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Biochar mitigated zerovalent iron-induced methane emissions in arsenic-contaminated paddy soil

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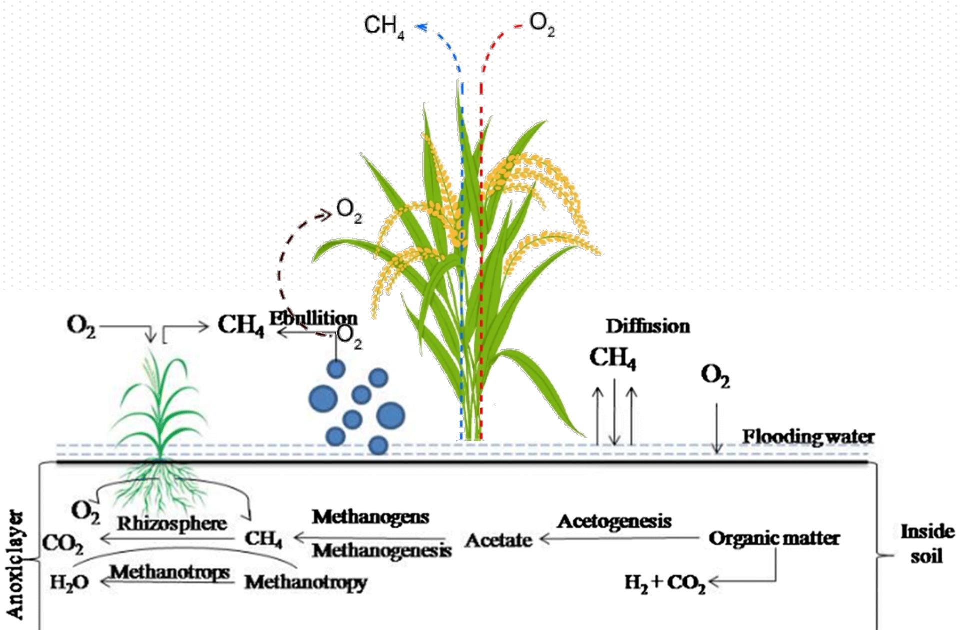
CONTENTS

1 Background

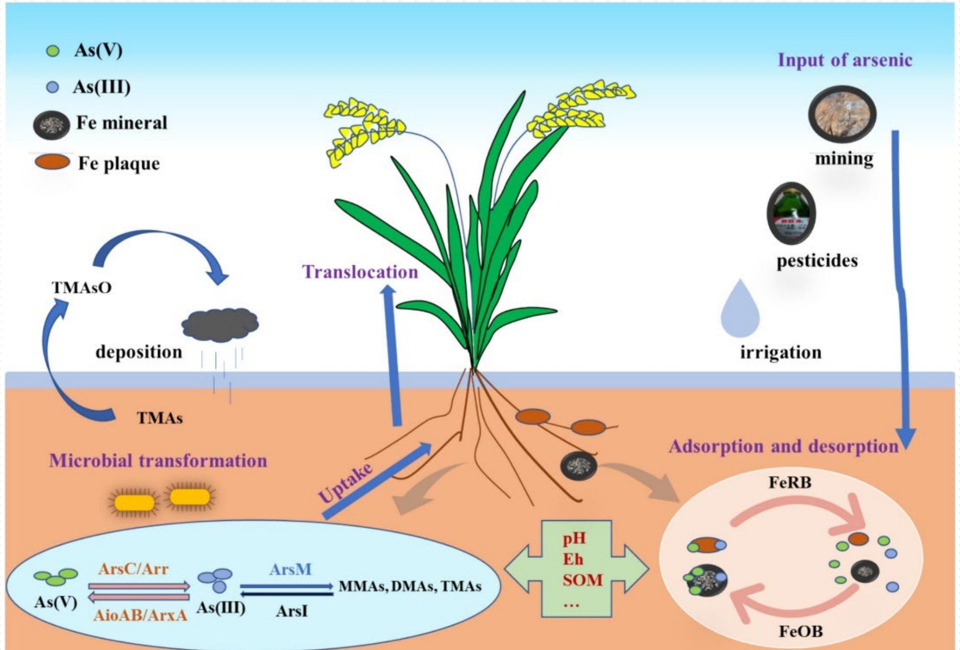
- Synergistic reduction of methane emissions and heavy metal pollution in paddy soil is crucial

