



# Contamination remediation and risk assessment of four typical long-residual herbicides: A timely review

Jiawen Li<sup>a</sup>, Haiyan Huang<sup>b</sup>, Yong Yang<sup>a</sup>, Caixia Wang<sup>a</sup>, Qingming Zhang<sup>a,\*</sup>

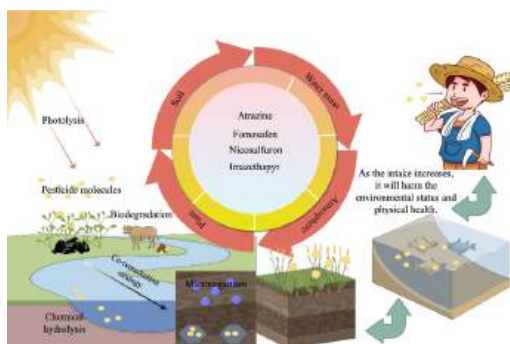
<sup>a</sup> Shandong Engineering Research Center for Environment-Friendly Agricultural Pest Management, College of Plant Health and Medicine, Qingdao Agricultural University, Qingdao 266109, China

<sup>b</sup> Department of Food Technology, Weifang Vocational College of Food Science and Technology, Anqiu 262100, China

## HIGHLIGHTS

- Contamination remediation and risk assessment of four long-residual herbicides were reviewed.
- The advantages and disadvantages of various remediation techniques were stated.
- The comprehensive application of remediation techniques is advocated to reduce pesticide residues.
- Effective risk assessment can help the selection of appropriate remediation methods.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

**Keywords:**  
Herbicides  
Long residue  
Pollution control  
Risk assessment

## ABSTRACT

In agricultural weed management, the use of long-residual herbicides provides benefits such as reduced application frequency and labor savings. However, as with any approach, there are potential limitations. Long-residual herbicides may have adverse effects on subsequent sensitive crops, soil health, and non-target beneficial organisms. Currently, numerous studies concentrate on contamination remediation technologies and risk assessment for effectively managing the environmental impacts of long-residual herbicides. This review highlights recent advancements in contamination remediation technologies and risk assessment for four representative long-residual herbicides (atrazine, nicosulfuron, fomesafen, and imazethapyr). Remediation techniques currently employed for long-residual herbicides, including bioremediation, physicochemical remediation, and hybrid remediation approaches, were systematically compared. Furthermore, the risk assessment framework integrates ecological and health dimensions to ensure a comprehensive evaluation. Additionally, future research priorities have been proposed. The overarching aim is to provide scientific insights and strategic recommendations for effectively controlling and mitigating contamination caused by long-residual herbicides in agricultural systems.

\* Corresponding author.

E-mail address: [qmzhang@qau.edu.cn](mailto:qmzhang@qau.edu.cn) (Q. Zhang).

<https://doi.org/10.1016/j.scitotenv.2025.180169>

Received 27 April 2025; Received in revised form 20 July 2025; Accepted 27 July 2025

0048-9697/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

1. Introduction

Persistent herbicides constitute a class of chemicals extensively employed in agricultural production for controlling a wide array of weeds, including grass and broadleaf species. Their effectiveness is attributed to their persistent nature and broad-spectrum herbicidal properties. These herbicides achieve precise and efficient weed control by inhibiting critical physiological processes in target weeds, such as the electron transport chain in photosynthesis, specific enzyme activities, branched-chain amino acid synthesis, or pathways related to cell division, thereby enhancing crop yield and quality.

Atrazine, nicosulfuron, fomesafen, and imazethapyr are four representative long-residual herbicides that are globally utilized, particularly in the cultivation of major food and cash crops like maize, beans, peanuts, and wheat. These four herbicides were selected as representative long-residual herbicides based on their widespread use, chemical diversity, and environmental persistence profiles. They represent different chemical classes—triazines, sulfonylureas, diphenyl ethers, and imidazolinones, respectively—enabling a broader analysis of structural effects on environmental behavior. Their high detection frequencies in soil, surface water, and agricultural products have been widely reported in North America, Europe, and East Asia. Moreover, these compounds have been listed among the priority contaminants by agencies such as the EPA, EFSA, and China's Ministry of Ecology and Environment (MEE) due to their ecotoxicity, potential for carryover, and endocrine-disrupting effects. Their persistence spans a broad range (DT<sub>50</sub>: 30–300 days), offering a spectrum for comparing remediation strategies and risk assessment models.

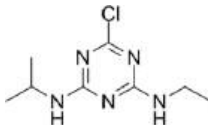
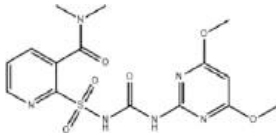
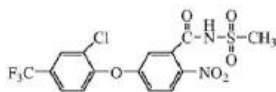
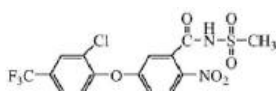
Long-residual herbicides can enter water bodies via soil leaching or accumulate through the food chain, exerting toxic effects on soil microbial communities, non-target plants, and aquatic organisms. For example, atrazine has endocrine-disrupting properties, posing a potential threat to both aquatic organisms and human health. Similarly, nicosulfuron has been shown to exhibit significant phytotoxic effects on subsequent crops, such as sorghum and oilseed rape. Moreover, long-term use of these herbicides could suppress soil enzyme activities and alter soil microbial community structures, thereby exacerbating their detrimental impacts on ecosystem services. Significant advancements have been achieved in the development of pollution remediation technologies aimed at addressing long-residual herbicide contamination. These technologies primarily include bioremediation, physical methods, chemical approaches, and integrated strategies. Bioremediation has

garnered substantial attention due to its environmentally friendly and highly efficient nature. Studies have shown that specific degrading bacteria, such as *Paenarthrobacter* sp. and *Chryseobacterium* sp., exhibit significant efficacy in breaking down herbicides like atrazine and nicosulfuron (Jiang et al., 2021). Furthermore, physicochemical methods and hybrid techniques have demonstrated considerable potential for enhancing restoration efficiency. However, challenges remain regarding the stability, cost-effectiveness, and long-term ecological impacts of these technologies in practical applications.

The physicochemical properties, degradation pathways and transport patterns of the four herbicides influenced their complex behavior in soil and water. For instance, the primary degradation pathways of atrazine in soil are photolysis and microbial degradation, and the degradation intermediates frequently exhibit heightened toxicity. The degradation of nicosulfuron is considerably influenced by soil pH and microbial communities, while imazethapyr and fomesafen demonstrate prolonged environmental persistence owing to their elevated stability (Poonia et al., 2022). To address the above problems, the establishment of a risk assessment framework, including toxicological assessment and environmental exposure modeling, is the key to optimize pollution management and reduce environmental risks.

This review focuses on four representative long-residual herbicides—atrazine, nicosulfuron, fomesafen, and imazethapyr (Detailed information is provided in Table 1)—and provides a critical evaluation of their environmental remediation strategies and risk assessment frameworks. Emphasis is placed on the multi-media transport and transformation behavior of these compounds, their persistence in agroecosystems, and the challenges posed by their long-term residues. To align with the aims of this review, we structure the discussion around four interrelated questions: (1) How do the physicochemical properties of long-residual herbicides affect their environmental fate and persistence across soil and water systems? (2) What are the strengths, limitations, and cost-performance tradeoffs of current remediation strategies—including biotic, abiotic, and co-remediation approaches—in both controlled and field conditions? (3) What major challenges hinder the field-scale implementation of these technologies, particularly under complex exposure scenarios involving co-contaminants and site-specific variability? (4) How can cross-compound evidence and critical appraisal support the development of standardized, transferable remediation frameworks and future research priorities? By answering these questions, this review aims to inform the design of more effective, scalable solutions for herbicide detoxification and to support the

Table 1  
Basic information of four long residual-herbicides.

Herbicide	Formula	Molecular weight (g/mol)	Water solubility (mg/L)	Soil adsorption coefficient	Chemical structure
Atrazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	215.68	33	100–300	
Nicosulfuron	C <sub>15</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub> S	410.41	9.7	14–40	
Fomesafen	C <sub>15</sub> H <sub>10</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>6</sub> S	438.76	1.79	200–500	
Imazethapyr	C <sub>15</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>	289.33	140	100–200	

scientific and sustainable use of herbicides in modern agriculture.

## 2. Contamination remediation and risk assessment of atrazine

### 2.1. Physicochemical properties and action mechanism

Atrazine is a triazine selective herbicide, but was originally introduced as a broad-spectrum herbicide by Ciba-Geigy in Switzerland in 1958. It is primarily utilized for controlling broadleaf weeds, annual grasses, and certain gramineous weeds in crops such as maize, sorghum, oilseed rape, and sugarcane. The chemical formula of atrazine is  $C_8H_{14}ClN_5$ , with a molecular weight of 215.68 g/mol. It exists as a white crystalline solid with a melting point of 175–177 °C and exhibits weakly alkaline properties ( $pK_a = 1.7$ ). Atrazine demonstrates a solubility of 33 mg/L in water at 25 °C, an octanol-water partition coefficient ( $\log K_{ow}$ ) ranging from 2.5 to 2.8, and a soil adsorption coefficient ( $K_{oc}$ ) between 100 and 300. These physicochemical characteristics influence its environmental behavior: its moderate polarity facilitates transport through the soil profile via runoff, while its relatively low  $K_{oc}$  values, particularly in soils containing less than 2 % organic matter, significantly elevate the risk of groundwater contamination.

Regarding its mechanism of action, atrazine has been demonstrated to inhibit the plastoquinone cycle within the photosynthetic electron

transport chain. This inhibition occurs via the competitive binding of atrazine to the QB site on the D1 protein of photosystem II (PSII), which induces the production of reactive oxygen species (ROS) and subsequently leads to the structural disintegration of chloroplasts (Tuncel et al., 2024). The selectivity of atrazine is attributed to the rapid glutathione-S-transferase (GST)-mediated detoxification process in crops such as maize, a metabolic pathway that is absent in sensitive weeds. Notably, prolonged use of this herbicide may result in the emergence of weed populations with reduced susceptibility. In recent years, mutations in the *psbA* gene, such as Ser264Gly, have been identified in certain weed populations, conferring target-site resistance.

### 2.2. Environmental behavior and risk assessment of atrazine

#### 2.2.1. Environmental distribution and transport

A transport model based on Monte Carlo simulations revealed that atrazine can leach to depths of 1.5–3.0 m/year in sandy soils in regions with annual rainfall exceeding 800 mm, whereas its movement is restricted to approximately 0.5 m in soils containing more than 30 % clay content. The half-life of atrazine in surface water has been shown to vary significantly with seasons, with the photolytic half-life ranging from 10 to 15 days during summer (light intensity: 200  $\mu\text{mol}/\text{m}^2/\text{s}$ ) to 60–90 days during winter. Recent studies have highlighted atmospheric

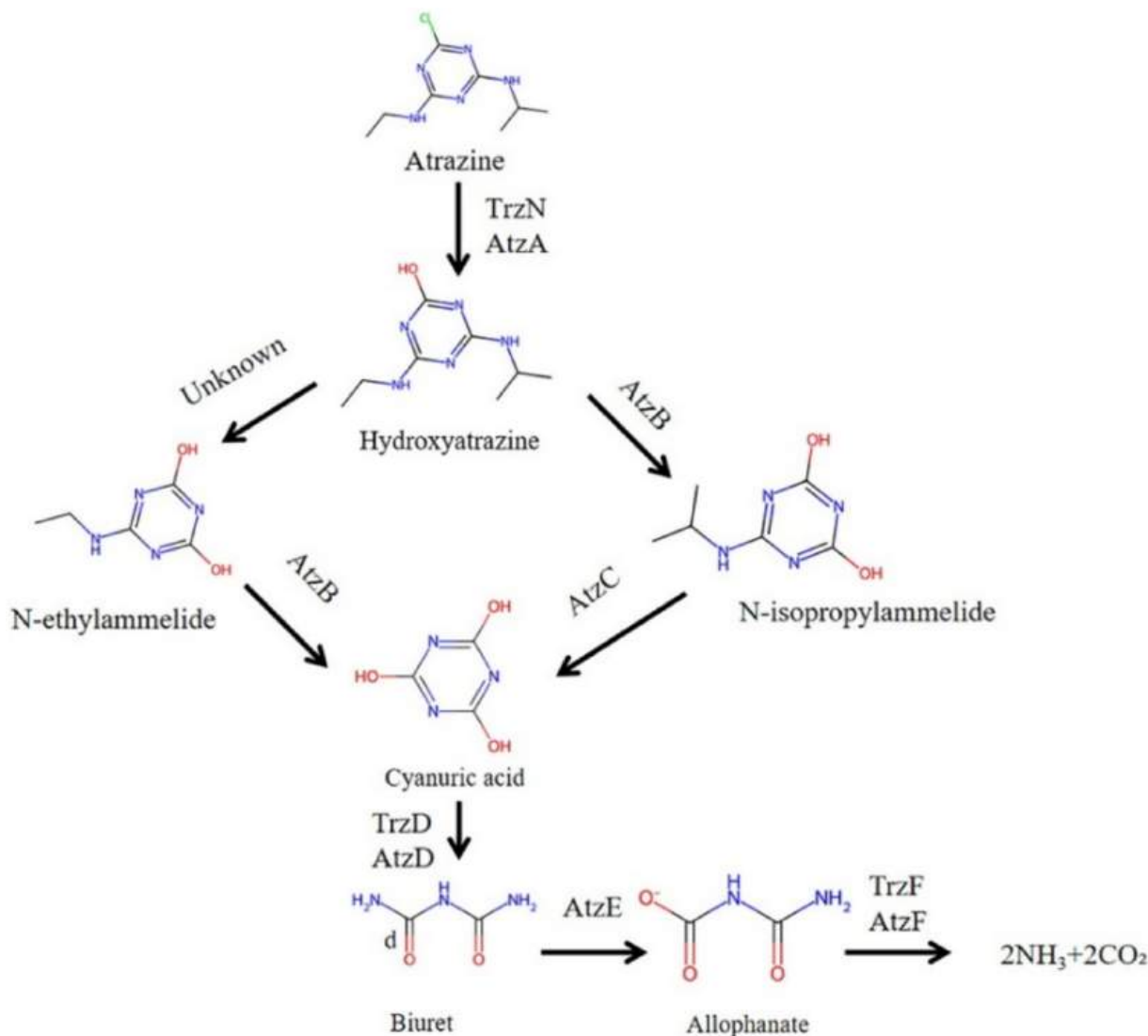


Fig. 1. Mineralization pathways for hydrolysis of atrazine (Udiković-Kolić et al., 2012).

wet deposition as a secondary transport pathway for atrazine, with concentrations of 0.8–1.2 µg/L detected in rainfall samples collected from intensive agricultural area (Taverna et al., 2018).

2.2.2. Degradation pathways and metabolites

The primary degradation pathways of atrazine involve photolysis, chemical degradation, and microbial degradation, with microbial degradation being the predominant elimination route. Specifically, the *atzABC* gene cluster in strains such as *Pseudomonas* sp. catalyzes a three-step dechlorination process: conversion of atrazine to hydroxyatrazine by *AtzA* (chlorohydrolase), formation of N-isopropylcyanuric acid by *AtzB* (amide hydrolase), and final mineralization of N-isopropylcyanuric acid into CO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> by *AtzC* (cyanuric acid amide hydrolase) (Sagarkar et al., 2014). The complete degradation pathway is illustrated in Fig. 1. However, recent metagenomic studies have shown that approximately 70 % of field-degrading bacteria harbor incomplete degradation gene clusters, resulting in the accumulation of intermediates such as deethylatrazine (DIA) and deisopropylatrazine (DDA). These intermediates exhibit enhanced ecotoxicological effects, with DIA and DDA showing 1.8-fold and 2.3-fold higher toxicity, respectively, compared to their parent compound (based on the *Danio rerio* LC<sub>50</sub> test) (Li et al., 2024). Of particular concern is the ability of these metabolites to form stable complexes with humic acids via π-π interactions, thereby extending their retention in sediments to 180–240 days.

2.2.3. Toxicology and risk assessment

Atrazine has been shown to induce a variety of biological effects, including but not limited to endocrine-disrupting impacts on aquatic organisms. For example: 1) Studies have demonstrated that the African clawed toad (*Xenopus laevis*) exhibited a 300 % increase in aromatase activity at an atrazine concentration of 0.1 µg/L, leading to an imbalance in sex ratios (Solomon et al., 2013). 2) Atrazine exhibits inhibitory effects on soil enzymes, with urease and dehydrogenase activities decreasing by 42 % and 57 %, respectively, after five years of continuous application (*p* < 0.01). Additionally, the microbial functional diversity index (Shannon index) decreased by 0.8–1.2 (Wang et al., 2024a). 3) Epidemiological studies indicate that long-term exposure (>0.5 µg/L) to atrazine increases the risk of breast cancer by 1.3-fold (95 % CI: 1.1–1.6), potentially due to abnormal activation of the ERα receptor (Meng et al., 2022).

