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Synchrotron Based Techniques in Soil Analysis: A Modern Approach

Surabhi Hota

Abstract

Soil is a highly heterogeneous system where a number of physical, chemical and biological processes are taking place. The study of these processes requires analytical techniques. The electromagnetic radiations in the form spectroscopy, X-Ray diffraction, magnetic resonance etc. have been used in the field of soil analysis since decades. The study of soil nutrients, mineralogy, organic matter and complex compounds in soils use these techniques and are successful tools till date. But these come with a limitation of lesser spatial and spectral resolution, time consuming sample preparation and destructive methods of study which are mostly ex-situ. In contrast to the conventional spectroscopic techniques, the synchrotron facility is of high precision and enables non-destructive study of the samples to a nano scale. The technique uses the high intensity synchrotron radiation which is produced in a special facility, where the electrons are ejected using very high voltage and accelerated in changing magnetic field, at a speed of light resulting in a very bright radiation that enables a very precise study of the subject. For example, in studying the dynamics of P and N in soils, SR aided XAS are used to study the K-edge spectra of these nutrients, without any matrix interference, which used to be a problem in conventional SEM, IR or NMR spectroscopy. These radiations provide high energy in GeV, which imparts high sensitivity and nanoscale detection. Basically, the SR facility improves the precision of the existing spectroscopic techniques. This chapter discusses how the Synchrotron radiations aid to improve precision in various field of soil analysis such as, carbon chemistry, nutrient dynamics, heavy metal and contaminant speciation and rhizosphere study. However, the technique also come with major limitations of requirement of very high skill for preparation of samples, inadequate availability of references for studies related to absorption spectrum and control of radiation damage. Applications and limitations of the technique thoroughly reviewed in this chapter with an aim to provide a brief idea of this new dimension of soil analysis.

Keywords: Soil, Synchrotron, analysis, energy, resolution

1. Introduction

Soil is a heterogeneous system and habitat for numerous flora and fauna, where umpteen chemical, physical and biological processes are operating to make it a living system. These processes are, element mineralization and immobilization, redox reactions, decomposition of organic matters by microbes, movement of nutrient elements towards the plant roots and related soil water movements, the complex processes near the rhizosphere, accumulation and distribution of elements and their chemical transformations into different complexes and valency, weathering of rocks and minerals

to form soil and related soil forming processes. To understand these processes, several techniques have been developed and experimented by the soil researchers from time to time. And there are numerous remarkable techniques that have aided to the human understanding of complex matters. Most of these techniques use source of energy and illumination for quantification of the elements and studying the complex structure of a system. Such techniques are Diffraction/scattering for crystallography; Polarimetry for measuring the shape of complex molecules and the properties of magnetic materials; Imaging for highly detailed imaging of small animals, and ultimately humans, to the substructure level of biological and physical material, using light from infrared to hard X-rays; Spectroscopy for analysis of chemical compositions and speciation of elements [1]. However, these techniques have several limitations in terms of their sensitivity, spatial resolution, lengthy sample preparation procedures and most of them are dependent upon destructive sampling and ex-situ analysis. With the development of synchrotron facility around the world, the exploitation and study of these processes have been made possible to the molecular level and in-situ because of the unique qualities of a synchrotron radiation viz.; high brightness, wide energy spectrum, highly polarized radiation and time structured emission. This gives the SR an advantage of due to high proton flux, possibility of beam tunability and weak scattering, high sensitivity resulted from acceleration of heavy ion beams to high energy.

Synchrotron Radiation (SR) is basically an electromagnetic radiation which is emitted when the charged particles are radially accelerated. Natural synchrotron radiation (SR) is as old as the stars produced due to charged particles spiraling around magnetic field lines in space [2], while short-wavelength synchrotron radiation generated artificially by in circular acceleration of relativistic electrons only ways back to early nineties [3, 4]. The synchrotron principle was invented by Vladimir Veksler in 1944 [5]. Edwin McMillan constructed the first electron synchrotron in 1945 [6]. The first ever synchrotron was successfully made in 1947 under the direction of Herbert Pollock at General Electric Research Laboratory, NY. And the first synchrotron radiation was observed by Floyd Haber on 24th April, 1947. This was a remarkable achievement in the field of physics which today has led to large, full-fledged synchrotron facilities around the world. The first-generation synchrotron facilities were only being used to study the fundamental properties of matter and was more of a particle accelerator [2]. Presently, the synchrotron facilities have upgraded to third generation, which enable the use of low energy or soft and high energy or hard X-rays, UV and longer wavelengths. The first ever third-generation hard X-ray source was European Synchrotron Radiation Facility (ESRF) in Grenoble followed by the Advanced Photon Source (APS) at Argonne National Laboratory with an energy of 7 GeV. The synchrotron is one of the first accelerator concepts to operate as large-scale facilities, where bending, beam focusing and acceleration could be separated into different components and where the magnetic field is guided in a time dependent manner, to synchronize with a particle beam of increasing kinetic energy.

