reviews on SSNMR and molecular modelling of clay minerals [49-51] for the earlier literature. Natural abundance of 100% and moderately strong quadrupolar interaction of $^{27}$Al (Table 1) render it a very popular NMR nucleus. A detailed review on the structures and SSNMR properties of aluminas (Al$_2$O$_3$) and aluminum (oxy)hydroxides (i.e., AIOOH and Al(OH)$_3$) has recently been published [6]. To avoid repetition, here we focus on some recent SSNMR studies on soil minerals relevant to environmental processes, e.g., binding and mobility of pollutants in soil, while Fe soil minerals are discussed in Section 6.1 due to the observed paramagnetic effects.

Fig. 4 illustrates the potential mechanisms of pollutant sequestration by clay minerals. SSNMR provides insight into the nature of pollutant bonding (e.g., inner- vs outer-sphere, mono vs bidentate surface complexes etc.).

Given the very favorable NMR properties of $^1$H, $^{27}$Al, $^{29}$Si, and $^{31}$P, the interactions of phosphate with aluminum (oxyhydr)oxides in soil have been probed by SSNMR using homo- and hetero-nuclear correlation experiments including simple CP with variable contact time, heteronuclear correlation (HETCOR), and rotational-echo adiabatic-passage double resonance (REAPDOR) experiments [21, 52, 53]. Fig. 4a illustrates a $^{31}$P{$^1$H}/$^{27}$Al CP-REAPDOR experiment which provided insight into the mechanism of phosphate adsorption on corundum ($\alpha$-Al$_2$O$_3$) [53]. The
elucidation of phosphate interactions with soil minerals can help evaluate the availability of P for plant uptake and the potential of P runoff into water bodies. However, these experiments require a sufficient concentration of phosphate, i.e., high P adsorption capacity to obtain NMR data within a reasonable time (1-7 days). Generally, a series of samples are exposed to different P concentrations as a function of time and/or pH with or without the presence of other ions (e.g., metal ions) in the solution. The solid product is characterized by SSNMR in combination with other techniques, e.g., powder X-ray diffraction (PXRD), electron microscopy, XAS, vibrational spectroscopy (IR and/or Raman), and additional adsorption studies (isotherms and kinetics). This has provided detailed insight into the binding nature of phosphate on bayerite, gibbsite, and boehmite as well as amorphous aluminum hydroxides [21, 52, 54]. A $^{31}$P SSNMR study of phosphate adsorption on gibbsite and kaolinite indicated precipitation of both amorphous and crystalline precipitates on the surface as well as the formation of both inner-sphere and outer-sphere surface complexes (Fig. 4b). Surface precipitation was dominant at low pH and high P concentrations whereas inner-sphere complexes were the major species at a pH of 8.0 [55]. In addition, the adsorption of more complex phosphate species such as inositol hexaphosphates [56, 57], glyphosate [58], and polyphosphates [59] has also been investigated. Under favorable circumstances, it is possible to perform *in situ* SSNMR studies of chemical reactions. For example, the transformation of gibbsite ($\text{Al(OH)}_3$) into lithium aluminum layered double hydroxides (LiAl-LDH) in highly alkaline lithium solutions mimicking nuclear waste, was followed by a combination of *in situ* $^{27}$Al MAS NMR on a gibbsite slurry (using slow 3-4 kHz spinning) and *ex situ* $^7$Li and $^{27}$Al SSNMR spectroscopy, and the results showed that the LDH formation mainly proceeded through a dissolution reprecipitation mechanism [60].

In addition, soil minerals are also widely used in environmental remediation and resource recovery due to their superior properties as sorbents. The SSNMR studies of soil minerals for sequestration of heavy metals, radionuclides, and phosphate are discussed in the following sections.
4. Environmental remediation

4.1. Sequestration and binding of heavy metals and radionuclides

Heavy metals are prevalent in everyday life, as they are (or have been) widely used in paints, textile, plastics, leather, batteries, pesticides, mining, electroplating, and other industry given their technological importance [61, 62]. Moreover, there is a sharp increase in the industrial use of radionuclides, e.g., lanthanides and actinides, due to their nuclear, electrical, optical, and biochemical properties [63]. As a result, considerable quantities of heavy metals and radionuclides inevitably enter the environment through solid waste (e.g., mine tailings) and wastewater (e.g., industrial streams) produced, and are hazardous to the ecosystems and human health [62]. A comprehensive understanding of the interactions of heavy metals and radionuclides with solid surfaces is not only necessary to understand the fate and transport of these harmful elements in the environment, but also helpful to enhance their sequestration by adsorption in a cost-effective way. As SSNMR can probe the chemical environment of solid samples in a non-destructive and non-invasive manner, it has been used to investigate the sequestration and binding of heavy metals and radionuclides by different adsorbents. The general approach is to characterize the adsorbents and probe their structural changes by $^{13}$C, $^{29}$Si, $^{31}$P, $^{27}$Al, and $^{15}$N SSNMR, whereas the NMR spectra of heavy metals/radionuclides themselves which should provide more direct information of binding mechanisms, are seldomly measured due to their unfavorable NMR properties [64-66]. For example, heavy metal nuclei are associated with large numbers of electrons, often resulting in large chemical shift anisotropies, long relaxation time, and wide chemical shift range (e.g., ca.-5500-6000 ppm for $^{207}$Pb in diamagnetic compounds) [67]. This renders the acquisition and analysis of heavy metal NMR spectra difficult, especially in environmental samples with relatively low concentrations of targeted nuclei.