In addition to partial toxicology discussed above, atrazine exerts broader ecological effects on non-target organisms and ecosystem functions. In aquatic ecosystems, atrazine acts as a potent photosystem II inhibitor in algae, leading to impaired primary productivity and potentially triggering trophic-level disturbances such as reduced zooplankton populations and hypoxic zones in eutrophic waters (DeLorenzo et al., 2001). In soil environments, atrazine exposure may shift microbial community structure, decreasing the relative abundance of nitrogen-cycling taxa such as *Nitrosospora* and *Bradyrhizobium*, and altering enzyme activities linked to organic matter turnover. These findings underscore the need for ecological risk assessments that go beyond organism-level toxicology and include functional endpoints such as photosynthesis, microbial nitrogen cycling, and biodiversity resilience.

Risk quotient (RQ) assessments based on the species sensitivity distribution (SSD) model revealed that RQ values for atrazine in surface water in North China's farmland regions range from 2.3 to 5.8, significantly exceeding the acceptable threshold (RQ > 1). Although atrazine has been banned in the European Union since 2004 (2004/248/EC), and the EPA maintains a water quality benchmark of 3 µg/L following reassessment in 2020, mitigation measures such as buffer zones (>30 m) and reduced application frequency (once per season) are still required (Gagneten et al., 2023). In China, the current Environmental Quality Standard for Surface Water (GB 3838-2002) sets a limit of 3 µg/L; however, specific standards for groundwater have yet to be established,

which may result in an underestimation of risks associated with exposure via drinking water pathways.

2.3. Advances in pollution abatement technology for atrazine

2.3.1. Bioremediation

The advancement of bioremediation technologies has emerged as a critical strategy for mitigating atrazine contamination, providing significant benefits in terms of environmental sustainability and ecological compatibility. A comprehensive overview of various atrazine-degrading bacterial species, along with their optimal conditions and degradation rates, is presented in Table 2. In microbial enhancement, Sagarkar et al. (2016) isolated an S-triazine-degrading *Arthrobacter* sp. AK-YN10 from a sugarcane field with long-term atrazine use. In liquid culture containing 1000 mg/L atrazine, strain AK-YN10 achieved a rapid and nearly complete degradation—99 % removal within just 30 h—demonstrating exceptional catabolic efficiency. Similarly, in microbial enhancement, Zhu et al. (2020) isolated *Bacillus safensis* ATR-Z5 and characterized its atrazine biodegradation capabilities. Under optimized lab conditions, ATR-Z5 utilized atrazine as the sole nitrogen source and achieved over 80 % degradation within 7 days. Liu et al. (2023) isolated *Pseudomonas rhizogenes* AT13, which exhibited exceptional degradation capacity, achieving 99.94 % degradation within 72 h at 30 °C. Transcriptomic analysis revealed a 5.7- to 8.3-fold upregulation of *atzABC* genes during the degradation process. Field applications demonstrated a 23 % increase in sesame germination rates and a 17 % enhancement in biomass accumulation. Several of the above bacterial strains have been identified as effective atrazine degraders, these include species from the genera *Pseudomonas*, *Paenarthrobacter*, *Arthrobacter*, *Bacillus*, and *Agrobacterium*, with various metabolic pathways such as hydrolytic dechlorination and ring cleavage. In addition to strains like *Arthrobacter* HB-5, such as *Agrobacterium rhizogenes* J14a, *Arthrobacter* AK-YN10, TES6, and ZXY-2 have demonstrated strong degradation capabilities under diverse soil conditions.

While native microbial consortia demonstrate robust herbicide degradation, emerging biotechnological approaches leverage genetically modified strains (GM) or engineered enzymes to overcome

**Table 2**  
Bacterial species degrading atrazine, degradation conditions and degradation rate.

Bacterial species	Degradation condition	Degradation rate (%)	Bibliography
<i>Rhodococcus</i> MBP1	30 °C, pH 7.5, 3 d	>90	(Fazlurrahman et al., 2009)
<i>Acinetobacter lwoffii</i> DNS32	30 °C, pH 7.0, 2 d	94	(Tao et al., 2019)
<i>Agrobacterium rhizogenes</i> AT13	30 °C, pH 8.57, 14 h	>99.7	(Liu et al., 2023)
<i>Agrobacterium rhizogenes</i> J14a	30 °C, pH 7.0, 3 d	94	(Struthers et al., 1998)
<i>Arthrobacter</i> sp. strain HB-5	40 °C, pH 7.0, 2 d	100	(Wang et al., 2011)
<i>Arthrobacter</i> sp. strain TES6	28 °C, pH 7.0, 4 d	>95	(El Sebaï et al., 2011)
<i>Arthrobacter</i> sp. strain AK-YN10	30 °C, pH 7.5, 30 h	>99	(Sagarkar et al., 2016)
<i>Arthrobacter</i> sp. strain ZXY-2	34 °C, pH 9.0, 12 h	>91.3	(Zhao et al., 2018)
<i>Nocardioidees</i> EAA3	28 °C, pH 7.0, 7 d	80–90	(Omotayo et al., 2013)
<i>Pseudomonas</i> AT13	30 °C, pH 7.0, 3 d	99.94	(Ye et al., 2016)
<i>Exiguobacterium</i> sp. BTAH1	35 °C, pH 7.5, 3 d	70–85	(Hu et al., 2005)
<i>Bacillus safensis</i> ATRZ5	35 °C, pH 7.5, 6 d	97.2	(Zhu et al., 2020)
<i>Streptomyces</i> sp. atz2	30 °C, pH 7.5, 3 d	98	(Mesquini et al., 2015)



metabolic limitations. For instance, transgenic *Escherichia coli* expressing optimized *atzABC* operons exhibit 2–3-fold higher atrazine mineralization rates than wild-type degraders, by bypassing rate-limiting steps in dichlorination (Wang et al., 2005). Similarly, laccases and cytochrome P450 enzymes fused to carbohydrate-binding modules show enhanced stability and substrate affinity when immobilized on biochar, achieving >95 % herbicide removal in 12 h (Shoseyov et al., 2006). However, field deployment faces regulatory and ecological hurdles, including horizontal gene transfer risks, unintended effects on soil microbiomes, and public acceptance barriers. Controlled encapsulation of GM microbes in alginate beads or lignin-based matrices may mitigate these concerns by restricting viability to contamination hotspots.

The synergy between phytoremediation and microbial activity showcases unique advantages. White clover (*Trifolium repens*) and alfalfa (*Medicago sativa*) enhanced rhizosphere *atzD* gene abundance by 2–3 orders of magnitude, achieving 68–73 % atrazine degradation within 40 days through root exudate-mediated stimulation of *Arthrobacter* populations (Motamedi et al., 2023). Recent studies have identified *Zea mays* as an effective phytoremediator when combined with mycorrhizal fungi, achieving 81 % atrazine removal in co-contaminated soils through enhanced cytochrome P450 expression (Brazier-Hicks et al., 2022). Organic amendments further enhance remediation efficacy. For instance, Luo et al. (2021) reported that goat manure amendment (4 % w/w) increased soil organic matter from 1.8 % to 3.4 %, enriching *Nocardioide*s (from 3.1 % to 11.2 %) and *Massilia* (from 2.4 % to 7.8 %), thereby improving degradation efficiency from 35.7 % to 84.3 % within 42 days. Subsequent vermicompost applications demonstrated 92 % atrazine degradation through synergistic effects between *Streptomyce*taceae (15.7 % abundance) and *Saccharimonadaceae* (9.3 %), while increasing deethylatrazine and deisopropylatrazine metabolite conversion rates by 38 % and 27 %, respectively (Luo et al., 2022). Comparatively, biochar-modified compost systems have shown 40 % faster degradation kinetics than conventional methods through enhanced microbial electron transfer processes.

### 2.3.2. Physicochemical remediation

Physicochemical methods provide rapid and effective solutions for contaminant remediation, with various materials demonstrating significant potential in enhancing the efficiency of degradation processes. Beyond adsorption-based approaches, ultraviolet (UV) photolysis and advanced oxidation processes (AOPs) represent cutting-edge strategies for atrazine mineralization. UV degradation alone achieves 40–60 % atrazine decomposition within 24 h via direct photolytic cleavage of C–Cl and C–N bonds, and the optimal half-life is even shorter than 5 min, though efficiency is highly matrix-dependent (e.g., reduced by dissolved organic matter) (Héquet et al., 2001). Coupling UV with oxidants dramatically enhances efficacy: UV/H<sub>2</sub>O<sub>2</sub> systems generate hydroxyl radicals (•OH) that achieve >90 % degradation in 1–2 h through non-selective oxidation, while UV/persulfate activates sulfate radicals (SO<sub>4</sub>•<sup>−</sup>) with 2–3× faster kinetics than conventional persulfate oxidation (Huang et al., 2018).

Among adsorption-focused methods, biochar and its modified forms have garnered considerable attention due to their dual roles in adsorption and enhancement of microbial degradation. The inherent porosity and large surface area of biochar render it an ideal material for removing atrazine from contaminated environments. For instance, Chen et al. (2024) developed a nano-hydroxyapatite-modified biochar that not only enhanced soil pH buffering within the range of 6.8–7.2 but also upregulated the expression of *atzABC* genes, achieving a degradation efficiency of 85.13 %, which represents a 50 % improvement over conventional biochar.

Beyond biochar, photocatalytic innovations leverage light energy to generate active free radicals, thereby degrading atrazine. For example, Ag/LaTiO<sub>3</sub> nanowire catalysts achieved 90 % degradation efficiency along with a 60–75 % reduction in metabolite ecotoxicity (Shawky et al., 2020). However, the high cost of materials and the substantial energy

requirements associated with photocatalysis pose major limitations, restricting its broader application. In this context, Rocha et al. (2024) introduced a more sustainable approach by utilizing green Ag nanoparticles supported on waste-derived carriers. This method achieved 92.4 % photodegradation efficiency while promoting environmental sustainability through the reuse of waste materials. Additionally, persulfate activation has been explored as a viable option for atrazine degradation, achieving 85–95 % degradation under alkaline conditions (pH > 9). While effective, the formation of chlorinated byproducts in groundwater remains a concern, underscoring the need for further optimization of this technology to minimize potential environmental risks.

### 2.3.3. Co-remediation strategy

Co-remediation strategy leverages synergistic effects to enhance degradation performance, with current approaches primarily focusing on integrating physical materials with microorganisms or enzymes. This strategy combines the strengths of different methods to address the complexities associated with contaminant degradation. For instance, microorganisms are frequently paired with adsorbents such as biochar or clay to increase biodegradation efficiency, while enzyme immobilization techniques are increasingly utilized to stabilize and enhance catalytic activity. The reaction mechanism of atrazine degradation through the combination of microorganisms and biochar is illustrated in Fig. 2, where microorganisms degrade atrazine by secreting a variety of enzymes, and biochar facilitates microbial degradation by adsorbing atrazine. Zhang et al. (2011) developed an integrated clay-straw copyrolysis biochar combined with strain DNS10, achieving a 42.6 % increase in atrazine removal and elevating soil available nitrogen and phosphorus by 35.2 % and 28.7 %, respectively. Song et al. (2020) implemented a dual-membrane electrokinetic-microbial system that achieved 1.8-fold higher degradation for Pb-atrazine co-contaminated soils while restoring enzymatic activity to 85–90 % of uncontaminated controls. Cutting-edge research by Zhang et al. (2024) established a biochar-biofilm system using *Acinetobacter lwoffii* DNS32, reducing the degradation half-life from 14.3 to 5.2 days via enhanced nitrogen cycling and microbial resilience. Recent breakthroughs in enzyme immobilization include Jia et al. (2024), who developed a novel laccase-HBT-Pd/BC co-immobilized biocatalyst achieving complete atrazine degradation (50 mg/L) within 5 h at pH 6.0, with LC-MS analysis confirming an 85 % reduction of cyanuric acid derivatives. The composite maintained 91 % efficiency after 10 reuse cycles, demonstrating potential for continuous-flow wastewater treatment. Emerging technologies include nano-bioremediation approaches, where Fe<sub>3</sub>O<sub>4</sub>/MOF-199 nanocomposites coupled with *Sphingomonas* sp. achieved 97 % atrazine removal in 6 h through combined adsorption-biodegradation mechanisms (Wang et al., 2022). These advancements underscore the importance of integrated remediation strategies combining biological, chemical, and physical processes for comprehensive atrazine management.

Techno-economic analyses indicate that bioremediation costs are significantly lower than those of thermal desorption. Although biological processes require longer durations (30–90 days compared to <24 h for advanced oxidation achieving >90 % degradation), future research must address interfacial effects in hybrid systems and long-term ecological impacts, particularly the bioaccumulation risks of metabolites in food chains. A comparative summary of key remediation technologies—adapted primarily from atrazine-focused studies but broadly reflective of structurally similar herbicides—is presented in Table 3.

## 3. Contamination remediation and risk assessment of nicosulfuron

### 3.1. Physicochemical properties and action mechanism

Nicosulfuron is a sulfonylurea herbicide that functions as a selective

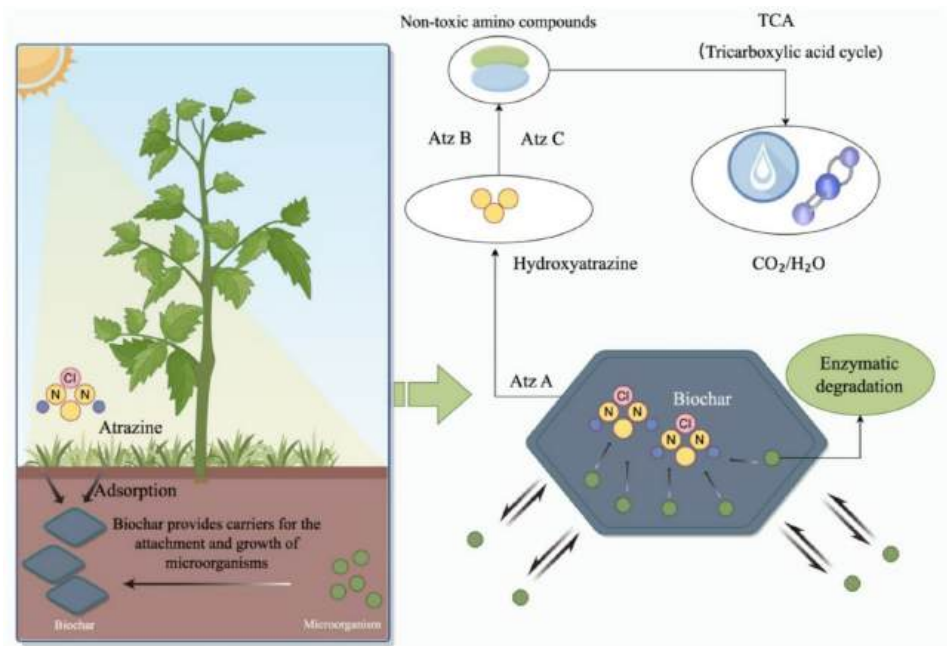


Fig. 2. Schematic diagram of co-remediation of atrazine contamination by biochar and microorganisms.

**Table 3**  
Comparative evaluation of atrazine remediation technologies across environmental media.

Remediation method	Medium	Efficiency (%)	Cost estimate (USD/ m <sup>3</sup> )	Field scalability	Key limitations	Bibliography
Bioremediation (consortium)	Soil	70–100	5–10	High	Slower rate, sensitive to pH/temp	(Singh and Singh, 2016)
Biochar + bacteria	Soil	90–96	8–12	High	Need soil amendment infrastructure	(Huang et al., 2022a)
UV photolysis	Water	40–60	15–25	Medium	Matrix interference; low mineralization	(Mu et al., 2021)
UV/H <sub>2</sub> O <sub>2</sub>	Water	>90	30–50	Medium	High H <sub>2</sub> O <sub>2</sub> consumption; <sup>•</sup> OH scavenging	(Poonia et al., 2022)
UV/persulfate	Water/ groundwater	85–98	40–65	Medium	SO <sub>4</sub> <sup>•−</sup> quenching by carbonates; Cl <sup>−</sup> byproducts	(Liu et al., 2022)
Photocatalysis	Water	~90	30–50	Low	High cost, energy intensive	(Dantas et al., 2024)
Fenton oxidation	Water	80–95	25–40	Medium	Sludge generation; pH-dependent efficiency	(Cheng et al., 2016)
Persulfate oxidation	Groundwater	85–95	23–35	Medium	Toxic byproducts possible	(Chen et al., 2018)
Enzyme-immobilized Pd/ BC	Water	~100	50–70	Medium	Reusability issues, synthesis cost	(Jia et al., 2024)

systemic conductive agent, primarily utilized in corn fields for the control of annual and perennial grasses as well as broadleaf weeds. With the chemical formula C<sub>15</sub>H<sub>14</sub>N<sub>6</sub>O<sub>6</sub>S and a molecular weight of 410.41 g/mol, it displays high water solubility (9.7 g/L at 25 °C) and low vapor pressure (1.2 × 10<sup>−9</sup> mPa at 25 °C), characteristics that enhance its environmental mobility. Notably, its soil adsorption coefficient (*K*<sub>oc</sub>: 14–40) indicates weak soil binding affinity, particularly in soils with low organic matter content (<2 %), thereby increasing its leaching potential.

