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Synchrotron-based techniques for elemental analysis in soil-plant system under polluted environment

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Abstract

Analytical techniques for elemental analysis in the soil-plant system have significance importance, especially emerging techniques such as synchrotron radiation (SR). Improved techniques allow samples to be examined in a non-invasive manner at high speed and resolution, resulting in better sample data. By applying various analytical techniques based on SR, it is possible to gather different information about the structure of the studied samples. In mining ecology, such techniques are widely used in assessing heavy metal-polluted sites, i.e., overburden dumps and areas around operating and mothballed mines. The present review elaborated insights into different analytical techniques for applying SR in plant-soil samples. The review also compared traditional research techniques with SR-based emerging and improved techniques. The need to use SR techniques for the complex diagnostics of sample structures to study their elemental and phase composition is substantiated. Using an integrated approach with SR, we can study the dynamics and speciation of HMs with carrier phases and uncover the mechanisms underlying the interactions between the adsorption centers of minerals, organic components, and heavy metals. It also improves the efficiency and accuracy of analysis and broadens the range of information obtained, which could lead to a more precise analysis of samples.

Keywords: Synchrotron radiation (SR), heavy metals, ore, spectroscopy, XRD, XAFS, FTIR, SRμCT.

Introduction

One of Earth Science's top concerns is understanding how human activity affects soil and plant health (Hazarika et al., 2022). Heavy metal (HM) pollution is one of the primary effects of human activity (Singh et al., 2015; Khasanova et al., 2023; Shi et al., 2023). Heavy metals (HMs) have the potential to enter the biosphere through various human interferences, including motor vehicles, mineral and organic fertilizers, and wastewater and industrial pollution sources (Masindi et al., 2021; Jamali et al., 2022; Konstantinova et al., 2023; Liu et al., 2023).

The HM content is among the most significant evaluation indices of soil quality. High-pH soil can and may encourage the adsorption of metal cations to soil particles as well as the precipitation of HMs, which may then influence the uptake of HMs by plants since high-pH soils are electronegative (Wang et al., 2017b). Many physiological processes in living things are inhibited when HMs accumulate in soils, leading to their

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degradation (Kulikov and Galiullina, 2006; Su et al., 2014). Excess HM exposure in living things poses major health hazards (Seth, 2012; Roy and McDonald, 2015). In humans, HMs cause the inactivation of enzymes by attaching themselves to their sulfhydryl groups. Furthermore, they can harm the central nervous system (Roy and McDonald, 2013). A variety of physical, chemical, and biological treatments (such as phytoremediation, microbial cleaning, etc.) can be used to clean up areas contaminated with HMs (Seth, 2012; Chandel et al., 2023; Schommer et al., 2023).

Considering this, the novel methods based on SR are crucial for examining the structure of soil and plant materials. Traditional methods of analyzing plant samples frequently result in their loss or damage, which reduces the accuracy of the data gathered during the analyses (Karunakaran et al., 2015). The researcher can identify the trace concentrations of elements using SR, which has higher parameters than standard X-ray tubes (Stańczyk et al., 2023). This reduces the sample exposure time significantly and prevents sample damages reported by Wang et al. (2017a). Synchrotron techniques in ore geology and mining have great potential for monitoring the biogeochemical behavior of ores, assessing contaminating impurities in ores, determining the presence of liquid fractions and inclusions, and conducting elemental and phase analyses of ores (Von der Heyden 2020; Loron et al., 2022).

Synchrotron Radiation (SR)-based Techniques

Radiation from electrons travelling at a high centripetal acceleration is known as Synchrotron Radiation (SR). Strong directivity and excellent brightness- orders of magnitude higher than in X-ray tubes- are its defining characteristics (Hofmann, 2007; Ternov, 2007). This study explains several SR-based techniques in detail in later sections.

Synchrotron Radiation X-ray Tomographic Microscopy (SRXTM or SRμCT) is a frequently used technique for SR. Since it enables the internal structures of fossils to be scanned with a resolution and accuracy not possible with other non-destructive techniques (Tafforeau et al., 2006), this technique is well-established in the study of plant parts and fossils (Smith et al., 2009). Synchrotron Phase-Contrast Imaging (SRPCI or SRPμCT) is a different sort of X-ray tomography where the sample is positioned at a variable distance from the detector, producing diffraction fringes (Brar et al., 2018). Low-density media interfaces in the sample can be seen thanks to this technique (Lauridsen et al., 2014). Thus far, SRPμCT has proven to be the least intrusive method for examining the internal structure of both soil and mineral samples. The method is also frequently used to analyze plant parts. Using this technology for spatial analysis, such as 3D tomograms and layer-by-layer sample scanning, is also usual practice.