*Heavy metals*
Chemical modification is frequently employed to introduce specific functional groups onto adsorbents [68] and to improve the properties of adsorbents [69]. SSNMR spectroscopy has been used to characterize adsorbents before and after modification to probe structural changes. The $^{13}$C CP-MAS NMR spectra of polyamine-functionalized mesoporous silicas confirmed the presence of bromopropylsilane chain groups in the functionalized silicas, which exhibited increased adsorption capacities on Cu$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$ [68]. The $^{27}$Al and $^{29}$Si MAS NMR spectra of zeolite-incorporated geopolymers, which were used for removal of Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Cr$^{3+}$ from aqueous solutions, indicated that zeolite was responsible for the more compact and firm microstructure of the blended geopolymers [69]. In addition to inorganic adsorbents, SSNMR spectroscopy has also been applied for characterization of biomass-based adsorbents, which usually have a complex and non-well-defined composition. The functional groups in orange waste were chemically blocked to investigate their roles in heavy metal sequestration, and $^{13}$C SSNMR verified the effective blocking of carboxyl groups by esterification according to the absence of their resonances in the $^{13}$C SSNMR spectrum after blocking [61]. Similarly, $^{13}$C CP-MAS NMR was also applied to identify alkyl-C, aromatic-C, hydroxyl and carboxylic groups as functional groups on three microbial biomass based biosorbents used for Pb(II) adsorption [62], and to probe cellulose-C, hemicellulose-C, pectin-C, and carboxyl groups in orange waste utilized for removal of Cd$^{2+}$, Zn$^{2+}$, and Cr$^{3+}$ [61]. It was also employed to verify the successful modification of chitosan with additional aromatic and aliphatic carbons for adsorption of Mn(II), Fe(II), Co(II), Cu(II), and Pb(II) [70], the amine cross-linking on reed for Cr(VI) removal [71], the esterification of Ocimum basilicum L. seed mucilage to succinate and formation of sodium salt for Cd(II) removal from ground water [72], the bifunctionalization of chitosan for Cu(II) and Cr(VI) sequestration [73], the modification of alginate with thiosemicarbazide for Pb(II) and Cd(II) removal [74], and the introduction of trimethylammonium group on cellulose nanofibrils for As(V) adsorption [75]. Solid-state $^1$H MAS NMR spectra of some biological adsorbents were also
collected [70, 71], but the overlap of the NMR resonances, a common challenge in $^1$H SSNMR spectra of environmental samples, prevented detailed analyses.

SSNMR studies of heavy metal nuclei sequestered by adsorbents can provide direct information of the active functional groups and the interaction between the heavy metals and adsorbents, as the chemical shifts depend on the nature, number, and geometry of the coordinating atoms surrounding the targeted heavy metal nuclei [64, 65]. By comparison of the $^{113}$Cd CP-MAS NMR spectra of Cd(II)-loaded *Datura innoxia* (isotope-enriched) and model ligands (model Cd complexes), Xia and Rayson [64] demonstrated the involvement of carboxylate-containing binding sites in Cd(II) sequestration. It is noteworthy that $^{113}$Cd MAS NMR spectra of dry samples failed due to inefficient CP conditions, highlighting that careful sample preparation is needed [64]. Furthermore, to investigate the Cd complex formed in Cd(II) adsorption by algae *Cladophora*, the researchers prepared a solid sample by soaking *Cladophora* in deionized water, mixing the supernatant with CdSO$_4$, and freeze-drying the solution to a solid residue. A resonance at 249.4 ppm in the $^{113}$Cd NMR spectrum (Cd(ClO$_4$)$_2$ = 0 ppm) of this solid residue revealed the involvement of N-containing ligand in Cd(II) complexation with the soluble extract of *Cladophora* [65]. However, this might not exactly reveal the nature of Cd(II) adsorption by *Cladophora* since only the soluble extract of *Cladophora* was used in the study.

Under the assumption that the isotropic chemical shift of a functional group will change upon its interaction with a heavy metal, comparison of SSNMR spectra of an adsorbent before and after heavy metal sequestration can also identify active binding sites. In Fig. 5, two new resonances at $\delta_{\text{iso}}(^{13}\text{C}) = 24.2$ and 21.2 ppm in the $^{13}$C CP-MAS NMR spectrum (tetramethylsilane (TMS) = 0 ppm) of a Pb(II)-loaded mercapto functionalized sepiolite (Pb-MSEP) were interpreted as strong chemical bonding between Pb(II) and mercapto groups (-SH), which caused a resonance shift of the connected methylene-C (-CH$_2$-SH, $\delta_{\text{iso}}(^{13}\text{C}) = 27.9$ ppm). The presence of the methylene-C (27.9 ppm) after
Pb(II) adsorption revealed that not all mercapto groups had reacted with Pb(II) [8]. In contrast, no difference was observed between $^{29}$Si CP-MAS NMR spectra of the mercapto functionalized sepiolite before and after Pb(II) adsorption, implying insignificant Pb(II) binding to siloxane groups [8]. In our previous study, we compared the $^{13}$C CP-MAS NMR spectra of watermelon rind before and after Pb(II)/Cd(II) adsorption (Pb loading: 232 mg/g Pb, Cd loading: 99 mg/g), and carboxyl groups in hemicellulose and pectin, ether and hydroxyl groups in pectin, hemicellulose and amorphous cellulose were identified as the active binding sites with assistance of spectral deconvolution and spectral references (e.g., cellulose, hemicellulose, and pectin) [76]. Moreover, adsorption of paramagnetic Ni(II) and Cu(II) on silicates was monitored by quantitative $^{29}$Si CP-MAS NMR spectra of silica as a function of metal ion loading and by varying the contact time during CP, as the interaction with the unpaired electrons leads to loss of signal intensity of $^{29}$Si species near the paramagnetic ion and changes in T$_1$ relaxation times [3].