There are more than 50 facilities in operation worldwide (<http://www.light-sources.org>) and are being used by more than 15,000 researchers. Some large facilities are listed in **Table 1**. There are a few large synchrotron facilities that have been operating with high electron energies, as high as 8 GeV (SPring-8 in Harima Science Garden City in Japan). PETRA III, which took up operation in 2009, is the most brilliant storage-ring-based X-ray radiation source in the world. As the most powerful light source of its kind (https://petra3.desy.de/index_eng.html). These machines are physically large (850 to 1,440 m in circumference) with a capability for 40 or more beamlines. There are also many smaller facilities (120 to 280 m in circumference) which have come in to existence in recent past, having lower electron energies (from 1.3 to 3 GeV). There are also some fourth-generation synchrotron facilities which have been conceptualized by few countries recently.

S.No.	Name of facility	Country	Energy (GeV)	Circumference (m)	Year of Operation
	Indus II	India	2.5	173	2005
1	National Synchrotron Light Source (NSLS-II)	US	3	792	2015
2	PETRA III	Germany	6	2304	2009
4	SPring-8	Japan	8	1436	1997
5	Advanced Photon Source (APS)	US	7	1104	1995
6	Progetto Utilizzazione Luce di Sincrotrone (PULS)	Italy	1.5	33.5	1980
7	Canadian light source	Canada	2.9	147	2004
8	Australian Synchrotron	Australia	3	216	2006
9	Shanghai Synchrotron Radiation Facility	China	3.5	432	2007
10	ALBA	Spain	3	270	2010
11	Sirius	Brazil	3	518.2	2018
12	Pohang Light Source II	South Korea	3	281.82	2011
13	Swiss Light Source	Switzerland	2.4	288	2001
14	European Synchrotron Radiation Facility	France	6	844	1992
15	Kurchatov Synchrotron	Russia	2.5	124	1999

Table 1.
Synchrotron facilities around the world.

Synchrotron facilities can generate frequencies over entire range of the electromagnetic spectrum. In addition to having a high intensity, the synchrotron light has other properties useful to researchers. Wavelengths produced by SR, may range from 10 to 11 m (hard X-rays) to 106 m (infrared light), emitted in short pulses (~100 ps wide spaced at 2 ns), partially coherent and arrives in parallel rays, highly polarized, isolation of specific wavelengths are possible with the use of diffraction or crystal gratings. And most importantly, light is released as a very narrow cone [7] which is then focused to provide a very narrow beam at the work station.

There are a number of techniques that have been used by the researchers for study of soils, they are: STXM- Scanning Transmission X-ray Microscopy, NEXAFS- Near Edge X-ray Absorption Fine Structure Spectroscopy, FTIR- Fourier Transform InfraRed Spectroscopy, μ XRD- Micro X-ray Diffraction, EELS- Electron Energy Loss Structure spectroscopy, EXAFS- Extended Absorption Fine Structure Spectroscopy, XANES- X-Ray Absorption Near Edge Structure Spectroscopy [8], HRTEM-High Resolution Transmission Electron Microscopy, SXRF- Synchrotron Based X-ray Radiation Fluorescence, XFS- X-ray fluorescence spectroscopy, X-ray

μ -computed tomography [9–11], SEM- Scanning Electron Microscopy, TEM- Transmission Electron Microscopy.

These synchrotron-based techniques have proved to increase the precision of determination of many soil parameters such as carbon chemistry of soil [12, 13], rhizosphere nutrient transport and other mechanisms [14, 15], heavy metal quantification and remediation, microbe-metal interaction mineral transformation, study of physical parameters of soil, soil fertility study.

Methodology: This chapter reviews the works done in the field of soil analysis for physical, chemical and biological parameters, using SR facility, all over the world and how it has aided to the improvement in precision and accuracy of the study.

2. Components and working of a synchrotron facility

A synchrotron facility in general, consists of:

1. **Electron gun:** It consists of a transformer which feeds a very high voltage (in hundred thousand Volts, approximately, 200000 V of DC) of electricity through a cathode which causes the electrons to jump off the surface. The cathode is made of tungsten-oxide disk, otherwise called a button. As electricity flows through the disk, the disk gets heated to about 1000° C, the temperature at which the electrons are released. A screen near the button is given a short, strong positive charge 125 times per second, which pulls the negative charge particles, the electrons, away from the disk.
2. **Linear Accelerator (LINAC):** The electron ejected from the electron gun, are fed into the LINAC. The energy of acceleration is provided by the Microwave radio frequency fields to accelerate the electrons to the speed of light. The speed of the electrons reaches approximately to 3×10^8 m/s. The LINAC produces electron pulses in a duration of approximately up to 132 nano seconds (ns). The electrons which become the photons now, must travel in a vacuum to avoid hinderance and reduction in velocity by colliding with other atoms and molecules. The vacuum chamber pressure is kept around 10–11 torr.
3. **Booster Ring:** The electrons circulate in the booster ring, to get a boost in energy from approximately 250 MeV (Mega electron volt) to approximately 2.9 to 6 GeV by the radio frequency cavity generated microwaves. The Booster Ring increases the speed of the electrons close to the speed of light (approximately 99.9999985 percent of the speed of light). There are two types of electro magnets in the booster ring. These magnets create the magnetic field, which is used by the synchrotron to guide the electrons around the booster ring. The magnetic field of the quadruple magnets are used to force the bunches of electrons into a fine beam within the vacuum chamber.
4. **Storage Ring:** After the electrons have gained sufficient energy to produce light, the injection system transfers them from the booster ring to the storage ring. The process of transferring electrons from booster to storage ring occurs approximately once per second up to 600 cycles which may take about 10 minutes. Once entered the storage ring, the electrons keep circulating for four to twelve hours and every time the dipole magnets/bending magnets bend the path of electron flow, photons are released. The bending magnets are aimed to circulate the electrons in a circular path [16]. After each turn of the bending

magnets, there is a photon port to allow the light to travel down the beam lines to the research stations.

5. Beam line: Each beam line consists of an optics cabin, experimental cabin, and control cabin. The optics cabin has optical instruments used to extract the type of radiation required for the experiment. The experimental cabin is for support mechanism, and provides environment for the sample study. Instruments called detectors record the information generated from the sample are recorded by the detectors. The control cabin, as the name suggest, allows the researchers to control the experiments and collect the data.
6. End Station: The final result is obtained at the end station. The components of end station are experiment specific. There is an optic hutch, consisting of mirrors by which the selected wavelengths of synchrotron light are focused onto the sample in an end station. The samples are placed in the experimental hutch, which consists of a sample holder and a detection system, specific to the technique adopted by the researcher. Also, includes computers through which the experiment is controlled by the researcher.

3. Organic carbon chemistry in soils observed by synchrotron based spectroscopy

Soil is believed to be the largest pool of terrestrial organic carbon containing about 1500 Pg C which is higher than the atmospheric and biotic pools combined [17, 18]. Organic C is crucial in maintaining the balance of inorganic form, specially, CO₂ in the atmosphere, which in turn, controls the global climate scenario [19]. The entire carbon cycle revolves around the organic C fraction. The decomposition of organic matter, from animal and plant residues and subsequent humification, leads to the formation of complex organic compound leading to significant structural and composition changes [20]. Organic compounds released from animals, plants, microbial cells, have a range of size and complexity from monomers to mixtures of biopolymers. This complexity makes chemistry of soil organic matters difficult to study. Organic C shows very high chemical and spatial complexity, creating significant analytical problems in the existing methods [21–24]. Soils characteristically have low amounts of C as compared to pure biological samples. They require relatively higher energy to substantially improve the detection limits and data that allow better quantification of C chemistry. The existing techniques are mostly destructive, or the samples are processed ex-situ, for analysis. This sometimes causes the loss of delicate structure of the complex organic matter. SR based spectroscopic techniques have proven to be an advanced tool to study the organic C chemistry of soils, as it enables the non- destructive micro and nano-scale analysis and enables keen study of reactivity, composition, heterogeneity, physical site of organic materials, and mineral-organic matter interactions. The high energy of SR provides very high spatial and spectral resolution.

SR-based scanning transmission Fourier transform infrared (FTIR) spectroscopy, X-ray microscopy (STXM) and C (1 s) near-edge X-ray absorption fine structure (NEXAFS), have proven to be unique and non-invasive in studying the complex processes of C chemistry in soils, in the recent past. These techniques have been used to reveal the Spatial organization of C forms in microstructures, functional group chemistry of C, interaction of C with soil matrix, surface Interactions of organic C and minerals.

The identification of the compound structure of the SOC and DOC involves basically, identifying the type of chemical bonds and functional groups in a molecule. And because of complex nature of the spectrum produced by the organic compounds, the identification and differentiation of the bond become difficult with low energy, conventional spectroscopic techniques. At low spectral resolution, the peaks seem to be overlapping and the fingerprinting becomes only partially useful. This limitation has been overcome by the incorporation of SR in to the spectroscopic techniques. The identification of the structural characteristics with high precision has become possible and even the study of impact of management on SOC cycle and composition could be successfully carried out by aid of SR based techniques in various studies [13, 23, 25–32].

