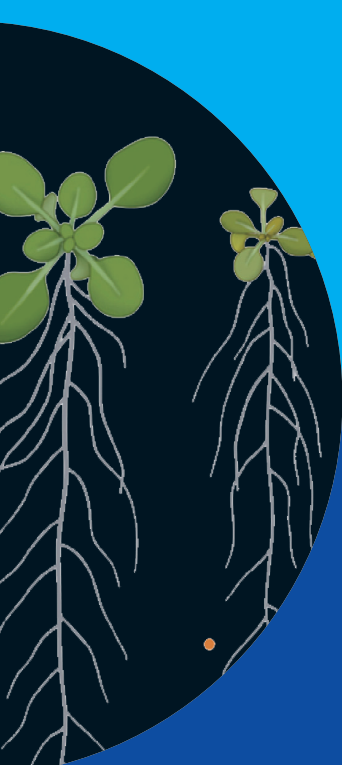


Environmental and Earth Sciences



Plants and their environment exhibit complex interactions. Through their relationship with soil, plants absorb nutrients and heavy metals, improving soil quality and fixing carbon. By absorbing and transpiring water, plants regulate the water cycle and purify water. In their interaction with air, plants absorb carbon dioxide for photosynthesis, regulate gas exchange, and reduce air pollution. Plants also form symbiotic relationships with microorganisms to enhance nutrient utilization and disease resistance, while interactions with animals support pollination and seed dispersal. Additionally, plants mitigate the greenhouse effect by absorbing carbon and adapting to extreme climates, thereby maintaining ecological balance. In 2024, research on plant–environment interactions using synchrotron radiation technologies at the NSRRC achieved significant progress.

Plants' ability to absorb and accumulate toxic substances makes them essential indicators for evaluating soil conditions. Understanding their absorption mechanisms is crucial for preventing harmful toxins from entering crops and improving soil health. Shan-Li Wang at National Taiwan University used X-ray absorption near-edge structure (XANES) technology to explore how soil conditions affect molybdenum (Mo) chemical forms and their absorption by rice.

Kuo-Chen Yeh at Academia Sinica applied the X-ray Nanoprobe beamline for X-ray fluorescence (XRF) analysis of *Arabidopsis*, mapping element distribution under varying soil conditions. This provided insights into element absorption and transport mechanisms.

Samir Gamil Mohammad Al-Solaimani at King Abdulaziz University (Saudi Arabia) used XANES and XRF imaging to study the effects of humic acid (HA) on nutrient availability, toxic elements, and plant growth. The results showed that HA improves soil fertility and reduces the absorption of toxic metals, offering practical solutions for enhancing soil and crop health.

Yu-Ting Liu at National Chung Hsing University focused on using plants and their derivatives to remove toxic metals from the environment. They demonstrated that thiol-functionalized biochar (BC) effectively removes hexavalent chromium [Cr(VI)] and uncovered how thermophilic acidic microalgae *Cyanidiales* detoxify trivalent arsenic [As(III)]. These findings highlight BC's effectiveness in Cr(VI) removal and *Cyanidiales*'s efficiency in As(III) detoxification, offering sustainable solutions *via* materials science and bioremediation.

Yu-Min Tzou at National Chung Hsing University investigated phosphorus regulation in soil to promote plant growth. His study examined citric acid adsorption on HA–ferric hydroxide co-precipitates (HAFHCPs) and competition between citric acid and phosphate (P) at different carbon-to-iron (C/Fe) ratios. Results revealed that HAFHCPs regulate phosphorus availability, which is influenced by C/Fe ratios, HA composition, and citric acid presence, as observed by XANES technology. Optimizing phosphorus availability is vital for sustainable phosphorus resource use.

These studies advance our understanding of plant–environment interactions and soil remediation strategies, providing critical insights for ecosystem sustainability. (by Chun-Chieh Wang)

Assessing Soil Conditions Through Plant Accumulation of Toxic Substances

Research reveals how absorption of soil toxins by plants can indicate soil health, guiding effective management and remediation strategies.

Plants can serve as the direct indicators of soil environmental conditions because they readily absorb and accumulate toxic substances from the soil. By studying the mechanisms through which plants accumulate chemical or toxic substances, we may prevent crops from taking up these harmful substances. Additionally, analysis of plants may be used to evaluate the effectiveness of soil remediation. Here, we present the research findings from 2024 conducted at the NSRRC, which focused on how plants accumulate toxic substances from the soil and how this process can be used to assess the effectiveness of soil