Methane emissions



Khushboo Gupta etal, 2021; Rajendran et al, 2024

Arsenic Contamination

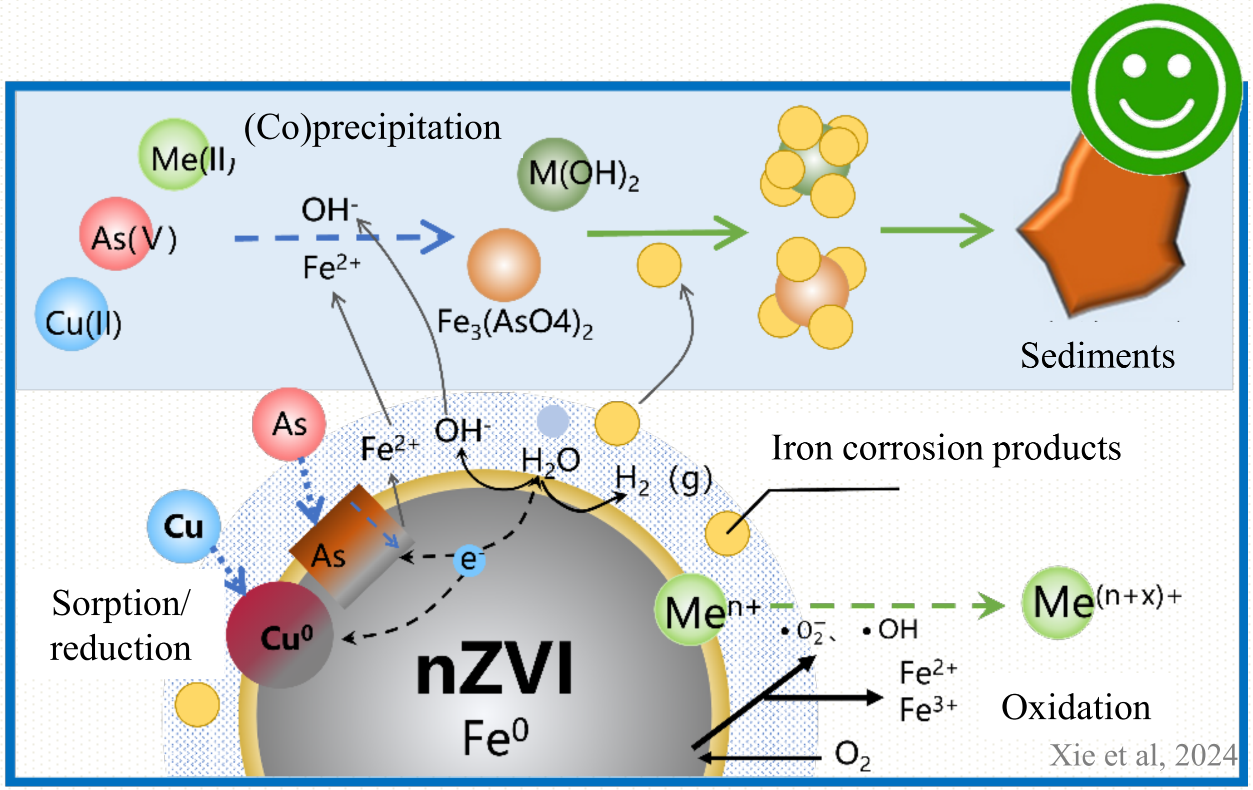


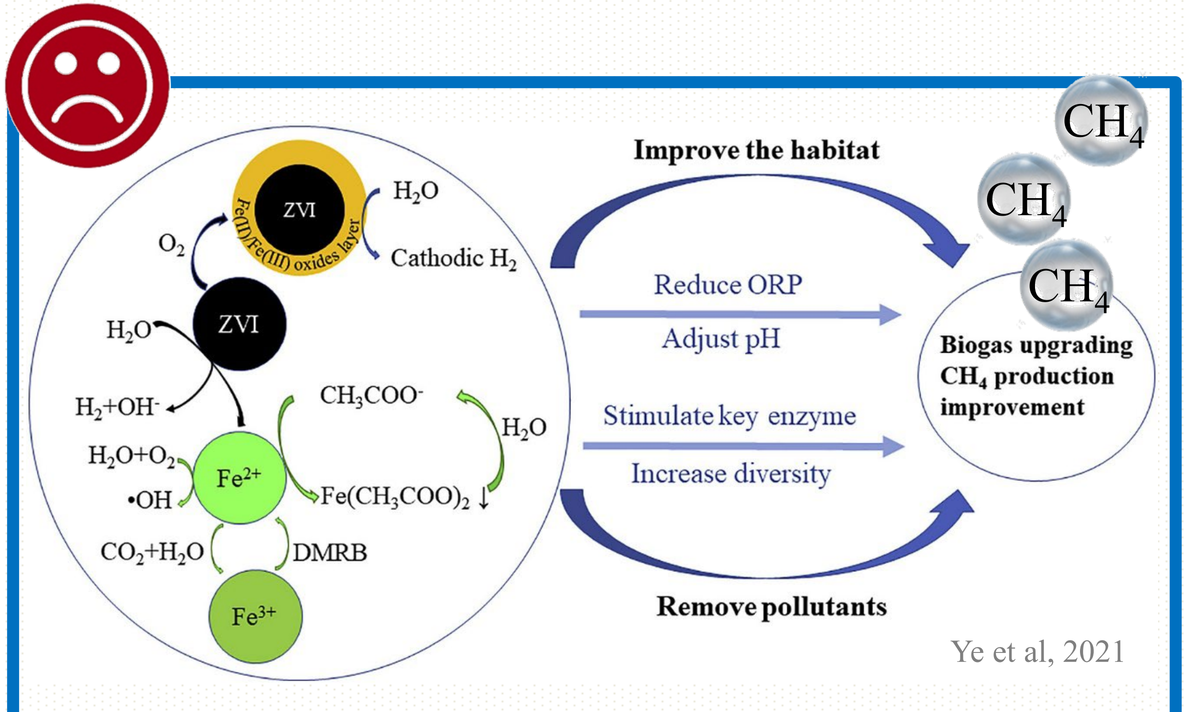
Zhang et al, 2024

Question: Effects of As of different concentrations on methane emission from paddy soil?

1 Ameliorant—Zerovalent iron

- Zerovalent iron (ZVI) has high surface area and strong reducing ability.
- ZVI efficiently immobilizes As via adsorption, reduction, and (co)precipitation.
- ZVI affects carbon mineralization and methane emissions by enhancing microbial electron bifurcation and direct inter-species electron transfer.



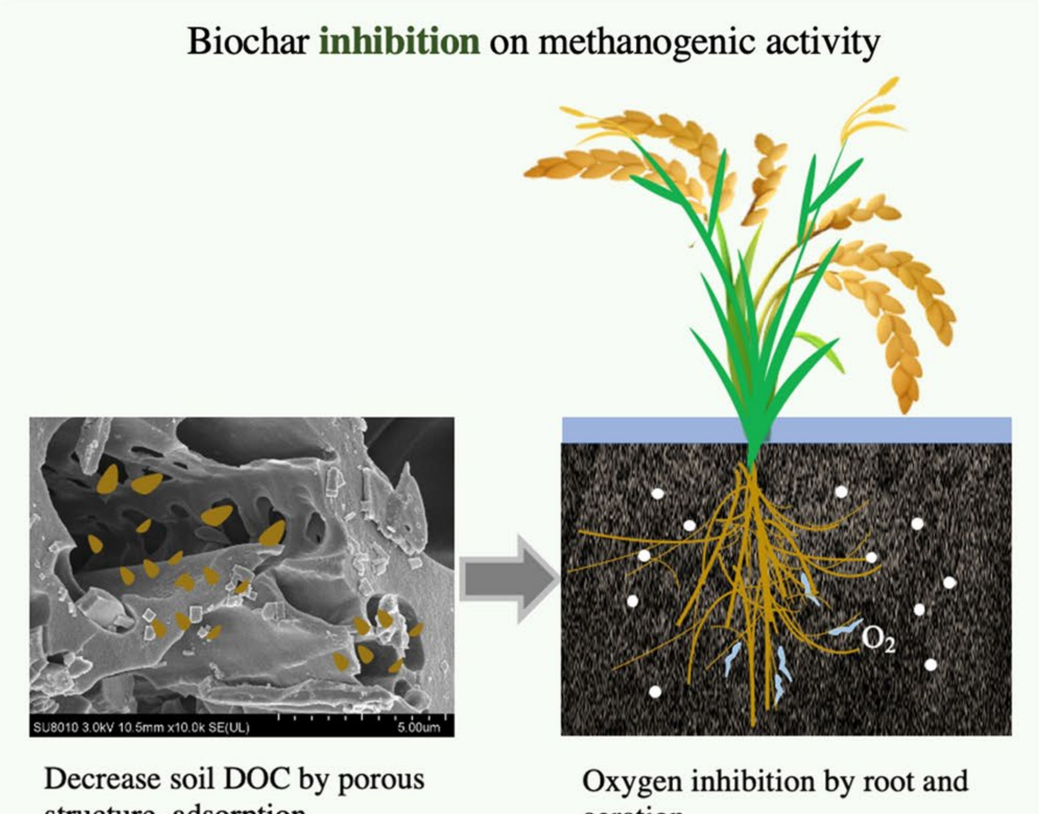


Effect of ZVI in anaerobic environment

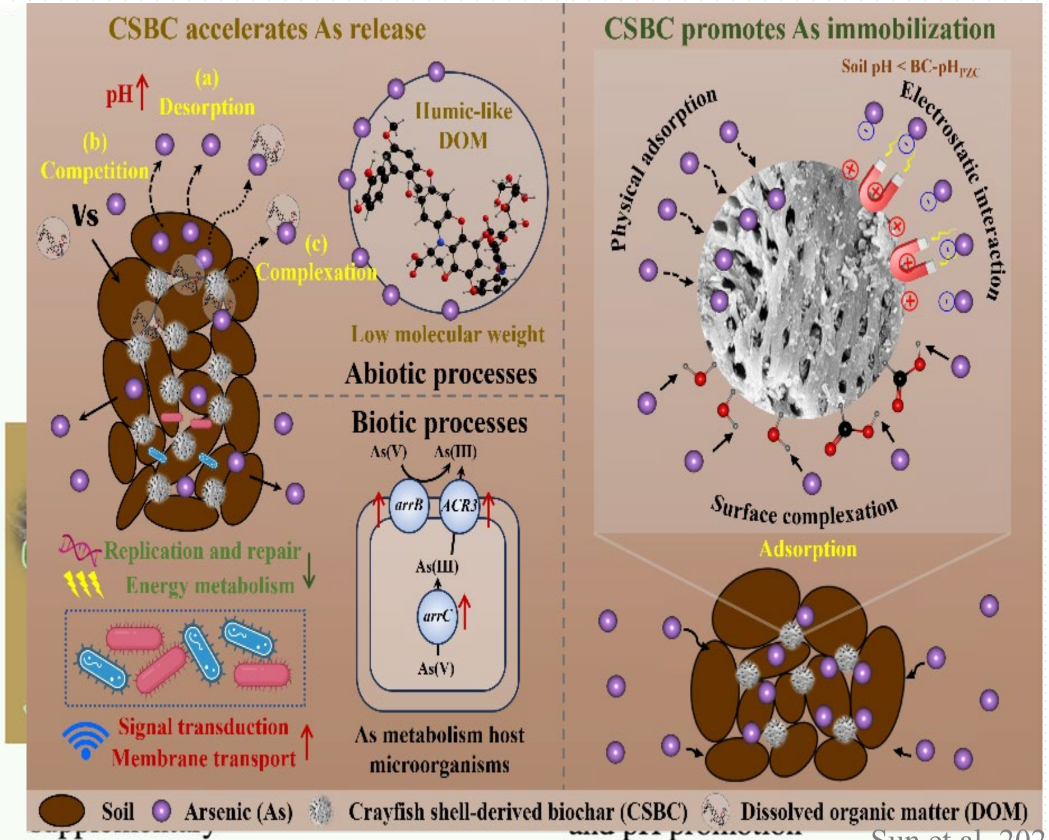
Question: How does ZVI contribute to CH_4 emission?

1 Ameliorant—Biochar

- Biochar (BC) inhibits methanogenic activity by decreasing dissolved organic carbon and increasing oxygen input.
- BC promotes aerobic methane oxidation activity through ameliorating soil aeration, increasing pH, and increasing O_2 availability of rhizosphere.
- BC promotes anaerobic methane oxidation activity due to its the electron accepting capacities.