The herbicidal mechanism of nicosulfuron involves the specific inhibition of acetolactate synthase (ALS), a critical enzyme in the biosynthesis of branched-chain amino acids (valine, leucine, isoleucine). This inhibition disrupts plant cell division by interfering with DNA synthesis and the development of meristematic tissue. Differential plant sensitivity to nicosulfuron arises from species-specific variations in ALS isoforms and metabolic detoxification capacities. Environmental persistence is influenced by pH-dependent degradation kinetics; acidic soils accelerate degradation via hydrolysis (*DT*<sub>50</sub> = 15–20 days), whereas alkaline conditions extend persistence due to reduced microbial activity (*DT*<sub>50</sub> = 190–250 days). Emerging evidence suggests that major metabolites, such as 2-amino-4,6-dimethoxypyrimidine (ADMP) and *N*, *N*-dimethyl-3-pyridinecarboxamide, retain phytotoxic properties, underscoring the need for comprehensive metabolite monitoring (Cheng

et al., 2022).

3.2. Environmental behavior and risk assessment

3.2.1. Environmental distribution and transport

The environmental fate of nicosulfuron is influenced by its physicochemical properties and application practices. Field monitoring studies conducted in major corn-producing regions, such as Northeast China and the USA Midwest, reveal substantial vertical transport, with detectable residues observed at depths of 90 cm within 90 days post-application. Incidents of groundwater contamination in permeable soils have reported concentrations exceeding 0.1 µg/L, approaching the European Union (EU) threshold for pesticide levels in drinking water. Hydrological modeling predicts that 12–18 % of applied nicosulfuron may infiltrate into high-permeability aquifers, posing potential chronic exposure risks to groundwater-dependent ecosystems. In aquatic systems downstream of agricultural areas, nicosulfuron exhibits bioaccumulation potential, with bioconcentration factors (BCF) ranging from 12 to 45 in macrophytes (e.g., *Lemna minor*) and benthic organisms. This transport pathway poses a threat to aquatic primary producers, as evidenced by 48-h *EC*<sub>50</sub> values of 0.007–0.015 mg/L for green algae (*Scenedesmus quadricauda*), which indicates high ecotoxicological

sensitivity (Li et al., 2024).

### 3.2.2. Degradation pathways and metabolites

The degradation of nicosulfuron occurs through three primary mechanisms: microbial degradation, plant-mediated degradation (phytodegradation), and chemical hydrolysis. Key bacterial genera involved in microbial degradation, such as *Pseudomonas*, *Bacillus*, and *Streptomyces*, produce acetolactate synthase (ALS)-degrading enzymes and sulfatases that mediate C–N/S bond cleavage. Secondly, phytodegradation involves transgenic crops expressing modified ALS enzymes, which exhibit enhanced metabolic capacity. These crops reduce soil residues by 40–60 % compared to conventional cultivars. During chemical hydrolysis, pH-dependent cleavage of sulfonylurea bridges predominates in acidic environments ( $\text{pH} < 6$ ), producing low-toxicity intermediates such as ADMP and  $\text{CO}_2$ . In contrast, alkaline conditions favor the formation of persistent sulfonamide derivatives (Grey and McCullough, 2012). The specific degradation pathways are shown in Fig. 3. Notably, the metabolite 2-(aminosulfonyl)-N,N-dimethylnicotinamide retains approximately 30 % herbicidal activity, necessitating its inclusion in comprehensive risk assessments (Rai et al., 2020).

### 3.2.3. Toxicology and risk assessment

Quantitative risk assessment utilizing species sensitivity distribution (SSD) models identifies aquatic ecosystems as the most vulnerable, with 5 % hazard concentration ( $\text{HC}_5$ ) values of 0.0032 mg/L for freshwater communities. Chronic exposure (21-day LOEC = 0.05 mg/kg) reduces soil microbial biomass carbon by 28 % and nitrogenase activity by 41 %, thereby impairing nutrient cycling functions (Cheron et al., 2022). Crop rotation studies demonstrate carryover effects in alkaline soils ( $\text{pH} > 7.5$ ), where residual nicosulfuron at 0.1 mg/kg causes 65 % germination inhibition in oilseed rape (*Brassica napus*), 42 % biomass reduction in sugar beet (*Beta vulgaris*), and 30 % yield loss in subsequent wheat crops (Ahmadi et al., 2017). Emerging concerns focus on sublethal effects: 90-day exposure to 0.01 mg/L alters the emergence timing of aquatic

insects and reduces fecundity by 18–25 % (Cheron et al., 2022). Regulatory frameworks now incorporate probabilistic risk assessment models, estimating a 23 % probability of exceeding ecological thresholds in intensive-use regions.

In addition to its direct toxicological impacts, nicosulfuron may induce broader ecological effects on non-target organisms and key ecosystem functions. Due to its high water solubility and weak adsorption to soil particles, it is highly mobile and prone to leaching and runoff, thereby increasing its environmental bioavailability. Studies have shown that nicosulfuron exposure inhibits photosynthesis in green algae by disrupting chlorophyll biosynthesis, which may suppress primary productivity in aquatic ecosystems. In soil systems, repeated application has been linked to reductions in microbial diversity and functional gene abundance, particularly among nitrifying bacteria and phosphorus-solubilizing taxa, potentially impairing soil fertility and nutrient cycling (Filimon et al., 2015). These ecological disturbances emphasize the need to incorporate microbial functionality and aquatic food web stability into environmental risk assessments for sulfonylurea herbicides.

### 3.3. Advances in pollution abatement technology for nicosulfuron

#### 3.3.1. Bioremediation

Microbial remediation has emerged as the most promising strategy for nicosulfuron elimination, with recent advancements in strain screening and metabolic pathway engineering. *Chryseobacterium* sp. LAM-M5, isolated by Ma et al. (2022), demonstrates exceptional degradation efficiency (92.39 % within 7 days) through hydrolase-mediated cleavage of the sulfonylurea bridge, reducing metabolite toxicity by 78 % compared to the parent compound. The discovery of *Pseudomonas* sp. LAM1902 further validates this approach, exhibiting dual functionality: 92.5 % herbicide degradation while upregulating antioxidant enzymes (SOD and CAT activities increased by 35–42 %) in sorghum roots, effectively mitigating phytotoxicity (Li et al., 2020). It is

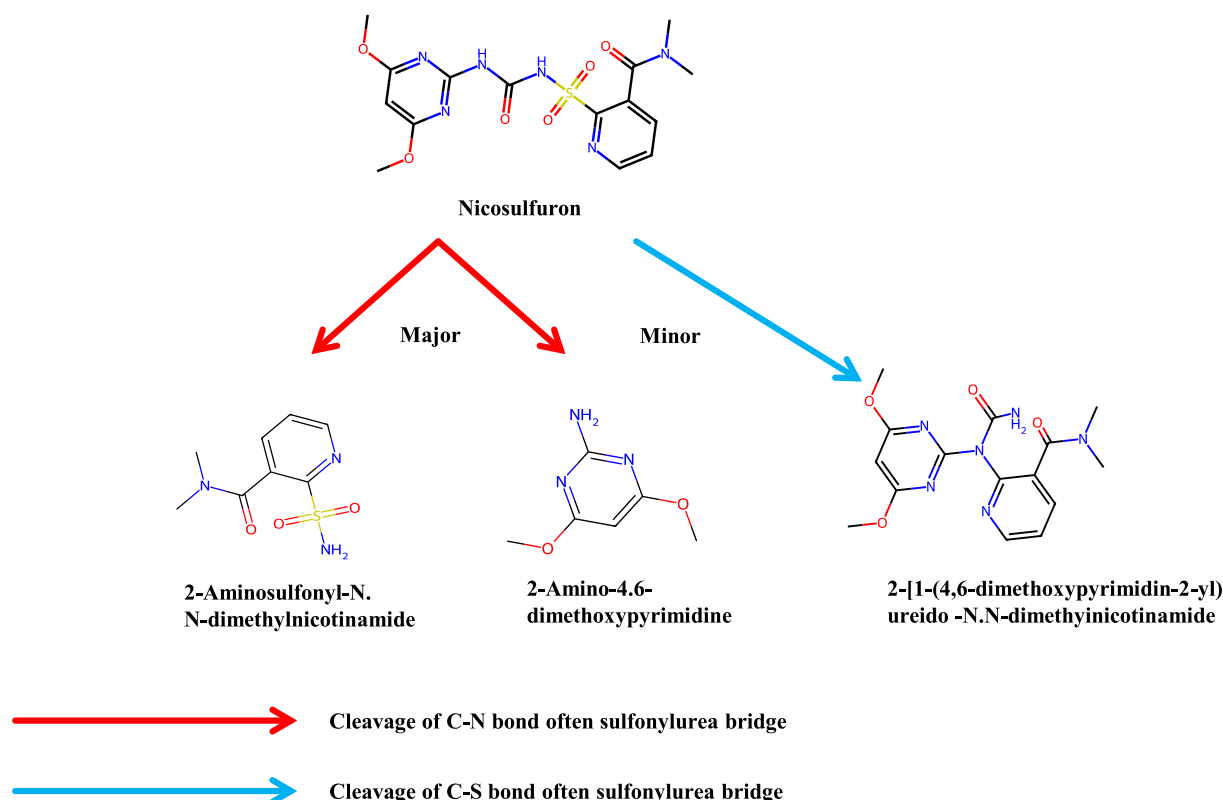


Fig. 3. Pathways of hydrolysis of nicosulfuron in the environment (Zhong et al., 2023).

worth noting that engineering microbial consortia has significantly enhanced degradation efficiency. Yang et al. (2024) developed a composite bacterium ES58, consisting of *Klebsiella oxytoca* ES5 and *grumontii* ES8, achieving 90.84 % degradation via complementary enzymatic systems (sulfonyleurea hydrolase and cytochrome P450), with the half-life reduced to 4.3 days. Wang et al. (2024b) introduced bacterial colony A12, comprising *Serratia marcescens* A1 and *Bacillus cereus* A2, which exhibits soil adaptability, degrading 91.2 % nicosulfuron in unsterilized soil while increasing dehydrogenase activity by 28 %, a critical indicator of soil functional recovery.

### 3.3.2. Physicochemical remediation

In the realm of nicosulfuron degradation methods, physicochemical techniques such as photocatalysis have gained prominence. Photocatalysts exposed to light generate holes that subsequently produce hydroxyl radicals and superoxide anions, which react with and degrade nicosulfuron, as illustrated in Fig. 4. Zhu et al. (2022) developed graphdiyne-modified biochar demonstrating dual adsorption-degradation capacity, achieving  $Q_{\max} = 98.6$  mg/g and 90 % photocatalytic degradation via OH radical generation, reducing acute toxicity to *Daphnia magna* from  $LC_{50} = 12.4$  mg/L to 46.8 mg/L. Xie et al. (2024) utilized acid-modified and nano zero-valent iron-loaded biochar, enhancing fomesafen adsorption (88 % in 6 h) through improved electron transfer, with adsorption capacity increased by 40 % compared to raw biochar. Persulfate activation exhibits pH-dependent efficiency, achieving >95 % degradation under alkaline conditions via  $SO_4^{\cdot -}$  dominance, outperforming conventional UV/ $H_2O_2$  systems.

Nonetheless, these technologies face significant practical challenges, including high energy demands, catalyst regeneration requirements, and limited demonstrations under real agricultural field conditions. In addition, the environmental safety of reaction intermediates and potential impacts on soil biota have not been systematically assessed.

### 3.3.3. Co-remediation strategy

Immobilization technology integrates biological and physicochemical mechanisms. Zhai et al. (2023) achieved a breakthrough by utilizing corn stover biochar to immobilize *Klebsiella jilinsis* 2N3, shortening the herbicide's half-life from 22.8 days to 5.1 days in non-sterile soil and achieving a maximum degradation rate of 92.62 %. This approach not only accelerates degradation but also improves soil microbial activity, aligning with circular economy principles. Zhang et al. (2023) developed an immobilized bacterial formulation of *Aspergillus terreus* DT2, achieving an 85 % reduction of soil nicosulfuron residues within 14 days through coupled biosorption and synergistic laccase production. While co-remediation technologies offer synergistic advantages, their reproducibility and performance under variable edaphic conditions (e.g., pH, CEC, organic matter) remain underexplored.

Crop rotations is an important method to reduce the contamination of nicosulfuron. For instance, maize-sorghum rotation systems enhance microbial degradation by 40–60 % compared to monoculture, with root exudates (e.g., 2.3  $\mu$ M/g phenolic acids) stimulating degrader abundance. Concurrently, biochar amendment (5 % w/w) in these systems increases soil cation exchange capacity (CEC) by 29 % and water-stable aggregates by 18 %, creating microhabitats for degradative consortia (Yang et al., 2023).

## 4. Contamination remediation and risk assessment of fomesafen

### 4.1. Physicochemical properties and action mechanism

Fomesafen, a diphenyl herbicide, is predominantly utilized in the cultivation of soybean, peanut, and cotton crops for controlling broad-leaf and grass weeds. Its chemical formula is  $C_{15}H_{10}ClF_3N_2O_6S$ , with a molecular weight of 438.76 g/mol and water solubility of 1.79 mg/L at 25 °C. Its soil adsorption coefficient ( $K_{oc}$ ) ranges from 200 to 500, indicating strong adsorption properties in soils containing  $\geq 2$  % organic matter.

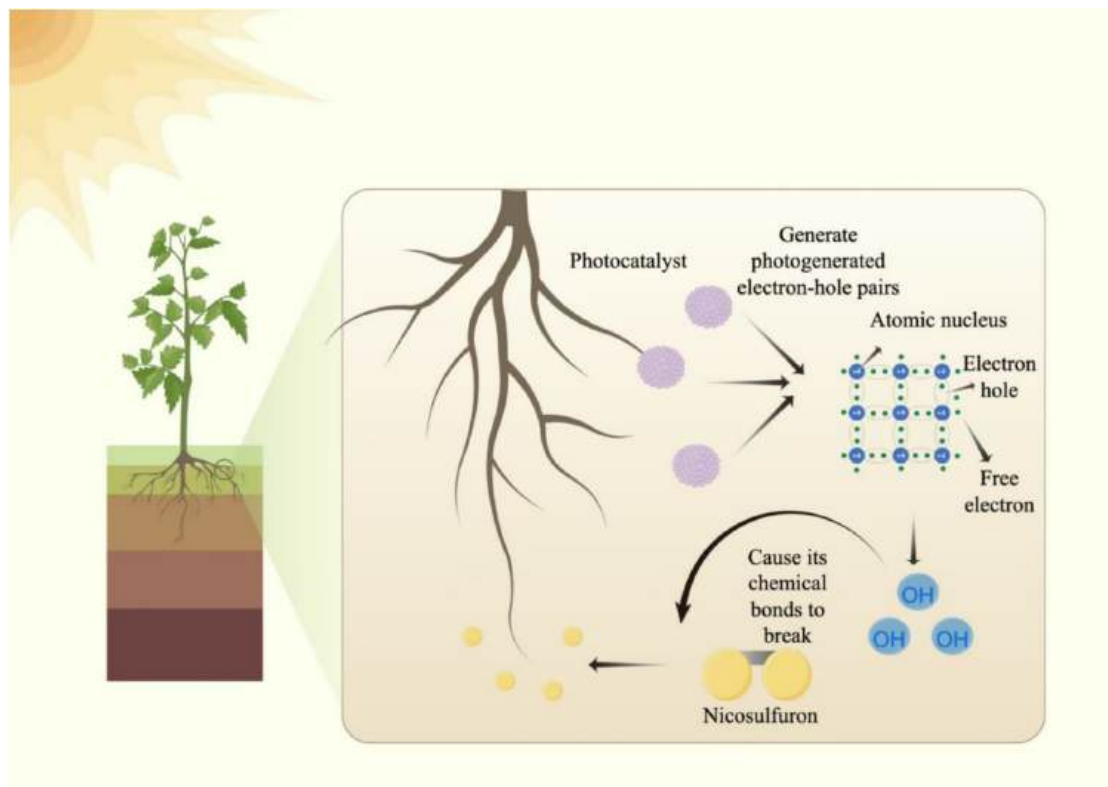


Fig. 4. Schematic diagram of photodegradation of nicosulfuron.



The herbicidal mechanism of fomesafen involves the inhibition of protoporphyrinogen oxidase (PPO) in plant cells, leading to an abnormal accumulation of protoporphyrin IX in the cytoplasm. This protoporphyrin IX is subsequently photoactivated to generate reactive oxygen species (ROS), which induce lipid peroxidation. This process results in increased cell membrane permeability (50–80 % increase in conductivity), electrolyte leakage ( $K^+$  loss up to 3.5 mmol/g FW), and ultimately water loss and wilting of target weeds. Notably, glutathione-S-transferases (GSTs) present in crop tissues facilitate the conjugation of fomesafen with glutathione, forming low-toxicity metabolites. This conjugation represents a critical mechanism contributing to the compound's selective toxicity.

Fomesafen induces visible symptoms such as chlorosis and necrosis typically within 3–7 days post-application. Its trifluoromethyl and chloroaromatic moieties confer notable chemical stability, resulting in a DT<sub>50</sub> of approximately 60–120 days in soils with pH 5–7. Under low temperature (<10 °C) and low humidity (<30 %) conditions, degradation rates decline by 40–60 %, leading to the persistence of residues primarily in the top 0–5 cm of soil. Field studies indicate that residues may remain at 10–15 % of the applied dose in soils under continuous use and suboptimal degradation conditions (Cobucci et al., 1998).