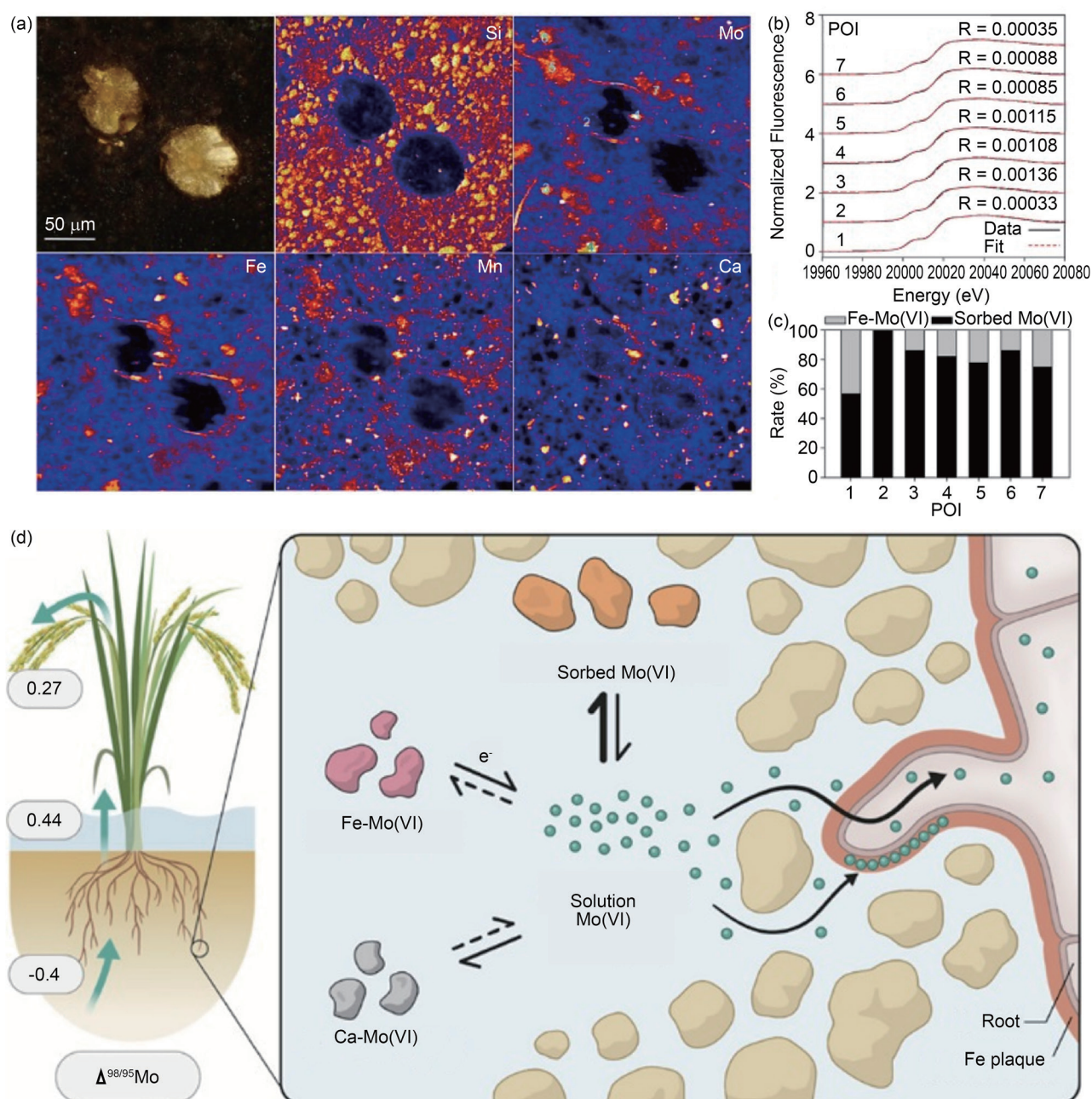


Fig. 1: (a) Microscopic view of rice roots, and spatial distributions of Si, Mo, Fe, Mn, and Ca; (b) μ -XANES spectra and (c) linear combination fits of the points of interest (POIs) indicated in (a). (d) Mechanism of rice uptake of soil molybdenum. [Reproduced from Ref. 1]

modification. With these discoveries, we aim to deepen our understanding of the interactions between plants and soil and to develop more effective soil management and remediation strategies.

Chemical Speciation and Uptake of Molybdenum by Rice

Molybdenum (Mo), a vital micronutrient for organisms, facilitates the metabolism of nitrogen, carbon, and sulfur and is crucial in enzyme catalysis. Although generally present in low concentrations in the Earth's crust, Mo levels can be elevated near industrial areas, potentially contaminating soil and accumulating in crops. This poses the health risks, including livestock poisoning and, in humans, conditions such as infertility and gout-like symptoms.

Rice, a major Mo dietary source for humans, often grows in submerged conditions that enhance Mo solubility and availability. This availability is further influenced by continuous flooding, which contrasts with the reduced Mo uptake seen in alternating wet–dry cycles. Key factors include soil redox processes driven by microbial activity and the dissolution of iron hydroxides, which affect the mobility of Mo compounds.

Shan-Li Wang (National Taiwan University) and his co-workers utilized X-ray absorption near edge structure (XANES) at **TPS 44A** and **TLS 16A1** and other microanalytical techniques to investigate how soil conditions affect Mo chemical forms and uptake in rice (**Fig. 1**). Their findings highlight the strong associations between Mo and Fe in the rice rhizosphere, which are facilitated by Fe plaques on root surfaces. This association promotes Mo dissolution/desorption, which is crucial for root absorption and subsequent transport to plant shoots, though only minimal amounts reach the grains.

The study reveals that Mo can accumulate significantly in rice without apparent toxicity, even in contaminated soils, raising concerns about Mo levels in consumed rice. Advanced studies in soil solution chemistry and Mo speciation provide the deeper insights into the complex dynamics of Mo availability and uptake, influencing the future research directions, particularly in Mo isotope fractionation. This study provides further understanding of the mechanisms affecting Mo's behavior in soil and its broader environmental and health impacts.