**Radionuclides**

SSNMR has been also utilized to investigate the sequestration and binding of radionuclides by different adsorbents. The two characteristic resonances at $\delta_{iso}(^{13}\text{C}) = 55.4$ ppm (indicative of methylene-C in the urea unit, -NH-CH$_2$-NH-) and 47.7 ppm (indicative the methylene-C between urea and phenolic rings, -Ph-CH$_2$-NH-) in the $^{13}$C CP-MAS spectrum of a urea-functionalized polymeric nanoparticle, which was synthesized for the removal of perrhenate anions (ReO$_4^-$), demonstrated the successful incorporation of urea groups in the polymeric nanoparticle [77]. Boyer et al. [78] recorded the $^{13}$C SP MAS NMR spectra of organic matter in wetland substrates to investigate the roles of organic matter in the transport of strontium (Sr) in natural wetlands. Similarly, the $^{13}$C and $^{29}$Si MAS NMR spectra of a chemically modified silica-gel, which was used as an ion exchange resin for lanthanides and actinides, were collected to characterize the silica-gel and confirmed the covalent binding of ethylene-di-amine-tri-acetate to the silica-gel matrix after
modification [63], and the $^{31}$P MAS NMR spectrum of a Zr(IV)-organophosphonate coordination polymer used for selective adsorption of lanthanides and actinides was acquired for structural characterization [79].

Similar to heavy metals, comparison of SSNMR spectra of an adsorbent with and without radionuclide loading can provide important information on the interactions between radionuclides and solid surfaces. Uribe et al. [80] observed a shoulder resonance ($\delta_{\text{iso}}^{(31)P} = 41.5$ ppm, assigned to phosphonate groups complexed to uranyl ions) on the main resonance ($\delta_{\text{iso}}^{(31)P} = 34.2$ ppm, assigned to phosphonate groups) in the $^{31}$P MAS NMR spectrum (85% phosphoric acid = 0 ppm) of a phosphonate-functionalized silica after uranium (U(VI)) adsorption, and its intensity was increased with increasing pH, which positively correlated to U(VI) uptake. The shift of the phosphonate groups to a higher frequency was caused by the de-shielding of the $^{31}$P nucleus due to complexation with U(VI), which removed electron density from the phosphoryl groups. The fraction of phosphonate groups interacting with U(VI) was estimated by the relative concentration of the resonance at $\delta_{\text{iso}}^{(31)P} = 41.5$ ppm, and the ligand-to-metal ratio was calculated to be 2:1 approximately [80]. As the limited solubility of many lanthanides and actinides species restricted the investigation of their interactions with solid surfaces, Mason et al. [81] employed Eu(III) as a model ion to examine the adsorption of trivalent lanthanide on amorphous silica at low surface loadings. The $^{29}$Si CP-MAS NMR spectra of Eu(III)-loaded silica were recorded at different CP contact time and Eu(III) concentrations. The results indicated the formation of inner-sphere Eu(III) complexes with an even distribution across the silica surface at all concentrations, possibly combined with precipitation at the highest surface loadings[81]. A weak interaction between uranyl and a chitin-based adsorbent was concluded given the insignificant changes of the $^{13}$C and $^{15}$N SSNMR spectra of the adsorbent after U(VI) adsorption (U loading: 188 mg/g) [82]. There are also a few SSNMR studies of radionuclides, which provide more straightforward information of interactions between radionuclides and solid surfaces.
Sequestration of cesium (Cs) on a mesoporous silica-gel as nine-coordinated Cs$^+$ was suggested due to the presence of a resonance at $\delta_{\text{iso}}(^{133}\text{Cs}) = -29.6$ ppm (CsCl solution in D$_2$O = 0 ppm) [66]. Moreover, the $^{133}$Cs MAS NMR spectra of Cs-loaded Na-type saponite (Na$_{0.66}$[Mg$_{5.34}$Li$_{0.66}$]Si$_8$O$_{20}$[OH]$_4$) at dehydrated and hydrated conditions were recorded to address the chemical form of Cs adsorbed on the mineral surface [83].