For a thorough examination of chemical composition, spectromicroscopy using SR-based Fourier Transform Infrared (SR-FTIR) is a relatively recent method (Wetzel and LeVine, 1999). Using the ability of their functional groups to absorb specific infrared wavelengths, these molecules can be identified in large numbers inside the sample being studied (Holman et al., 2003). Furthermore, the absorption intensity is directly correlated with the concentration of each individual group of atoms, and its value is also specific to those groups. Thus, it is possible to find the concentration of a particular component in the sample by measuring the absorption intensity. Only employing the FTIR approach is uncommon (Xiao et al., 2018). Typically, FTIR is used in conjugation with methods like XRF or XRD that reveal the sample's elemental composition (Xiao et al., 2022; Hou et al., 2023). FTIR spectroscopy is used to analyze the organic component of soils, as opposed to XRD and XANES spectroscopy techniques, which study the mineral composition. FTIR approach allows the tracking of the primary mechanisms of immobilization, transformation, and movement of HMs in soils and plants.

The near-edge structure of the X-ray absorption spectrum (X-ray absorption near-edge structure method, or XANES) or the far-edge structure (EXAFS technique: Extended X-ray absorption fine structure) of samples can be investigated using X-ray Absorption Fine Structure (XAFS) spectroscopy. According to Tsitsuashvili et al. (2021), XAFS is the fluctuations close to a structureless step curve that should be monitored for an isolated atom. XANES provides information on atom charge states and the symmetry of the local atomic environment. Coordination numbers, some angles between chemical bonds, and the radii of coordination spheres are among the details of the absorbing atom's local geometry contained in EXAFS. Using XAFS, scientific teams can monitor the samples' redox potential, evaluate the oxidation state of metal pollutants, and examine the local atomic structure of soil and ore components.

Similar to the other methods mentioned, XAFS functions best when used in conjugation with other methods of physicochemical analysis (Manceau et al., 2004; Bauer et al., 2022). However, the technique's applicability is restricted by the heterogeneity and polydispersity of soil samples. It is challenging to extrapolate, using only the XAFS technique, the spectra of heavily contaminated soils that contain a wide variety of HM mineral forms from the spectra of regular samples.

Large (> 100 μm) single crystals are not necessary to ascertain the atomic structure of crystalline materials through X-ray diffraction (XRD) analysis. The atomic structure of a crystalline sample, unit cell parameters, spatial symmetry, position, and atom type can all be ascertained using this technique. It is feasible to ascertain properties like valence and interatomic distances using the unit cell parameters. Without prior knowledge of the structure or elemental composition of the microcrystals under study, XRD allows for determining their structure. It is an effective analytical tool for examining how atoms are arranged in crystalline materials (Tsitsuashvili et al., 2021). For XRD analyses, laboratory radiation sources are most frequently utilized. Simultaneously, SR is increasingly used because of its enhanced parameters, which primarily relate to high resolution (Nevidomskaya et al., 2021; Kumari et al., 2023). Analyses of soils and soil-like environments, including sediments, dust from the side of the road, and individual soil components, such as ores and their components, are conducted (Brown, 2002; Fan and Gerson, 2011).

Applications of Synchrotron Radiation-based Techniques

A significant number of works (Lauridsen et al., 2014; Meneses et al., 2018; Ma et al., 2020) use SRμCT. SRμCT for instance, has been applied to detect gas deposits on hydrophobic surfaces visually. The 3D tomograms that showed the spatial distribution of gas in the tissue and on the leaf's surface when submerged in water were made public by Lauridsen et al. (2014). On the superhydrophobic adaxial side of the leaf, the gas film formed elongated triangular gas volumes by filling the surface tissue furrows at the base and the tip of the leaf segment. The entire observed exterior gas volume was gas-phase coupled as a result of the comparatively high volume of gas layers within each furrow being connected by a thin network of gas film covering the tissue ridges between each furrow. On the other hand, no gas films were observed on the leaf's abaxial side (Lauridsen et al., 2014).