Physiology and Molecular Basis of Thallium Toxicity and Accumulation in *Arabidopsis thaliana*

Thallium (Tl) is a heavy metal with extensive applications across several industries, including chemical, pharmaceutical, optical, electronics, energy, and aerospace, as well as in superconducting materials and high-energy physics. Despite its limited annual production—approximately 10 tons globally—industrial processes inadvertently release an estimated 2,000 to 5,000 tons into the environment each year. This can significantly elevate Tl concentrations in contaminated soils, with well above the typical background level of less than 1 mg/kg found in most uncontaminated soils. Recognized for its extreme toxicity, Tl has been classified as a priority pollutant, which necessitates thorough research into its environmental impact, exposure routes, and toxicity.

Tl is particularly concerning because of its ability to be readily absorbed by plants, where it can disrupt potassium (K)-dependent biological processes and accumulate in the edible parts of plants, such as the roots and leaves. This accumulation poses the significant risks of food chain contamination. The model plant *Arabidopsis thaliana* (hereafter *Arabidopsis*), which is known for its fully sequenced genome, provides an excellent subject for mutagenesis studies aimed at understanding the physiological and molecular impacts of Tl. These studies are crucial for developing strategies to mitigate Tl toxicity and accumulation in plants.

Kuo-Chen Yeh (Academia Sinica) and his co-workers utilized the NSRRC **TPS 23A** X-ray nanoprobe beamline to perform X-ray fluorescence (XRF) analyses on *Arabidopsis* (**Fig. 2(a)**). These studies reveal that different concentrations of Tl not only inhibit growth and cause leaf chlorosis but also result in Tl accumulation in both roots and shoots, illustrating the plant's transport capabilities and the mechanisms of Tl toxicity.

Further investigations showed that Tl absorption occurs primarily through the roots, moving to the stems with increasing concentrations in the growth media. At peak levels, Tl concentrations reached 1,775 mg/kg in roots and 1,219 mg/kg in shoots. The plant demonstrated a significant transfer factor from roots to aerial parts, but this accumulation adversely affects the growth of both. The similarity in the distribution patterns of Tl and K within *Arabidopsis* suggests that they might share transport proteins or channels.

In addition to physiological studies, genetic and transcriptomic analyses aim to identify mutants with altered responses to TI and to explore the genes involved in its uptake and transport. Early transcriptional response studies have identified several TI-responsive genes associated with oxidative stress, antioxidant defense, K channel activity, and photosynthesis. These findings are integral to understanding TI's behavior in plants and the potential mechanisms of bioaccumulation (Fig. 2(b)), paving the way for future research and mitigation strategies.

Lemongrass and Sage Fertilized with Humic Acid Accumulate Toxins in Soil Treated with Heavy Oil Fly Ash

Saudi Arabia relies on over 40 million tons of heavy oil annually

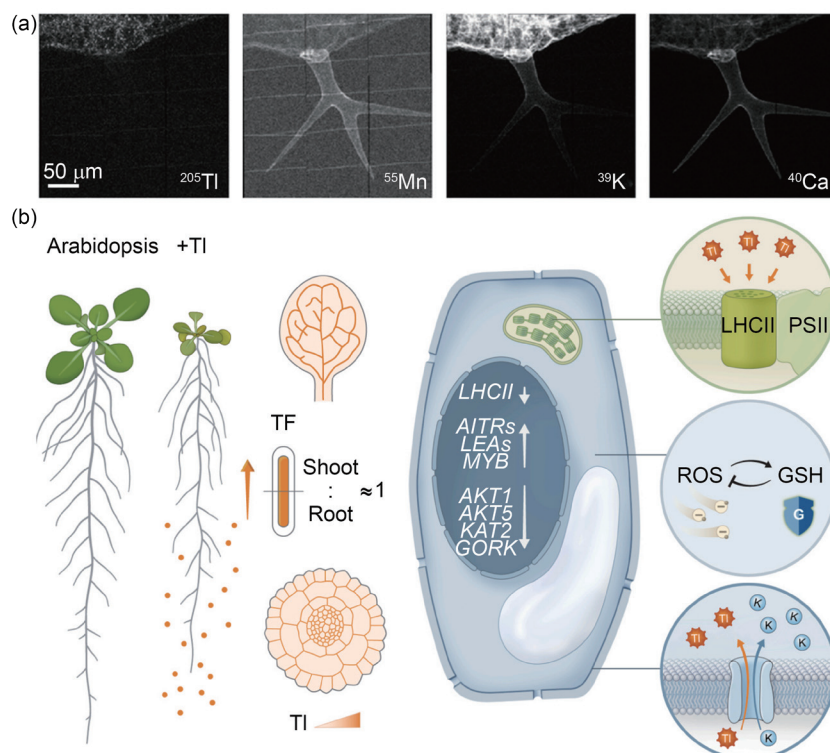


Fig. 2: (a) Synchrotron μ -XRF images of TI, Mn, K, and Ca distribution in TI-treated leaves. The elemental signal is shown in white. (b) A schematic representation of the uptake, toxicity, and accumulation of TI in Arabidopsis plants. [Reproduced from Ref. 2]