4.2. CO$_2$ mineralization

Given the growing concern about the increasing content of the greenhouse gas CO$_2$ in the atmosphere, extensive research is now focused on the geosequestration of CO$_2$ from the atmosphere via formation of carbonate minerals (e.g., magnesium carbonates, Eq. 1 as an example) as this is the only known long-term removal and storage of CO$_2$ [84, 85].

\[
\text{Mg}_2\text{SiO}_4\text{(s) + 2CO}_2\text{(g) + 2nH}_2\text{O(l) \rightarrow 2MgCO}_3\cdot n\text{H}_2\text{O(s) + SiO}_2\text{(s)}}
\]  
(Eq. 1)

Thus, a detailed understanding of the reaction mechanisms of CO$_2$ with minerals, e.g., forsterite (Mg$_2$SiO$_4$), under conditions for mineralization is of importance. However, it is not easy to identify the composition of the complex product obtained after C mineralization given that (1) it usually consists of amorphous (PXRD invisible) and crystalline species, and (2) the existence of several magnesium carbonates, which differ in their chemical composition e.g., by the number of crystallographic water or hydroxyl groups including magnesite (MgCO$_3$), hydromagnesite (4MgCO$_3$·Mg(OH)$_2$·4H$_2$O), dypingite (4MgCO$_3$·Mg(OH)$_2$·(5-8)H$_2$O), and nesquehonite (Mg(OH)(HCO$_3$)·2H$_2$O) [86].

SSNMR has been reported as a powerful approach for the identification of various carbonates even with small structural differences among each other by using standard minerals as spectral references. The $^{13}$C SP MAS NMR spectra of forsterite reacted with water-saturated supercritical CO$_2$ for 14 days revealed a mixture of nesquehonite (MgCO$_3$·3H$_2$O, $\delta_{\text{iso}}(^{13}\text{C}) = 164$-$166$ ppm, TMS = 0 ppm) and magnesite (MgCO$_3$, $\delta_{\text{iso}}(^{13}\text{C}) = 170$ ppm) as well as that magnesite constitute 95 % of...
the sample at a reaction temperature of 50 °C (Fig. 6a) [87]. The magnesite mineral species grown on the surface of forsterite during CO₂ mineralization was investigated (Fig. 6b) by the use of both ¹³C static and MAS NMR, which yielded the precise determination of the chemical shift anisotropy tensor and precise determination of isotropic chemical shifts, respectively [86]. The anisotropic parts of the CSA tensor allow for the distinction between carbonate and bicarbonate. Furthermore, ²⁹Si and ¹³C SP- and CP-MAS NMR combined with high power ¹H decoupling were used to characterize the mineralization products of supercritical CO₂ with forsterite at variable H₂O content to investigate the role of H₂O in CO₂ mineralization [88, 89]. In addition to magnesium bearing phases, calcium minerals in hydrated cement are also capable of CO₂ storage via carbonation. ²⁹Si and ²⁷Al MAS NMR were employed to investigate the chemical phases in carbonation of synthetic calcium silicate hydrate (the main hydration product of cement) [90] and cement pastes [91] at different CO₂ concentrations. Furthermore, the capture and long-term storage of CO₂ in solid sorbents, e.g., amine-modified porous silicas [7, 10, 92, 93] and LDH [94], are regarded as promising alternatives for CO₂ mineralization at local point sources. Chemical conversion of CO₂ into carbamate after reaction of CO₂ with sodium amide encapsulated in porous silica was confirmed by ¹³C and ²³Na MAS NMR [7], whereas ¹³C and ¹⁵N MAS NMR provide important insight into the complex CO₂ reactions with amine-bearing moieties on solid sorbents [92, 93]. A dynamic exchange of CO₂ by MgAl LDHs was identified by ¹³C CP-MAS NMR and exchange spectroscopy (EXSY), which showed a fast chemical exchange between carbonate and atmospheric CO₂ in the interlayer [94].

5. Resource recovery: Phosphorus (P)

P is an essential element for living organisms. However, it is a non-renewable resource and the global P rock may be exhausted in 50-100 years [95]. On the other hand, P release from anthropogenic activities, e.g., agriculture runoff, wastewater treatment plants, and industrial streams, results in eutrophication in receiving water bodies. Hence, the speciation of P in environmental samples such
as sewage sludge, lake sediments, soil, and adsorbents has drawn attentions from researchers attempting to remove and recover P from wastewater and to understand the fate of P in nature. Liquid-state $^{31}$P NMR preceded by P extraction (e.g., alkaline extraction and sequential fractionation of P) is usually employed to examine the molecular configuration of P (e.g., pyrophosphate and orthophosphate monoester) in targeted samples [96]. For example, orthophosphate (ortho-P), organic phosphate (organic-P, including orthophosphate monoesters and orthophosphate diesters), and pyrophosphate (pyro-P) were identified in sewage sludge by using liquid-state $^{31}$P NMR preceded by NaOH-EDTA extraction. It was observed that organic-P transformed to ortho-P and pyro-P after pyrolysis [97]. This technique is also widely used to investigate P speciation in different types of soil such as manure-amended soil [98], forest soil after wildfire [99], and marine sediments [100]. However, incomplete extraction as well as the possible degradation/alteration of the P species by extractants may happen as lyophilization and redissolution of the extracts are often required to achieve a P concentration detectable by NMR. This may render the identification and quantification of P in environmental samples less precise [101].