The aided advantage of SR is its brightness, which can be defined as the photon flux or power emitted per source area and solid angle, is 100–1000 times greater than the brightness obtained from a conventional source [33, 34]. FTIR spectroscopy has been considered the most powerful technique for identifying types of chemical bonds and functional groups in a molecule which produces IR absorption spectrum, in the form similar to fingerprint. FTIR combined with microscopy allows probing of small areas in shorter time intervals and with an optimum signal-to-noise ratios. However, SR-FTIR spectroscopy could reveal the quantity, structure composition, and distribution of chemical constituents in humus fractions [13, 23]. In some studies, it has also been used to identify stable soil aggregates and black C particles chemistry [27, 35] and these studies show that, the SR-FTIR spectra has stronger band width compared to conventional FTIR. Studies revealed that, FTIR spectra below 1450 cm^{-1} normally leads to overlapping bands of indefinite quantity. SR-FTIR has a spectrum ranging from 4000 to 400 cm^{-1} and could measure the molecular level vibration of organic and inorganic functional groups [36, 37]. SR-FTIR can also identify the changes in intensities and vibrational characteristics of bands, shifts in frequencies and shapes of a particular band [38]. These properties have been exploited to study the molecular level changes in SOM composition due to management practices [13, 23, 39]. It was also made possible by this technique to study organo-mineral assemblages [27, 35].

NEXAFS is also such a technique which is being used by many researchers for similar studies in recent past. It is highly element-specific as the different elements show X-ray absorption peaks at different energies [40]. NEXAFS when combined to STXM, information as precise as 30–50 nm spatial resolution could be obtained. This technique is termed as NEXAFS spectromicroscopy. This technique has been used in study of humic fractions mined from highly complex soil matrices [13, 23, 24, 29, 41, 42], study nanostructures of polymers [43] and fingerprinting of C in biological materials [44, 45].

The results obtained from the SR-based techniques are basically an improvement over the pre-existing spectroscopic techniques, where the bond stretch (eg. C-O or O-H), π and σ transitions [23] are taken as the reference for speciation of the C containing species. However, the spectral signatures, or fingerprints of pure biological materials obtained from SR based spectroscopy can serve as a reference for interpretation of the results obtained from conventional spectroscopy. The results can then be quantified using chemometrical methods, multivariate analysis, regression modeling, principal component analysis or predictive modeling [27, 46]. In laboratory analysis of samples, chemical analysis of C samples can only provide the total OC, or different pools of C or fractions of humus, which are mostly quantitative. But the SR based techniques can reveal what is the actual composition of the TOC fraction or humus fraction. These revelations can be related to the stage of weathering of a soil, its pedogenesis and can also correlate the data to predict the responsible chemical, physical and biological processes. Information related to

fingerprints of organic compounds such as proteins, nucleic acids, carbohydrates and lipids, predictive models and algorithms can be developed, which can be used by researchers with basic facilities, to predict the organic C chemistry and related processes. However, the data from fingerprints of standard substances is still inadequate to fully identify functional group chemistry for soil organic C and a strenuous effort is required to fill that breach.

4. Synchrotron based techniques in elemental speciation in soils

Soil is a very heterogenous system and the chemical and biological processes happening inside it are even more complex. The important processes, as mentioned in the introductory section, are dependent upon the concentration of different elements involved in process, their distribution and their chemical behavior, which makes their speciation very much crucial. Also, the speciation of environmental contaminants such as heavy metals are important as they lead to degradation of soils [47, 48]. XAS is a powerful technique to provide answer to questions related to the chemistry of an element present in ant system starting from minerals, to biological specimens and solutions [49–52]. The XAS technique basically scans the object of study using a range of X-ray energies. Hence, with the advent of synchrotron, the energy of X-ray could be increased. XANES and EXAFS are the two techniques XAS techniques which have been used in many studies for studying the elements in heterogenous environments, by selecting appropriate energies of the incoming X-ray photon with the aid of SR facilities and thereby generating chemical maps of an element in relation to its oxidation state and chemical bonding [53]. K-edge XANES has been used to test the speciation of Al on the thin surface coatings of quartz and feldspar grains in a loess soil [54], and studying the coordination of Al in imogolite and allophones [55].

X-ray techniques such as low-energy XRF (LEXRF) has been used to quantify Al in plant tissues to determine the toxicity levels. A study was carried out to determine Al accumulation in tea plants, in the soils with high acidity, resulted to high concentration of Al. it revealed that Al accumulated mainly within the cell walls of the leaf epidermal cells, also confirming that the apoplast are the tolerance mechanism of toxicity in tea plants because of results showing Al accumulation in apoplast and traces in symplast. Similar study in soybean showed higher accumulation of Al in roots [56] using LEXRF. Cr speciation has been done by using EXAFS in soils contaminated by leather tanning, reporting the dominant form as Cr (III) with low levels of Cr (VI) [57]. Different industrially contaminated soils have been studied for determination of and speciation of Cr using this technique [58, 59]. XANES has been used to identify associations of metals in contaminated environments. Fandeur et al. [60] reported that Cr (VI) was found in closed association with Mn-oxides concluding the role of Mn-oxides in oxidation of Cr (III) to Cr (VI). Jacobson et al. [61] reported Cu to be present in hotspots that are associated with organic matter within the soil matrix using in-situ XANES. Similarly, a study by [62], revealed the Cu hotspots not to be associated with calcium (Ca) carbonates, Fe oxides, or Cu sulfates. EXAFS has been used for speciation of As, based on the absorption spectra of As-O distances. Grafe et al. [63] used m-XRF and m-XAS to study the speciation of As in a chromated copper-arsenate (CCA) contaminated soil to determine the effects of co-contaminating metal cations (Cu, Zn, Cr) on As speciation. X-ray computed μ -tomography (SR- μ CT) is also a powerful technique that enables study of internal structure and composition of sample without sectioning it physically. Other advantage over conventional technique is enables a 3D study of the subject. 2D study of the samples limit the projection of metals present in the