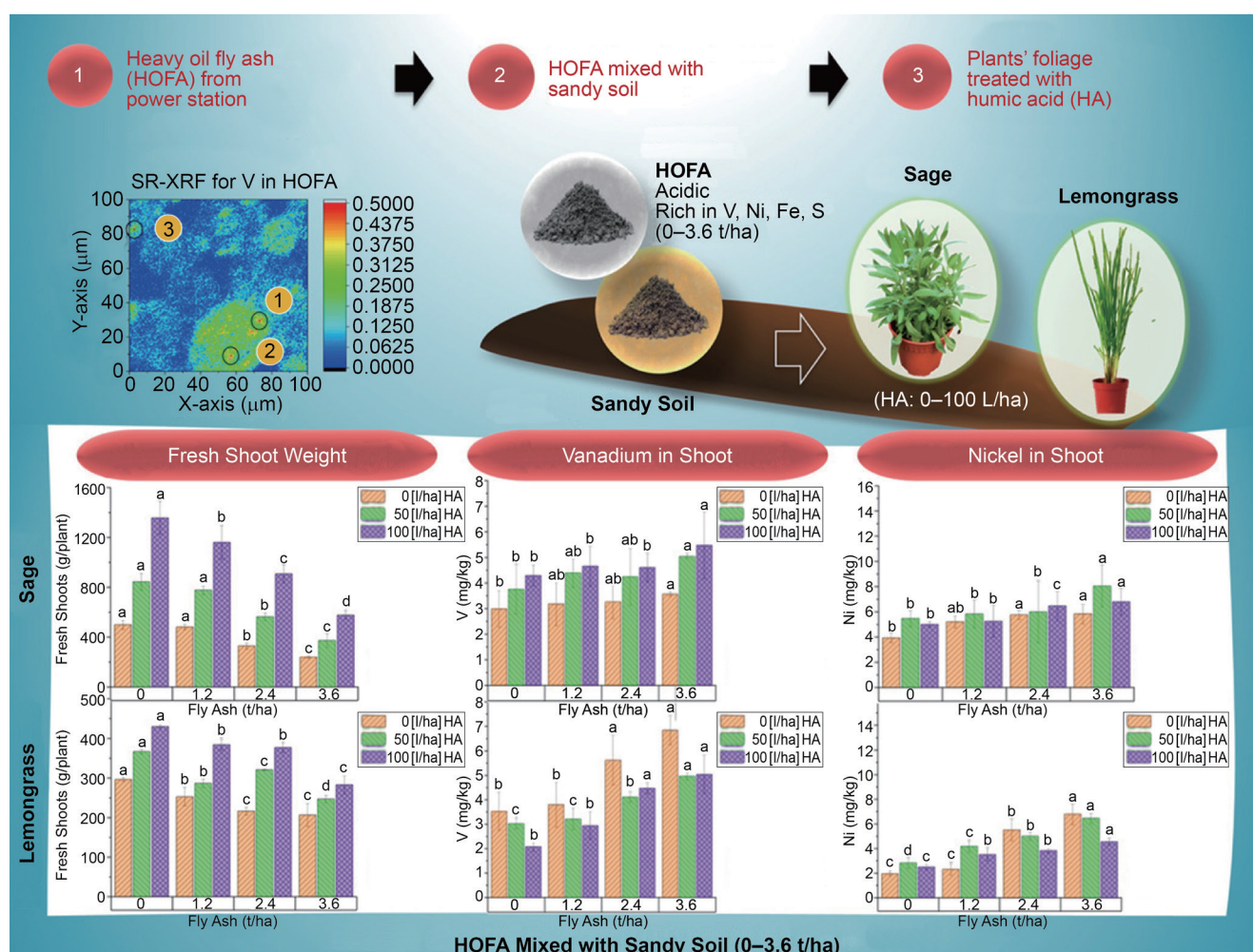


Fig. 3: Evaluating the effect of soil amendment with HOFA using sage and lemongrass as indicators. [Reproduced from Ref. 3]

for electricity and desalination, which contribute to 70% of its energy output, and it consumes about 320 million barrels of oil each year. This process results in the production of roughly 250,000 tons of heavy oil fly ash (HOFA) annually, with the individual facilities like the Rabigh power plant generating around 10,000 tons. Predominantly, HOFA is disposed of in landfills, a method that increases the risk of air, surface water, and groundwater pollution due to its content of unburned carbon and toxic inorganic compounds like vanadium and nickel.

Efforts to manage and mitigate HOFA's environmental risks are crucial. It has found uses in construction as a stabilizing material in cement, concrete blocks, asphalt mixtures, and in synthesizing glass ceramics. Additionally, HOFA serves economical roles in recovering valuable metals and as a water treatment adsorbent. However, its application in agriculture as a soil amendment is less explored because of the high levels of toxic elements it contains, which can harm soil quality and plant growth.

Samir Gamil Mohammad Al-Solaimani (King Abdulaziz University, Saudi Arabia) and his co-workers conducted research using the NSRRC **TPS 23A** beamline, including XRF imaging and XANES analysis. These techniques aided in assessing the impact of varying HOFA doses on sandy soils' nutrient and toxic element profiles and explored the effects of humic acid on plant growth and elemental uptake (**Fig. 3**).

Results indicated a significant presence of vanadium, nickel, iron, and sulfur in HOFA, with lower levels of chromium and manganese and minimal silicon. Notably, about 17.3% of vanadium exhibited high mobility, potentially increasing the environmental risks. Experiments demonstrated that low HOFA doses (1.2 to 3.6 tons per hectare) slightly affected soil pH, electrical conductivity, and element content, while higher doses adversely impacted plant growth. Treatment with humic acid significantly improved plant resilience to HOFA-induced stress.