$^{31}$P SSNMR can complement liquid-state $^{31}$P NMR for better qualitative and quantitative analysis of P in environmental samples. To determine the extraction efficiency of a modified EDTA-NaOH extraction protocol, liquid-state $^{31}$P NMR was used to quantify polyphosphates in extracts of activated sludge, whereas $^{31}$P SSNMR was employed to estimate the polyphosphates content in the sludge before and after extraction to validate the extraction protocol [101]. Moreover, $^{31}$P SSNMR successfully identified Ca and Al ortho-P as the main P-containing phases in sewage sludge, whereas only the total inorganic ortho-P was identified as the major P fraction by liquid-state $^{31}$P NMR spectroscopy [96]. It should be noted that common iron phosphate species such as vivianite ($\text{Fe}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O}$), strengite ($\text{FePO}_4\cdot2\text{H}_2\text{O}$), and phosphate adsorbed on iron minerals are not observed (vide infra, Section 6.1). SSNMR is also a powerful tool to provide information about the
mechanism of P sequestration by sorbents used in wastewater and eutrophicated water bodies. $^{31}\text{P}$ MAS NMR combined with static $^{139}\text{La}$ NMR indicated that all phosphate sequestered by a lanthanum (La) modified bentonite clay (Phoslock®, used in chemical lake restoration) existed as rhabdophane ($\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, $n \leq 3$, $\delta_{\text{iso}}(^{31}\text{P}) \approx -3.5$ ppm, 85% $\text{H}_3\text{PO}_4 = 0$ ppm) in a laboratory study (Fig. 7b), and a small amount of phosphate species (surface-P, $\delta_{\text{iso}}(^{31}\text{P}) \approx -0.5$ ppm, 9% of the total intensity) was adsorbed on the surface [102]. In contrast, PXRD proved ambiguous with respect to the formation of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and monazite ($\text{LaPO}_4$) due to similar PXRD diffractograms and strong overlap with the bentonite reflections (95 wt% of the sample, Fig. 7a) [102]. The conversion of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ to the anhydrous, more stable $\text{LaPO}_4$ ($\delta_{\text{iso}}(^{31}\text{P}) = -4.5$ ppm, 85% $\text{H}_3\text{PO}_4 = 0$ ppm) was also observed in the sediment of a lake treated with La modified bentonite a decade ago by a combination of $^{31}\text{P}$ MAS NMR and La EXAFS [103, 104]. Li et al. [52] recorded the $^{31}\text{P}$ SP MAS NMR spectra of phosphate-loaded boehmite at different P concentrations, pH, ionic strength, and reaction time. The formation of bidentate binuclear surface complexes was identified as the predominant sorption mechanism under the conditions investigated. Recently, the adsorption of biogenic P (e.g., organic-P and pyro-P) by a La/Al-hydroxide (LAH) composite was investigated and the $^{31}\text{P}$ SSNMR spectra of the P-loaded LAH indicated biogenic P binding on the LAH surface via inner-sphere complexes ($\delta_{\text{iso}}(^{31}\text{P}) = 0$ to -11 ppm), and there is no formation of surface precipitates ($\delta_{\text{iso}}(^{31}\text{P}) = -11$ to -30 ppm) [105]. SSNMR has also been used to monitor struvite precipitation [106] and P speciation in bio-char formation [107], as it provides quantitative insight into the P speciation of both crystalline and amorphous phases.

Notably, the chemical shift of ortho-P in SSNMR can be shifted and broader (e.g., from 9 to -30 ppm) compared with that in liquid-state NMR due to hydration, cation complexation, and adsorption on minerals. Moreover, the loss of signal intensity is often observed for ortho-P bound to paramagnetic species such as Fe and Mn[108]. These characteristics make the resonance assignment
of \textsuperscript{31}P SSNMR spectra difficult for complex and heterogeneous environmental samples. More measures to mitigate paramagnetic effects on SSNMR are discussed in the next section.