sample, only in the direction of beam. SR- μ CT has higher sensitivity, resolution and speed. SR-XRF is also a powerful technique devised to study the elements in environment. It has a very précised detection limit for many elements (<0.01 ppm).

5. Synchrotron based techniques in study of mineral structure, their occurrence and abundance in soils

It is known that X-ray diffraction (XRD) is a basic technique which has been used widely for the characterization and identification of crystalline structure of minerals. But it comes with some imitations like it cannot be used to study amorphous minerals, the slide preparation procedures are very much time consuming, requires invasive sampling. Also, the low energy and low flux make the diffractometer geometry very limited. The use of diffracted X-rays, instead of transmitted X-rays restricts the analysis of hydrated and oxygen samples. Compared to the conventional technique, the SR-XRD provides very high sensitivity due to energy tunable nature and high flux. It enables the non-invasive study of trace matters, amorphous minerals, hydrated and oxygen samples, thin films and solution phase. The study of areas as small as 1 mm^2 can be done with a beam spatial resolutions of $<5\text{ mm}$.

synchrotron-based techniques of XRD and XAFS, have greatly improved the understanding about the structural and chemical properties of amorphous minerals, such as iron oxide minerals like lepidocrocite, goethite and hematite. Their transformations of metastable phases to stable phases of iron oxides [64] and chemical reactions occurring on their surfaces have also been possible to study with the aid of these techniques., and chemical reactions occurring on their surfaces. [65] used XANES spectroscopy for identification and quantification of iron compounds in soils. Massive improvements have been achieved in understanding the structure of poorly crystalline and nanosized iron oxides species like ferrihydrite, by synchrotron XRD, EXAFS, and total X-ray scattering data. Studies also have used laboratory XRD to determine changes in the structural properties of goethite and hematite due to substitution by Al^{3+} than Fe^{3+} in mineral structure (up to 33 mol.%). Atomistic and long-range scales data regarding substitution of trace to low amounts of other elements in the structure of iron oxides on the basis of indirect, dissolution data have been predicted using synchrotron XRD and EXAFS [66–70]. The valence state of substituent elements, coordination states and their effects on element substitution in iron oxides nave been revealed by XANES spectroscopy [66].

6. Synchrotron based techniques in study of microbial interactions with contaminants/pollutants in the soil

SR-FTIR spectromicroscopy is a powerful technique which has come in to use in recent years for study of microbial activities with high spatial resolution to μm scale and temporal resolution to seconds scale, enabling keen study of processes at cellular level [71]. It combines three techniques viz.; microscopy, mid IR spectroscopy and SR based light source, which makes it possible to precisely locate the target, obtain its vibrational spectra and obtain very high signal to noise ratio.