#### 4.2. Environment behavior and risk assessment

#### 4.2.1. Environmental distribution and transport

The environmental fate of fomesafen is primarily characterized by strong soil sorption and low mobility. Following field application, over 80–90 % of the herbicide remains confined to the top 0–5 cm of soil, particularly in clay-rich or organic matter-enriched soils. Its high soil adsorption coefficient and low water solubility (0.11 mg/L at 25 °C) result in minimal leaching under standard agricultural conditions. However, in coarse-textured soils or under heavy rainfall, trace amounts may leach to depths of 15–30 cm. Fomesafen is largely immobile in aquatic environments due to its strong affinity to soil and sediment particles. Partitioning to suspended matter is moderate ( $K_d \approx 50\text{--}120\text{ L/kg}$ ), and photolysis in surface water is relatively slow, with a reported half-life of >20 days under natural light. Therefore, fomesafen is not

considered a significant contaminant in surface waters under standard application scenarios. Its main environmental concern lies in the persistence in surface soil under cool or dry conditions, where degradation may be inhibited, prolonging residue retention (Cobucci et al., 1998).

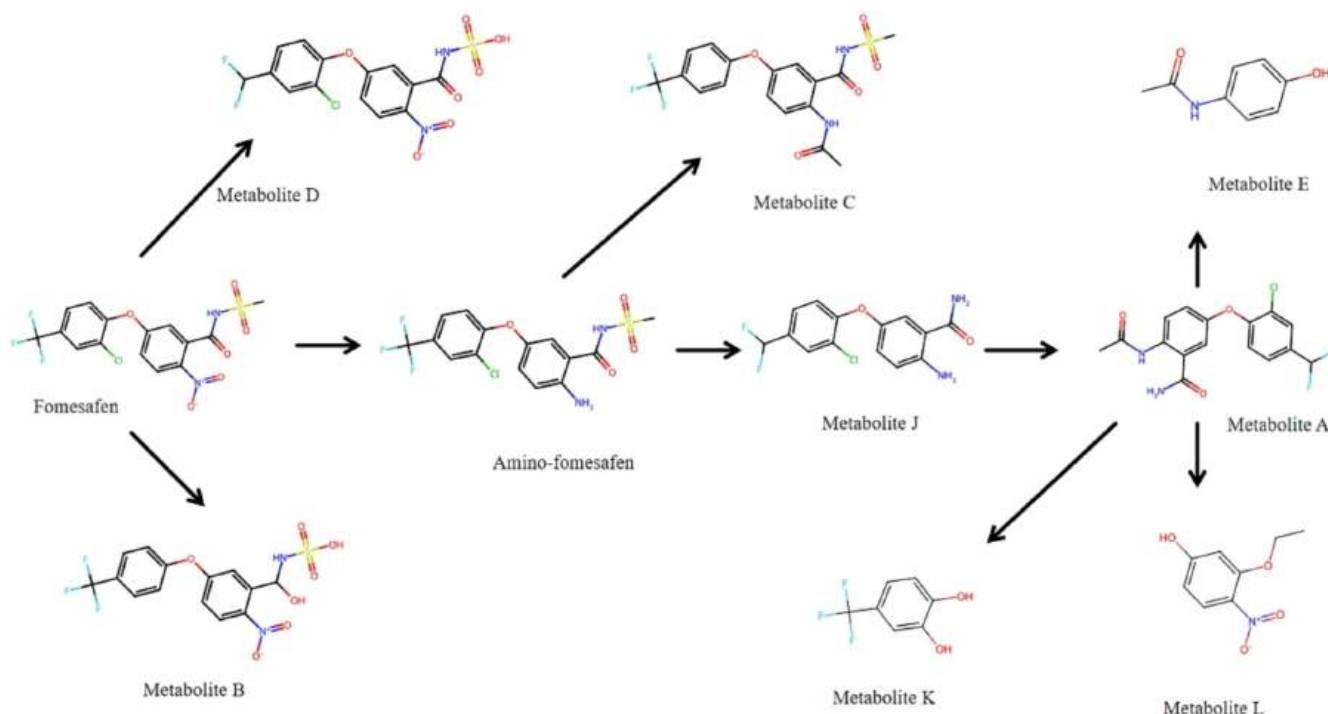
#### 4.2.2. Degradation pathways and metabolites

The degradation of fomesafen in the environment is predominantly governed by microbial processes, while photolysis plays a minor role, and hydrolysis is considered negligible. Aerobic soil microbes—especially species within the genera *Pseudomonas*, *Rhodococcus*, and *Sphingomonas*—are known to metabolize fomesafen via oxidative dealkylation and ring cleavage pathways. The major transformation product identified in soil is desmethyl-fomesafen, which has markedly reduced herbicidal activity and environmental persistence (Fig. 5).

Photolytic degradation in natural surface waters is slow, with half-lives typically exceeding 20 days under sunlight. Studies confirm that sunlight generates hydroxylated metabolites in trace amounts, without producing highly toxic or persistent photoproducts. Chemical hydrolysis under environmental pH (5–9) remains insignificant, confirming the structural stability of fomesafen across typical agricultural settings. Under anaerobic or waterlogged conditions, especially in paddy soils, fomesafen degradation is significantly suppressed. DT<sub>50</sub> values have been recorded in the range of 150–200 days, accompanied by accumulation of desmethyl and hydroxylated metabolites (Wang et al., 2024b).

#### 4.2.3. Toxicology and risk assessment

The long-term application of fomesafen in agricultural soils raises notable concerns regarding its sublethal effects on soil health, microbial function, and non-target organisms. Laboratory and field investigations have demonstrated that fomesafen residues may suppress soil microbial activity, particularly affecting enzyme functions essential for nutrient cycling. For example, significant reductions in soil dehydrogenase (−35 %) and urease activity (−48 %) have been reported after 60 days of exposure to fomesafen at field-relevant concentrations (0.1–0.2 mg/kg), especially at low temperatures and under low organic matter conditions. Metagenomic analysis showed that the relative abundance of nitrogen-



**Fig. 5.** Degradation pathways of fomesafen in soil (Zhao et al., 2023).

fixing genera (*Rhizobium*, *Sinorhizobium*) recorded after repeated use of fomesafen was reduced, as was the abundance of *nifH* genes in the inter-root of plants (Chen et al., 2025). However, these shifts were transient and partially reversible after a single growing season without herbicide exposure, suggesting a non-persistent ecological disturbance.

Crop phytotoxicity remains a relevant issue, particularly in sandy soils. Sugar beet (*Beta vulgaris* L.) is especially sensitive to fomesafen residues, with 50 % inhibition of primary root elongation observed at soil concentrations above 0.025 mg/kg. Gibberellin pathway suppression has also been implicated, with fomesafen exposure downregulating GA20ox expression by up to 37 % in root tips. To mitigate risk, recommend rotational intervals of  $\geq 12$  months for maize following fomesafen use in sandy soils, and  $\geq 8$  months in clay soil (Li et al., 2025).

In aquatic systems, fomesafen displays moderate to high acute toxicity toward invertebrates and fish. The 48 h-LC<sub>50</sub> for *Daphnia magna* is 0.01–0.03 mg/L, while for zebrafish *Danio rerio*, the 96 h-LC<sub>50</sub> ranges from 1.8 to 3.0 mg/L. Sublethal effects include increased oxidative stress, developmental delays, reduced motor behavior, and cardiac developmental defects associated with exposure to low concentrations in *D. rerio* (Jumel et al., 2002). As a PPO inhibitor, fomesafen disrupts chlorophyll biosynthesis and cell membrane integrity. While this mode of action is highly specific to target weeds, unintended impacts on plant–microbe symbiosis and aquatic primary producers highlight the need for cautious application in ecologically sensitive zones.

#### 4.3. Progress in pollution abatement technologies

##### 4.3.1. Bioremediation

Bioremediation has emerged as a pivotal approach for mitigating fomesafen contamination, primarily through microbial degradation and phytoremediation mechanisms. Notably, *Pseudomonas aeruginosa* FB5, isolated by Yang (2014), exhibited robust degradation capabilities toward fomesafen, achieving an 86.75 % degradation efficiency within 28 days under controlled laboratory conditions. This strain significantly reduced the herbicide's half-life from 93 to 30 days, thereby alleviating

soil phytotoxicity and enhancing microbial diversity in contaminated soils. Further investigations revealed that degradation efficiency correlates with the metabolic activity of cytochrome P450 enzymes, which facilitate the cleavage of fomesafen's ether bonds. Similarly, *Bacillus* sp. FE-1 demonstrated complete mineralization at 20 mg/L through N-dealkylation and aromatic ring cleavage, with strong tolerance to environmental fluctuation (Cui et al., 2018).

Phytoremediation of fomesafen-contaminated soils is primarily mediated by plant–microbe interactions in the rhizosphere. Root exudates—comprising organic acids, phenolics, amino acids, and sugars—act as both carbon sources and signaling molecules, stimulating the growth and enzymatic activity of contaminant-degrading microbial taxa such as *Pseudomonas*, *Arthrobacter*, and *Nocardioideis* (Zhao et al., 2022). These microbes, in turn, express key degradative enzymes including oxidoreductases, laccases, and cytochrome P450s, enhancing herbicide transformation rates.

Although direct studies on fomesafen are limited, recent experiments using *Zea mays* and *Medicago sativa* demonstrated that rhizosphere soils planted with these species showed significantly higher dehydrogenase activity and faster herbicide dissipation—up to 50–60 % reduction in soil residues compared to unplanted controls (Tarla et al., 2020). These effects are attributed to both microbial recruitment and rhizosphere oxygenation. Fig. 6 illustrates the mechanism of plant degradation of fomesafen, highlighting several metabolic transformations occurring after root uptake. In addition, plant presence improved soil nitrogen cycling and organic carbon storage, suggesting co-benefits in soil restoration.

Fomesafen, as a diphenyl ether herbicide, shares structural motifs with other PPO inhibitors. Therefore, rhizosphere-enhanced degradation observed for similar compounds (e.g., acifluorfen) may be extended to fomesafen. However, current evidence remains indirect. Controlled experiments with isotope-labeled fomesafen, transcriptomic profiling of rhizosphere microbes, and time-resolved metabolite tracing are needed to definitively establish plant-assisted degradation pathways. Until then, phytoremediation should be regarded as a promising but under-

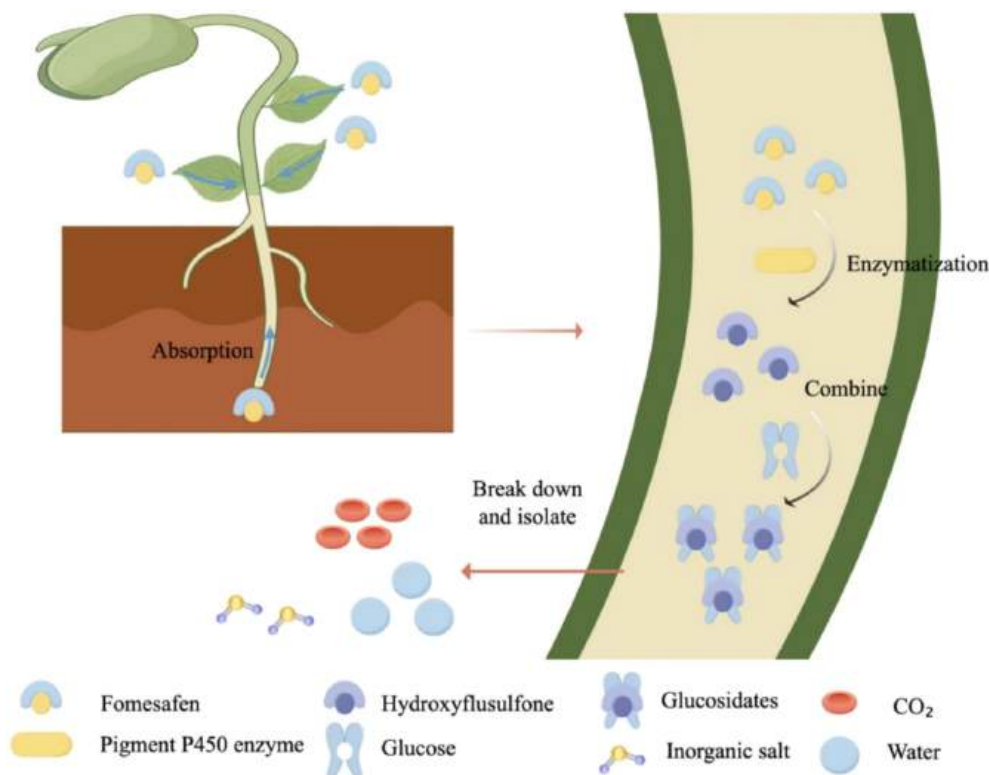


Fig. 6. Schematic diagram of phytodegradation of fomesafen.

validated approach for long-residual herbicide remediation.

#### 4.3.2. Physicochemical remediation

Physicochemical methods are more prominent in the treatment of fomesafen due to their high efficiency and applicability. Yang et al. (2020) developed a solar-driven Fenton system using Fe<sup>3+</sup>-loaded biochar, achieving 94 % fomesafen degradation within 2 h via hydroxyl radical (•OH) generation. This method reduced maize kernel residues to 0.05 mg/kg (below EU MRLs) while increasing crop yield by 22 % through iron micronutrient supplementation. Similarly, Wei (2023) engineered a g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> photocatalyst that degraded 84 % fomesafen under visible light, with intermediates (e.g., 2-chloro-4-fluoroacetophenone) exhibiting negligible ecotoxicity (EC<sub>50</sub> > 100 mg/L). Despite their high degradation efficiencies, these methods often face limitations related to energy input, catalyst recovery, and reaction byproduct management.

#### 4.3.3. Co-remediation strategies

Co-remediation strategies combining biological and physicochemical mechanisms have shown promise in improving fomesafen degradation efficiency and adaptability to complex environments. Biochar–microbe systems are among the most studied, where pyrolyzed biochar (typically at 400–500 °C) provides porous surfaces and electron-buffering capacity, facilitating colonization by degraders and enhancing biofilm formation. These systems have demonstrated up to 3-fold acceleration in fomesafen dissipation compared to single-strain inoculation (Zhao et al., 2022). Enzyme-based approaches also contribute to co-remediation progress. Recent studies reported that laccase immobilized on magnetic graphene oxide retained over 85 % catalytic activity after multiple cycles and enhanced fomesafen removal through combined adsorption and oxidative degradation (Wong et al., 2021). However, these systems are primarily tested under lab-scale, pH-controlled conditions, and their scalability remains uncertain.

Overall, co-remediation offers operational flexibility and synergy, but future work should focus on optimizing material–microbe compatibility, reducing system complexity, and validating long-term ecological safety in real-world scenarios.

### 5. Contamination remediation and risk assessment of imazethapyr

#### 5.1. Physicochemical properties and action mechanism

Imazethapyr, a member of the imidazolinone class of herbicides, is a systemic and selective herbicide widely employed for pre- and post-emergence control of broadleaf weeds and certain grass weeds in leguminous crops such as soybeans (*Glycine max*), peas (*Pisum sativum*), and oilseed rape (*Brassica napus*). Its chemical formula is C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>, with a molecular weight of 289.33 g/mol. The compound exhibits water solubility of 140 mg/L at 25 °C and a soil adsorption coefficient (*K*<sub>oc</sub>) ranging from 100 to 200, indicating its high mobility in low-organic-texture soils and susceptibility to leaching into groundwater.

Imazethapyr exerts its function by inhibiting the synthesis of branched-chain amino acids (valine, leucine, and isoleucine) in target plants through the suppression of acetolactate synthase (ALS) or acetohydroxyacid synthase (AHAS). This inhibition disrupts protein synthesis and cell division, leading to cessation of plant growth and eventual plant death. The selectivity of imazethapyr between crops and weeds is attributed to differential metabolism and the presence of insensitive ALS isozymes in tolerant species. Despite its relatively low application rate (50–100 g/ha), the environmental persistence of imazethapyr is concerning, with a half-life ranging from 30 to 120 days in most soils and extending up to 150 days under alkaline conditions (Laskar et al., 2024). This persistence has led to its classification as a persistent organic pollutant in certain agricultural regions.

#### 5.2. Environment behavior and risk assessment

##### 5.2.1. Environmental distribution and transport

The environmental fate of imazethapyr is primarily determined by its physicochemical properties, particularly its water solubility and soil sorption characteristics. In soils with low organic matter content (<1.5 %), imazethapyr exhibits high mobility, with leaching potential being more pronounced in sandy and loamy soils (Liu et al., 2024). Recent studies employing <sup>14</sup>C-labeled imazethapyr have shown that approximately 60–70 % of the applied herbicide remains within the top 30 cm of soil, while 10–15 % may leach to deeper soil layers within 60 days post-application. In saline-alkaline soils, the mobility of imazethapyr is significantly enhanced due to reduced adsorption capacity, thereby increasing contamination risks in arid and semi-arid regions.

##### 5.2.2. Degradation pathways and metabolites

The environmental degradation of imazethapyr occurs through three primary pathways: photolysis, microbial degradation, and chemical hydrolysis. Fig. 7 illustrates the complex interplay between microbial degradation, photolysis, and hydrolysis pathways in the environmental fate of imazethapyr, highlighting the formation of various intermediate and terminal metabolites. Photodegradation is most efficient under strong UV irradiation ( $\lambda > 290$  nm), with a half-life of 15–20 days under natural sunlight, producing low-toxicity metabolites such as 2-hydroxyimazethapyr and imazethapyr acid. However, this process is significantly slower (DT<sub>50</sub> > 60 days) under shaded or low-light conditions, particularly in no-till farming systems.

