PRO AGRO LECTORIUM

Inhibiting release of phenanthrene from rice-crab coculture sediments to overlying water with rice stalk biochar: Performance and mechanisms

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Research significance

- Bioturbation is an important factor in the secondary release of contaminants from the sediments. Clarifying the mechanism of crab bioturbation on the release of PAHs from paddy field sediments is an important basis for correctly assessing the ecological risk of rice-crab co-cropping production model.

Rice and Crab Cultivation Income Increases by About **Two Times**

Comprehensively implement the requirements of the Fourteenth Five-Year Plan and promote the **high-quality development of the rice-fishing industry.**

Variety Selection

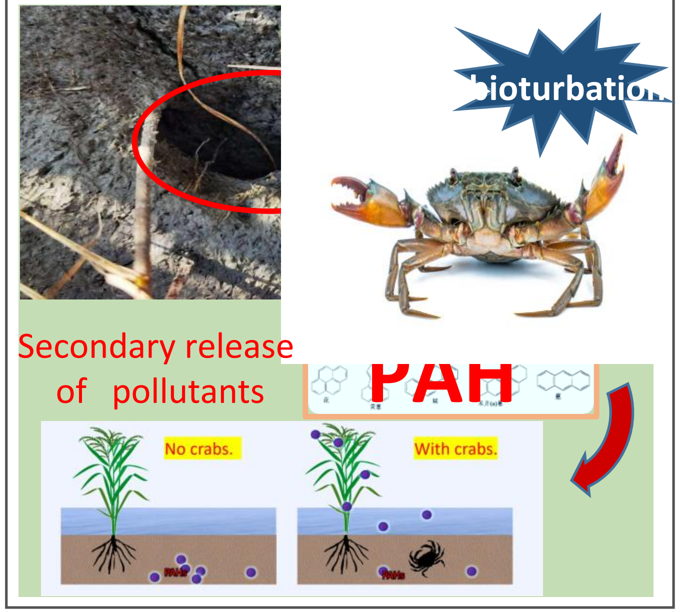
Irrigation pattern

fertilizer ratio

Farming management

Tillage measures

Reduction of pesticides



Rice and crab farming became one of the priorities in the structural adjustment of the agricultural industry due to its significant income-generating benefits.

Currently, it only focused on enhancing the experimentation and research on the rice-crab co-cropping eco-agricultural system, while ignoring the potential risks posed by bioturbation.

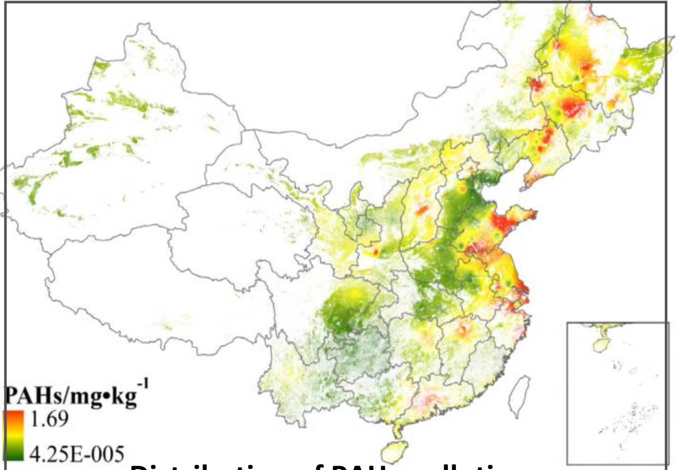
Bioturbation refers to various activities of benthic animals, such as feeding, burrowing, defecation, and migration. Bioturbation was prone to secondary releases of contaminants from the sediments.

Research background

- Inhibition the release of PAHs from the sediment of rice-crab co-cultivation paddy fields in the Northeast alpine region is an important way to reduce the ecological risk, and guarantee the green agriculture and food safety.

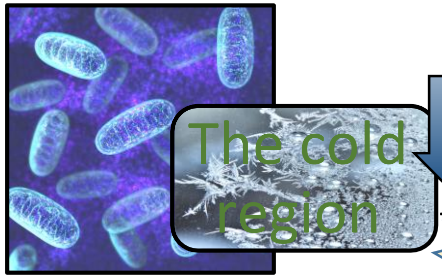
As the "ballast" of China's food security, the total grain output of Heilongjiang Province in 2021 exceeded 150 billion pounds, accounting for 11.5% of the country's total grain output.

As of 2022, 12 cities (prefectures) and 57 counties (cities and districts) in Heilongjiang Province were actively developing rice-fishery integrated farming in their main rice production areas, with a total area of 3.32 million mu.

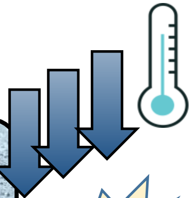


Distribution of PAHs pollution in China by region

PAHs were found as high as 355 μg/kg in soil and sediment of Heilongjiang farmland, which was higher than organic pollutants such as pesticides and reached a moderate pollution level.