6. Challenges

6.1. Paramagnetic effects in environmental samples

Paramagnetic effects originate from the unpaired electrons that are an intrinsic feature of many transition metal ions such as Fe, Mn, and Ni, which are often present in environmental samples. A paramagnetic ion interacts with the surrounding nuclear spins and alters the shape of their NMR spectra by increasing their relaxation rates and changing their chemical shifts [109]. SSNMR is a powerful tool for characterization and structural analysis of diamagnetic systems in solids, but many samples of interest in environmental science (e.g., soil, sewage sludge, and sediments) contain paramagnetic ions in significant concentrations [35, 100, 110]. It is reported that the median concentrations of Fe and Mn are 26 mg/g and 0.55 mg/g in soil, respectively [111], but can be substantially higher (ca. 32.8 mg/g) in sludge samples from wastewater treatment plants with intensive iron dosing [110]. Given the magnetic properties of Fe(II,III) and Mn(II, II, IV) minerals, strong paramagnetic effects are observed and the NMR signals of nearby nuclei may be broadened beyond detection. The \textsuperscript{31}P chemical shift of strengite (FePO\textsubscript{4} \cdot 2H\textsubscript{2}O) is around 15800 ppm (85\% H\textsubscript{3}PO\textsubscript{4} = 0 ppm), which is far beyond the standard spectral window for \textsuperscript{31}P SS NMR (e.g., -500 - 500 ppm) [112]. It was also observed that the increasing Fe content in calcium aluminoferrite dramatically broadened the \textsuperscript{27}Al MAS NMR spectra and reduced the intensity of the NMR signal (Fig. 8a) [113]. In addition, a significant interaction between \textsuperscript{29}Si spins and the unpaired electron spins of Fe(III) ions was revealed by the roughly linear relationship between the spinning sidebands (ssbs) intensity and the Fe\textsubscript{2}O\textsubscript{3} content in 10 cements (Fig. 8b) [114]. This has limited the studies of environmental samples by SSNMR to paramagnetic phases, where the fast electron spin relaxation facilitates NMR and (ultra)fast MAS is often necessary to ensure sufficient resolution. To remove paramagnetic inorganic
constituents, it is common to pretreat soil samples with 2-10 wt\% hydrofluoric acid (HF) before $^{13}$C SSNMR studies to dissolveminerals and thereby concentrate soil organic matter [35, 41-45, 115]. However, such a treatment might alter the composition of organic matter to some extent even though the accuracy of NMR can be improved after the removal of paramagnetic materials [41]. It is still an ongoing scientific debate whether demineralization by HF yields residual soil organic matter, which mimic the original composition, or leads to removal of C groups with high affinity to oxyhydroxides (e.g., O/N-alkyl C) [35, 116].

$^1$H SSNMR studies of hydrogen species in paramagnetic samples are hampered by the strong broadening due to electron-nuclear dipolar interactions, whose strength can be reduced by a factor of about six ($\gamma(^2\text{H})/\gamma(^1\text{H}) \approx 6.5$) if deuterium ($^2$H) is studied. Deuteration may be possible for some environmental samples by soaking them in D$_2$O. $^2$H MAS NMR provided information about the local hydrogen environment in three common iron oxyhydroxides, i.e., goethite, lepidocrocite, and akageneite, as well as the effects of Al doping and particle size on the magnetic properties [117-119]. Moreover, lithium and phosphate binding sites were identified using $^{6,7}$Li MAS NMR [118, 119] and $^{31}$P SSNMR [120], respectively. The broadness of the $^{31}$P resonances rendered MAS obsolete and the NMR spectra were obtained by spin-echo mapping, i.e., piece-wise addition of static NMR spectra recorded with a Hahn echo, with signals spanning from 0 to 8000 ppm [112, 120]. Despite the broad NMR spectra, the formation of bidentate phosphate binding on iron oxyhydroxides surfaces was suggested, as the hyperfine shifts were smaller than that for condensed iron phosphate [112] and larger than that for a monodentate organophosphate model complex[120]. Alternatively, the amount of $^{31}$P bound to paramagnetic minerals (e.g., iron phosphate and P adsorbed on Fe oxides) can be estimated by spin counting as the difference between the total P content determined by elemental analysis (e.g., inductively coupled plasma-optical emission spectroscopy (ICP-OES)) and the P content determined from quantitative $^{31}$P MAS NMR spectra of the diamagnetic P species [110]. The
Na sites in different polymorphs of birnesite, a layered and hydrous manganese oxide, have been probed by $^1$H and $^{23}$Na MAS NMR [121, 122].

Jarosite are a class of acid mine drainage minerals, which can sequester heavy metals such as Zn(II), Pb(II) and arsenate. $^2$H MAS NMR of synthetic samples established the defect mechanism and local magnetic properties, thereby resolving the ambiguity about the existence of hydronium ($\text{H}_3\text{O}^+$) in these minerals [123]. The presence of solid acids ($\text{H}_3\text{O}^+$ and $\text{H}_2\text{O}_5^+$ ions) in iron sulfates such as hydronium jarosite and rhombooclase has been proven by $^2$H MAS NMR [123-125]. Many important binding sites for contaminants are often ill-defined mineral phases such as ferrihydrite and basaluminite, where SSNMR provides key information about the local environment and their relative concentrations. For example, structural ambiguities and local atomic structure of basaluminite (ideally $\text{Al}_4(\text{OH})_{10}(\text{SO}_4)\cdot5\text{H}_2\text{O}$), a poorly crystalline aluminum hydroxysulfate, were obtained from $^{27}$Al SSNMR combined with S EXAFS, XRD and pair distribution function (PDF) analysis as well as electron microscopy, and the $^{27}$Al SSNMR revealed close structural similarities with Felsőbányite (a highly crystalline mineral) and the presence of structural Al defects ($\text{AlO}_4$ and $\text{AlO}_5$) [126]. Similarly, doping of Al in ferrihydrite allowed for indirect quantification of the Al doping level [127, 128], and the observation of broad NMR resonances from $^{27}$Al substituted in iron (oxy)hydroxides provided an example of how element doping modifies the properties of minerals [128]. Thus, given the recent improvements in both fast MAS NMR probes and pulse sequences for detection of paramagnetic samples, there are many opportunities within this area.