In the field of earth sciences, SRμCT is effectively utilized for the morphological examination of rocks and soil as well as the evaluation of their internal structures. Meneses et al. (2018) employed layer-by-layer SRμCT scanning of pumice to ascertain the porosity and friability- two key characteristics of this igneous rock. Artificial neural networks were trained on the acquired images using a variety of segmentation techniques. The statistical analysis of the Krasker-Wallace test revealed significant differences between the segmentation techniques. In the study by Ma et al. (2020), SRμCT was used to evaluate the influence of pore characteristics on the stability of black soil in freeze-thaw cycles. Porosity rose with the number of freeze-thaw cycles, leading to the development of macropores, linked channels, blocks, and fracture structures. Additionally, there was a shift in the shape of pores: there were more oblong pores and less regularly and irregularly formed pores. The increase in the number of pores was related to volumetric changes in ice during freezing, which caused soil particles to separate from each other. Furthermore, the capacity to recover from deformation brought on by ice crystal extrusion progressively diminished with an increase in the frequency of freeze-thaw cycles. In another study, Scheckel et al. (2007) examined the features of the distribution and compartmentalization of thallium (Tl) in Iberis intermedia using synchrotron X-ray differential absorption-edge computed microtomography (CMT). CMT studies were conducted at the GeoSoilEnviroCARS (GSECARS) bending magnet beamline 13-BM-Dat at the Advanced Photon Source (APS) at the Argonne National Laboratory, USA. According to the authors, CMT is the only method that can identify the compartmentalization of Tl in the vascular system of cotyledons and leaves of Iberis intermedia.

According to research conducted by Von der Heyden (2020) and Lahlali et al. (2015), SRPμCT is currently the least invasive method for investigating the internal structure of samples. In order to optimize data quality in wheat and rapeseed, Karunakaran et al. (2015) demonstrated the advantages of SRPμCT for visualization and quantification of internal plant and root structures over a wide range of imaging parameters. The linear profiles of the samples clearly showed the details of the sample's internal structure and the presence of cavitations in the stem vessels and their connecting structures. The authors state that the relatively low dose of radiation absorbed by the samples will enable future longitudinal studies in which the same living plant can be photographed in a series of time-separated exposures. In another study, Lahlali et al. (2015) applied the SRPμCT technique to wheat varieties infected with Fusarium root rot and confirmed the structural differences between resistant and susceptible varieties. The artificially infected and uninfected rachis and ears scanned showed different resistance in Sumai3, FL62R1, and Muchmore varieties. Differences in mass density and phase contrast signals between healthy and infected sections were observed and proved most pronounced in the Muchmore variety. Healthy ones appeared in white and were filled with internal structures, while infected ones were mostly empty and transparent due to water and tissue loss.

The Synchrotron radiation-Fourier transform infrared (SR-FTIR) spectroscopy can be used to reveal and demonstrate the composition and distribution of components in humus fractions. In their study, Solomon et al. (2005) used SR-FTIR to observe the effect of land use change on the content, composition, and stability in the soil of various organic forms of carbon occurrence in the extracted humic compounds. Easily degradable components of soil organic matter (polysaccharides, labile components of aliphatic fragments) were more prominent in the humic matter of forest soils, while aromatic and recalcitrate aliphatic forms prevailed in the humic deposits of the permanently cultivated fields. In another study, Lehmann et al. (2007) employed the SR-FTIR technique for the spatial description of carbon forms in soil organic matter, revealing the distribution of total carbon and spatial patterns in the distribution of some of its forms. The correlation analysis confirmed these empirical data. Observations on carbon distribution in soil microaggregates allowed a new look at the mechanisms of their formation and stabilization of organic carbon.

The authors suggested that in the studied soils, microaggregate formation is initiated mainly by the accumulation of organic matter on the surfaces of clay particles rather than by the occlusion of organic debris by clay particles. Clay cluster and biopolymer distribution exhibited spatial heterogeneity, as demonstrated by Xiao et al. (2019) using SR-FTIR. According to the authors, all soil microaggregates in clay soil samples were dominated by the OH, C-H, C=C, Si-O, and Al-O functional groups, and there was a significant association between these functional groups. The absorptions of Si–O (1030 cm^{-1}, silicates) and Al–O (915 cm^{-1}, kaolinite, and smectite) functional groups were stronger than others. These findings demonstrated that the biopolymers and clay clusters had a diverse spatial distribution. The correlation suggested that mineral clusters could bind various biopolymers.

Holman et al. (2002) investigated the catalysis of polycyclic aromatic hydrocarbons (pyrene) by humic acid using the SR-FTIR spectroscopy method. SR-FTIR spectra were recorded during pyrene degradation on magnetite surfaces by Mycobacterium sp. JLS bacteria, both in the presence and absence of Elliott Soil Humic Acid. Based on the collected data, SR-FTIR mapping of the samples revealed the spatial distribution of the infrared absorption peaks related to pyrene, Elliott Soil Humic Acid, and Mycobacterium sp. JLS bacteria.