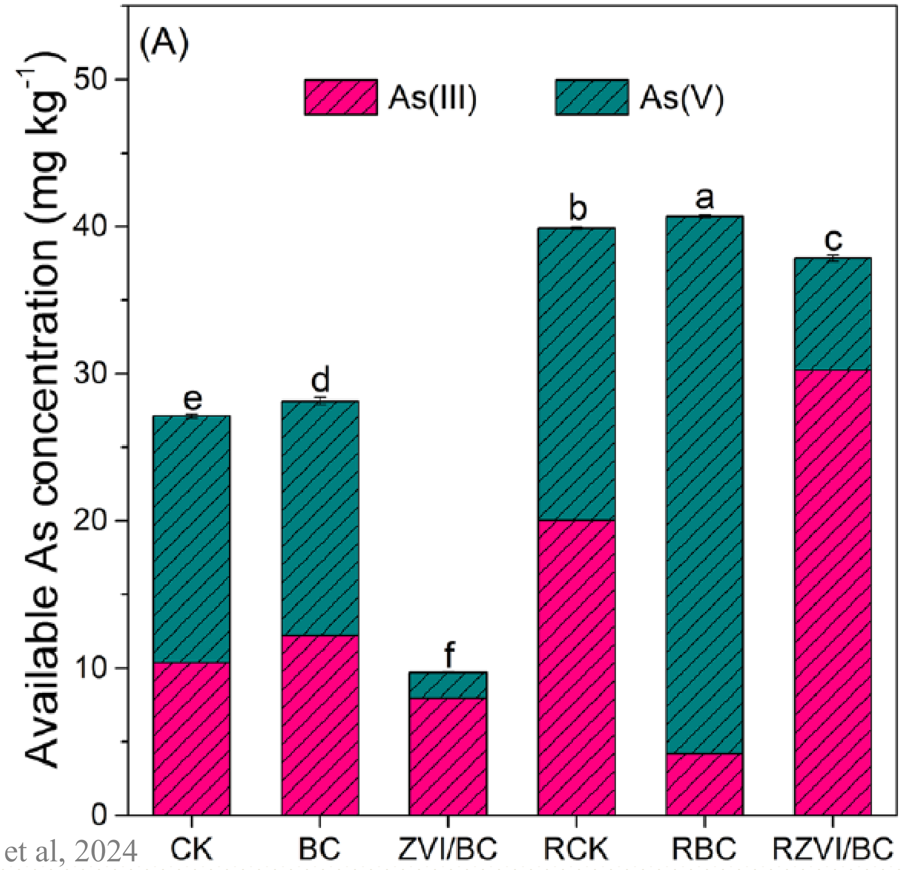
Nan et al, 2021



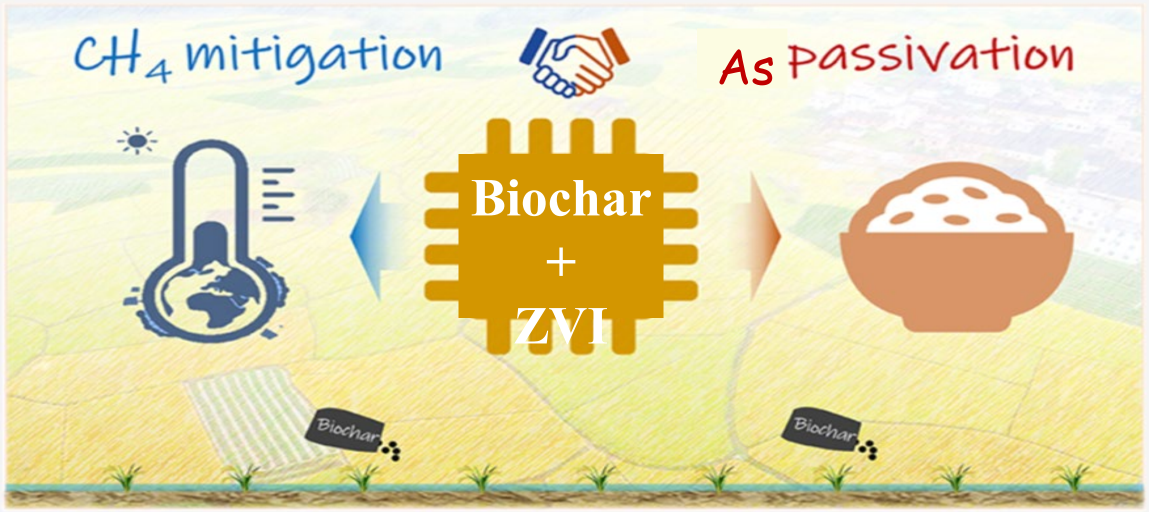
Sun et al, 2025

1 Synergistic effects of BC+ZVI for dual goals

❒ BC+ZVI resulted in enhanced As immobilization and reduced CH_4 emission.



Wang et al, 2024



Combined application of Biochar and ZVI has potential for both arsenic and methane mitigation

1 Research objectives & Hypothesis

Research objectives

Effects of As of different concentrations on methane emission from paddy soil

Effects of ZVI on As immobilization and methane emission

Role of BC in mitigating ZVI–induced CH_4 emissions in As-polluted paddy soil

Hypothesis

BC can regulate Fe/C cycling and microbes in ZVI amended As-spiked soil, leading to enhanced As immobilization and reduced CH_4 emission.

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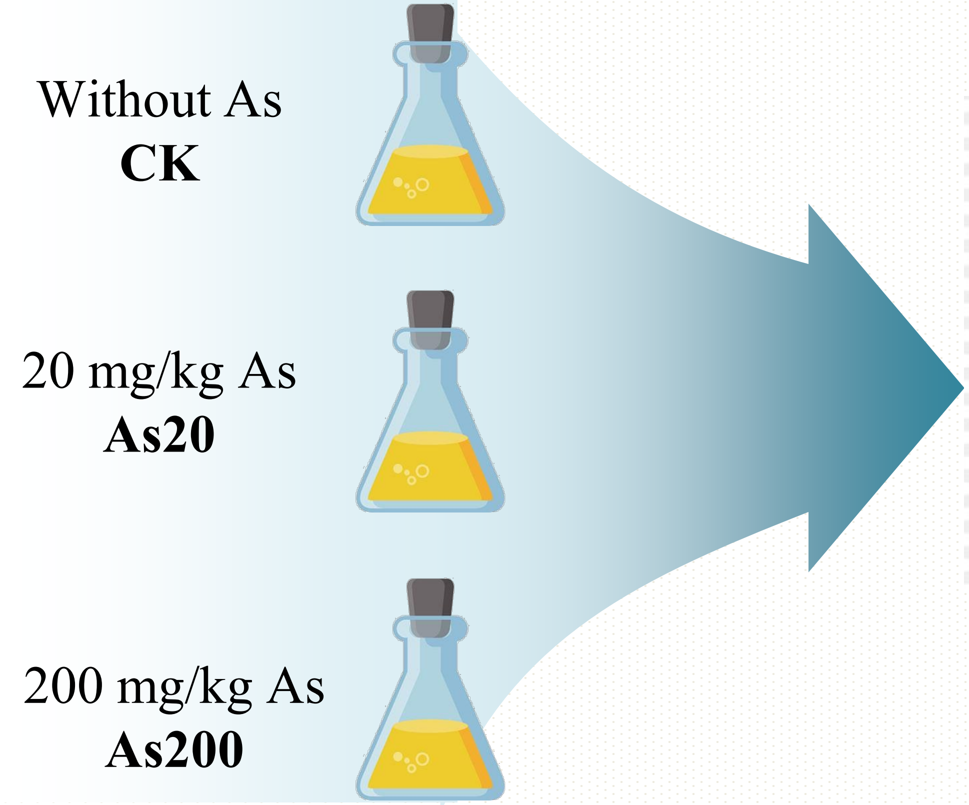
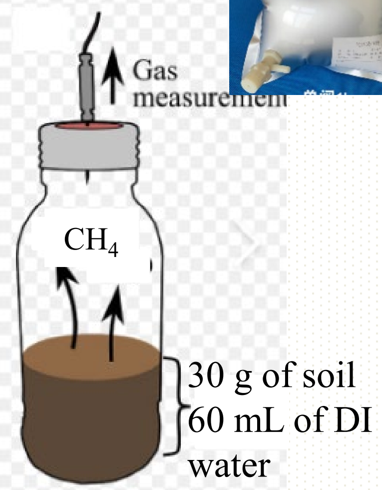
Methane emission from Arsenic-contaminated paddy soil

2 Experimental setup

Effects of As of different concentrations on methane emission from paddy soil

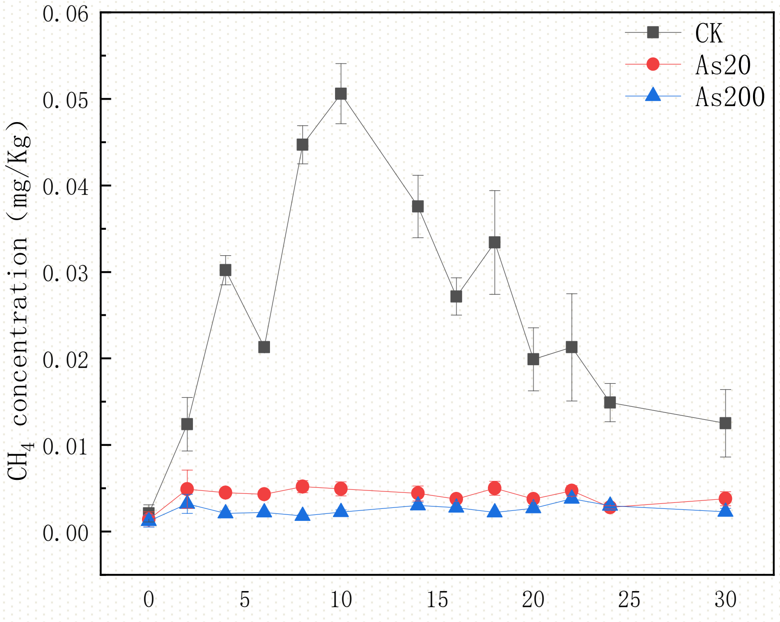
- 250 mL serum bottle: 30g soil + 60 mL deionized water (flooded)
- The serum bottle was sealed, flushed with high-purity N_2 to maintain anaerobic conditions, and incubated at 25 °C for 30 d