Among the species tested, common sage showed the superior capability in accumulating elements compared to lemongrass, though both remained below critical toxicity thresholds. The findings suggest that controlled application of HOFA could enhance nutrient levels in low-fertility soils without severely altering their properties, particularly when combined with humic acid. Common sage also displayed potential for phytoremediation in HOFA-treated soils containing nickel and vanadium. These insights confirm the potential of HOFA as a resource for improving soil health in arid environments and offer new strategies for its disposal that are relevant both within Saudi Arabia and globally.

These studies underscore the critical role of plants in monitoring and improving soil health, providing the valuable data that can inform soil management strategies and mitigate pollution. The findings from the NSRRC in 2024 emphasize the complex dynamics of substance accumulation in plants and offer new insights into effective environmental management practices. (Reported by Chun-Chieh Wang)

*This report features the work of Shan-Li Wang and his collaborators published in Sci. Total Environ. **949**, 175141 (2024); the work of Kuo-Chen Yeh and his collaborators published in Ecotox. Environ. Safe. **276**, 116290 (2024); and the work of Samir Gamil Al-Solaimani and his collaborators published in Sci. Total Environ. **945**, 173998 (2024).*

TPS 23A X-ray Nanoprobe

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

TLS 16A1 Tender X-ray Absorption, Diffraction

- Quick-scanning XAS, XRF, XANES
- Environmental and Earth Sciences, Physics, Materials Science, Chemistry

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Sustainable Remediation Materials for Toxic-Metal Removal: Insights into Arsenic and Chromium Detoxification Mechanisms

Heavy metal remediation is achieved using an environmentally sustainable approach that involves thiol-functionalized black carbon and thermoacidophilic Cyanidiales.

The remediation of toxic metals, such as chromium (Cr) and arsenic (As), is vital for public health and ecological balance. The 2024 studies at the NSRRC explores the advanced materials and biological pathways for hexavalent Cr(VI) and arsenite [As(III)] removal. Utilizing synchrotron-based techniques, the research highlights thiol-functionalized black carbon for Cr(VI) remediation and thermoacidophilic Cyanidiales for As(III) detoxification, offering effective and sustainable solutions through materials science and bioremediation advancements.

Thiol-Functionalized Black Carbon as Effective and Economical Materials for Cr(VI) Removal:

Hazardous Cr(VI) continues to raise critical environmental and public health concerns, necessitating the development of effective remediation methods. Yu-Ting Liu (National Chung Hsing University) and her collaborators recently discovered the removal mechanisms of Cr(VI) by modifying black carbon (BC), which is synthesized from rice straw residue and contains thiol groups. This is the first study that alters BC with thiol groups to target Cr(VI) removal. Here, the designated samples were evaluated: i) BC and ii) thiol-functionalized black carbon (S-BC) with BC/thioglycolic acid ratios (g mL^{-1}) of 1:20 (S-BC20), 1:30 (S-BC30), and 1:40 (S-BC40).

The research team conducted X-ray absorption spectroscopy (XAS) at TLS 17C1 and TPS 44A to determine the related Cr speciation on solid samples.

The results revealed that Cr species on solid samples primarily transformed from Cr(VI) to Cr(III), as shown in Fig. 1. At pH 3.5, over 86.2% of Cr(VI) was reduced to Cr(III), with S-BC retaining only 4.1–6.8% Cr(VI) compared to 13.8% for BC. At pH 5.5, all Cr(VI) was converted to Cr(III) on both materials. Finally, at pH 7.5, S-BC retained no Cr(VI), while BC retained 13.2% Cr(VI).

Sorption isotherms confirmed that S-BC40 demonstrated high Cr(VI) sorption capacities—201.2, 145.8, and 106.6 mg g^{-1} at pH 3.5, 5.5, and 7.5—exceeding BC sorption capacities by 2.0–2.3 times. Notably, S-BC40 converted all sorbed Cr into Cr(III) at $\text{pH} \geq 5.5$, forming Cr(OH)_3 and organic Cr(III) complexes. These findings highlight thiol functionalization as a promising strategy for effective Cr(VI) remediation and waste reutilization.

Accumulation and Bio-Oxidation of Arsenite Mediated by Thermoacidophilic Cyanidiales:

As contamination from geogenic and anthropogenic sources poses a critical

environmental and public health threat due to the high toxicity and mobility of As(III). Liu and her team unveiled the molecular mechanisms of As(III) removal by thermoacidophilic microalga Cyanidiales. This red alga, thriving in acidic, metal-rich environments, exhibits unique detoxification characteristics ideal for As remediation. This pioneering study evaluated As(III) removal by *Cyanidium caldarium* (Cc) and *Galdieria partita* (Gp) across a pH range of 2.0–7.0.

The team employed transmission X-ray microscopy (TXM) at TLS 01B1 to reveal the related As distribution on Cyanidiales, as shown in Fig. 2 (see next page). 3D tomography revealed that As present on Cc was distributed both near their surface and internally, particularly at pH 5.0, which suggests intracellular tolerance mechanisms. In contrast, Gp relied on surface-level As immobilization. These findings indicate that Cc is more resilient to As stress, particularly at $\text{pH} \leq 5.0$ due to its superior intracellular detoxification capacity.