In another report, Wan et al. (2019) used the SR-FTIR spectroscopy method to study the concentration and characteristics of Fe-linked carbon in twelve agricultural soil samples obtained from different areas of central and eastern China, which demonstrated a direct correlation between the spatial distribution of aliphatic compounds, carboxylic acids, peptides, lignin derivatives, and polysaccharides and the Fe-O distribution. The correlation coefficients of Fe-O with organic compounds had the following order: polysaccharides or aliphatic compounds > peptides > carboxylic acids > lignin derivatives. Stronger associations occurred between Fe-O and polysaccharides, aliphatic compounds, or peptides than between carboxylic acids or lignin derivatives. In addition, the correlation coefficients between Fe-O and organic compounds showed that these three compounds were closely related to iron oxides. Therefore, assuming that more polysaccharides, aliphatic compounds, and peptides are associated with Fe oxides than carboxylic acids and lignin derivatives, it can be concluded that iron oxides preferentially stabilize polysaccharides and aliphatic compounds in arable soils.

The distribution of HMs in soil has been examined using SR-FTIR. The study by Yu et al. (2017) demonstrated the association of Cu with mineral elements and functional groups within soil particles. Through SR-FTIR, the non-uniform distribution of Cu in soil particles was shown. The areas of high and low Cu concentrations represented the newly added and original Cu, respectively. Information about the distribution pattern of functional groups in the soil particles was also obtained. All functional groups had a distribution similar to Cu, which may indicate their ability to bind Cu.

The XAFS technique is not as commonly used in earth sciences as XRF or XRD, for example, but the frequency of its application has expanded considerably in recent years. Most studies with this technique use SR, as laboratory facilities are very scarce. In geology, XAFS can be used to probe crystalline and weakly crystalline materials. Based on the chemical composition of weakly crystalline materials, conclusions can be drawn about the contaminants in the mined rock (McNear et al., 2010). Analysis of XANES spectra provides information on the redox properties and coordination numbers of metals in mineral and metal-ligand compositions (Cook et al., 2011). In-situ XANES spectral imaging has been used to study the dynamics of the oxidation degree of a particular HM in a particular ore (Etschmann et al., 2017).

Prietzel et al. (2007) identified various Fe (II) and Fe (III) compounds in soil samples using the XANES method. The contribution of various organic and inorganic Fe-containing compounds was evaluated using the linear combination fitting method. In another study, Strawn and Baker (2009) analyzed five soil samples using the XAFS method, in which they determined the molecular structure of Cu compounds and the energy transitions of electrons by the peaks splitting and their intensity. Using these data together with statistical analysis and theoretical modeling allowed the authors to suggest that Cu-SOM (soil organic material) complexes are the predominant species in soils. Based on these results, it was hypothesized that more than 90% of Cu in soil samples is present in the form of Cu-SOM complexes.

Using XAFS to analyze the dynamics of toxic heavy metals, such as cadmium (Cd), allows determining the ability of soils and plants to accumulate them and studying the speciation of pollutants and their extractability. A study conducted on six soil samples from different regions of Brazil showed a progressive natural attenuation of soil contamination by Cd-containing phases. Cd (II) entering these soils was mainly immobilized by organic matter and oxide minerals binding to the soil. The degree of Cd extractability dynamics was evaluated four months after contamination using chemical fractionation. By analyzing the XANES spectra of the samples, a high content of Cd bound to soil organic matter was determined (Colzato et al., 2017). In another study, Kim et al. (2002) investigated Cr speciation and dynamics. By analyzing XANES spectra, the authors obtained information on soil and plants' sorption and extraction capacities concerning Cr-containing compounds. Cr (III) and Cr (VI) were found in the samples. It is emphasized that Cr (VI) is a strong oxidant and poses a danger to plants, even in small amounts. The conversion of Cr (III) to Cr (VI) was initiated by manganese, a strong oxidant present in the samples.