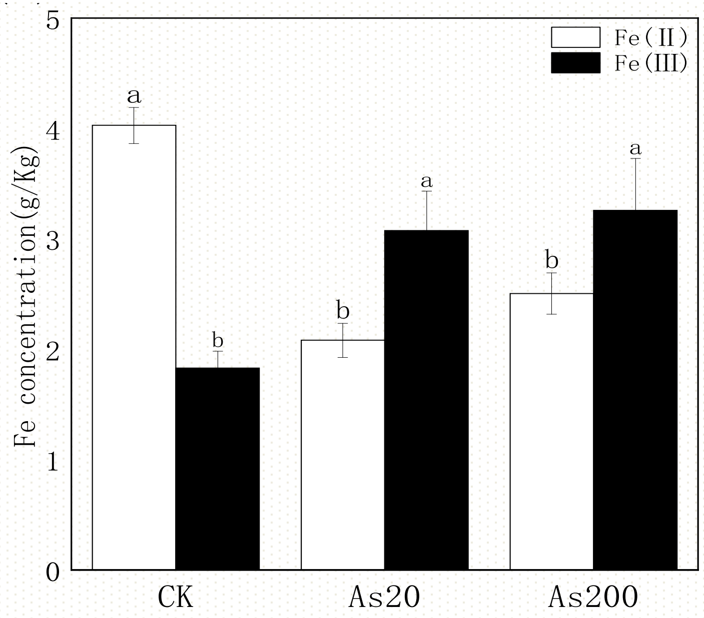


Gas Chromatography

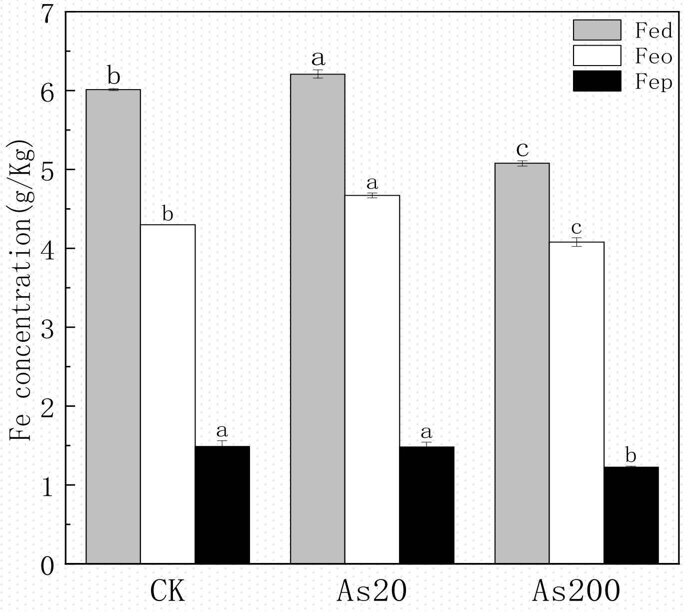
2 Methane emission from Arsenic-contaminated paddy soil



Methane emissions



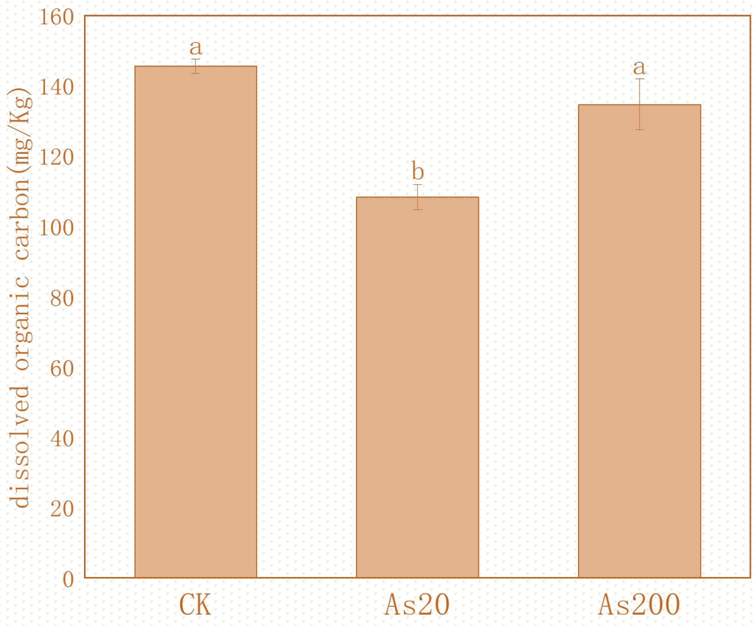
Fe ions



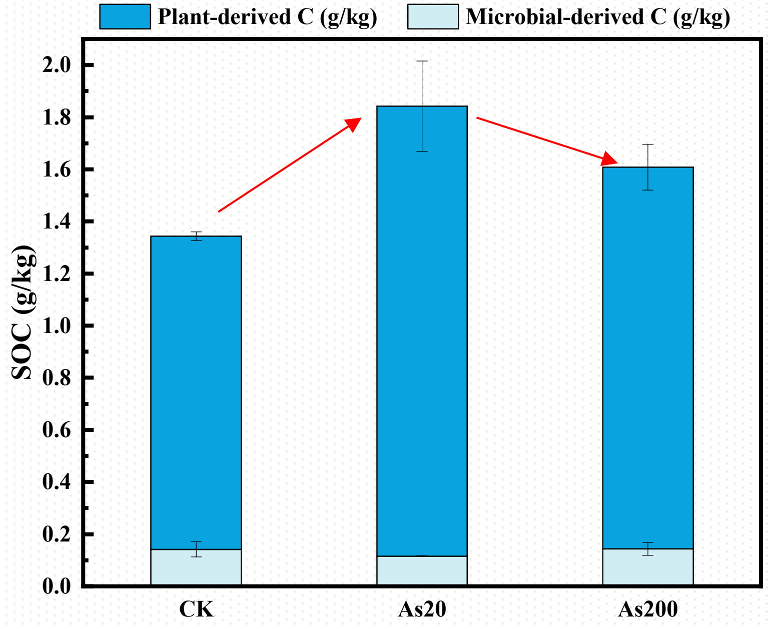
Fe oxides

- Methane emissions were inhibited by As @ 20& 200 mg/kg.
- As significantly promoted the oxidation of Fe(II) to Fe(III).
- Low concentration As increased free iron oxide (Fed) and amorphous iron oxide (Feo), while high concentration As decreased Fed, Feo, and complexed iron oxide (Fep).