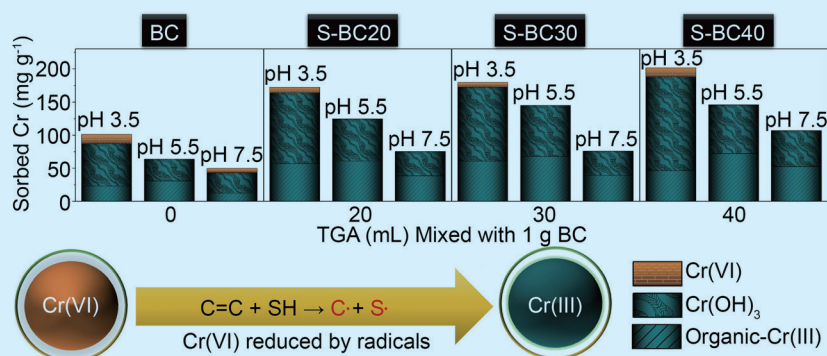


Fig. 1: Proposed removal mechanisms for Cr(VI) by thiol-functionalized black carbon. [Reproduced from Ref. 1]

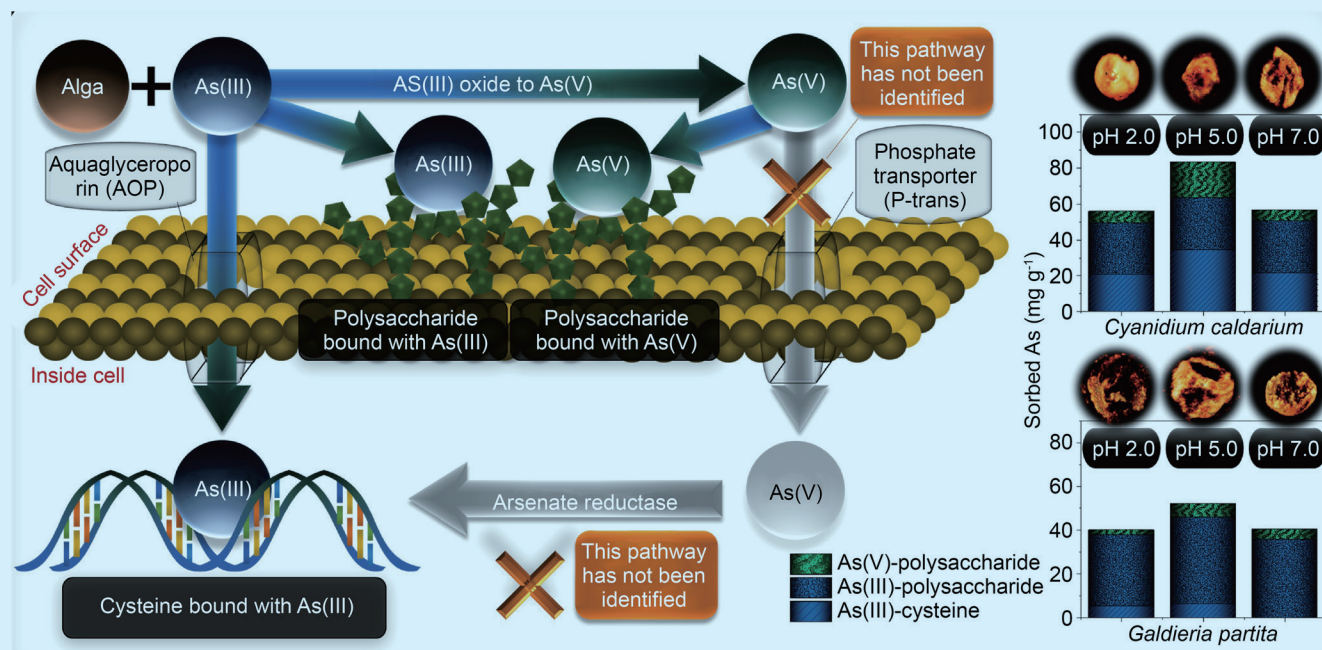


Fig. 2: Proposed mechanisms for As(III) removal by Cyanidiales. [Reproduced from Ref. 2]

The team conducted XAS analysis at **TLS 17C1** and **TPS 44A** to determine the related As speciation on Cyanidiales. As species were identified as arsenate [As(V)]-polysaccharide, As(III)-polysaccharide, and As(III)-cysteine, as illustrated in **Fig. 2**. At pH 5.0, Cc showed the highest sorption capacity that was dominated by As(III)-cysteine, while Gp retained mainly As(III)-polysaccharide. At pH 2.0 and 7.0, Cc exhibited balanced As(III)-polysaccharide and As(III)-cysteine with minimal As(V). These results highlight Cyanidiales' reliance on surface complexation and intracellular sequestration, with Cc exhibiting superior detoxification capacity.

To study As interactions in Cyanidiales, the team conducted synchrotron-based Fourier transform infrared spectroscopy at **TLS 14A1** to examine the changes in functional groups and protein secondary structures under As(III) exposure. The results show that α -helix/ β -strand ratios correlated with sorbed As levels. However, Gp exhibited a negative correlation between α -helix/ β -strand ratios and sorbed As levels, indicating structural fragility. In contrast, Cc displayed positive correlations at pH $\leq$ 5.0, reflecting strong protein

adaptation. Notably, Cc exhibited fewer unordered structures, suggesting intracellular protein proliferation as a key response to As toxicity, further highlighting its superior resilience.