Microbial degradation, primarily mediated by soil bacteria such as *Pseudomonas* sp. and *Bacillus* sp., plays a crucial role in imazethapyr breakdown through demethylation and ring cleavage reactions, the degradation pathway in soil is depicted in Fig. 8. The major microbial metabolites include *N*-methylimidazole-2-carboxylic acid and 5-ethyl-3-pyridinecarboxylic acid, both of which exhibit reduced phytotoxicity compared to the parent compound. Chemical hydrolysis of imazethapyr is pH-dependent, with degradation rates being 5–7 times faster in acidic soils (pH 5.0–6.0) compared to alkaline conditions (pH 7.5–8.5) (Huang et al., 2022b).

##### 5.2.3. Toxicology and risk assessment

The ecological impacts of imazethapyr residues extend beyond its herbicidal activity, significantly affecting soil microbial communities and biochemical processes. Long-term application (>5 years) has been shown to reduce soil dehydrogenase activity by 40–60 % and alkaline phosphatase activity by 30–50 %, indicating substantial disruption to microbial metabolic functions (Vishwakarma et al., 2023). Recent metagenomic studies have revealed shifts in microbial community structure, with a notable decrease in nitrogen-fixing bacteria (*Rhizobium* sp.) and mycorrhizal fungi populations in imazethapyr-treated soils. Furthermore, its environmental behavior—particularly its mobility and persistence in soil—can lead to indirect ecological effects under field conditions. Residual imazethapyr has been reported to alter root exudate profiles, affecting the structure of rhizosphere microbial communities. This may result in decreased abundance of plant growth-promoting rhizobacteria, with potential consequences for crop performance (Liu et al., 2020).

In aquatic ecosystems, while the acute toxicity of imazethapyr to macrophytes is relatively low (EC<sub>50</sub> > 10 mg/L), chronic exposure at sub-lethal concentrations (0.1–1.0 mg/L) has been shown to inhibit photosynthesis in phytoplankton communities by 20–40 %. Besides, chronic low-dose exposure in aquatic environments has been linked to shifts in benthic macroinvertebrate diversity, suggesting subtle but ecologically relevant food web disruptions. These findings point to a need for long-term ecological evaluations that extend beyond organism-level acute toxicity assays (Fowlkes et al., 2003).

The human health risks associated with imazethapyr exposure are primarily mediated through two pathways: consumption of

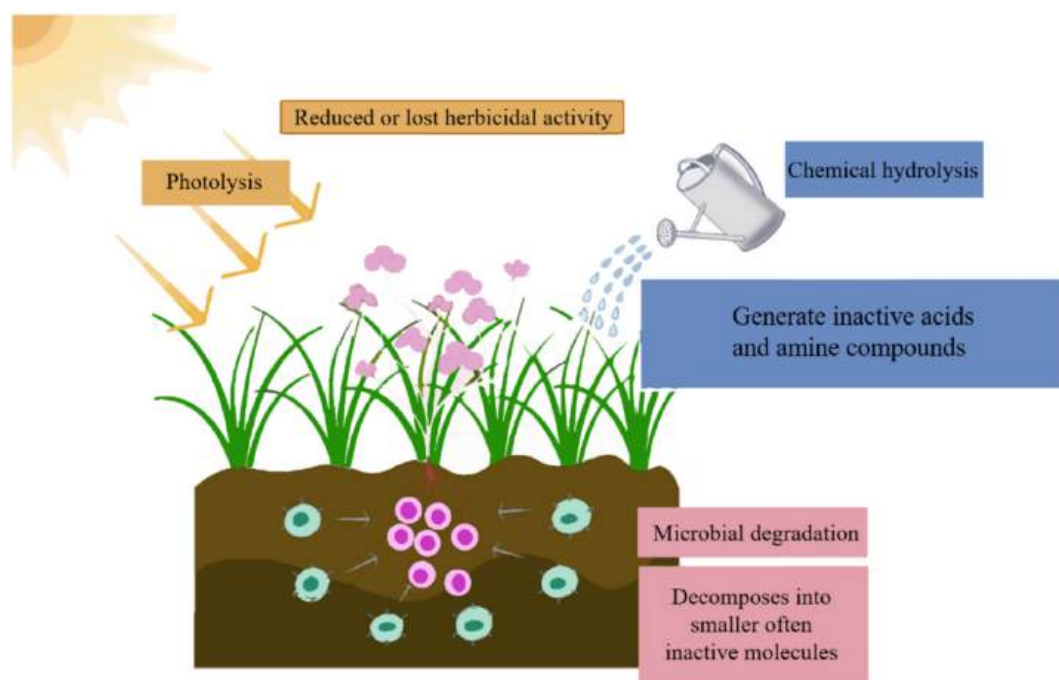


Fig. 7. Microbial degradation, photolysis, and hydrolysis of imazethapyr.

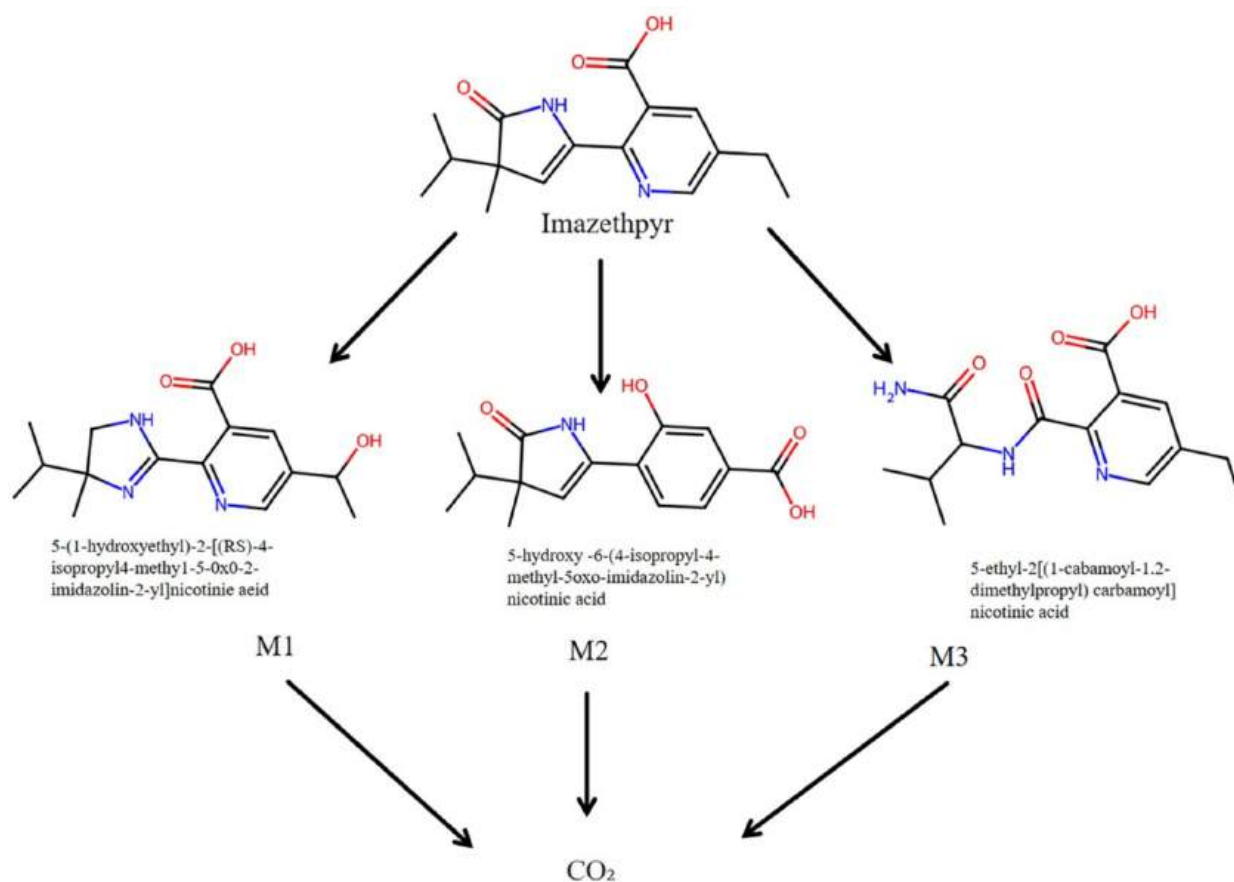


Fig. 8. Metabolic pathway of imazethapyr degradation (Kaur and Kaur, 2022).

contaminated drinking water and dietary intake of agricultural products. Chronic exposure has been linked to hepatotoxicity and nephrotoxicity in animal models, with observed no-effect levels (NOEL) of 2.5

mg/kg body weight/day. Recent epidemiological studies suggest potential neurotoxic effects, including impaired cognitive function, at exposure levels exceeding 0.1 mg/kg/day (Costa et al., 2022). The



establishment of maximum residue limits (MRLs) for imazethapyr in various crops (0.05–0.5 mg/kg) and drinking water (0.1 µg/L) by regulatory agencies reflects these health concerns.

### 5.3. Progress in pollution abatement technologies

#### 5.3.1. Bioremediation

Bioremediation has emerged as a pivotal strategy for mitigating imazethapyr contamination, leveraging microbial degradation and soil microbiome modulation. Tang et al. (2024) demonstrated the efficacy of *Bacillus marcorestinum* YN1, achieving 88 % degradation efficiency of imazethapyr within 15 days while significantly enhancing soil microbial diversity and functional gene expression related to xenobiotic metabolism. This aligns with findings by Cheng et al. (2023), who reported that cow dung-corn stover organic fertilizer augmented imazethapyr degradation by 30 % through enriching *Proteobacteria* and *Actinobacteria* populations, which are associated with herbicide metabolism, while simultaneously improving soil nutrient dynamics (e.g., organic carbon and nitrogen cycling). Further advancements include the isolation of *Brevibacterium* sp. IM9601 by Xu et al. (2024), which achieved 90.08 % degradation efficiency under response surface-optimized conditions (pH 7.2, 30 °C, 1.5 % inoculum). This strain's enzymatic machinery, particularly cytochrome P450 monooxygenases, enables rapid cleavage of imidazolinone rings, a critical step in detoxification.

#### 5.3.2. Physicochemical remediation

Physicochemical methods offer rapid and scalable solutions for imazethapyr removal, particularly in heterogeneous soil and aquatic environments. Kaur and Kaur (2020) pioneered the use of low molecular weight chitosan-β-cyclodextrin biocomposites (LCD) synthesized via ultrasound, achieving 59.42–99.44 % herbicide removal efficiency depending on soil texture and organic matter content. Adsorption mechanisms involve electrostatic interactions and hydrogen bonding between LCD's functional groups and imazethapyr's polar moieties. Nanomaterial-based strategies have also gained traction: Ag-C<sub>3</sub>N<sub>4</sub> photocatalysts degrade 95 % of imazethapyr within 2 h under visible light by generating hydroxyl radicals (•OH), while persulfate activation in alkaline soils (pH > 8) achieves 85–90 % efficiency via sulfate radical (SO<sub>4</sub>•<sup>-</sup>) oxidation (Kaur and Kaur, 2024). Membrane technologies modified with TiO<sub>2</sub> nanoparticles exhibit >90 % removal in aqueous systems through size exclusion and hydrophobic interactions. Despite their efficiency, these physicochemical strategies raise concerns regarding nanoparticle leaching, high energy consumption, and secondary pollution, particularly in poorly buffered soils or aquatic habitats.

#### 5.3.3. Co-remediation strategies

Synergistic approaches combining biological and physicochemical methods have shown superior performance in imazethapyr management. A landmark study by Miao et al. (2025) immobilized *Bacillus cereus* MZ-1 on corn stover biochar, achieving 79.85 % removal efficiency while reducing phytotoxicity to oilseed rape (*Brassica napus*). The biochar carrier enhanced bacterial viability by 40 % through pH buffering and nutrient retention, illustrating the dual role of adsorption and biodegradation. Similarly, β-cyclodextrin-chitosan composites coupled with *Pseudomonas* sp. accelerated degradation kinetics by 2.5-fold compared to standalone treatments, attributed to microbial utilization of chitosan-derived oligosaccharides as growth substrates (Kaur and Kaur, 2020).

## 6. Comparative analysis of four herbicides behavior and remediation strategies

### 6.1. Environmental modulators of herbicide fate and remediation efficiency

The fate and remediation performance of long-residual herbicides are influenced not only by their molecular structures but also by intricate interactions with environmental variables, such as soil texture, organic matter content, pH, redox potential, and climatic conditions. For example, fine-textured soils with high clay and organic carbon content often enhance herbicide sorption, thereby reducing bioavailability while simultaneously limiting mobility and microbial access. In contrast, sandy or low-organic soils may increase leaching risks and reduce retention time for degradation. In addition to abiotic variables, plant species identity also modulates rhizosphere degradation potential. Leguminous crops such as *Medicago sativa* can enhance microbial recruitment and enzymatic activity through root-secreted flavonoids and organic acids, particularly enriching degraders like *Pseudomonas* and *Arthrobacter* (Jiang et al., 2023). The success of co-remediation approaches is therefore highly context-dependent, necessitating site-specific evaluations.

In addition to modulating microbial enzyme activity, fertilization practices may facilitate complex interactions within the rhizosphere, especially in the context of nutrient competition. High levels of nitrogen or phosphorus inputs can alter microbial community dynamics by promoting fast-growing copiotrophic taxa while inhibiting specialized degraders, thereby inducing antagonistic effects that diminish bioremediation efficiency (Geisseler and Scow, 2014). Conversely, moderate nutrient availability may foster synergistic interactions by supporting both plant growth and microbial metabolism, thereby enhancing root exudation and microbial enzyme induction. These nutrient-mediated interactions often vary across soil types and climatic regimes, influencing herbicide persistence and mobility. For instance, in coarse-textured soils or under high rainfall, nutrient leaching may indirectly suppress microbial activity and herbicide degradation (Huang et al., 2014). Therefore, comprehending nutrient-microbe-plant feedbacks under diverse fertilization scenarios is essential for refining rhizosphere-driven remediation strategies.

These plant-soil interactions also modulate herbicide behavior in distinct compound-specific ways across soil-climatic gradients. Atrazine, due to its moderate sorption and chemical persistence, accumulates more readily in low-organic, high-rainfall soils, where microbial activity may be delayed due to nutrient saturation or altered root exudation profiles. Nicosulfuron is more readily degraded, yet its transformation is sensitive to soil pH and microbiome composition, which can be destabilized in intensively farmed systems. Fomesafen's strong affinity for organic matter makes it more stable in clay-rich soils, yet its phytotoxicity may increase in root zones with reduced aeration. Imazethapyr exhibits high mobility in alkaline, sandy soils with low cation exchange capacity, making its leaching more likely under irrigation or rainfall events, especially when root nodulation is impaired.

Furthermore, the intensity of agricultural practices, including tillage, cropping systems, and fertilizer application, can indirectly affect herbicide persistence and toxicity by modifying soil structure, rhizodeposition patterns, and microbial community resilience. These effects are additionally modulated by climatic factors; for instance, atrazine photolysis predominates in low-latitude regions, whereas microbial degradation is significantly reduced under temperate conditions, thereby enhancing carry-over effects and toxicity to non-target organisms. Consequently, a systems-level understanding of how biotic and abiotic stressors converge on herbicide fate is critical for achieving effective field remediation (Kaur and Kaur, 2022).

It is noticed that a variety of tools are available for predicting the environmental transport and impacts of herbicides. Recent advances in predictive modeling, such as machine learning (e.g., Random Forests,

Generalized Boosted Regression) and chemometric approaches (e.g., Partial Least Squares regression), offer promising tools to integrate these multifactorial interactions for real-time of herbicide transport and persistence. For instance, binomial-gamma hurdle models and LASSO regression models have demonstrated high accuracy in detecting atrazine concentrations in water by taking into account soil properties and spatial autocorrelation (Beaulieu et al., 2020). Similarly, ensemble methods like Boosted Regression Trees can handle non-linear relationships between atrazine degradation rates and edaphic-climatic variables, enabling dynamic risk assessments across heterogeneous landscapes. Future frameworks could leverage such tools to optimize remediation strategies by predicting metabolite mobility and long-term residue accumulation under varying agricultural practices.

6.2. Cross-herbicide comparison of key properties and risks

The four herbicides reviewed—atrazine, nicosulfuron, fomesafen, and imazethapyr—share long-residual characteristics but differ significantly in environmental behavior, toxicity, and treatment responsiveness. As shown in Table 4, they exhibit moderate-to-high persistence ( $DT_{50}$  = 35–150 days), but diverge in leaching potential, metabolite types and their risk profiles, and sorption behavior. Atrazine and imazethapyr are relatively mobile in aqueous environments, while fomesafen tends to sorb tightly to soil particles, reducing leaching but prolonging residue retention. These comparative traits inform compound-specific remediation approaches and highlight the need for metabolite-focused toxicity monitoring and regulatory evaluation across diverse environmental settings.