2 Methane emission from arsenic-contaminated paddy soil



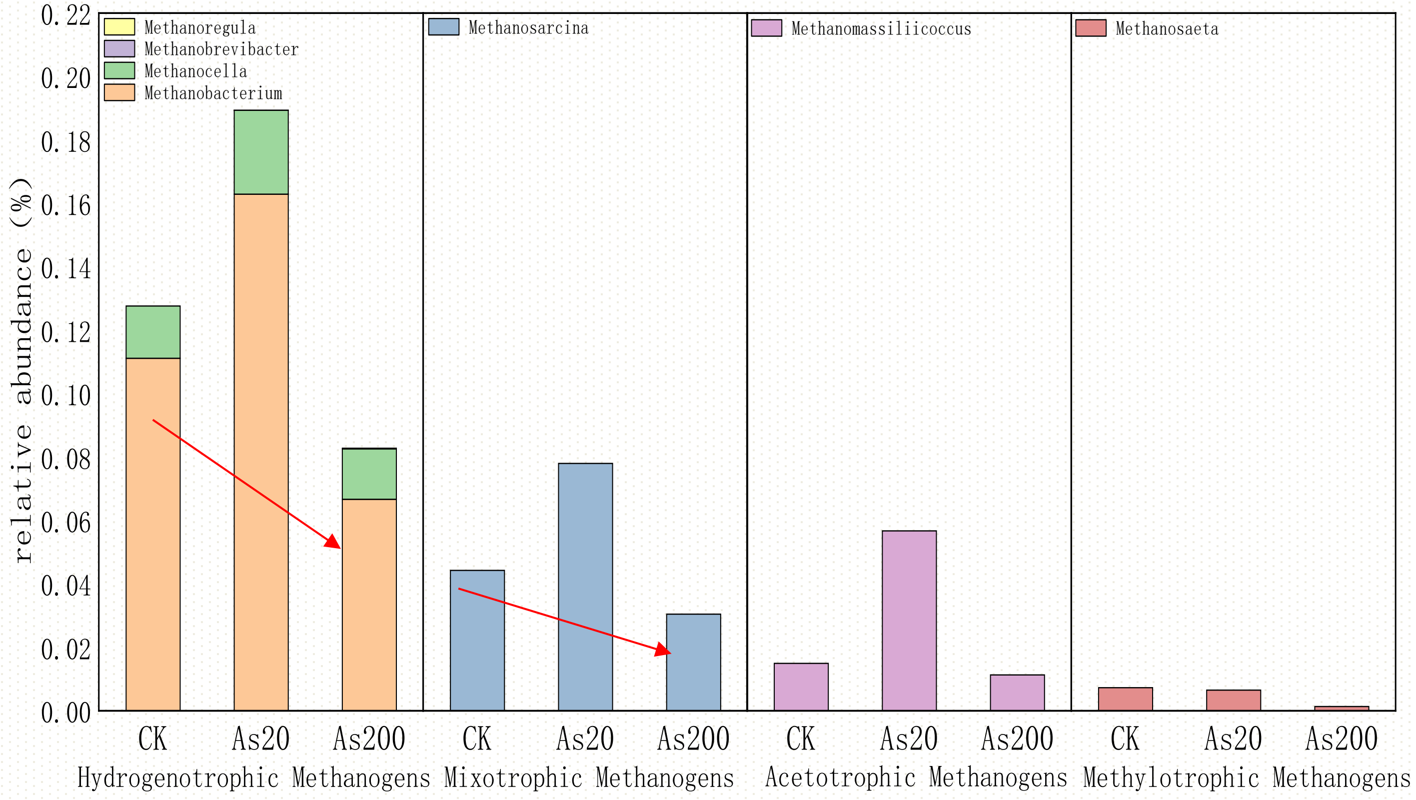
DOC



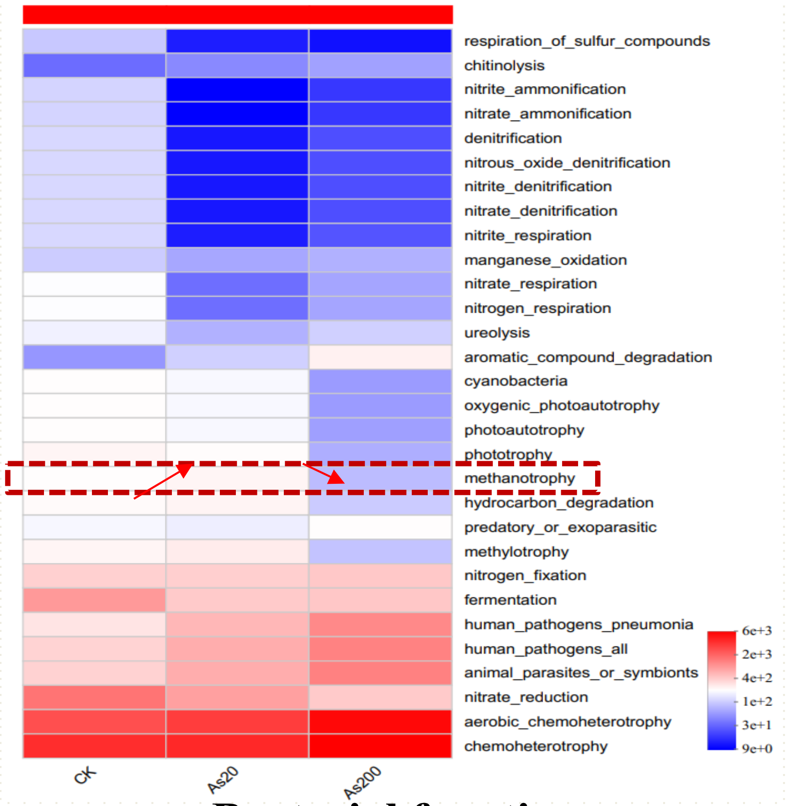
Plant derived C/ Microbial derived C

- As20 reduced DOC content in the soil, indicating lower available substrates for methane production.
- As significantly increased plant derived carbon, indicating the limited utilization.
- Low As concentration decreased microbial derived carbon, while high dose As increased microbial derived carbon, indicating high As levels severely damaged microorganisms.

2 Methane emission from Arsenic-contaminated paddy soil



Methanogens at genus level



Bacterial functions

- Low As concentration increased bacterial and archaeal diversity and richness, and enriched CH_4 oxidation bacteria and function Methanotrophy, inhibiting CH_4 emissions.
- High As concentration severely damaged microorganisms, reduced bacterial and archaeal diversity and richness, and decreased methanogens relative abundance, inhibiting C utilization and CH_4 emissions.

2 Summary

- As changed microbial living environment by oxidizing Fe ions, affected C metabolism bacteria and methanogens.

- The mechanism associated with compromised CH_4 emissions is concentration-dependent:

  As20 inhibited C decomposition and promoted CH_4 oxidation

  As200 severely damaged microorganisms associated with methanogenesis.

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Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil

3 Experimental setup

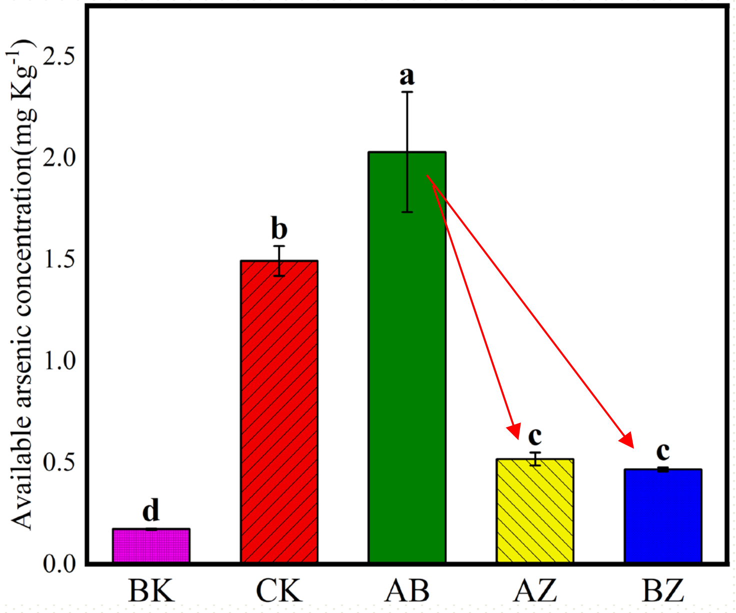
Effects of ZVI and Biochar on methane emissions in As-contaminated paddy soil

- Polyethylene pots with 6 L capacity: 4.5 kg of uncontaminated/As-contaminated soil + 0.99 g urea, 0.225 g KH_2PO_4, and 0.225 g + 2 cm overlying tap water (174% of field capacity, flooded state)
- Polyethylene pots with soils and ameliorant were incubated for 46 d.

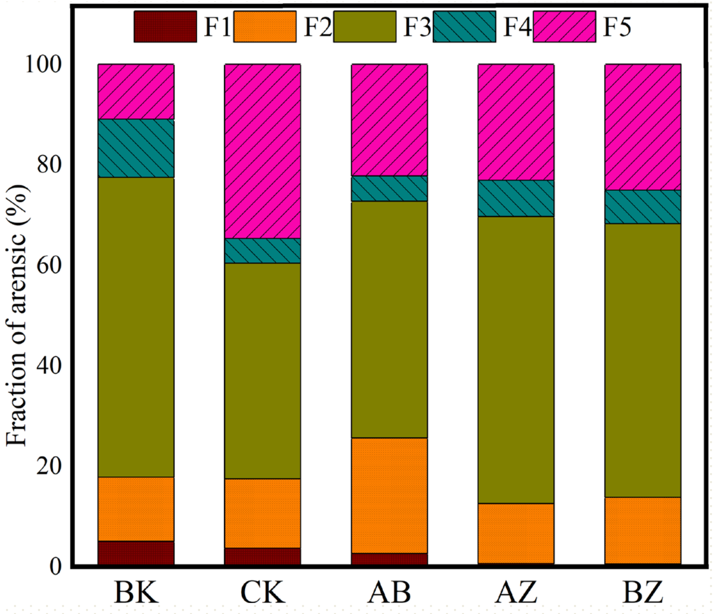
Without As	200 mg/kg As	200 mg/kg As +1%BC	200 mg/kg As +1%ZVI	200 mg/kg As +1%BC+1%ZVI
BK	**CK**	**AB**	**AZ**	**BZ**