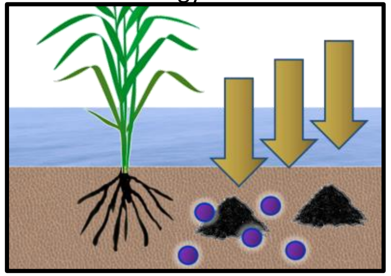


Microbial degradation technology



The effect is not significant

suppression technology



Reduces or prevents the transport and transformation of pollutants in the soil and mitigates soil contamination.

Heilongjiang Province was an important grain-producing area in China, with 60 million mu of rice planted annually, ranking first in the country." Rice-crab co-cropping" has become a key recommended production model.

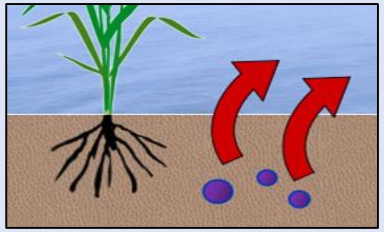
PAHs were common pollutants in agricultural fields in Heilongjiang. Secondary release of PAHs under crab bioturbation entered the food chain via the water-soil-plant-animal pathway, jeopardizing human health and food security.

The climatic characteristics of the cold region make microbial degradation of PAHs less effective. Therefore, the inhibitory technology to control PAHs release should be the first choice for remediation.

Technical Optimization

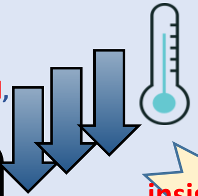
- **Research on control technology of PAHs release from bottom mud pollutants**

Technologies for controlling the migration and release of bottom mud pollution mainly include: ① pollutant removal technologies (e.g. microbial remediation) ② pollutant inhibition technologies (in-situ and ex-situ inhibition technologies).



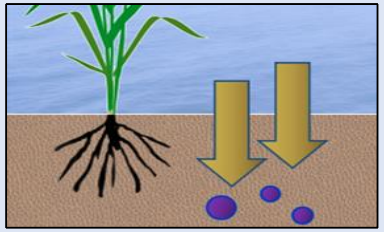
① Pollutant removal technology

Pollutants Removal technologies (e.g., microbial, etc.)



Biodegradation removal techniques were ineffective in the cold northeast region for low temperature.

Inhibition technology has become hotspot for controlling the release of pollutants from bottom mud



② Pollutant Suppression Technology

Ectopic suppression technology is costly,and needs large space requirement.

In-situ suppression technology has better feasibility and applicability.

√ In situ suppression technology

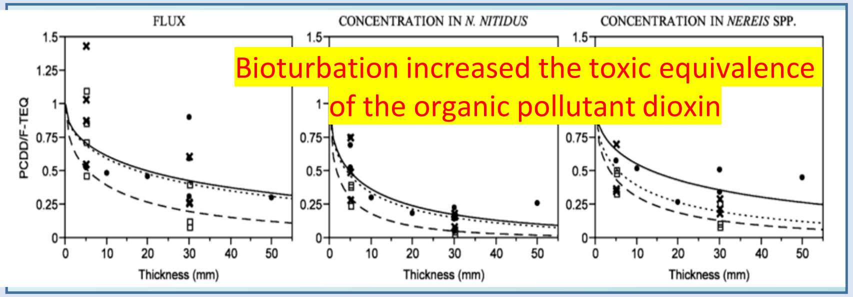
× Anisotropic suppression technology

In-situ control technology is subdivided into: adsorbent in-situ modification, In situ active cover, etc.

Active cover technology is affected by benthic disturbance.

In-situ improvement technology has more advantages and potential.

However, the existing in-situ adsorbents are not effective for organic pollutants.



(Josefsson et al., 2012)

Benthic bioturbation by benthic fauna reduced the remediation efficacy of in situ active mulching techniques.

In conclusion: Finding suitable adsorbents is the key to inhibiting the release of PAHs from paddy field sediments in the cold region.