Cc demonstrated superior sorption capacity, achieving 83.2 mg g⁻¹ at pH 5.0. Cc outperformed Gp across all tested conditions, driven by mechanisms such as As(III) oxidation, surface complexation with polysaccharides, and intracellular formation of As(III)-cysteine complexes, as shown in **Fig. 2**. These findings highlight Cyanidiales' ability to transform and immobilize As, paving the way for innovative and effective detoxification strategies.

In summary, this report showcases two sustainable approaches for heavy-metal remediation: i) thiol-functionalized BC for Cr(VI) removal and ii) thermoacidophilic Cyanidiales for As(III) removal. Leveraging NSRRC's synchrotron-based techniques, both methods demonstrated high levels of toxic-metal removal, offering promising solutions to environmental contamination. (Reported by Yen-Lin Cho, National Sun Yat-sen University, and Kamonchanok Huangmee, National Chung Hsing University)

This report features the work of Yu-Ting Liu and her collaborators published in *J. Environ. Manage.* **360**, 121074 (2024) and *Bioresource Technol.* **406**, 130912 (2024).

TPS 44A Quick-scanning X-ray Absorption Spectroscopy
TLS 01B1 X-ray Microscopy
TLS 14A1 IR Microscopy
TLS 17C1 EXAFS

- TXM, FT-IR, EXAFS, XAS
- Environmental and Earth Sciences, Biological Science, Chemistry

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Citric Acid Enhances Phosphate Release from Humic Acid-Iron Hydroxide Coprecipitates

The presence of citric acids could mildly obstruct the structural development of the Fe domain in humic acid-iron hydroxide coprecipitates, as shown by X-ray absorption spectroscopy techniques.

Recent research led by Yu-Min Tzou (National Chung Hsing University) and his team has demonstrated the sorption of citric acid onto two humic acid-iron hydroxide coprecipitates (HAFHCPs), as well as the mutual effects of citric acid and phosphate (P) sorption on these HAFHCPs at different C/Fe ratios. Their findings show that as the C/Fe ratio increases to 0.5, the maximum sorption capacity (MSC) of citric acid on HAFHCP-Y50 and HAFHCP-A50 decreases by 9.1–16.7% (Fig. 1). In addition, the citric acid sorption capacity of HAFHCP containing humic acid was extracted from volcanic soil of Yangmingshan (HAFHCP-YHA) is approximately 92% of that of HAFHCP containing the Sigma-Aldrich humic acid (HAFHCP-AHA). This trend is likely due to competition for sorption sites on iron hydroxide (FH) surfaces between YHA and citric acid, which is driven in part by the electrostatic repulsion between negatively charged HA and citric acid at pH 5.5.

Using X-ray absorption spectroscopy (XAS) at TLS 16A1, Tzou and coworkers observed through Fe K-edge X-ray absorption fine structure (EXAFS) analysis that the k^3 -weighted $\chi(k)$ data for iron hydroxide (FH) and FH with sorbed citric acid were largely similar. However, slight differences emerged at $k \approx 5.0, 7.5$, and $8.5 \text{ \AA}^{-1}$ between free HAFHCP-Y50/A50 and HAFHCP-Y50/A50 with sorbed citric acid. These findings suggest that citric acid impedes the structural development of Fe domains in HAFHCP, increasing dissolved Fe content and reducing the sorption capacity for citric acid (Fig. 1). A previous study by Tzou and his colleagues showed that HAFHCP-Y50 likely contains a relatively homogeneous distribution of C and Fe domains. In contrast, HAFHCP-A50 appears to have a ferrihydrite core with humic acid growing on its surface and possesses fewer polar functional groups. This arrangement results in greater Fe dissolution when citric acid is sorbed.

Understanding how HAFHCPs influence P availability is critical, particularly when organic acids and P coexist. To explore this, three experimental systems were developed to

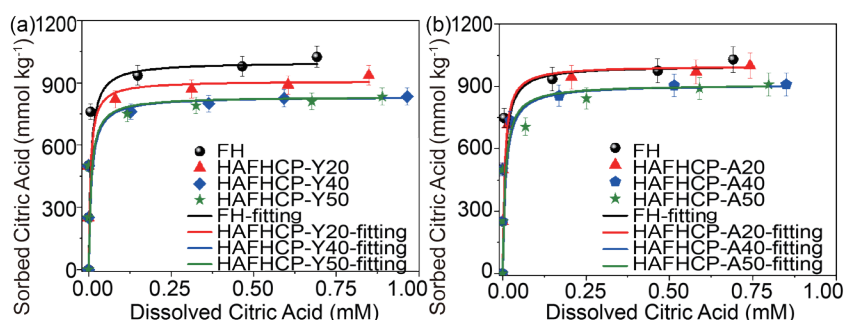


Fig. 1: Citric acid sorption isotherms for iron hydroxide (FH) and HAFHCP containing (a) YHA and (b) AHA with initial C/Fe ratios of 0.2, 0.4, and 0.5 (HAFHCP-Y20, Y40, Y50, A20, A40, and A50) fitted with the Langmuir isotherm model (solid lines). [Reproduced from Ref. 1]