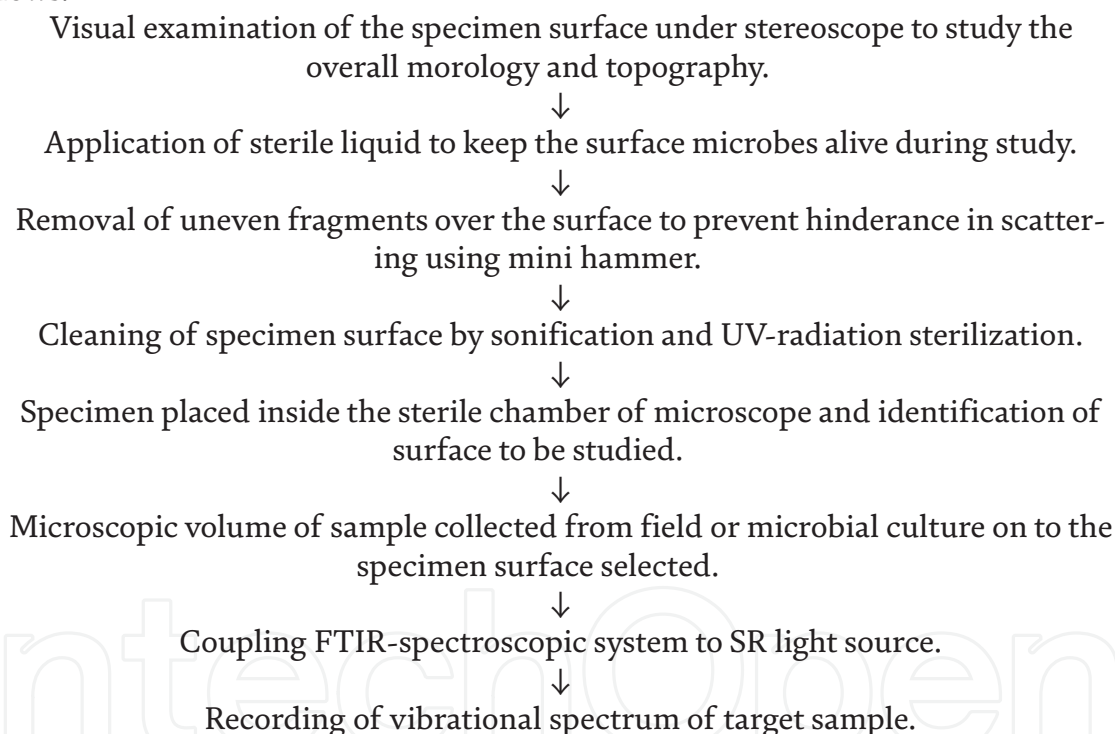
Earlier FTIR spectromicroscopy technique used an aperture to take reading of smaller areas within the sample, because to take reading, one had to adjust the incoming light to either eliminate some part of it or to distribute it among detectors, uniformly. This resulted to reduction in signal strength. The thermal emission sources are limited to focus an area of 75–100 mm in diameter only. In contrast to these conventional sources, a synchrotron infrared source can obtain spectra from

smaller target areas without using aperture [72]. In SR-FTIR Spectro microscopy, one can use the infrared beam to visualize a spot as small as the diameter of its wavelength resulting to 0.7 times of spatial resolution [73–75].

The study of action of microbes over a geological surface (here, soil) is based on the fact that, the changes carried out by microbial action (mineralization, immobilization, biodegradation) is monitored by the study of the vibrational spectra of the substrate (heavy metal or pollutant). Many studies have been carried out to find out the reference spectra of several contaminants such as, Chromium and molybdenum hexacarbonyls [76], Pentacyanonitrosyl-complexes of chromium and molybdenum [77], Aromatic chromium tricarbonyls [78], Explosive molecule vapors [79], polycyclic aromatic hydrocarbons (PAH) [80–83], Fluoranthene and benzofluoranthenes [84], Organo-arsenic (III), –antimony (III) and -bismuth (III) thiolates [85], PAHs incorporating the peropyrene structure [86], Nonregular PAHs [87], large PAHs [88] Naphthalene and anthracene [89], 1-nitropyrene [72] Toluene-

3,4-dithiolatoantimony (III) derivatives [90], Trimethylarsine oxide [91] phosphorus tricyanide [92] Oil spill [93] Quinoline and Phenanthridine in Solid Argon and H₂O [94] 6-nitrochrysene [95, 96] Arsenate on Fe-Ce bimetal oxide [97].

A general step-by-step scheme of studying the microbe interaction is given as follows:



Apart from the above-mentioned organic contaminants, metal contaminants speciation and bioavailability has also been widely determined using SR techniques. In a study [98] XAS was used to explore the short-term aging profile and the long-term speciation of dissolved Cu, CuO, and CuS nanoparticles, concluding that the short-term reactions with nanoparticles are dependent on the Cu form and soil chemistry, while the long-term reaction are independent of the form of Cu and transformed into iron oxyhydroxide or natural organic matter bound Cu. Similarly, Colzato et al. [99] used Cadmium L-edge XANES to study short-term temporal changes in Cd speciation and long-term changes in Cd extractability to conclude that highly weathered Oxisols and less weathered Entisols and Mollisols contain Cd bound to organic matter and Fe and Al oxides. Mariet et al. [100] used EXAFS to study a century old Pb leftover from metallurgical activities and reported the presence of Pb mainly as sorbed to Fe oxy(hydr)oxides, which was a significant finding of great consequence to environment. SR based techniques have also been used

recently to study real time biodegradation of organic chemicals [101], where it was predicted that humic acid accelerates the degradation of polyaromatic hydrocarbons (PAHs) by enhancing the solubility of the PAH, thereby increasing PAH bioavailability to microorganisms. SR-FTIR was used to study the effect of HA on the degradation kinetics of pyrene by *Mycobacterium* sp. on a magnetite surface [101].