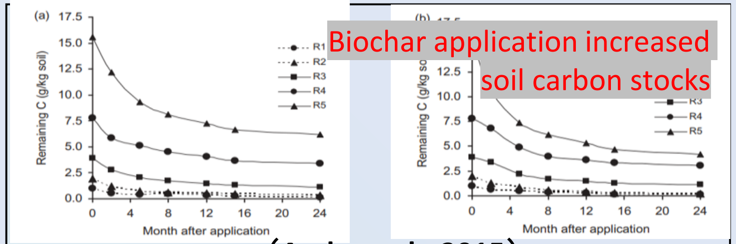
Technical Optimization

- ## Research on biochar in pollution remediation

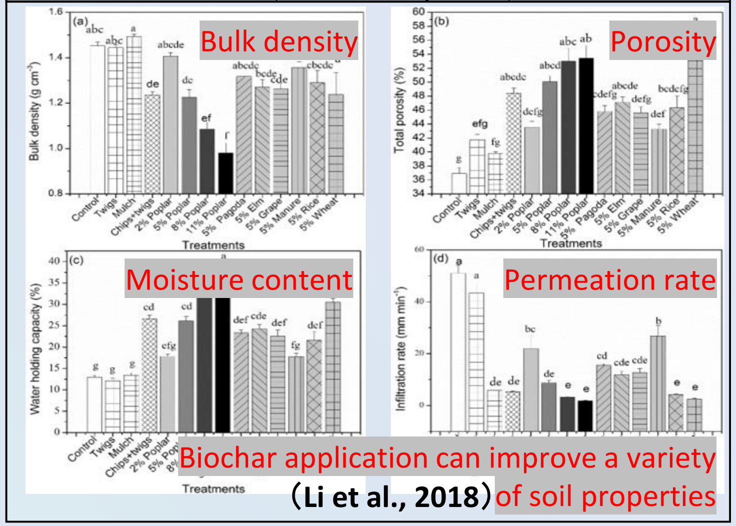
Various types of biochar

Rice Husk Biochar - Recycling of Rice Field Waste

Broad application prospects in the field of soil remediation

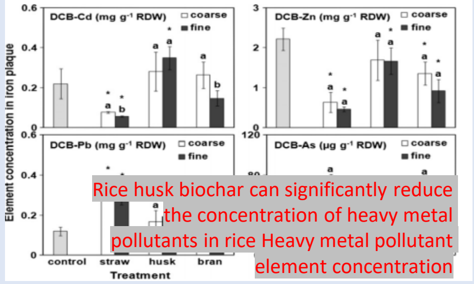


（Anda et al., 2015）

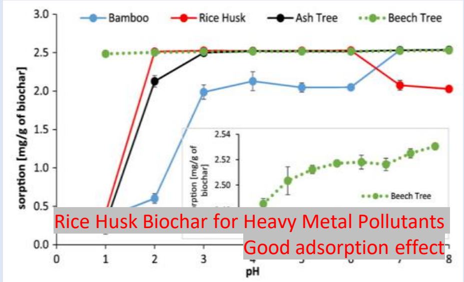


（Li et al., 2018）

Soil application of biochar improves soil properties (pH, moisture, microbial load, and activity), increases soil fertility and crop yields, increases carbon sequestration time, and reduces CO_2 emissions.



（Zheng et al., 2012）



（Soudek et al., 2017）

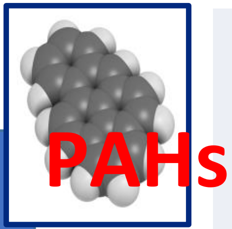
Due to its adsorption capacity, **rice husk biochar has better application value in situ remediation of contaminated soil**. Existing studies focused on heavy metals, **and fewer studies on organic contaminated soils such as PHE.**

Existing problem

1

It has been shown that benthos disturbance can cause the structure and properties changes of the sediments. However, the current research on bioturbation is centered on the disturbance of benthic organisms in large ecosystems such as oceans, estuaries, and lakes. Rice-crab farming has not been adequately studied as a small ecosystem with bioturbation.

2



Currently, most current studies on the remediation of PAHs contamination in the environment by straw biochar have been conducted in water and soil environments. Sediment systems are more complex and variable than individual water and soil environments, and the remediation of PAHs in the sediments of paddy systems is of substantial significance for food security and human health reasons.

3

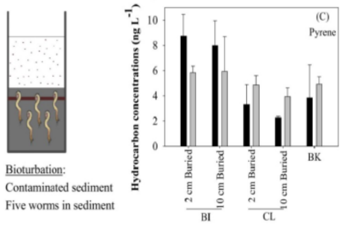
Little research has been reported on the remediation of PAHs contamination in sediments of integrated rice farming systems containing bioturbation conditions, the effect of biochar addition on the biological effectiveness of PAHs in integrated rice farming systems is unclear. The mechanism of this release is unknown and needs to be explored.

Existing problem

- **The mechanism of this release is unknown and needs to be explored.**

(Qin et al.，2014)

Various bioturbation effects



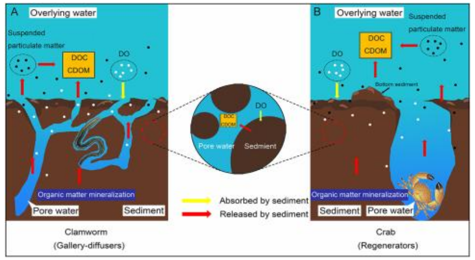
(Tian et al.，2019)

Disturbance of sandworms in double-toothed enclosures (marine)

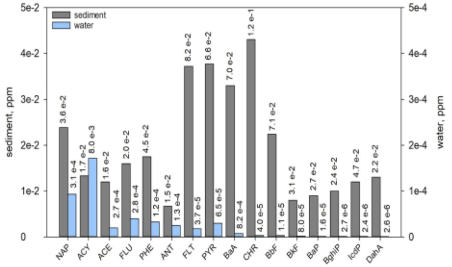
(Mermillod-Blondinet al.，2008)

Perturbation of tubular worms (freshwater)

Significant effects of bioturbation effects on PAHs release



(Nie et al.，2021)



(Jesus et al.，2022)

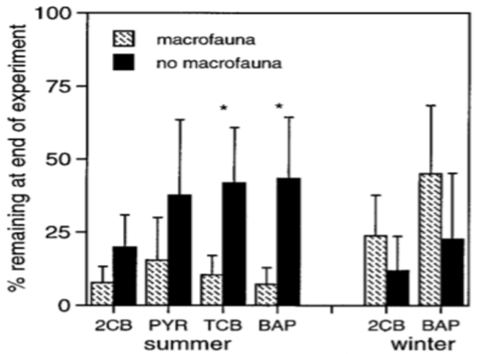
Related studies have shown that bioturbation significantly enhanced DOC concentration in overlying water, which has a strong adsorption capacity for organic matter, thus **promoting** the release of PAHs from sediments.