3 Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil

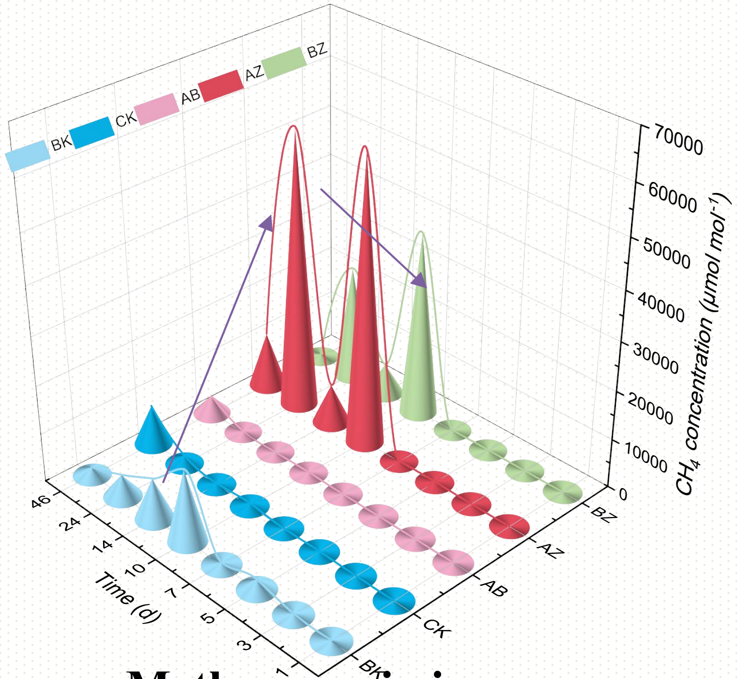
BK: Blank, **CK:** As-spiked soil, **AB:** Biochar+CK, **AZ:** ZVI+CK, **BZ:** BC+ZVI+CK



Available arsenic in soil



Arsenic fractionation



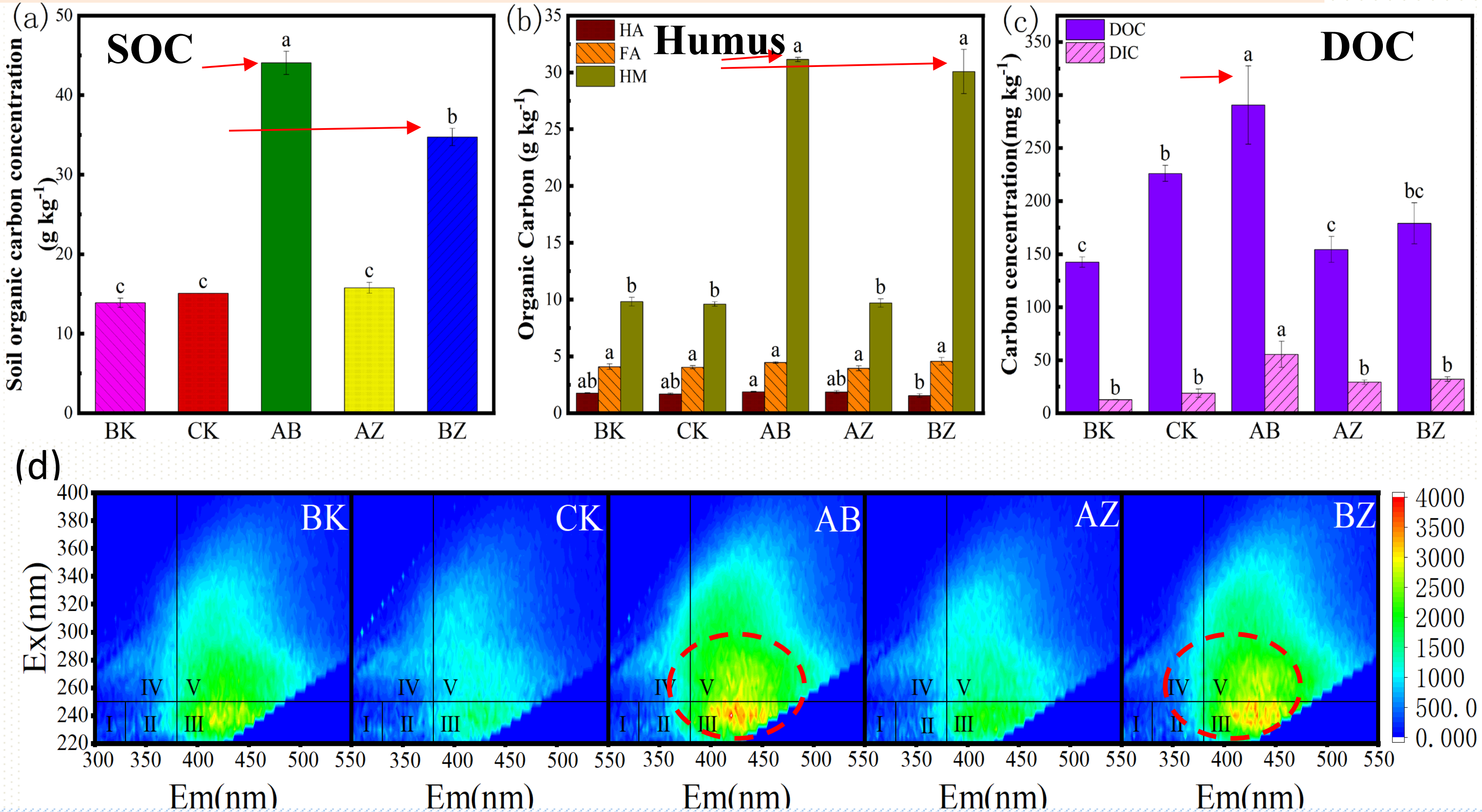
Methane emissions

- ZVI and BC+ZVI significantly decreased available As by 65% and 69%, respectively.
- As forms in ZVI and BC+ZVI treated soil: Fe and Al amorphous and poorly-crystalline hydrous oxides bonded As (F3)>residual As (F5)>specifically adsorbed As (F2)>Fe and Al well-crystallized hydrous oxides bonded As (F4).
- ZVI stimulated CH_4 emissions, while BC and BC+ZVI decreased CH_4 emissions.

3 Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil

BK: Blank, **CK:** As-spiked soil, **AB:** Biochar+CK, **AZ:** ZVI+CK, **BZ:** BC+ZVI+CK

C related parameters

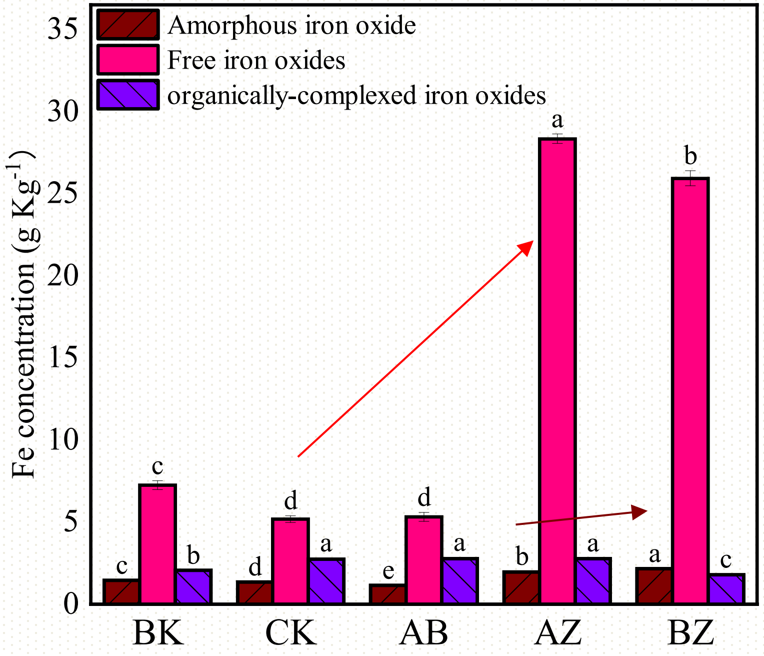


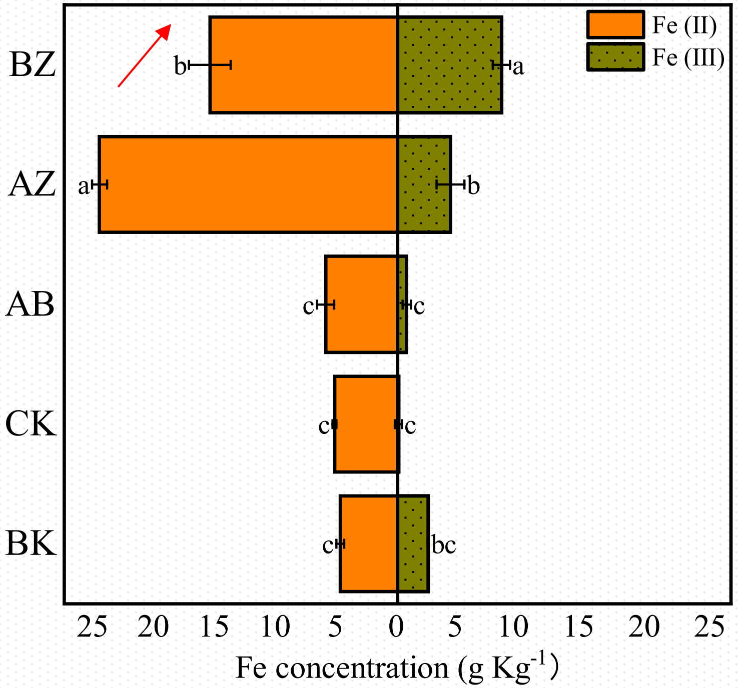
- BC and BC+ZVI significantly increased the contents of SOC, DOC, and humins (HM).
- BC and BC+ZVI increased humic acid-like substances (region V) and fulvic acid-like substances (region III).