6.2. Low-gamma NMR nuclei

SSNMR provides valuable information about the local environment around the NMR active nuclei, as illustrated above. However, several elements, which have high occurrence in nature are often inaccessible for studies of natural samples or at low concentrations due to the unfavorable NMR properties, especially $^{17}$O ($I = 5/2, 0.04\%$) and alkaline earth metals ($^{25}$Mg, $^{43}$Ca, $^{87}$Sr, and $^{136/137}$Ba),
which are low-gamma nuclei often with a low natural abundance of the NMR active isotope and quadrupole nuclei (I > ½), c.f., Table 1. In contrast most of the alkaline metals are NMR favorable except $^{39}$K, which is a low-gamma nuclei, but of high abundance (Table 1). Thus, SSNMR studies of these nuclei in natural abundance are mainly restricted to natural samples with a high concentration of the low gamma nuclei of interest. Alternatively, synthetic analogues can be synthesized using isotope enrichment. High-field (20 T) SSNMR of $^{43}$Ca enriched amorphous calcium carbonates combined with molecular dynamic simulations and DFT calculations showed a high degree of structural disorder in this material and probed the structural changes as a function of Mg substitution [22]. Detailed insight into the weathering of forsterite (Mg$_2$SiO$_4$), an endmember in the olivine (Mg$_2$-$\alpha$FeSiO$_4$) minerals, was obtained using $^{25}$Mg quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) NMR and $^1$H-$^{25}$Mg CP NMR recorded at ultra-high field combined with $^{29}$Si CP-MAS NMR, which showed the formation of an amorphous Si-rich surface layer (Fig. 9) [129]. The changes in chemical speciation were monitored electrochemically, and the combination of SSNMR with electron microscopy and PXRD showed that leaching of Mg(II) into solution led to the formation of an amorphous polymeric silicate on the surface of the particles [129]. Only a few studies of quadrupolar nuclei with large quadrupole moments including $^{67}$Zn, $^{75}$As, $^{87}$Sr, and $^{139}$La have been reported [102, 130], as the NMR spectra can span several MHz and often ultra-high magnetic fields are needed to obtain the NMR spectra.

7. Summary

SSNMR spectroscopy is a powerful characterization technique for studies of environmental samples and processes, as it provides detailed insight into the speciation and quantification of different species. Environmental samples are often a mixture of different amorphous and crystalline mineral phases along with organic fractions. SSNMR can characterize these solid phases as well as
their interactions with pollutants, which are adsorbed on the surface or sequestered, in diamagnetic and to some extent also in paramagnetic systems. However, a multi-technique approach combining SSNMR with other complementary techniques (e.g., XAS and PXRD) is necessary to have a detailed understanding of environmental samples and environmental processes on different length scales. Thus, a collaborative, interdisciplinary effort is recommended.

Currently, assignment of NMR data is mainly based on the isotropic chemical shift using empirical correlations from studies of model systems, while the use of correlation experiments is limited to samples where the NMR isotope of interest is present in a sufficiently high concentration. Future directions, which will strengthen SSNMR spectroscopy as an analytical technique in environmental science, include implementation (and development) of computational methods for assignment of NMR parameters as well as more advanced data analysis, i.e., not only isotropic chemical shifts.

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Figures and Tables

Fig. 1 $^{31}$P MAS NMR spectra of a mineral specimen (Limfjorden, Denmark), a precipitate from reject water (Vandcenter Syd, Odense, Denmark), and fertilizer-quality struvite crystallized from wastewater (Marselisborg wastewater treatment plant, Aarhus, Denmark) illustrating the identification of minerals species and quantitative SSNMR. All samples contain struvite ($\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$, $\delta_{\text{iso}}(^{31}\text{P}) = 6$ ppm, 85% $\text{H}_3\text{PO}_4 = 0$ ppm) [106] and the spectral intensity (integral) can be used for quantitative determination of the different phosphate species. The $^{31}$P MAS NMR spectra shows that the mineral specimen mainly consists of newberyite ($\text{MgHPO}_4\cdot3\text{H}_2\text{O}$, $\delta_{\text{iso}}(^{31}\text{P}) = -7$ ppm) [106]) due to conversion of struvite by loss of ammonia to the atmosphere. The struvite samples were kindly provided by Assoc. Prof. Tonci Balic Zunic, Mineralogical Museum, Copenhagen, Denmark (mineral specimen), Nina Almind-Jørgensen, Vandcenter Syd, Odense, Denmark (reject water precipitate), and Professor Per Halkjær, Aalborg University, Denmark (struvite).
Fig. 2 - $^{13}$C CP-MAS NMR spectra of (a) original soil, (b) straw-amended soil under aerobic, and (c) straw-amended soil under anaerobic incubation, and (d) the general assignment of the resonances (A/O-A denotes the alkyl C/O-alkyl C ratio which reflects the organic C stability in soil). Adapted from Ref [44] with permission from Elsevier.
Fig. 3 Three different mechanisms for pollutant interaction with a mineral: Inner- and outer-sphere complexation as well as ion-exchange illustrated using cation (green) interaction with a clay mineral.