Facilitating release

Release inhibition

?

③



(Schaffner et al.，1997)

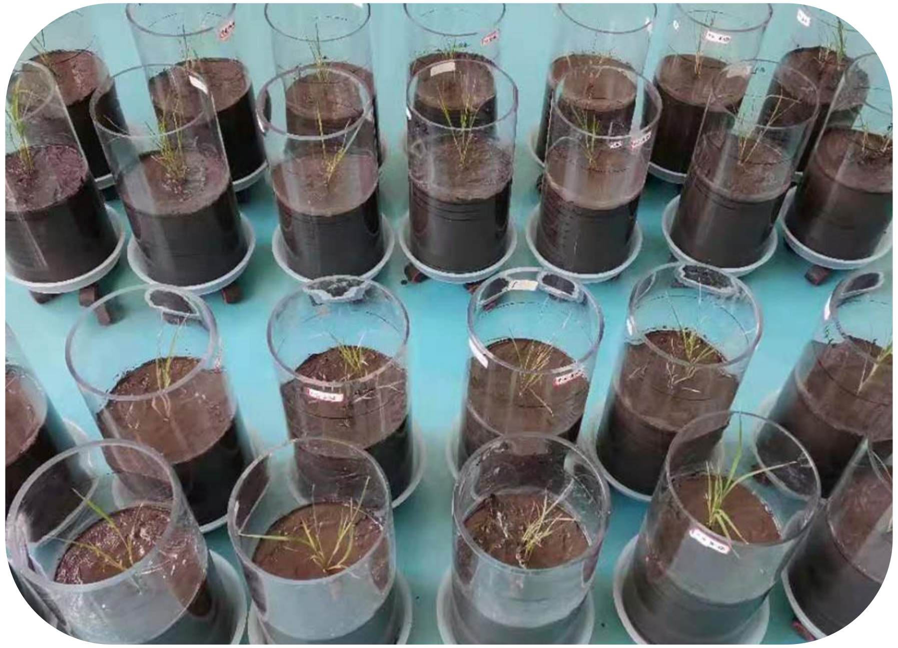
Some studies have shown that bioturbation **inhibits** the release of PAHs from sediments

1. It indicates that the release of PAHs from sediments in freshwater ecosystems is influenced by a variety of environmental factors, such as sediment, benthic fauna.

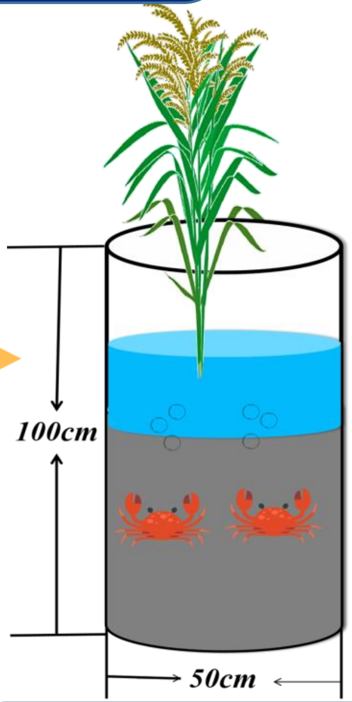
2. The mechanism of this release is unknown and needs to be explored.