7. Synchrotron based techniques in studying soil nutrient (nitrogen and phosphorus) dynamics

Phosphorus is a major essential nutrient to plants and directly involved in the metabolic activities of plants, maintain structural integrity and directly affecting the economic yield of crops due to its crucial role in fruit setting and flower development. P found in many forms in soil, organic or inorganic. The form of P in a soil decides its fate of mineralization, fixation, and availability as well as interaction with other compounds in soil. This makes the study of P speciation very much important. But low concentrations of P in chemical and organic species make it difficult to specify the form of occurrence of P due to matrix interferences [102, 103] using conventional techniques like SEM, IR spectroscopy and NMR spectroscopy.

But due to the aided advantages of SR-XAS, a matrix interference free data has been made possible. The technique uses XAS spectra for identification of the species. However, it represents the average of spectra of all the P species present, hence, model analogues of P species are used as reference to extract the individual spectra from the overall spectra. The conventional techniques involve the chemical processing of sample followed by colorimetric analysis, or other extractant methods, which mostly involves the removal of P from its natural environment (soil matrix or colloid) and resulting to possible alteration of original form of occurrence. However, use of SR techniques such as XANES and EXAFS have proved to be promising in soil P speciation. These techniques involve the study of spectrum produced by only one element (i.e., K-edge spectrum of P) of target irrespective of other elements present. Brandes et al. [104] have studied the phosphorus K-edge XANES spectra of potassium phosphate and various organic P species. The K-edge spectrum of P species in XANES can be identified by characteristic line feature, for example, a pre-white line feature indicated the PO_4 tetrahedra in coordination with a transition metal. Similarly, a weak pre-white line showing absorption peak at 2–5 eV indicated Fe (III) phosphate and adsorbed Phosphate on it [16]. Such features are very prominent for P minerals like phosphorsiderite and strengite [105]. Similar studies have been carried out by few researchers till date, which uses XANES for speciation of Soil P [106–113]. XANES has been used to study adsorbed species of P on Fe and Al oxides [110].

N is also a major essential plant nutrient involved in structural integrity to metabolic activities of plants. The inorganic forms of N have been well explored and its analysis procedure in soil system is well established. But the nature of soil organic nitrogen (SON) has still remained relatively unexplored given its importance in the N cycle [114], as half of the SON have been termed as the unknown N [115]. The dissolved organic N (DON) also has the same fate as SON in terms of its characterization [116]. There are several methods that have been devised to characterize the SON fraction as hydrolysable N, $\text{NH}_3\text{-N}$ and unidentified N, such as, acid hydrolysis [117], pyrolysis, mass spectrometry and NMR spectroscopy [118, 119]. The use of X-ray spectroscopic methods in this field has come in to existence in recent past only [25, 120–124], which come with their obvious limitations of low energy, sensitivity and incapability to determine very small fraction of samples and limited number of reference spectra.

As mentioned in the previous regarding P determination, XANES K-edge N spectra has been used in few recent studies for speciation of SON and DON, which

are present in very low concentrations, due to their highly sensitive beamline characteristics. And these works have been focusses in the direction of developing appropriate N reference standards [125]. The N K-edge XANES requires very high flux beamline critical of the study subject, and it occurs at photon energy of around 400 eV. An N-XANES represents the average of spectra of all the N species present, hence, reference spectrum of N species is used to extract the individual spectra from the overall spectra. This is almost like a fingerprinting technique where reference spectra and resultant K-edge spectra are compared to conclude the speciation. The peak resonance spectra of ammonium compounds were found to be around 401 eV [126], for KNO₃ and Ca (NO₃)₂ it is around 412 eV, pyridine-based compounds at 398.7 eV. N-XANES has been used to characterize Maillard reaction-produced humic substances in DOM-related geomaterials [122], to study the aquatic sediment humic acids and their characterization to pyridines and oxidized pyridines [123]. These approaches had the major disadvantages of physical alteration and poor correlation between soil properties and chemical characteristics of extracts [125]. Because organic N fraction is closely associated with the clay size fractions of soil, the analytical technique that did not involve much chemical alteration, came in to popularity in the recent years, with the advent of SR based XANES. N-XANES has been used to study the dynamics of N-compounds in the rhizosphere of field pea (*Pisum sativa* L.) [127], characterizing heterocyclic (pyridinic) N in pyridines, pyrazines, nitrilic-N, $-N^{1/4}$, amide N and $-NH-$ and nitroaromatic-N. N K-edge XANES was used to derive the spectra of soil to study the changes in SON compound by changes in pedoclimatic properties and cultivation duration [128].

8. Synchrotron based techniques in soil rhizosphere studies

Soil rhizosphere is a very complex yet important part of soil–plant root interaction. The microbes inhabiting the rhizosphere, the root exudates from plants, their interactions with each other and with the surrounding environment is crucial for nutrient cycling, nutrient release from SOM and ultimately plant growth. However, the study of rhizosphere has not been easy due to its complexity. The very fine root structures are not easily identifiable with existing techniques. The visualization of complex processes taking place in the rhizosphere require very high intensity beam as well as nanoscale spatial resolution, which have been met recently by some interventions which use SR for study.