3 Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil

BK: Blank, **CK:** As-spiked soil, **AB:** Biochar+CK, **AZ:** ZVI+CK, **BZ:** BC+ZVI+CK

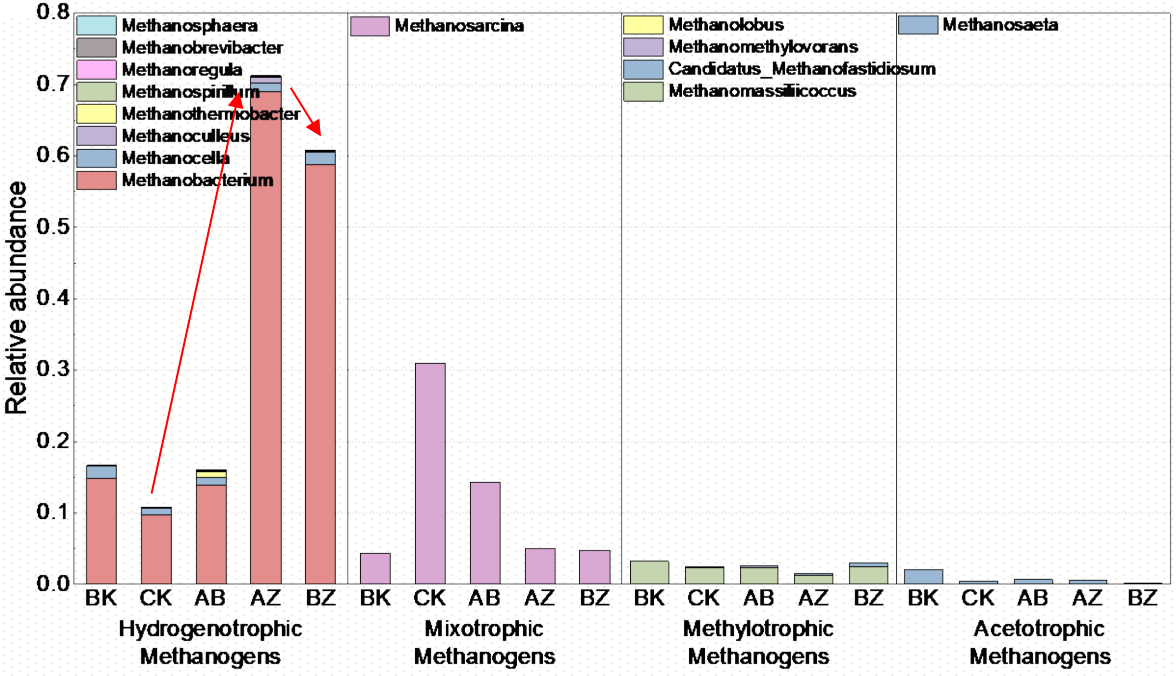
Fe related indicators



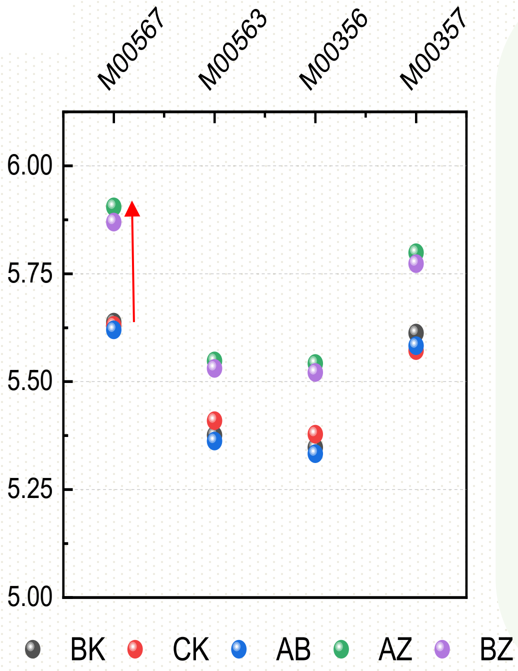


- ZVI addition significantly increased free Fe oxide and amorphous Fe oxide concentrations
- BC significantly promoted the transformation of free Fe oxide and organically-complexed Fe oxide in ZVI-treated soil to amorphous Fe oxide.
- BC significantly promoted the oxidation of Fe(II) to Fe(III).

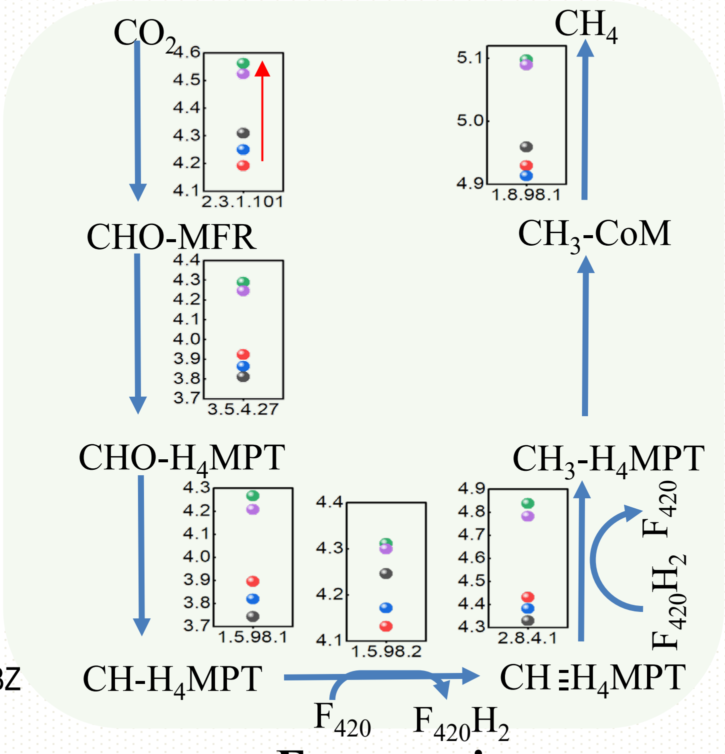
3 Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil



Methanogens at genus level



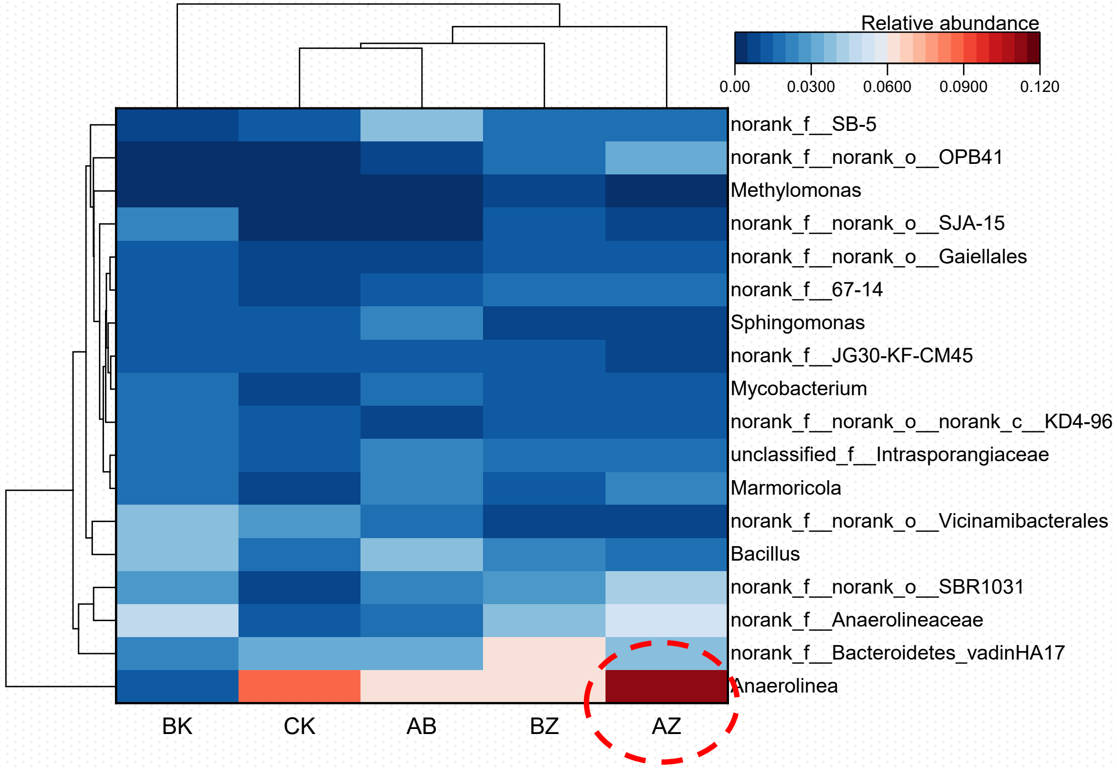
Modules involved in methane metabolism



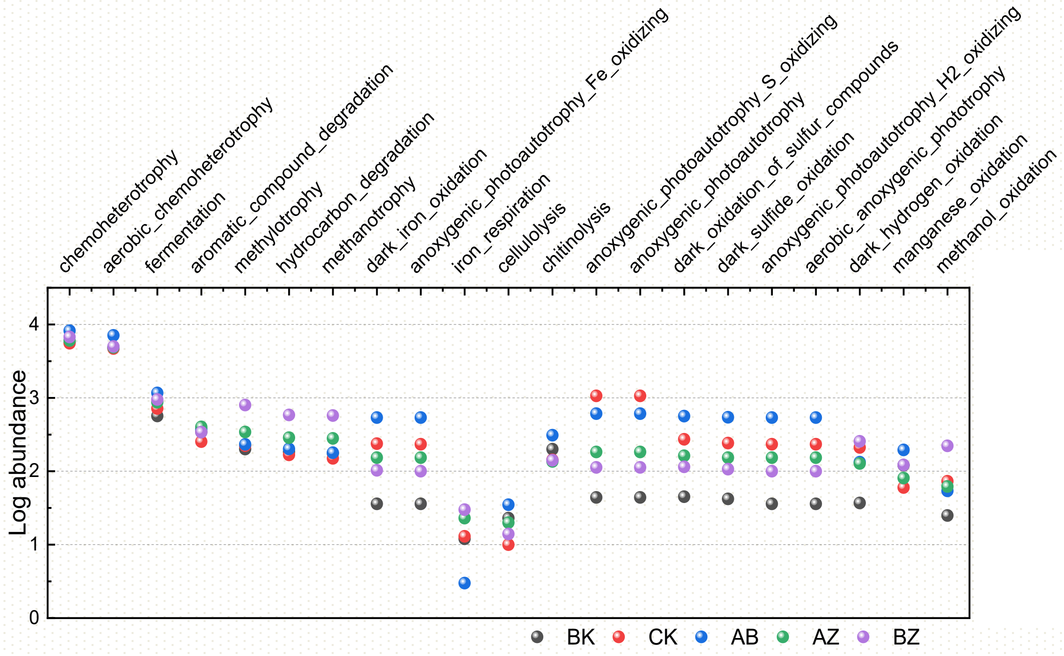
Enzymes in hydrogenotrophic methanogensis

- ZVI and BC+ZVI increased the relative abundance of hydrogenotrophic methanogen *Methanobacterium*.
- ZVI and BC+ZVI promoted four methanogenesis pathways, especially hydrogenotrophic methanogenesis (M00567) pathway, and increased genes encoding hydrogenotrophic methanogenesis related enzymes.
- BC+ZVI showed lower relative abundance of hydrogenotrophic methanogen and related genes than ZVI.

3 Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil



Bacterial communities at genus level



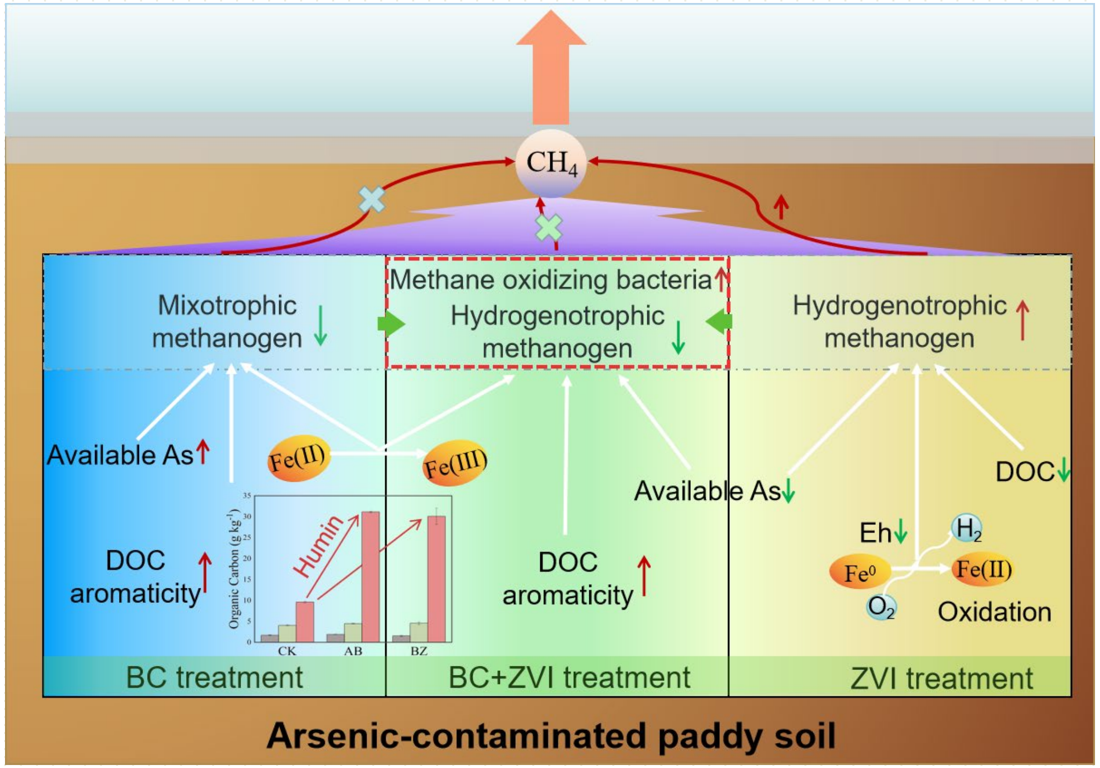
Bacterial functions predicted according to FAPROTAX database

- ZVI enriched As detoxification related bacteria (e.g., *Anaerolinea*).
- Treatment with ZVI (AZ and BZ) increased methynotrophy and hydrocarbon degradation abundance.
- BC increased methane oxidation bacteria *Methylocystis* and corresponding function Methanotrophy abundance.

3 Biochar mitigated ZVI-induced methane emissions in As-contaminated paddy soil

Summary

- ZVI stimulated methane emissions by decreasing soil redox potential, promoting decomposition of organic substrates, and enhancing hydrogenotrophic methanogen *Methanobacterium*.
- BC synergistically reduced CH_4 emissions from As contaminated paddy soils amended with ZVI by promoting Fe oxidation, enriching methanotroph *Methylomonas*, and decreasing carbon bioavailability and hydrogenotrophic methanogens abundance.



04

Conclusions & Acknowledgement

4 Conclusions

As suppressed methane emissions from paddy soil

- As changed microbial living environment by oxidizing Fe ions, affected C metabolism bacteria and methanogens.
- Different As dose had different inhibition mechanism on CH_4 emissions: low As dose inhibited C decomposition and promoted CH_4 oxidation, while high As dose severely damaged microorganisms.

ZVI promoted As immobilization but stimulated CH_4 emissions

- ZVI relieved arsenic toxicity, promoted C decomposition, reduced DOC aromaticity, decreased soil Eh, enriched hydrogenotrophic methanogens *Methanobacterium*, and enhanced four methanogenesis modules, resulting in increased CH_4 emissions.

BC+ZVI achieved As immobilization and mitigated ZVI-induced CH_4 emissions

- BC+ZVI enhanced methane oxidation and inhibited methanogenesis by promoting Fe oxidation, enriching methanotroph Methylomonas, and decreasing carbon bioavailability and hydrogenotrophic methanogens abundance. **BC+ZVI provides a sustainable option for soil remediation and global climate change.**

4 Acknowledgement

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Contributors

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- Prof. Jörg Rinklebe, Prof. Ashok Kumar Alva

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