Research Design

Release of benthic phenanthrene(PHE) by bioturbation



Indoor microcosmic system



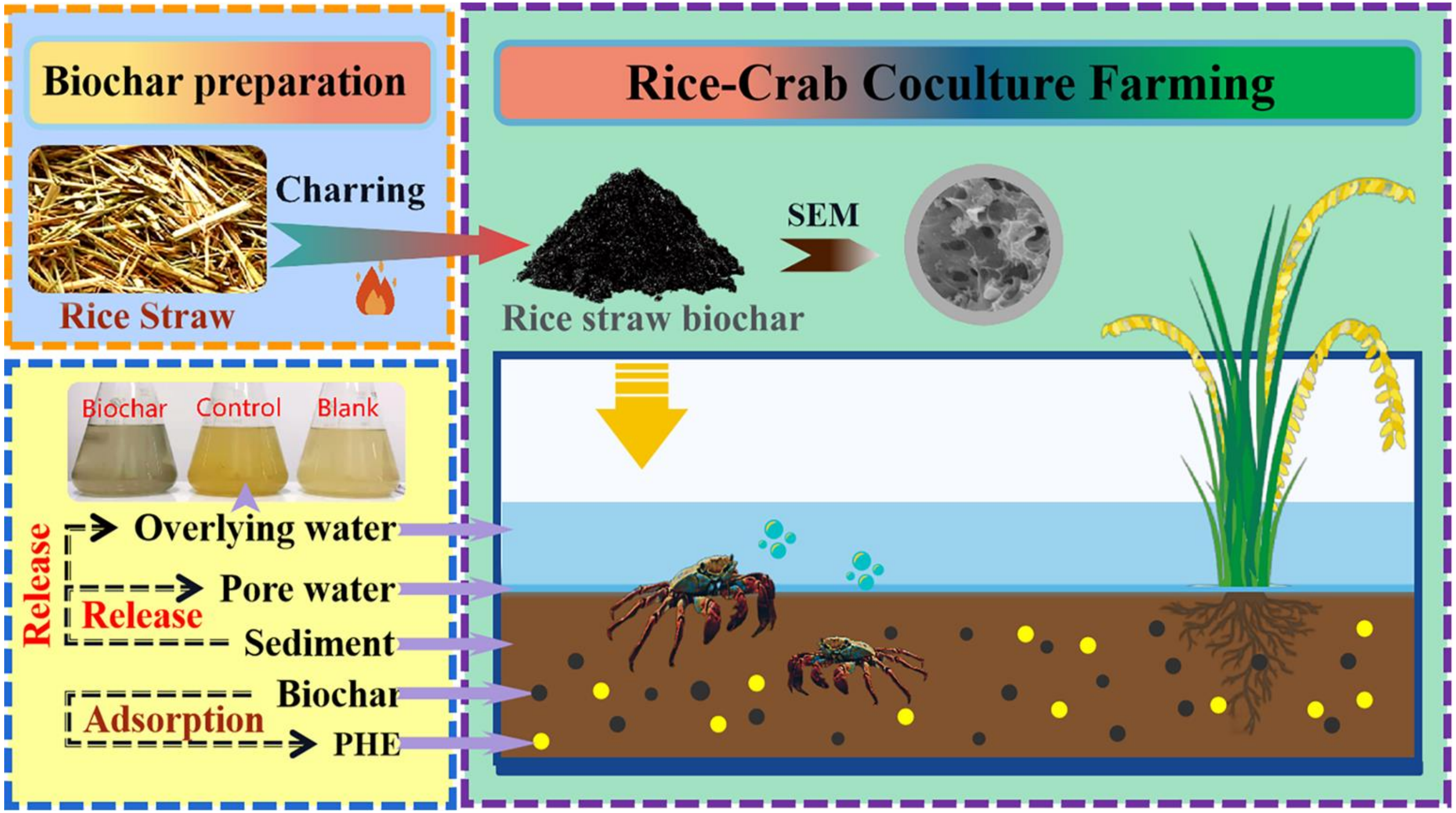
microcosmic device

Microcosmic experimental design

Two treatment groups, the control group and the crab disturbance group were set up. The experimental period was 30 d. Overlying water samples with a volume of 1 L were collected every 5 d. The physicochemical properties of the overlying water, such as dissolved phenanthrene(PHE), particulate phenanthrene(PHE), total suspended solids (TSS) and dissolved organic carbon (DOC), were measured.

The microcosmic system was a cylindrical device with a diameter of 50 cm and a height of 100 cm.
The device contained rice, Chinese mitten crab, overlying water, and sediments.