The lower Cr (VI) content in the near-surface soil horizons compared to the deeper soil horizons was due to different kinetics of Cr (III) oxidation to Cr (VI). The content and dynamics of Cr (VI) in soil were also controlled by the anion-exchange capacity of Fe oxides (Garnier et al., 2013). In addition to Cr, its compounds are also toxic, particularly Cr_2O_3, which is most dangerous in the form of nanoparticles (NPs). Using EXAFS in the study, Kumari et al. (2023) determined the functional groups of Cr oxide, which had phytotoxic effects such as stunting the germination of plant samples. Another illustrative example of work centered around the analysis of a single HM is the paper by Prietzel et al. (2023). The study examined the speciation of aluminum (Al) in soils, which is important for Al cycling and toxicity in terrestrial ecosystems. Three forest soil profiles were analyzed using synchrotron-based XANES and XRD techniques (Synchrotron Light Research Institute, Thailand). Al K-edge XANES allowed us to estimate the relative contribution of different Al species to the total Al in soil samples. The authors claimed that XANES, in combination with XRD and elemental analysis, is a promising methodological complex for the speciation of Al in soils with a great potential to promote the understanding of Al biogeochemistry in terrestrial ecosystems.

The XANES spectroscopy was used to investigate the structure of various soil samples and soil phases saturated with Cu^{2+} and Zn^{2+} ions (Minkina et al., 2014). Soil samples of ordinary black soil were saturated with $Cu(NO_3)_2$ and CuO. Samples of individual soil components (calcite, kaolinite, bentonite, and humic acid preparations isolated from ordinary black soil) were saturated with Zn^{2+} and Cu^{2+} ions. The analysis of XANES spectra of the K-edge of the zinc absorbed by the carbonate phase (Figure 1) showed that Zn ions substitute Ca ions in octahedral positions and demonstrate the 1s → 4p electronic transition. When comparing the intensity of maximum A and the energy position of spectral features B and C in the XANES spectra of the K-edge for Zn in humic acid, it was observed that metal ions, regardless of what minerals they consist of, have similar mechanisms of interaction with soil organic matter.

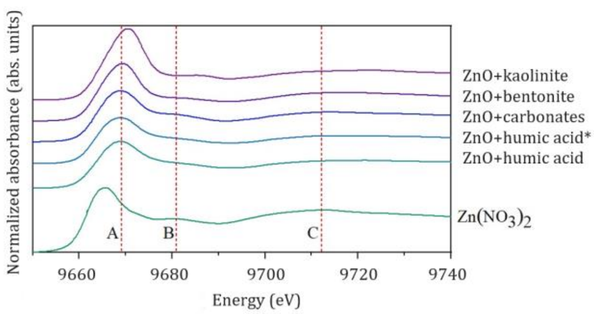

Figure 1. XANES absorption spectra of the Zn K-line (Minkina et al., 2014)

An urgent interdisciplinary goal is to study soil and plant contamination in order to gather comprehensive information on the dynamics and speciation of HMs. Adding various metal NP concentrations to the soil sample under investigation while maintaining other experimental conditions is one of the most effective approaches for studying the accumulation and transformation of HM NPs. In order to determine the phases of copper-containing compounds under various circumstances, a sample of black soil was examined (Burachevskaya et al., 2021). Based on a comparison with model compounds, XANES measurements demonstrated a high sensitivity to the geometry of bonds produced by Cu atoms, which characterizes the near surroundings of Cu atoms in soil samples (Figure 2). After the soil was incubated with the tested compounds, XANES analysis was carried out. When comparing the soil sample saturated with CuONPs to the control sample, there were no noticeable changes to the X-ray absorption spectra.

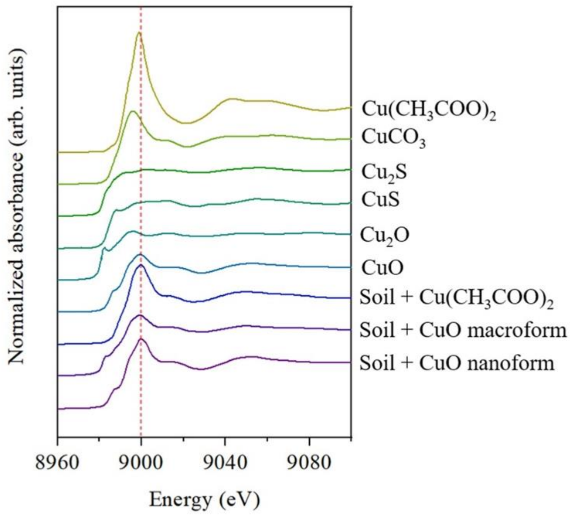

Figure 2. XANES spectra of Cu compounds in the Hordeum sativum (Burachevskaya et al., 2021)