In terms of ecotoxicity, atrazine poses considerable risks to aquatic organisms, while nicosulfuron and imazethapyr primarily affect rhizosphere microbes and sensitive crops. Increasing evidence shows that certain metabolites of long-residual herbicides can exhibit higher toxicity, mobility, and persistence than their parent compounds. For instance, DACT (from atrazine) and ADMP (from nicosulfuron) are more water-soluble, increasing the risk of groundwater leaching and long-distance transport. Hydroxyatrazine, though less acutely toxic, demonstrates high persistence in soil–water matrices. These metabolites may also bioaccumulate in aquatic food webs, particularly under continuous herbicide application or in irrigation-intensive regions. However, current data on bioaccumulation factors, biomagnification, and chronic endocrine effects remain sparse.

Beyond environmental persistence, metabolites of herbicides also pose potential risks through bioaccumulation and trophic transfer in food chains. Due to their increased water solubility and membrane permeability, metabolites such as DACT and ADMP can be absorbed by aquatic invertebrates, benthic organisms, and even crop root systems, entering food webs through irrigation or sediment contact.

However, systematic studies on bioaccumulation factors (BAFs), bioconcentration factors (BCFs), and biomagnification across trophic

levels remain scarce. Most available data focus on acute toxicity endpoints, while chronic low-dose exposure via drinking water or contaminated produce—especially in regions with intensive herbicide use—remains under-investigated. These data gaps hinder the implementation of science-based regulatory thresholds. To address this, multi-trophic bioaccumulation models, coupled with targeted metabolite monitoring in agricultural products, are urgently needed. High-resolution tools such as metabolomics and stable isotope tracing may support better risk evaluation of herbicide-derived residues in food systems. Furthermore, Regulatory frameworks (e.g., EPA, EFSA) often lack compound-specific guidance values for metabolites, creating blind spots in exposure monitoring. Future risk assessments must address this gap through dedicated studies and international harmonization of metabolite monitoring protocols.

6.3. Strengths and limitations of remediation technologies

Different remediation strategies offer distinct advantages and constraints, shaped by environmental conditions and compound properties. Bioremediation is low-cost, sustainable, and suitable for in situ applications in biologically active soils. It excels in rhizosphere-rich systems, particularly under neutral to slightly alkaline pH and moderate temperature conditions (25–35 °C), which support optimal microbial metabolism and enzyme activity. However, it performs poorly in nutrient-depleted, saline, or acidic soils, where microbial viability and catabolic gene expression are often suppressed. Low redox potential (e.g., waterlogged fields) may also limit oxygen-dependent degradation pathways.

Physicochemical techniques—including photocatalysis, persulfate oxidation, and zero-valent iron activation—enable rapid and high-efficiency degradation, especially under well-aerated conditions with sufficient redox potential, which favor oxidative mechanisms. Advanced oxidation processes (AOPs) perform best in environments with neutral to slightly acidic pH, which enhances radical formation and catalyst stability (Héquet et al., 2001). Photocatalysis further requires adequate light intensity and temperature to activate semiconductors like  $TiO_2$ . Nonetheless, such methods may yield toxic byproducts under certain soil chemistries, necessitating careful environmental matching (Wei, 2023).

Co-remediation systems, such as biochar-immobilized bacteria, enzyme–nanoparticle hybrids, or plant-assisted consortia, integrate the strengths of both biological and physicochemical mechanisms. These systems are particularly attractive in heterogeneous field conditions, where environmental parameters may fluctuate. For instance, enzyme–nano hybrids can maintain catalytic activity across a wider pH and temperature range than free enzymes, while biochar matrices buffer soil pH and enhance microbial colonization in otherwise suboptimal soil. Their multifunctional nature allows for greater flexibility, but robust site-specific assessments are still required for performance prediction.

Despite the conceptual appeal of co-remediation strategies—which

**Table 4**  
Comparative overview of four long-residual herbicides.

Herbicide	$DT_{50}$ (soil)	Koc (mL/g)	Leaching risk	Ecotoxicity profile	Key metabolites & risk	Effective remediation strategies	Bibliography
Atrazine	35–50 d	~100	High	High (RQs > 1 in aquatic species; chronic effects)	DEA, DIA, DACT, HA (toxic, persistent)	Bioremediation, biochar adsorption	(Ralston-Hooper et al., 2009)
Nicosulfuron	15–200 d	<20	High	Low-moderate (algae, aquatic invertebrates, soil microbes, sensitive crops)	ASDM, ADMP (higher, more mobile, cytotoxic)	Biochar-assisted biodegradation	(Zhong et al., 2023)
Fomesafen	60–120 d	60–1467	Low-medium	Moderate (soil enzymes affected, aquatic low risk)	FHBA (low risk, persistent)	Photocatalysis, phytoremediation	(Wang et al., 2025)
Imazethapyr	30–120 d	~150	Medium	Medium (soil microbial shifts, aquatic algae)	OH-imazethapyr (persistent)	Bioremediation, co-remediation	(Liu et al., 2024)

Note: Toxicity ranking based on current studies; regulatory thresholds may not fully reflect metabolite-specific risks; HA is hydroxyatrazine, DACT is diamino-chlorotriazine, ASDM is 2-aminosulfonyl-N,N-dimethylnicotinamide, ADMP is 2-amino-4,6-dimethoxypyrimidine, FHBA is 2-(2-fluoro-4-hydroxyphenyl)butanoic acid.

integrate microbial activity with abiotic techniques such as photocatalysis, adsorption, or oxidation—their functional interactions under field conditions remain insufficiently characterized. Evidence suggests that synergistic effects can emerge when abiotic processes increase pollutant bioavailability (e.g., via desorption or oxidative cleavage), thereby enhancing microbial access and enzymatic degradation. For instance, biochar amendment not only provides sorption sites but also buffers pH and supplies microbial habitats, boosting bacterial survival and herbicide breakdown.

However, antagonistic interactions are also possible. Some oxidants (e.g., sulfate radicals from persulfate) may damage cell membranes or denature microbial enzymes, reducing biodegradation capacity. Similarly, metal leaching from nanomaterials can alter microbial diversity or suppress sensitive strains. In saline, nutrient-poor, or extreme pH environments, abiotic agents may exacerbate stress, further limiting biological activity. Therefore, co-remediation system design must consider material compatibility, application timing, and soil biological status, ideally validated through field-scale pilot studies. Future research should incorporate multi-factorial assessments of microbial viability, pollutant transformation pathways, and long-term soil functional recovery in co-treatment contexts.

#### 6.4. Agrochemical co-exposure: an overlooked constraint in field remediation

The stability and effectiveness of herbicide remediation systems in real-world agricultural soils are increasingly influenced by the simultaneous presence of other agrochemicals, such as fertilizers (e.g., urea, phosphate) and residual pesticides. These co-applied inputs can interact at multiple levels—within the spray tank, on plant surfaces, and most critically, in the soil—leading to physicochemical interference, shifts in microbial community composition, and modulation of degradative pathways. Such interactions may yield additive, synergistic, or more commonly, antagonistic outcomes, posing significant challenges to the predictability and robustness of biotic and abiotic remediation strategies. Among these, nitrogen and phosphorus fertilizers have been reported to suppress key microbial degradation pathways by altering enzyme synthesis or diverting microbial metabolism away from xenobiotic transformation toward resource acquisition. In contrast, certain organic amendments such as composted manure or green manure have demonstrated the ability to enhance microbial resilience and functional diversity, potentially accelerating herbicide breakdown indirectly. Likewise, co-occurrence of multiple pesticide residues—either from prior applications or through runoff—may induce competitive substrate inhibition, increase oxidative stress, or inhibit horizontal gene transfer, collectively reducing the functional capacity of degradation consortia. Notably, herbicide–herbicide antagonism has been more frequently observed than synergism, emphasizing the compound-specific and highly context-dependent nature of these interactions (Barbieri et al., 2023).

To improve field applicability and ensure ecological safety, future research should adopt experimental frameworks that simulate realistic multi-chemical exposure scenarios. This includes tracking dynamic interactions across different soil types, climatic regimes, and cropping systems, while using integrated endpoints such as enzyme activity, microbial functional genes, and compound-specific degradation rates. Regulatory assessments should also move beyond single-compound ecotoxicology to embrace mixture-based evaluations, in line with the environmental complexity encountered in actual remediation sites.

#### 6.5. Evidence quality and critical appraisal in comparative analysis

One critical limitation in drawing cross-study comparisons lies in the uneven quality of the existing evidence. In this review, we adopted a simplified evidence appraisal approach to reflect differences in study design, scale, and methodological transparency. Studies conducted

under real-world conditions—such as multi-site field trials, long-term monitoring programs, and meta-analyses—were treated as high-confidence sources. In contrast, conclusions based on laboratory simulations, un-replicated experiments, or insufficiently described methods were interpreted more cautiously. This differentiation allowed for a more nuanced comparative synthesis in Sections 6.1–6.4, where trends were highlighted only when supported by consistent, well-documented evidence.

Moreover, methodological heterogeneity across the literature, including differences in degradation metrics, soil types, microbial inoculum formulations, and exposure durations, further complicates robust cross-study comparisons. The adoption of standardized reporting practices and clearer distinctions between experimental reliability levels would substantially enhance future reviews and evidence integration. Strengthening these aspects is essential not only for improved scientific synthesis but also for guiding evidence-based recommendations in policy and land management.

In summary, while a substantial body of research has advanced our understanding of long-residual herbicide behavior and remediation, the heterogeneity in study quality and methodological rigor presents a key limitation to drawing universally applicable conclusions. Recognizing and accounting for this variability is crucial to avoid overgeneralization and to support more targeted, evidence-informed remediation strategies. This insight also underscores the urgent need to move beyond laboratory-based efficacy reports toward addressing the practical barriers that constrain large-scale implementation. Accordingly, the following chapter shifts focus to these real-world challenges, emphasizing economic feasibility, technological readiness, and the need for more integrative, resilience-based frameworks.

### 7. Challenges, systemic risks, and future directions in herbicide remediation

Despite the progress in understanding the environmental fate and remediation of long-residual herbicides, significant challenges remain in translating laboratory findings into field-scale applications. Complex soil heterogeneity, variable climatic conditions, and the co-occurrence of multiple agrochemicals often compromise the consistency and effectiveness of current remediation strategies. Moreover, ecological and human health risk assessments are still limited by narrow scopes and outdated models that fail to capture chronic, system-level impacts.

This chapter critically examines the major technical and practical barriers to large-scale remediation (Section 7.1), and evaluates emerging tools—economic and technological—that can enhance operational feasibility and monitoring efficiency (Section 7.2). We further argue for a paradigm shift toward resilience-based, integrated risk assessment frameworks that account for microbial dynamics and environmental complexity (Section 7.3). The potential and constraints of genetically engineered microbial systems are also explored as promising yet debated innovations (Section 7.4). In addition, we highlight how fragmented analyses and the lack of unified evaluation frameworks hinder knowledge integration and comparative assessment in herbicide research (Section 7.5). Finally, the chapter concludes by outlining specific research priorities that will be essential for developing robust, scalable, and sustainable remediation strategies moving forward (Section 7.6).

#### 7.1. Current barriers to field-scale application

While extensive progress has been made in elucidating the environmental behavior and remediation strategies of four long-residual herbicides—atrazine, nicosulfuron, fomesafen, and imazethapyr—several critical limitations continue to impede their effective management at the field scale. A large proportion of current research remains confined to laboratory conditions, where environmental variables such as soil heterogeneity, fluctuating moisture regimes, and

microbial community dynamics are either controlled or oversimplified. These studies often lack sufficient replication, error analysis, or standardized performance metrics, resulting in inconsistent data and reduced comparability across experiments.

Moreover, the diversity of soil types, initial contaminant concentrations, and experimental protocols across studies hampers the identification of robust and transferable remediation solutions. Cross-study comparisons are further complicated by the limited use of formal evidence evaluation frameworks (e.g., GRADE), and systematic assessments across different herbicides or treatment conditions are still rare. This has led to a fragmented evidence base with poor external validity and limited guidance for field-scale implementation.

An additional constraint lies in the narrow scope of many studies, which primarily focus on the parent herbicides while neglecting their transformation products. Notably, only a small fraction—less than 15 %—of the reviewed literature examines metabolite behavior under field conditions. Yet, metabolites such as diaminochlorotriazine (from atrazine) and ADMP (from nicosulfuron) are known to exhibit greater persistence and higher groundwater mobility than their parent compounds. Despite their toxicological relevance, ecotoxicity data for these metabolites remain scarce, limiting the reliability of current ecological risk assessments and potentially underestimating long-term risks to non-target organisms.

To bridge these gaps, future work must prioritize the inclusion of metabolite monitoring and toxicity profiling within field trials. Establishing a more comparative, evidence-based, and application-driven research paradigm will be critical for developing environmentally sustainable and scalable remediation strategies.

## 7.2. Enhancing practical feasibility through economic assessment and monitoring tools

While numerous biotic and abiotic remediation strategies have demonstrated promising results at laboratory or pilot scale, their field applicability remains constrained by practical considerations such as cost-effectiveness, process monitoring, and mechanistic resolution. Most current studies focus on removal efficiency under controlled conditions, often overlooking the economic and operational feasibility of scaling these interventions in diverse agricultural settings.

Bioremediation technologies (e.g., microbial community application, bioaugmentation) frequently exhibit a cost-effectiveness that is largely attributable to their site-specific deployment. The avoidance of excavation and energy-intensive treatment processes results in cost savings, while concurrently enhancing biodiversity and reducing carbon emissions. However, it should be noted that input costs encompass a variety of expenses, including the preparation of microbial cultures, the potential addition of nutrients, and the ongoing monitoring of the process. Furthermore, their remediation performance may be diminished in nutrient-poor soils, which are characterized by a scarcity of essential nutrients. In contrast, physicochemical methods (e.g., advanced oxidation processes, zero-valent iron, photocatalysis) typically achieve high removal efficiencies, but tend to be more energy intensive. These methods may require specialized equipment and a continuous supply of reagents. The cost-benefit ratio is contingent upon the scale of the treatment. On-site applications generally entail higher capital expenditure and operating expenditure. Key constraints include the durability of the catalyst, energy costs, and the control of toxic by-products. Conversely, co-remediation remediation systems (e.g., biochar-microbial cascade, enzyme-nanoparticle hybridization technologies) are classified as mid-cost. While the integration of multiple technologies may result in increased initial capital expenditures, it can also lead to substantial improvements in the stability of field applications and the breadth of their applicability. For instance, the production of biochar can incur costs ranging from approximately \$51 to \$386/ton (Fang et al., 2025). The primary expenses associated with such systems encompass the procurement of feedstock, pyrolytic carbonization,

biochar functionalization, microbial immobilization, and long-term performance monitoring.

Cost-benefit analyses are rarely integrated into remediation research, yet are essential for determining the viability of technologies in resource-limited or large-scale contexts. Factors such as input cost (e.g., amendments, microbial consortia), labor, infrastructure, and post-remediation land usability should be systematically assessed and compared across strategies. Without such evaluation, even highly efficient methods may remain academically promising but practically unadoptable.

Advanced characterization tools—such as metagenomics, stable isotope probing (SIP), and high-resolution mass spectrometry (HRMS)—can deepen our understanding of microbial community shifts, metabolic pathways, and degradation intermediates. For example, metagenomic sequencing allows for the identification of degradative gene clusters and keystone taxa involved in herbicide breakdown, even under complex environmental backgrounds. SIP enables the direct tracking of labeled herbicide-derived carbon or nitrogen through microbial food webs, revealing active degraders in situ (Malla et al., 2022). HRMS, when combined with non-target screening, can uncover previously uncharacterized transformation products and metabolic bottlenecks. These technologies not only support mechanistic understanding, but also enhance process monitoring and optimization—especially when embedded into adaptive remediation frameworks. However, their application in herbicide-contaminated agricultural systems remains sporadic, with limited integration into field-scale monitoring or feedback-controlled management. Future efforts should focus on combining these tools with real-time environmental data (e.g., soil redox, enzyme activity, metabolite flux) to develop dynamic remediation protocols and early-warning systems for functional failure or rebound contamination.

To ensure field reliability, real-time and portable monitoring tools such as biosensors, smartphone-based detectors, and wireless soil probes could be integrated to track remediation progress and detect residual contaminants and microbial activity. Such innovations not only enhance process transparency but also support adaptive management, especially under fluctuating environmental conditions. Moving forward, coupling these advanced analytical and monitoring platforms with economic evaluation will be crucial for translating laboratory findings into practical, scalable, and regulatory-compliant remediation systems.

## 7.3. Toward resilient and integrated risk assessment frameworks

As agricultural herbicide application is often seasonal and recurrent, effective risk assessment frameworks must extend beyond short-term exposure snapshots to account for the resilience and stability of microbial and ecological systems involved in natural attenuation. Prolonged or repeated herbicide inputs can disrupt microbial community composition, reduce functional redundancy, and impair long-term degradation capacity. These ecological shifts, though subtle, can lead to cumulative ecosystem dysfunction—particularly in soils with low buffering capacity or under intensive monoculture systems.

In this context, ecological resilience—defined as a system's ability to resist, adapt to, or recover from chemical stress—should be considered a core component of bioremediation performance and risk modeling. Incorporating resilience-related metrics such as microbial diversity, keystone degrader persistence, or enzymatic recovery trajectories can enhance the predictive power and long-term relevance of risk assessments.