Research Design



Preparation of rice straw biochar

Characterization of rice straw biochar

Adsorption mechanism of biochar

Biochar addition to sediments

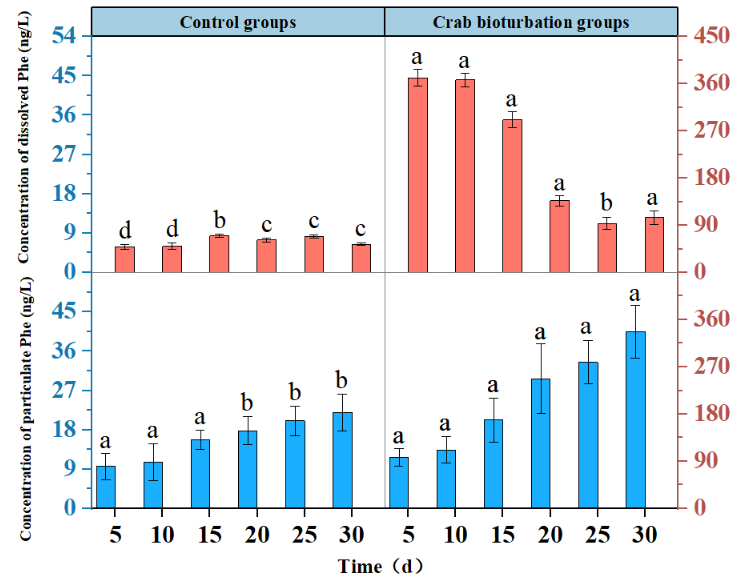
Inhibitory effect of biochar

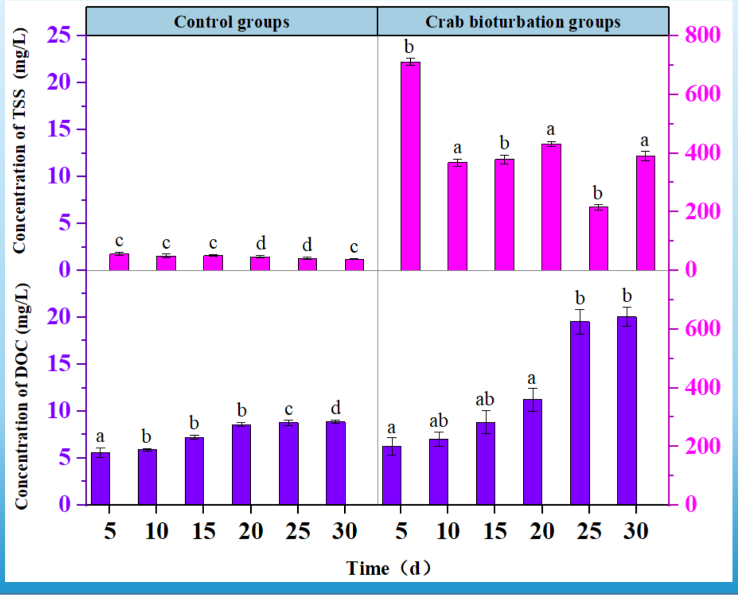
Biological validity analysis

Research result 1:
Effect of bioturbation on the release of PHE from sediments

Effects of bioturbation on the release of PHE from the sediments

Changes in physicochemical properties of TSS and DOC in overlying water





Results： The release concentrations of PHE in the particulate and dissolved states of the sediments in the crab bioturbation groups were 5.3 and 1.8 times higher than those in the control group without crab bioturbation, respectively.
Analyze： Bioturbation significantly contributed to the release of PHE from the sediments to the overlying water.

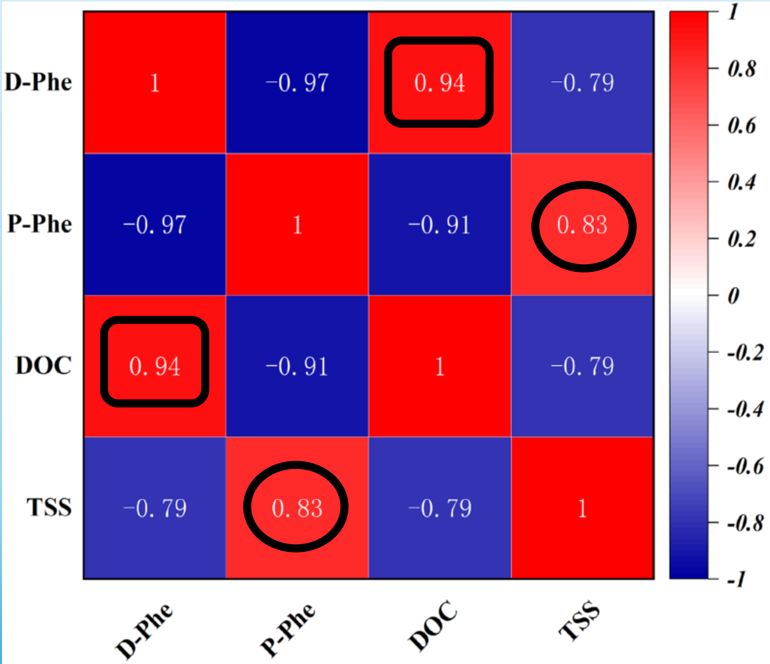
Results：TSS and DOC concentrations in the overlying water of the crab bioturbation group were 18.3 and 3.6 times higher than those of the control group without crab bioturbation, respectively.

Analyze：Bioturbation significantly contributed to TSS and DOC concentrations increase in overlying water.

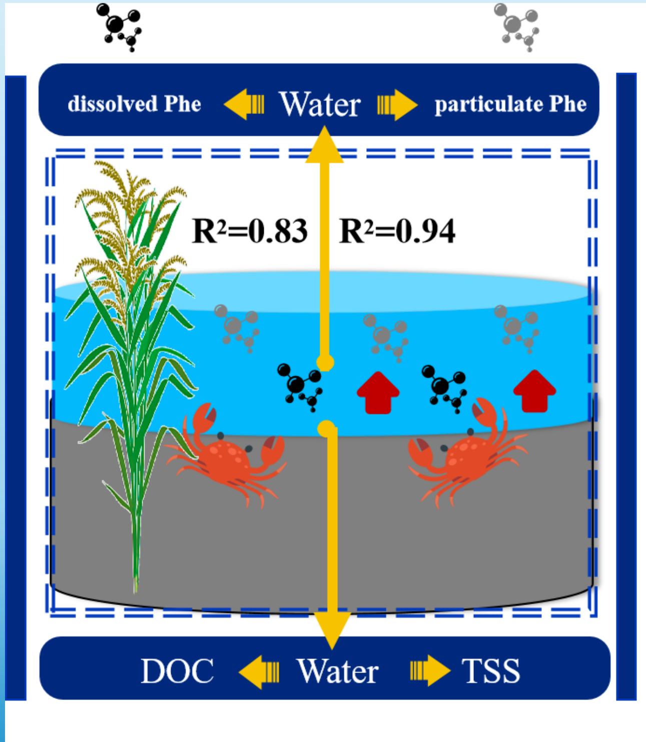
Research result 1:
Effect of bioturbation on the release of PHE from sediments

Pearson correlation analysis(p<0.05)

PHE mechanistic analysis of upward water releases



D-Phe:dissolved phe
P-Phe:particulate phe



Results： ①The correlation between dissolved PHE and DOC was R^2=0.94, p<0.05.