The presence of heavy metals (Pb and Sb) in the soils of military ranges causes pollution of surface and ground waters, a decrease in biological activity, and an increase in the uptake of metals by biota. The evaluation of the immobilization capacity of soil organic matter by the EXAFS technique carried out by Ahmad et al. (2013) made it possible to develop remediation measures for Pb-polluted soils. EXAFS spectra of soil samples in which organic sorbents (mussel shells, cattle bone meal, and biochar) were added showed a significant presence of organically bound Pb compounds, and introducing additives led to an increase in pH. EXAFS spectra, in combination with SEM and XRD, revealed stable Pb compounds in samples containing organic additives, which, according to the authors, suggests a mechanism of Pb immobilization. In another example of Pb research (Nevidomskaya et al., 2015), analyses of the connection between metal ions and different soil components using XANES (Figure 3a) and EXAFS (Figure 3b) showed that the local atomic environment of Pb can vary greatly depending on the structure of the mineral phase. Lead (Pb^{2+}) ions in bentonite, kaolinite, hydromuscovite, gibbsite, and calcite are included in the positions of the intra-muscovite complex, replacing some aluminum ions in the octahedral sites. This results in a change in the Pb-O distances in the Pb-bearing octahedrons. Pb^{2+} is also sorbed by dimeric (Pb-Pb) silicate and aluminum groups. The adsorbent surface structure plays a key role in the sorption of Pb^{2+} across mineral phases.

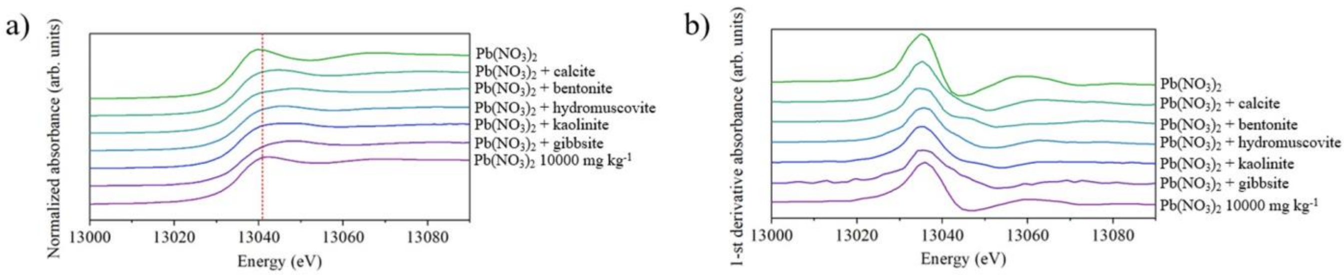

Figure 3. XANES spectra of L-lines (a) and their derivatives (b) for $Pb(NO_3)_2$, different soil samples, and a soil sample at 10000 mg Pb kg^{-1} (Nevidomskaya et al., 2015)

During mining and subsequently processing minerals, coastal floodplains, which play a key role in transporting nutrients and HMs between surface water and groundwater, are heavily polluted. This type of pollution often involves arsenic (As), which is present in coastal soils as As (V) and the more toxic As (III). Using the EXAFS technique, it was found that most of the As is represented by As (V). As was mostly bound to Fe hydroxyl compounds in the studied samples and concentrated around the roots. The As bound to Fe proportion reached up to half or more of the total arsenic content. This was explained by the highest adsorption affinity of As with Fe (Voegelin et al., 2007).

The EXAFS technique is used to study adsorption properties and forms of radionuclides in soils. As a result of intensive nuclear and thermonuclear weapons testing, as well as the Chornobyl and Fukushima accidents, a large amount of Caesium (^{137}Cs) was released into the soil through atmospheric precipitation. Fan et al. (2014) revealed that the species of adsorbed Cs depend mainly on the clay minerals contained in the soil. The authors observed a strong affinity for Cs binding on illite $(K_{0.75}(H_3O)_{0.25})Al_2(Si_3Al)O_{10}((H_2O)_{0.75}(OH)_{0.25})_2$ and vermiculite $(Mg^{+2},Fe^{+2}, Fe^{+3})3\ [(Al,Si)_4O_{10}]\cdot(OH)_2\cdot4H_2O$. The Cs was also well sorbed on the zeolite. In the study of ores, Newville (2004) used the XANES and EXAFS spectroscopy methods to determine the information on coordination numbers, degrees of disorder in the local coordination environment, bond lengths, and the chemical identity of HM atoms. Most of the works related to the application of EXAFS spectroscopy in ore research are related to the study of the formation of metal-ligand complexes in the hydrothermal fluid model in a wide elemental range, e.g., gold (Liu et al., 2014) or platinum group elements (Mei et al., 2015).