Moreover, conventional risk assessments often focus narrowly on single-chemical toxicity or endpoint concentrations, which may not capture the full spectrum of ecological and human health risks associated with long-residual herbicides. Yet, studies show that herbicide residues can persist across seasons, influencing microbial succession and nutrient cycling. Additionally, the toxicological relevance of herbicide metabolites—such as DACT and aminomethylphosphonic acid



(AMPA)—is receiving increased attention due to their greater persistence, mobility, and in some cases, higher toxicity compared to parent compounds. However, systematic studies on their bioaccumulation, chronic toxicity, and trophic transfer remain scarce. Most available data focus on acute endpoints, while long-term low-dose exposures via drinking water or food crops are poorly characterized. Regulatory frameworks, including those of the EPA and EFSA, often lack compound-specific guideline values for key metabolites, leaving important blind spots in environmental and food safety monitoring.

To address these gaps, future risk assessments must integrate metabolite-specific monitoring, multi-trophic bioaccumulation modeling, and high-resolution analytical tools—such as metabolomics, isotope tracing, and ecological network analysis—to improve mechanistic understanding and predictive capability. These components should not operate in isolation, but rather be incorporated into a unified systems-based risk assessment framework that captures chronic exposure patterns, mixture effects, non-target responses, and site-specific ecological thresholds. Only through such integrative approaches can we develop resilient and scalable strategies to manage the long-term ecological and health risks posed by herbicide residues and their transformation products.

#### 7.4. Technical and ecological challenges in GEMs deployment under field conditions

The application of genetically engineered microorganisms (GEMs) and synthetic enzymes represents a promising direction for enhancing the degradation efficiency of persistent herbicides, especially those with recalcitrant chemical structures. Advances in synthetic biology and omics technologies have enabled the tailoring of microbial strains to express specific degradative pathways or enhance co-metabolic capacity, targeting herbicides such as atrazine, sulfonylureas, and imidazolinones (He et al., 2022).

Nevertheless, the field application of GEMs faces significant technical, ecological, and regulatory hurdles. Concerns include the ecological fitness of engineered strains in open environments, horizontal gene transfer, and unintended impacts on native microbial communities and ecosystem functions. Additionally, stringent biosafety regulations in many countries limit the use of GEMs outside contained systems. Similar concerns extend to engineered enzymes, which may require stabilization strategies (e.g., immobilization or encapsulation) to function effectively under variable field conditions.

To balance innovation with safety, future research should explore hybrid approaches, such as bioaugmentation with semi-engineered consortia, or gene-editing of native degraders to minimize ecological disruption. Integrated risk-benefit assessments and environmental fate modeling of GEMs are also essential before field-level adoption. While the technological potential is undeniable, widespread use of engineered solutions in herbicide remediation will depend on both scientific progress and regulatory evolution.

#### 7.5. Fragmented analysis in herbicide research and lack of unified frameworks

A major limitation in current herbicide remediation research lies in the fragmented, compound-specific approach. Most studies isolate each herbicide as an independent entity, overlooking shared environmental behaviors, toxicity profiles, and treatment mechanisms. This prevents the development of generalizable remediation frameworks applicable to multi-contaminant systems, which are common in modern agriculture.

Although comparative traits exist—such as metabolite persistence or microbial responsiveness—they are rarely leveraged in remediation design. To improve knowledge transfer and practical deployment, future research should adopt cross-compound experimental designs and unified evaluation matrices.

#### 7.6. Research priorities

Based on the limitations discussed above, we propose the following prioritized directions to guide future work:

- (1) Strengthen field-based validation of remediation strategies, with systematic consideration of site heterogeneity, cost-effectiveness, and operational scalability under real-world conditions.
- (2) Design and optimize adaptable co-remediation systems that address co-contamination scenarios and demonstrate stability across varying soil types and climates.
- (3) Develop integrative ecological and health risk assessment frameworks that link herbicide fate, microbial shifts, and biomarker-based responses across exposure levels.
- (4) Establish standardized protocols and evidence grading systems to enhance the comparability, reproducibility, and synthesis of herbicide remediation studies.
- (5) Extend cross-compound analytical frameworks to enable transferable remediation designs based on shared properties, transformation pathways, and risk profiles.

These priorities highlight the urgent need for interdisciplinary, implementation-oriented, and data-harmonized research to ensure herbicide pollution management aligns with long-term environmental and agricultural sustainability goals.

#### 8. Conclusion

Atrazine, nicosulfuron, fomesafen, and imazethapyr are four frequently utilized long-residual herbicides in agricultural production, which play a crucial role in enhancing crop yields and reducing labor costs. However, their persistence and potential ecological risks in soils and water bodies present significant challenges to environmental quality and human health. Although progress has been made in current technologies for managing their pollution, substantial research gaps remain in the optimization of combined remediation strategies, metabolite toxicity assessments, and long-term risk evaluations. In the future, it will be essential to refine the pollution abatement technology system and establish a comprehensive, scientific risk assessment framework through multidisciplinary collaboration, thereby achieving efficient management of long-residual herbicides and promoting the sustainable development of agroecosystems.

#### CRediT authorship contribution statement

**Jiawen Li:** Writing – original draft, Visualization, Investigation, Data curation. **Haiyan Huang:** Investigation, Data curation. **Yong Yang:** Methodology. **Caixia Wang:** Funding acquisition. **Qingming Zhang:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to invent the work reported in this paper.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (32372593) and Shandong Province Modern Agricultural Industry Technology System (SDAIT-30-06).

#### Data availability

Data will be made available on request.

## References

- Ahmadi, A.R., Shahbazi, S., Diyanat, M., 2017. Analysis of nicosulfuron residues in maize field soil by high-performance liquid chromatography. *Qual. Assur. Saf. Crop.* 9 (2), 229–235.
- Barbieri, G.F., Young, B.G., Dayan, F.E., Streibig, J.C., Takano, H.K., Merotto Jr., A., Avila, L.A., 2023. Herbicide mixtures: interactions and modeling. *Adv. Weed Sci.* 40, e020220051.
- Beaulieu, M., Cabana, H., Taranu, Z., Huot, Y., 2020. Predicting atrazine concentrations in waterbodies across the contiguous united states: the importance of land use, hydrology, and water physicochemistry. *Limnol. Oceanogr.* 65 (12), 2966–2983.
- Brazier-Hicks, M., Franco-Ortega, S., Watson, P., Rougemont, B., Cohn, J., Dale, R., Hawkes, T.R., Goldberg-Cavalleri, A., Onkokesung, N., Edwards, R., 2022. Characterization of cytochrome P450s with key roles in determining herbicide selectivity in maize. *ACS Omega* 7 (20), 17416–17431.
- Chen, L., Hu, X., Yang, Y., Jiang, C., Bian, C., Liu, C., Zhang, M., Cai, T., 2018. Degradation of atrazine and structurally related s-triazine herbicides in soils by ferrous-activated persulfate: kinetics, mechanisms and soil-types effects. *Chem. Eng. J.* 351, 523–531.
- Chen, W., Li, Y., Shi, G., Fan, G., Tong, F., Liu, L., Li, J., Gao, Y., 2025. The role of symbiotic nitrogen-fixing bacteria, *Rhizobium* and *Sinorhizobium*, as “bridges” in the rhizosphere of legumes after fomesafen application. *Appl. Soil Ecol.* 209, 106013.
- Chen, Y., Zhen, Z., Wu, W., Yang, C., Yang, G., Li, X., Li, Q., Zhong, X., Yin, J., Lin, Z., Zhang, D., 2024. Biochar modification accelerates soil atrazine biodegradation by altering bacterial communities, degradation-related genes and metabolic pathways. *J. Hazard. Mater.* 479, 135693.
- Cheng, L., Wang, L., Wang, X., Ou, Y., Liu, H., Hou, X., Yan, L., Li, X., 2023. The various effect of cow manure compost on the degradation of imazethapyr in different soil types. *Chemosphere* 337, 139325.
- Cheng, M., Zeng, G., Huang, D., Lai, C., Xu, P., Zhang, C., Liu, Y., Wan, J., Gong, X., Zhu, Y., 2016. Degradation of atrazine by a novel fenton-like process and assessment the influence on the treated soil. *J. Hazard. Mater.* 312, 184–191.
- Cheng, S.H., Yu, C.H., Xue, M.M., Wang, X.J., Chen, L.P., Nie, D.X., Zhang, N., Zhang, J., Hou, Y.H., Lin, R.H., 2022. Toxicity and risk assessment of nine pesticides on nontarget natural predator *Harmonia axyridis* (Coleoptera: Coccinellidae). *Pest Manag. Sci.* 78 (12), 5124–5132.
- Cheron, M., Costantini, D., Brischoux, F., 2022. Nicosulfuron, a sulfonylurea herbicide, alters embryonic development and oxidative status of hatchlings at environmental concentrations in an amphibian species. *Ecotoxicol. Environ. Saf.* 232, 113277.
- Cobucci, T., Prates, H.T., Falcão, C.L., Rezende, M.M., 1998. Effect of imazamox, fomesafen, and acifluorfen soil residue on rotational crops. *Weed Sci.* 46 (2), 258–263.
- Costa, G., Fernandes, A., Santos, T., Brito, L., Rodrigues, L., Valadares, M., Felzenszwalb, I., Ferraz, E., Morais Leme, D., Oliveira, G., 2022. *In vitro* and *in vivo* cytotoxicity assessment of glyphosate and imazethapyr-based herbicides and their association. *J. Toxicol. Environ. Health A* 85 (12), 481–493.
- Cui, N., Wang, S., Khorram, M.S., Fang, H., Yu, Y., 2018. Microbial degradation of fomesafen and detoxification of fomesafen-contaminated soil by the newly isolated strain *Bacillus* sp. FE-1 via a proposed biochemical degradation pathway. *Sci. Total Environ.* 616, 1612–1619.
- Dantas, Á.d.O.S., Rocha, A.C.d., Cardoso, V.L., Vieira, P.A., 2024. A review of approaches to atrazine treatment employing advanced oxidation processes technologies. *Eng. Sanit. Ambient.* 29, e20230021.
- DeLorenzo, M.E., Scott, G.L., Ross, P.E., 2001. Toxicity of pesticides to aquatic microorganisms: a review. *Environ. Toxicol. Chem.* 20 (1), 84–98.
- El Sebai, T., Devers-Lamrani, M., Changey, F., Rouard, N., Martin-Laurent, F., 2011. Evidence of atrazine mineralization in a soil from the Nile delta: isolation of *Arthrobacter* sp. Tes6, an atrazine-degrading strain. *Int. Biodeterior. Biodegrad.* 65 (8), 1249–1255.
- Fang, H., Zhou, C., Guan, D.X., Azeem, M., Li, G., 2025. Synergistic approaches for sustainable remediation of organic contaminated soils: integrating biochar and phytoremediation. *Agriculture* 15 (8), 905.
- Fazlurrahman, Batra, M., Pandey, J., Suri, C.R., Jain, R.K., 2009. Isolation and characterization of an atrazine-degrading *Rhodococcus* sp. strain MB-P1 from contaminated soil. *Lett. Appl. Microbiol.* 49 (6), 721–729.
- Filimon, M.N., Vlad, D.C., Verdes, D., Popescu, R., 2015. Enzymatic and biological assessment of sulfonylurea herbicide impact on soil bacterial communities. *Afr. J. Agric. Res.* 10 (14), 1702–1708.
- Fowlkes, M.D., Michael, J.L., Crisman, T.L., Prenger, J.P., 2003. Effects of the herbicide imazapyr on benthic macroinvertebrates in a logged pond cypress dome. *Environ. Toxicol. Chem.* 22 (4), 900–907.
- Gagneten, A.M., Regalado, L., Carriquiriborde, P., Reno, U., Kergaravat, S.V., Butinof, M., Agostini, H., Alvarez, M., Harte, A., 2023. Atrazine characterization: an update on uses, monitoring, effects, and environmental impact, for the development of regulatory policies in Argentina. *Integr. Environ. Assess. Manag.* 19 (3), 684–697.
- Geisseler, D., Scow, K.M., 2014. Long-term effects of mineral fertilizers on soil microorganisms—a review. *Soil Biol. Biochem.* 75, 54–63.
- Grey, T.L., McCullough, P.E., 2012. Sulfonylurea herbicides' fate in soil: dissipation, mobility, and other processes. *Weed Technol.* 26 (3), 579–581.
- He, B., Hu, Y., Wang, W., Yan, W., Ye, Y., 2022. The progress towards novel herbicide modes of action and targeted herbicide development. *Agronomy* 12 (11), 2792.
- Héquet, V., Gonzalez, C., Le Cloirec, P., 2001. Photochemical processes for atrazine degradation: methodological approach. *Water Res.* 35 (18), 4253–4260.
- Hu, J., Dai, X., Li, S., 2005. Effects of atrazine and its degrader *Exiguobacterium* sp. BTAH1 on soil microbial community. *J. Appl. Ecol.* 16 (8), 1518–1522.
- Huang, J., Bao, M., Li, J., Chen, H., Xu, D., Chen, Z., Wen, Y., 2022a. Enantioselective response of wheat seedlings to imazethapyr: from the perspective of Fe and the secondary metabolite DIMBOA. *J. Agric. Food Chem.* 70 (18), 5516–5525.
- Huang, X., Yang, X., Lin, J., Franks, A.E., Cheng, J., Zhu, Y., Shi, J., Xu, J., Yuan, M., Fu, X., 2022b. Biochar alleviated the toxicity of atrazine to soybeans, as revealed by soil microbial community and the assembly process. *Sci. Total Environ.* 834, 155261.
- Huang, X.F., Chaparro, J.M., Reardon, K.F., Zhang, R., Shen, Q., Vivanco, J.M., 2014. Rhizosphere interactions: root exudates, microbes, and microbial communities. *Botany* 92 (4), 267–275.
- Huang, Y., Han, C., Liu, Y., Nadagouda, M.N., Machala, L., O'Shea, K.E., Sharma, V.K., Dionysiou, D.D., 2018. Degradation of atrazine by  $Zn_xCu_{1-x}Fe_2O_4$  nanomaterial-catalyzed sulfite under UV-vis light irradiation: green strategy to generate  $SO_4^{\cdot-}$ . *Appl. Catal. B.* 221, 380–392.
- Jia, J., Xue, P., Ma, L., Li, P., Xu, C., 2024. Deep degradation of atrazine in water using co-immobilized laccase-1-hydroxybenzotriazole-Pd as composite biocatalyst. *J. Hazard. Mater.* 468, 133779.
- Jiang, D., Li, Y., Wang, J., Lv, X., Jiang, Z., Cao, B., Qu, J., Ma, S., Zhang, Y., 2023. Exogenous application of *Bradyrhizobium japonicum* AC20 enhances soybean tolerance to atrazine via regulating rhizosphere soil microbial community and amino acid, carbohydrate metabolism related genes expression. *Plant Physiol. Biochem.* 196, 472–483.
- Jiang, W., Zhai, W., Liu, D., Wang, P., 2021. Coexisting antibiotic changes the persistence and metabolic profile of atrazine in the environment. *Chemosphere* 269, 129333.
- Jumel, A., Coutellec, M.A., Cravedi, J.P., Lagadic, L., 2002. Nonylphenol polyethoxylate adjuvant mitigates the reproductive toxicity of fomesafen on the freshwater snail *Lymnaea stagnalis* in outdoor experimental ponds. *Environ. Toxicol. Chem.* 21 (9), 1876–1888.
- Kaur, L., Kaur, P., 2022. Degradation of imazethapyr in soil: impact of application rate, soil physicochemical properties and temperature. *Int. J. Environ. Sci. Technol.* 19, 1877–1892.
- Kaur, P., Kaur, P., 2020.  $\beta$ -Cyclodextrin-chitosan biocomposites for synergistic removal of imazethapyr and imazamox from soils: fabrication, performance and mechanisms. *Sci. Total Environ.* 710, 135659.
- Kaur, P., Kaur, P., 2024. Insights into adsorption performance and mechanism of chitosan-bentonite biocomposites for removal of imazethapyr and imazamox. *Int. J. Biol. Macromol.* 262 (Pt 1), 129903.
- Laskar, N., Das, K., Kancheti, M., Senthilkumar, M., Kumar, V., Tewari, K., Nath, C.P., 2024. Dissipation kinetics and residue distribution of imazethapyr in urdbean (*Vigna mungo* (L.) Hepper) and urdbean field soil and its effect on soil microbial population. *B. Environ. Contam. Toxicol.* 113 (2), 21.
- Li, D., Liu, Y., Xu, L., Yu, H., Kan, Y., Liu, R., Li, G., 2025. Dichlormid protect wheat from fomesafen residual injury by increasing PPO expression and the photosynthesis characterize. *Ecotoxicol. Environ. Saf.* 289, 117701.
- Li, M., Song, J., Ma, Q., Kong, D., Zhou, Y., Jiang, X., Pares, R., Ruan, Z., Zhang, Q., 2020. Insight into the characteristics and new mechanism of nicosulfuron biodegradation by a *Pseudomonas* sp. LAM1902. *J. Agric. Food Chem.* 68 (3), 826–837.
- Li, R., Hu, W.Y., Liu, H.Q., Huang, B., Jia, Z.J., Liu, F., Zhao, Y.G., Khan, K.S., 2024. Occurrence, distribution and ecological risk assessment of herbicide residues in cropland soils from the Mollisols region of Northeast China. *J. Hazard. Mater.* 465, 133054.
- Liu, L., Chen, Z., Zhang, N., Liu, J., Tian, Z., Sun, C., 2024. Transcriptomic and metabolomic analysis provides insight into imazethapyr toxicity to non-target plants. *Environ. Sci. Pollut. Res. Int.* 31 (19), 28368–28378.
- Liu, W., Zhao, Q., Zhang, Z., Li, Y., Xu, N., Qu, Q., Lu, T., Pan, X., Qian, H., 2020. Enantioselective effects of imazethapyr on *Arabidopsis thaliana* root exudates and rhizosphere microbes. *Sci. Total Environ.* 716, 137121.
- Liu, Y., Ji, X., Yang, J., Tang, W., Zhu, Y., Wang, Y., Zhang, Y., Zhang, Y., Duan, J., Li, W., 2022. Degradation of the typical herbicide atrazine by UV/persulfate: kinetics and mechanisms. *Environ. Sci. Pollut. Res.* 29 (29), 43928–43941.
- Liu, Y., Li, M., Wu, J., Liu, W., Li, Y., Zhao, F., Tan, H., 2023. Characterization and novel pathway of atrazine catabolism by *Agrobacterium rhizogenes* AT13 and its potential for environmental bioremediation. *Chemosphere* 319, 137980.
- Luo, S., Zhen, Z., Zhu, X., Ren, L., Wu, W., Zhang, W., Chen, Y., Zhang, D., Song, Z., Lin, Z., Liang, Y.Q., 2021. Accelerated atrazine degradation and altered metabolic pathways in goat manure assisted soil bioremediation. *Ecotoxicol. Environ. Saf.* 221, 112432.
- Luo, S., Ren, L., Wu, W., Chen, Y., Li, G., Zhang, W., Wei, T., Liang, Y.Q., Zhang, D., Wang, X., Zhen, Z., Lin, Z., 2022. Impacts of earthworm casts on atrazine catabolism and bacterial community structure in laterite soil. *J. Hazard. Mater.* 425, 127778.
- Ma, Q., Jiang, X., Li, Q., Song, J., Zhou, Y., Ruan, Z., 2022. Isolation and identification of nicosulfuron degrading strain *Chryseobacterium* sp. LAM-M5 and study on its degradation pathway. *Biotechnol. Bull.* 38 (2), 113–122.
- Malla, M.A., Dubey, A., Kumar, A., Yadav, S., 2022. Metagenomic analysis displays the potential predictive biodegradation pathways of the persistent pesticides in agricultural soil with a long record of pesticide usage. *Microbiol. Res.* 261, 127081.
- Meng, W., Wang, D.F., Li, S.Z., Wang, Y.Y., Jiang, C., Tian, H.Z., Ji, M.S., 2022. Residual characteristics of atrazine and its metabolites in the Liaoning province of China. *Separations* 9 (12), 397.
- Mesquini, J.A., Sawaya, A., López, B.G.C., Oliveira, V.M., Miyasaka, N.R.S., 2015. Detoxification of atrazine by endophytic *Streptomyces* sp isolated from sugarcane and detection of nontoxic metabolite. *B. Environ. Contam. Toxicol.* 95 (6), 803–809.
- Miao, J., Fan, Q., Li, H., Yang, Y., Zhang, Q., 2025. Combination of the degrading bacterium *Bacillus cereus* MZ-1 and corn straw biochar enhanced the removal of imazethapyr from water solutions. *Next Sustain.* 5, 100077.