②The correlation between particulate PHE and TSS was R^2=0.83, p<0.05.

Analyze： The transport of particulate PHE from sediment by crabs bioturbation led to TSS concentration increase in the overlying water, which in turn led to an increase in particulate PHE concentration in the overlying water. Crab bioturbation significantly increased DOC concentration in the overlying water, and due to the adsorption of dissolved PHE on DOC, the dissolved PHE concentration in the overlying water increased accordingly.

Research result 2:
Characterization of PHE adsorption on rice straw biochar

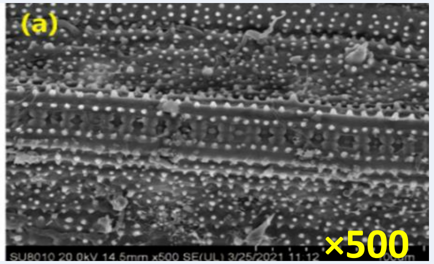
Explored the surface topography of biochar

Selected thick and complete rice straw, washed and rinsed the surface impurities repeatedly.

characterization

(SEM)

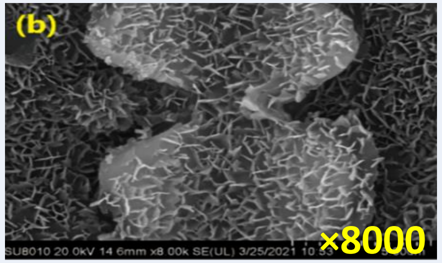
Rice straw had an intact tubular vascular structure within it.



(SEM)

magnification

Magnification revealed that the interior of the foramen contained fibrous protrusions.



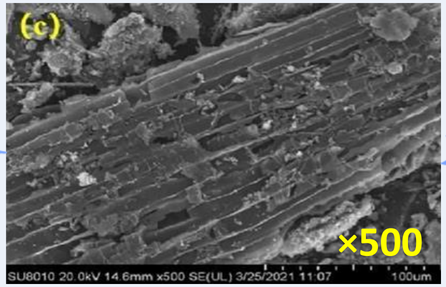
Rice straw dried and crushed, was placed in a muffle furnace and slowly increased to 500 ℃, was carbonized at constant temperature for 3h.

RSC

characterizatio
n

(SEM)

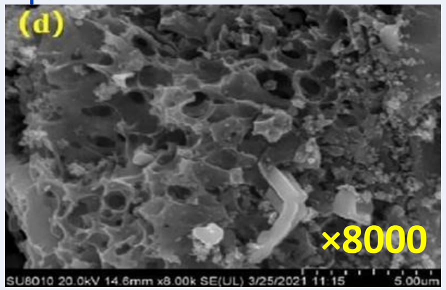
The vascular bundle structure was found to be disrupted with a large number of irregular pits.



(SEM)