XAFS is actively used for other purposes besides analyzing the content of heavy metals in soil samples. An example is the study by Lombi et al. (2006), where phosphorus (P) speciation and distribution in fertilized soil were investigated. Studies have shown that P is highly heterogeneously distributed in soil samples. Evidence also showed that P is invariably associated with Ca rather than Fe on the nanoscale. It was also shown that near fertilizer granules, P precipitation in the form of octacalcium phosphate or apatite-like compounds is the dominant mechanism responsible for decreases in P lability. In another study, Alotaibi et al. (2018) used a combination of synchrotron-based XANES and sequential chemical extraction to study phosphorus speciation in a prairie soil after growing Canola plants with the addition of meat and bone meal ash (MBMA) and dried distiller's grains ash (DDGA). The phosphorus sequential extraction protocol used is based on the Hedley et al. (1982) procedure. According to the research results, P transformed from the initial ash sources into a much less crystalline form when it was added to the soil, and Canola plants were grown on the soil for five weeks. The authors argue that the lack of differences in XANES spectra of MBMA and DDGA after adding them to soil may indicate that some transformations of P-form ash have occurred.

The advantage of using XRD with SR is the possibility of obtaining an extremely thin, high-intensity, parallel beam of X-rays, which reduces the heterogeneity of elemental composition in the investigated area of the soil sample. The XRD method is often combined with other methods of analysis: XRF, FTIR, and XAFS. The most common analyses are performed on agricultural soils. Another intensively studied area is technogenic soils polluted with HMs, i.e., soils around factories, industries, and various active and abandoned mines.

The analysis of the elemental composition of soil NPs by XRD using SR was considered in the study conducted by Tsao et al. (2013) on the example of clay minerals of different fractions. In the 2000 nm fraction, quartz was the dominant mineral phase. In the 450-2000 nm fraction, intense diffraction peaks of illite, kaolinite, goethite, and haematite were detected. The NPs of illite, kaolinite, goethite, and haematite were also identified in the 1-100 nm fraction. The analysis of diffraction peaks showed an increase in kaolinite content with decreasing particle size in red soils. The proportion of illite, on the contrary, decreased with decreasing fractions. When interacting with Pb, the phosphorus contained in bones forms the pyromorphite $Pb_5(PO_4)3Cl$. This was demonstrated by Landrot et al. (2020), who examined soil samples at three locations in a residential area of Klithi village (Kanchanaburi, Thailand) near a landfill and a house and in a garden. Analyses of the soil sample near the landfill revealed diffraction peaks of hydroxyapatite, a component of fish bones. On the contrary, analyses of the soil samples near the house and in the garden did not show the presence of pyromorphite mineral phases. Huynh et al. (2003) used synchrotron-based XRD to study the partial substitution of Cd for Fe in goethites. The authors claimed that Cd could be incorporated by isomorphous substitution of up to ~9.5% of the Fe3+ ions in the octahedra of goethite. XRD and TEM revealed that incorporating Cd increased all unit-cell parameters but an overall decrease in crystallite size.

XRD mapping using SR can provide new insights into the mineralogy and orientation of clay particles during the formation of soil crusts. Only the general morphological state of such processes on the soil surface was investigated for a long time, but the mineral composition was uncertain due to the clay particles being too small. A quantitative description of such processes is also lacking. XRD mapping is an efficient way to establish the composition and texture of soil crusts at a depth of a few centimetres with high resolution. This is well illustrated by the XRD mapping of clay layers in soil crust samples studied by Geoffroy et al. (2022). Fitzpatrick et al. (2019) presented an exemplary work that used both laboratory- and synchrotron-based XRD methods. Soil samples on the surface of the fabric (pyjamas) were examined. Synchrotron-based investigations were conducted on the powder diffraction beamline at the Australian Synchrotron Facility. Laboratory XRD results showed that all samples contain similar amounts of quartz (dominant), layer silicate clays (minor and trace amounts of chlorite, smectite, kaolin, and illite), feldspars (minor amounts of albite and orthoclase), and rutile (traces). Synchrotron-based XRD data showed the mineralogy of very small amounts of the soil samples, which comprises tiny soil particles and fragments on the fabric in the in-situ mode using the high-throughput stage.