- Motamedi, M., Zahedi, M., Karimmojeni, H., Baldwin, T.C., Motamedi, H., 2023. Rhizosphere-associated bacteria as biofertilizers in herbicide-treated alfalfa (*Medicago sativa*). *J. Soil Sci. Plant Nutr.* 23 (2), 2585–2598.
- Mu, Y., Chen, Y., Chen, P., Qin, L., Zou, J.-P., Wu, M., Luo, S.-L., 2021. New insights into the degradation of atrazine by ultraviolet-based techniques. *ACS ES&T Water.* 1 (4), 958–968.
- Omotayo, A.E., Ilori, M.O., Radosevich, M., Amund, O.O., 2013. Metabolism of atrazine in liquid cultures and soil microcosms by *Nocardioides* strains isolated from a contaminated Nigerian agricultural soil. *Soil Sediment Contam.* 22 (4), 365–375.
- Poonia, K., Hasija, V., Singh, P., Parwaz Khan, A.A., Thakur, S., Thakur, V.K., Mukherjee, S., Ahamad, T., Alshehri, S.M., Raizada, P., 2022. Photocatalytic degradation aspects of atrazine in water: enhancement strategies and mechanistic insights. *J. Clean. Prod.* 367, 133087.
- Rai, P.K., Kim, K.H., Lee, S.S., Lee, J.H., 2020. Molecular mechanisms in phytoremediation of environmental contaminants and prospects of engineered transgenic plants/microbes. *Sci. Total Environ.* 705, 135858.
- Ralston-Hooper, K., Hardy, J., Hahn, L., Ochoa-Acuña, H., Lee, L.S., Mollenhauer, R., Sepúlveda, M.S., 2009. Acute and chronic toxicity of atrazine and its metabolites deethylatrazine and deisopropylatrazine on aquatic organisms. *Ecotoxicology* 18, 899–905.
- Rocha, V., Franco, S., Bertão, A.R., Neves, I.C., Tavares, T., 2024. Recycling of natural and waste materials as supports for green silver nanoparticles as efficient catalysts in photodegradation of organic pollutants. *Environ. Technol. Innov.* 34, 103576.
- Sagarkar, S., Nousiainen, A., Shaligram, S., Björklöf, K., Lindström, K., Jorgensen, K.S., Kapley, A., 2014. Soil mesocosm studies on atrazine bioremediation. *J. Environ. Manag.* 139, 208–216.
- Sagarkar, S., Bhardwaj, P., Storck, V., Devers-Lamrani, M., Martin-Laurent, F., Kapley, A., 2016. S-triazine degrading bacterial isolate *Arthrobacter* sp. Ak-YN10, a candidate for bioaugmentation of atrazine contaminated soil. *Appl. Microbiol. Biotechnol.* 100, 903–913.
- Shawky, A., Mohamed, R.M., Mkhald, I.A., Youssef, M.A., Awwad, N.S., 2020. Visible light-responsive Ag/LaTiO<sub>3</sub> nanowire photocatalysts for efficient elimination of atrazine herbicide in water. *J. Mol. Liq.* 299, 112163.
- Shoseyov, O., Shani, Z., Levy, I., 2006. Carbohydrate binding modules: biochemical properties and novel applications. *Microbiol. Mol. Biol. Rev.* 70 (2), 283–295.
- Singh, B., Singh, K., 2016. Microbial degradation of herbicides. *Crit. Rev. Microbiol.* 42 (2), 245–261.
- Solomon, K.R., Giesy, J.P., LaPoint, T.W., Giddings, J.M., Richards, R.P., 2013. Ecological risk assessment of atrazine in North American surface waters. *Environ. Toxicol. Chem.* 32 (1), 10–11.
- Song, Y., Cang, L., Zuo, Y.L., Yang, J.L., Zhou, D.M., Duan, T.G., Wang, R.Q., 2020. EDTA-enhanced electrokinetic remediation of aged electroplating contaminated soil assisted by combining dual cation-exchange membranes and circulation methods. *Chemosphere* 243, 125439.
- Struthers, J., Jayachandran, K., Moorman, T., 1998. Biodegradation of atrazine by *Agrobacterium radiobacter* J14A and use of this strain in bioremediation of contaminated soil. *Appl. Environ. Microbiol.* 64 (9), 3368–3375.
- Tang, Y., Zhai, Q., Zhang, Z., Lu, Z., Li, R., Zhang, H., 2024. Exploration of the biodegradation pathway and enhanced removal of imazethapyr from soil by immobilized *Bacillus marcorestinctum* YN1. *Chemosphere* 351, 141178.
- Tao, Y., Hu, S.B., Han, S.Y., Shi, H.T., Yang, Y., Li, H.X., Jiao, Y.Q., Zhang, Q., Akindolie, M.S., Ji, M.Y., Chen, Z.B., Zhang, Y., 2019. Efficient removal of atrazine by iron-modified biochar loaded *Acinetobacter lwoffii* DNS32. *Sci. Total Environ.* 682, 59–69.
- Tarla, D.N., Erickson, L.E., Hettiarachchi, G.M., Amadi, S.I., Galkaduwa, M., Davis, L.C., Nurzhanova, A., Pidlisnyuk, V., 2020. Phytoremediation and bioremediation of pesticide-contaminated soil. *Appl. Sci.* 10 (4), 1217.
- Taverna, M.E., Busatto, C.A., Lescano, M.R., Nicolau, V.V., Zalazar, C.S., Meira, G.R., Estenoz, D.A., 2018. Microparticles based on ionic and organosolv lignins for the controlled release of atrazine. *J. Hazard. Mater.* 359, 139–147.
- Tuncel, M.E., Yildiz, U., Uras, Y., Akyol, G., Ozkul, C., Akyol, N.H., 2024. Sorption and transport of atrazine for stable manure-amended agricultural soil from Kahramanmaraş, Turkey. *Soil. Sediment Contam.* 33 (7), 1117–1133.
- Udikić-Kolić, N., Scott, C., Martin-Laurent, F., 2012. Evolution of atrazine-degrading capabilities in the environment. *Appl. Microbiol. Biotechnol.* 96 (5), 1175–1189.
- Vishwakarma, A.K., Meena, B.P., Das, H., Jha, P., Biswas, A.K., Bharati, K., Hati, K.M.P., Chaudhary, R.S.K., Shirale, A.O., Lakaria, B.L., Gurav, P., Patra, A., 2023. Impact of sequential herbicides application on crop productivity, weed and nutrient dynamics in soybean under conservation agriculture in Vertisols of central India. *PLoS One* 18 (1), e0279434.
- Wang, H.Z., Ren, W.J., Xu, Y.F., Wang, X., Ma, J., Sun, Y., Hu, W.B., Chen, S.S., Dai, S.X., Song, J.Y., Jia, J.F., Teng, Y., 2024a. Long-term herbicide residues affect soil multifunctionality and the soil microbial community. *Ecotoxicol. Environ. Saf.* 283, 116783.
- Wang, J., Zhu, L., Liu, A., Ma, T., Wang, Q., Xie, H., Wang, J., Jiang, T., Zhao, R., 2011. Isolation and characterization of an *Arthrobacter* sp. strain HB-5 that transforms atrazine. *Environ. Geochem. Health* 33 (3), 259–266.
- Wang, L., Samac, D.A., Shapir, N., Wackett, L.P., Vance, C.P., Olszewski, N.E., Sadowsky, M.J., 2005. Biodegradation of atrazine in transgenic plants expressing a modified bacterial atrazine chlorohydrolase (atza) gene. *Plant Biotechnol. J.* 3 (5), 475–486.
- Wang, L., Xie, C., Sui, J., Yang, J., Zhou, Y., Wang, T., Chen, F., Cui, X., Yang, Y., Zhang, W., 2025. Microbial degradation of diphenyl ether herbicides past, present and future. *J. Environ. Chem. Eng.* 13 (3), 116357.
- Wang, S., Yang, Y., Li, D., Xie, L., Wu, Y., Li, G., 2024b. Current research status, opportunities, and future challenges of nine representative persistent herbicides. *J. Agric. Food Chem.* 72 (40), 21959–21972.
- Wang, W., Huang, Y., Han, G., Liu, B., Su, S., Wang, Y., Xue, Y., 2022. Enhanced removal of P (V), Mo (VI) and W (VI) generated oxyanions using Fe-MOF as adsorbent from hydrometallurgical waste liquid: exploring the influence of ionic polymerization. *J. Hazard. Mater.* 427, 128168.
- Wei, 2023. Adsorption, Degradation and Phytotoxicity Assessment of Fomesafen by Biochar/G-C<sub>3</sub>N<sub>4</sub>. Shanxi University, Taiyuan.
- Wong, E.L., Vuong, K.Q., Chow, E., 2021. Nanozymes for environmental pollutant monitoring and remediation. *Sensors* 21 (2), 408.
- Xie, W., Peng, C., Chen, A., Wang, H., Tholley, M.S., Qian, R., Lu, S., Zhang, W., Zhan, X., 2024. Synergistic adsorption and degradation of sulfonylurea herbicides by biochar-supported nano zero-valent iron composites in in-situ soil remediation. *Chem. Eng. J.* 500, 156927.
- Xu, Z., Li, B., Jia, Y., Guo, X., Lv, F., 2024. Biodegradation of imazethapyr by bacterial strain IM9601 isolated from agricultural soil. *Curr. Microbiol.* 81 (1), 33.
- Yang, B., Xiao, Y., Dong, M., Wang, S., Zhang, H., Wu, X., 2024. Bioremediation of soils contaminated with nicosulfuron by the bacterial complex ES58. *Process Biochem.* 146, 176–187.
- Yang, C., Wang, H., Duan, Y., Bei, F., Jia, S., Wang, J., Wang, H., Liu, W., 2023. Enhanced herbicide metabolism and target-site mutations confer multiple resistance to fomesafen and nicosulfuron in *Amaranthus retroflexus* L. *Biology-Basel* 12 (4), 592.
- Yang, F., Wang, Y., Sun, C., He, J., Wang, S., Ma, Y., Fu, H.Y., Liu, C., 2020. Highly efficient degradation bacteria: remediation effect on soil polluted by fomesafen. *Chin. Agric. Sci. Bull.* 36 (15), 68–73.
- Yang, L., 2014. Study on Soil Remediation and Degradation Mechanism of Flumesafen Degrading Bacteria. Heilongjiang University, Harbin.
- Ye, J., Zhang, J., Gao, J., Li, H., Liang, D., Liu, R., 2016. Isolation and characterization of atrazine-degrading strain *Shewanella* sp. YJY4 from cornfield soil. *Lett. Appl. Microbiol.* 63 (1), 45–52.
- Zhai, Q., Chen, X., Zhang, M., Zhang, C., Zhang, Z., Pan, H., Zhang, H., Sun, F., 2023. Immobilization of *Klebsiella jilinsis* strain 2N3 by corn straw biochar enhanced the degradation of nicosulfuron and restores the soil microbiome function and composition. *Appl. Soil Ecol.* 189, 104917.
- Zhang, B., Zhang, J., Wang, Y., Qu, J., Jiang, Z., Zhang, X., Tao, Y., Wang, Y., Kang, Z., Han, S., Zhang, J., Zhang, Y., 2024. Biodegradation of atrazine with biochar-mediated functional bacterial biofilm: construction, characterization and mechanisms. *J. Hazard. Mater.* 465, 133237.
- Zhang, J.H., Wang, X.T., Bai, W.B., Cao, C.L., 2023. Study on remediation of soil contaminated of nicosulfuron by *Aspergillus terreus* DT2 solid inoculum. *Chin. J. Biol. Control.* 39 (6), 1463–1473.
- Zhang, Y., Jiang, Z., Cao, B., Hu, M., Wang, Z., Dong, X., 2011. Metabolic ability and gene characteristics of *Arthrobacter* sp. strain DNS10, the sole atrazine-degrading strain in a consortium isolated from black soil. *Int. Biodeterior. Biodegrad.* 65 (8), 1140–1144.
- Zhao, G., Tian, Y., Yu, H., Li, J., Mao, D., Faisal, R.M., Huang, X., 2022. Development of solid agents of the diphenyl ether herbicide degrading bacterium *Bacillus* sp. Za based on a mixed organic fertilizer carrier. *Front. Microbiol.* 13, 1075930.
- Zhao, G., Zhou, J., Tian, Y., Chen, Q., Mao, D., Zhu, J., Huang, X., 2023. Remediation of fomesafen contaminated soil by *Bacillus* sp. Za: degradation pathway, community structure and bioenhanced remediation. *Environ. Pollut.* 336, 122460.
- Zhao, X., Wang, L., Ma, F., Yang, J., 2018. Characterisation of an efficient atrazine-degrading bacterium, *Arthrobacter* sp. Zxy-2: an attempt to lay the foundation for potential bioaugmentation applications. *Biotechnol. Biofuels* 11, 1–10.
- Zhong, J., Wu, S., Chen, W.J., Huang, Y., Lei, Q., Mishra, S., Bhatt, P., Chen, S., 2023. Current insights into the microbial degradation of nicosulfuron: strains, metabolic pathways, and molecular mechanisms. *Chemosphere* 326, 138390.
- Zhu, J., Xiang, S., Zhang, B., Wang, J., Li, C., Pan, C., Xu, Y., Ma, Y., 2022. Oxygen-defective graphdiyne for ultra-efficient removal of sulfonylurea herbicides from aqueous solution. *J. Environ. Chem. Eng.* 10 (3), 107724.
- Zhu, J.W., Meng, Z.L., Fu, L., Jin, C.H., 2020. Study on the biodegradation characteristics of atrazine and isolation of an atrazine degrading bacterium, *Bacillus safensis* ATR-Z5. *Fresenius Environ. Bull.* 29 (8), 6412–6419.