STXM has been used to investigate the rhizosphere in few recent studies, for studying OC distribution within bacterial biofilms at fine scale [129–131] soil micro-aggregates [12, 26, 51] and bacteria-soil mineral interfaces [132]. Along with STXM, NEXAFS has been used to study oxidative damage of lignocellulosic materials [133] in bleaching and if such technique could be used in soil, it may help in quantifying the degradation of plant cells [134]. Synchrotron -IR microscopy (SIRM) is such a technique which has enabled the non-invasive mapping of root zone by using mid-IR spectroscopic signature. For SIRM studies, seedlings are sown in rhizoboxes, with modification of Lexan faces with windows such as Zn Selenide windows [135] and diamond window [136]. These windows allow direct observation of root-soil interface using SIRM. SIRM enables to focus the IR ton area as small as 6–10 mm [74, 75].

9. Limitations

SR based techniques have proven to be a boon in the field of soil analysis. However, it is still unexplored and there is a lot of scope for further research in this

field. No technique is perfect and SR based techniques also come with several limitations. For example, μ -XRF uses hard X-ray beamlines for metal and metalloids with $Z > 20$, and at this beam line the lighter elements (N, P and S) cannot be studied. Similarly, soft X-ray cannot be used for heavy elements. The interpretation of data in K-edge XANES requires very much skill and accuracy, also when a specific element is being detected, there are chances of self-absorption leading to faulty interpretation. Also, the low energy of K-edge shell and low concentrations of the elements in soil pose limitations to this technique. Studies involving preparation of thin sections require very high skill. Detailed mapping of spatial distribution of organic C also poses challenges when information on single locations needs to be interpolated to processes encountered at the Pedon or landscape scale. Also, constraints such as sample preparation, control of radiation damage, or spectral quantification are faced in SR-FTIR studies. Other limitation of SR-FTIR is that it cannot be applied to all geological materials, because it is not possible to obtain IR-spectrum for those elements which are opaque at IR e.g., Iron oxides or sulfides and non-silica bearing minerals. The data from spectral information of standard substances is still insufficient to fully identify functional group chemistry for soil organic C and a concerted effort is required to fill that gap as soon as possible. However, these limitations also indicate the areas where the future research should be focused.

10. Future perspective

The SR based techniques are far more improved in terms of their accuracy compared to the pre-existing techniques that use EM radiation for chemical and physical analysis of soils. Soils are inseparable entity of agriculture production systems and environment as a whole. The advent of SR techniques has provided a better insight into the soil nutrient dynamics, organic C speciation, soil mineralogy, fate of trace elements, metal contaminants, organic pollutant bioavailability and microbial interactions. These results obtained from SR based techniques can be used to make significant predictions for sustainability of an agricultural system. For example, the forms of nutrient in a soil can indicate the underlying biogeochemical process which is occurring in real time and can be a good indicator of soil health. The correlation of the different forms with soil microbial flora and fauna will give insight into the health status of a soil. The forms of OC in soils are very good indicator of soil genesis, aggregate stability and capacity of a soil to provide nutrition for the microbial population. The clay coatings on the ped faces, cutans and other micromorphological features can be accurately visualized to understand the soil development processes and their stage of weathering, which in turn, decides the nutrient holding capacity, permeability, infiltration etc. and these are important parameters to decide cropping systems. The future researches should be focused towards overcoming the short falls of the techniques. For SR absorption techniques, a wide range of spectral libraries should be priority. The different techniques should be combined together to increase the array of analysis of the samples. In addition to this, significant constraints like need sample preparation, control of radiation damage and spectral quantification should be addressed.

11. Conclusion

The SR based techniques are remarkable improvement over the pre-existing spectroscopic techniques. The use of SR in soils is quite new and fairly unexplored dimension. Not a very less but also not a lot of research has been done towards


analysis of soil parameters. The techniques such as XAS, FTIR and XRD have been widely used in soil studies, for soil nutrient dynamics, organic C speciation, soil mineralogy, fate of trace elements, metal contaminants, organic pollutant bioavailability and microbial interactions. The exploration of unexplored at nano scales has been possible with the advent of this technique. However, some limitations such as unavailability of adequate spectral references, converting the qualitative data in to quantifiable terms high skill requirements for handling and sample preparations and most importantly, the confinement of SR facilities to select places have restricted their wide adoption. Hence, future researches focused in this direction to popularize and further explore this technique to make it reachable in public domain.

Author details

Surabhi Hota
ICAR—National Bureau of Soil Survey and Land Use Planning, Regional Centre,
Jorhat, Assam, India

*Address all correspondence to: surabhi.hota@gmail.com; surabhi.hota@icar.gov.in

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