The XRD method was found to have an application in studying exchange processes in the rhizosphere. Fancello et al. (2019) stated that quartz, phyllosilicates, feldspars, and ore metal sulphides are probably inherited from the bedrock, while other phases are the product of biological or geochemical secondary processes. HM sulphates, and carbonates are the result of alteration and oxidation of Pb-Zn-Fe, and kaolinite is the result of feldspar weathering.

XRD performs best when combined with other techniques. A clear example is the study by Fischel et al. (2023). The combination of μXRD and μXRF mapping allowed the authors to determine the phase and elemental composition of the Graskop manganiferous soil samples and nodules of concentric bands of Mn and Fe that form during redox cycles. Moreover, the study showed the correlation between Si and Ca in stabilizing these metal oxides in the soil matrix and nodules. The authors claimed that using SR makes it possible to analyze Mn at the micron scale and determine its species and distribution in diverse geochemical systems, including soils with trace Mn concentrations. In another study, Kumari et al. (2023) used a combination of synchrotron-based XRD and XAFS to study the total content, mobility, and factor toxicity index of the Cr macro- and NPs in contaminated barley (*Hordeum vulgare* L.). For this study, Cr_2O_3 macro- and NPs were injected into the Haplic Chernozem samples, where barley plants were subsequently grown. All studies were performed using ash-fertilized plants. The presence of the Cr crystalline phase in plants from both sets was indicated and confirmed by the narrow and intense diffraction peaks in the respective spectra (Figure 4). The most intense peaks in the patterns correspond to crystalline Cr_2O_3 (eskolaite). The sample contaminated with NPs also contained a noticeable amount of KCl (sylvite). The accumulation and translocation of Cr in barley plants were confirmed by synchrotron XAFS analysis.

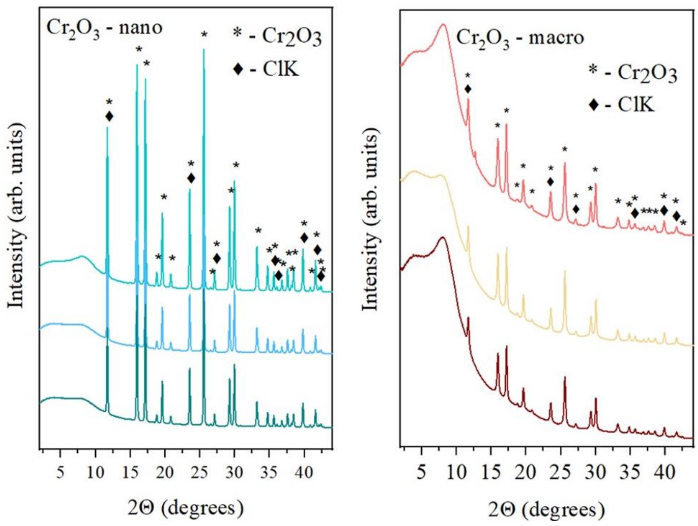

Figure 4. X-ray diffraction pattern of ash fertilized Hordeum vulgare L. plants grown on soils polluted with Cr_2O_3 nanoparticles (left) and Cr_2O_3 macroparticles (right) compounds

XRD is a technique used in geology and ore studies to determine details about the unit cell characteristics of mineral phases and the geometry and orientation of a mineral's crystal lattice (Lavina et al., 2014). Working with small samples is made possible by the X-ray spot's small size, high brightness, low noise, and intensity (Reynolds et al., 2010), for instance, to research the properties of the manganese nodule's surface crystallites (Manceau et al., 2014).

Conclusion

The review showcases the advancements of contemporary techniques for studying metalloid forms and heavy metals. Although XAS is a powerful analytical tool, it is best applied as one of several analytical techniques to obtain the clearest picture of the processes controlling HM mobility in soil environments. This is based on the generalization of the literature and our data obtained using synchrotron analysis. Other sophisticated spectroscopic methods are frequently employed in addition to the conventional analytical methods in soil chemistry to supplement the elementally specific data acquired from XAS. Based on the analysis of the reviewed works, it can be concluded that using SR-based methods is preferable when analyzing polydisperse samples. This is because these methods allow one to study the distribution of metalloids and HMs in soil and plant samples without destroying them, as well as the oxidation degree of elements of variable valence and solid-phase sample elemental and phase compositions in micro volumes. Using an integrated approach, we can study the dynamics and speciation of HMs with carrier phases and uncover the mechanisms underlying the interactions between the adsorption centres of minerals, organic components, and heavy metals. It also improves the efficiency and accuracy of analysis and broadens the range of information obtained.

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