Fig. 4 (a) $^{31}\text{P}\{^1\text{H}\}/^{27}\text{Al}$ CP-REAPDOR experiments was used to determine the $^{31}\text{P}-^{27}\text{Al}$ heteronuclear dipolar coupling, for phosphorus species adsorbed on corundum for the resonances at $\delta_{\text{iso}}(^{31}\text{P}) = -2.6$ ppm (blue dot, $85\% \text{ H}_3\text{PO}_4 = 0$ ppm) in NMR spectra of the sample prepared at pH 5 and at $\delta_{\text{iso}}(^{31}\text{P}) = -2.2$ ppm (red circle) for the pH 9 sample. The dashed lines are calculated curves based on geometry-optimized structural models of phosphate adsorption on corundum surfaces. Inset shows typical control ($S_0$) and $^{27}\text{Al}$-dephased (S) NMR spectra acquired with 8 kHz spinning rate, 0.5 s repetition
delay, 1 ms CP contact time, 2 rotor cycles, and 101588 scans. Reprinted from Ref [53] with permission from Elsevier. (b) The $^{31}$P SP MAS NMR spectrum of phosphate-loaded gibbsite with assignment of the different species using deconvolution (1 mM phosphate, 500 m$^2$/L gibbsite, pH 6.7. Adapted from Ref [55], copyright (2020) American Chemical Society.
Fig. 5 $^{13}$C CP-MAS NMR spectra of mercapto functionalized sepiolite (MSEP) with and without Pb loading. The appearance of resonances at 24.2 ppm. and 21.2 ppm was interpreted as the evidence of SH-Pb interactions (TMS = 0 ppm). Adapted from Ref [8] with permission from Elsevier.
Fig. 6 ¹³C SSNMR studies of magnesium carbonates phase formed in CO₂ mineralization with (a) SP (Adapted from Ref [87] with permission from Elsevier), (b) static CP (A) and CP-MAS (C) experiments with simulation (B) of the static line shape. The ¹³C CP-MAS NMR spectra were used for precise determination of the mineral phases present (isotropic chemical shifts), whereas the static NMR spectra allowed for precise determination of the anisotropic elements of chemical shift tensor. Adapted with permission from Ref [86], copyright (2020) American Chemical Society
Fig. 7  (a) PXRD diffractograms of Phoslock®, rhabdophane (LaPO₄·1.4H₂O), monazite (LaPO₄), and La phosphate minerals (LaP100 and LaP100-HA₁₀₀) formed by P sequestration of a La modified bentonite clay. The reflections marked by ○, ■, and ◊ originate from Phoslock®, rhabdophane, and monazite, respectively. The low intensity of the La phosphate phase reflects the only 4.4 w/w% La in Phoslock®. (b) ³¹P⁻¹H CP-MAS NMR used for identification of the La phosphate mineral (LaP 100) formed. Rhabdophane and monazite were used as the model compounds. The similar ³¹P chemical shift and CP build-up curves confirmed the formation of rhabdophane. The more intense spinning sidebands are due to a few percent iron in the natural clay. Reprinted with permission from Ref. [102], copyright (2015) American Chemical Society.
Fig. 8 (a) $^{27}$Al MAS NMR spectra of synthetic ferrites Ca$_2$Al$_{1.33}$Fe$_{0.67}$O$_5$ (Fe/Al = 0.5), Ca$_2$AlFeO$_5$ (Fe/Al = 1.0), and Ca$_2$Al$_{0.93}$Fe$_{1.07}$O$_5$ (Fe/Al = 1.2). The NMR spectra for Fe/Al = 1.0 and 1.2 are shown on identical intensity scales, which correspond to a vertical expansion by a factor of 2 relative to the spectrum for Fe/Al = 0.5. The asterisk and squares indicate the resonances from the central transition and ssbs, respectively. Adapted from Ref [113] with permission from Elsevier. (b) The ratio of the spinning sides bands to the total intensity ($I_{ssb}/I_{tot}$) as a function the Fe$_2$O$_3$ concentration in the $^{29}$Si MAS NMR spectra of 10 cements recorded with 6 kHz (filled circles) and 13 kHz (open circles) spinning speed. Adapted from Ref [114] with permission from Elsevier.
Fig. 9 (a) $^1$H-$^{25}$Mg CP QCPMG NMR spectrum of forsterite reacted for 310 hours, (b) $^1$H-$^{25}$Mg CP QCPMG NMR spectrum of Mg(OH)$_2$ after 16 scans, (c) $^{25}$Mg QCPMG NMR spectra of Mg(OH)$_2$ after 16 scans, and (d) $^{25}$Mg QCPMG NMR spectrum of a clinohumite standard. The $^{25}$Mg NMR spectra were recorded at ultra-high field (21.1 T) using 10 kHz spinning. The use of $^1$H-$^{25}$Mg CP QCPMG allowed for observation of the surface precipitate, which was assigned to a clinohumite species based on similarities of the $^{25}$Mg QCPMG NMR spectra of these two species [129]. It is noted that conventional static $^{25}$Mg NMR spectra did not give a signal for forsterite (Mg$_2$SiO$_4$). Moreover, the $^{25}$Mg QCPMG NMR spectra of forsterite (without CP) before and after reaction were similar and did not give insight into the surface species formed (not shown). Reprinted from Ref [129] with permission from Royal Chemical Society.
Table 1. NMR properties of common elements in environmental samples.

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<th>Quadrupole moment (fm²)</th>
<th>Frequency (MHz)²</th>
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<td>79.47</td>
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<td>Phosphorus</td>
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(Notes: *Larmor frequency at 9.4 T. Data from Ref [11].)