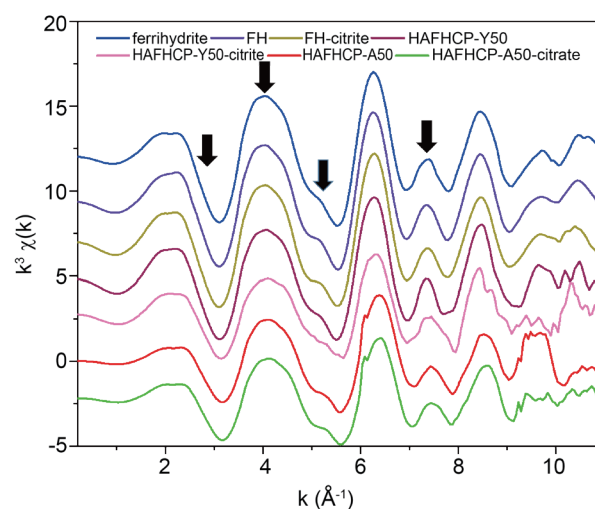


Fig. 2: Fe K-edge EXAFS spectra after sorption of citric acid on FH, HAFHCP-Y50, and HAFHCP-A50. Initial amounts of added citric acid were 0 and 2500 mmol kg⁻¹. [Reproduced from Ref. 1]

assess the cross-competitive sorption of P and citric acid on FH and HAFHCPs. Across all three systems, P sorption onto FH, HAFHCP-YHA, and HAFHCP-AHA followed the same order: P-C > S > C-P (Fig. 3, see next page). In the P-C, S, and C-P systems, P sorption on FH, HAFHCP-Y50, and HAFHCP-A50 differed significantly, having a decreasing trend of 1669–1780, 1245–1365, and 1018–1132 mmol kg⁻¹, respectively (Fig. 3). Notably, in the C-P system, pre-sorbed citric acid reduced P sorption by 50% compared with the MSC of P on FH (2250 mmol kg⁻¹) likely because of citric acid acting as a diffusion barrier for P. In

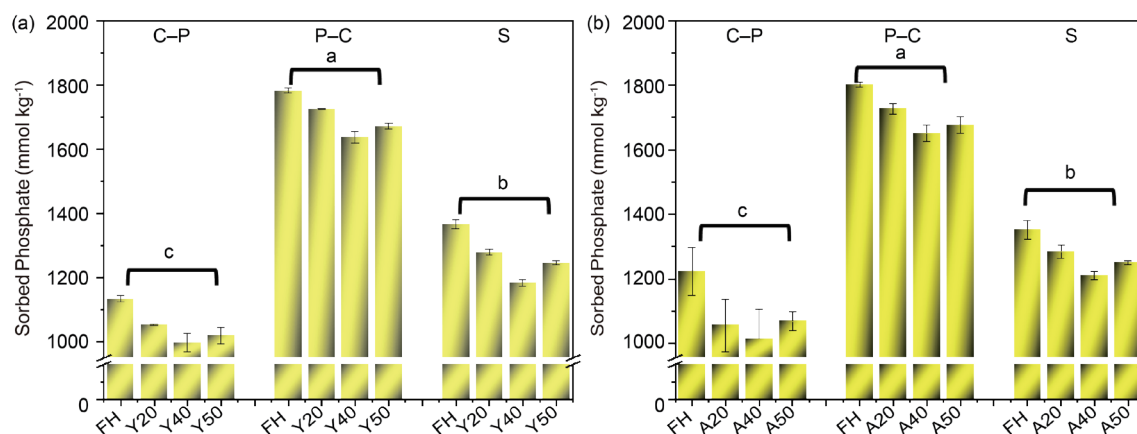


Fig. 3: The P sorption capacity for FH and HAFHCP containing (a) YHA and (b) AHA with initial C/Fe ratios of 0.2, 0.4, and 0.5 (HAFHCP-Y20, Y40, Y50, A20, A40, and A50) on cross-competitive sorption systems of C–P, P–C, and S. The order of addition for the different sorption systems are as follows: (1) For the C–P system, 1000 mmol kg^{−1} of citric acid was first added into FH/HAFHCP suspensions for 42 h, and then 2250 mmol kg^{−1} of P was added and allowed to react for another 42 h. (2) For the P–C system, 2250 mmol kg^{−1} of P was added and allowed to react with FH/HAFHCP for 42 h prior to the addition of 1000 mmol kg^{−1} of citric acid. The mixtures were then allowed to react for another 42 h. (3) In the S system, both P and citric acid were added simultaneously and allowed to react for 42 h. Statistical analysis was performed using one-way analysis of variance followed by Fisher's least-significant-difference (LSD) multiple-comparisons test at a significance level of $P < 0.05$. Significant differences between groups are denoted by different letters (a, b, c), as determined by Fisher's protected LSD test at a significance level of $P = 0.05$. [Reproduced from Ref. 1]

contrast, in the P–C system (where P was pre-sorbed), the presence of citric acid reduced P sorption by approximately 20%. Such effects may result from dissolved Fe functioning as a bridging agent between citric acid and P. Overall, these results indicate that citric acid strongly enhances P release in the C–P system.

In summary, this study emphasizes the role of HAFHCPs in the cross-competitive sorption of citric acid and P. The findings show that factors such as C/Fe ratios, the organic composition of humic acids, and the presence of citric acids (as observed through XAS) are key to understanding P availability. Consequently, the implementation of soil management strategies that foster favorable conditions for P availability is crucial for the sustainable utilization of P resources. (Reported by Kai-Yue Chen, National Chiayi University)

*This report features the work of Yu-Min Tzou and his collaborators published in Environ. Res. **240**, 117517 (2024).*

TLS 16A1 Tender X-ray Absorption, Diffraction

- EXAFS
- Environmental and Earth Sciences, Chemistry

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