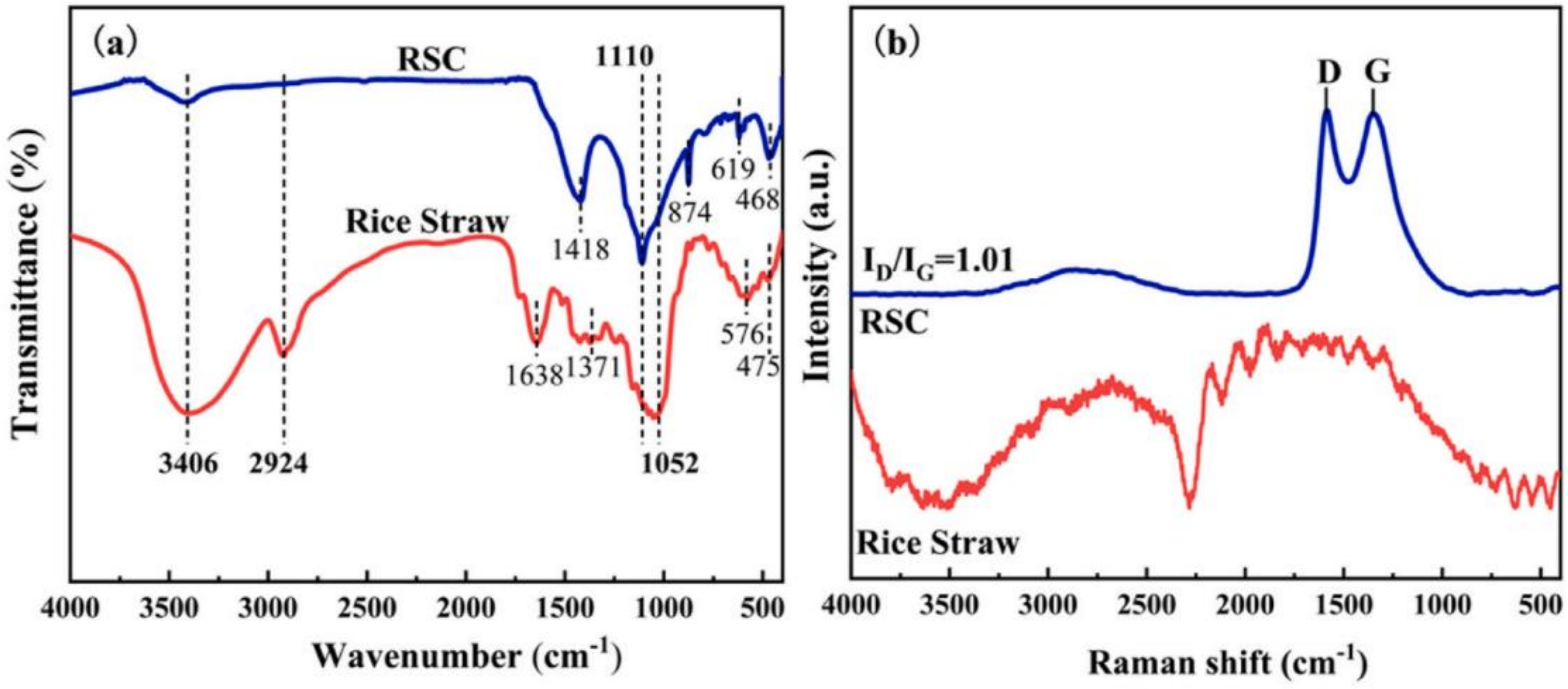
magnification

The laminar distribution of pore structure further increased the number of active sites inside the RSC, which provided favorable conditions for the adsorption of pollutants.



Research result 2:
Characterization of PHE adsorption on rice straw biochar

Explored Fourier transform infrared spectra and Raman spectra

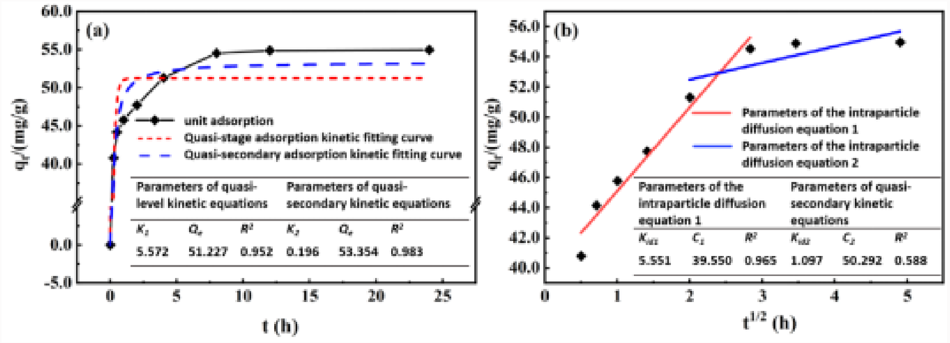


FTIR showed that the high degree of carbonization and high aromaticity of RSC can also improve the carbon content of soils and the stability of biochar in soils, improving soil nutrient conditions and thus promoting crop growth.

Research result 2:
Characterization of PHE adsorption on rice straw biochar

Explored Biochar Adsorption Characterization

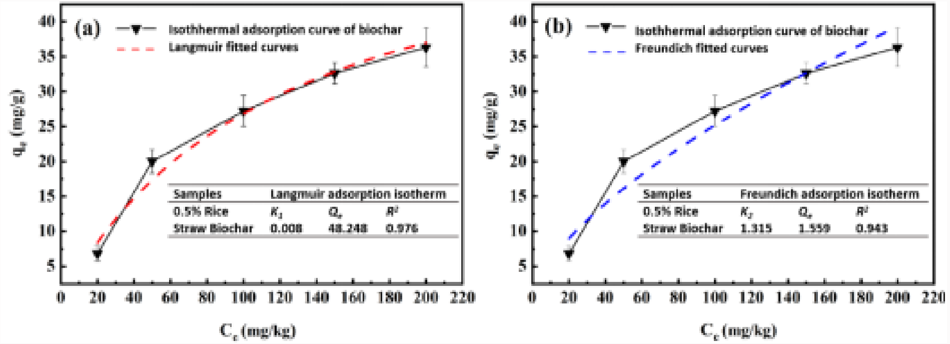
Adsorption kinetic model fitting for PHE adsorption from sediment by rice straw biochar



Results: PHE adsorption by rice straw biochar increased rapidly in the first 3h, then the adsorption rate slowed down after 6h, and basically reached the adsorption equilibrium after 15h. The coefficient of the second-order kinetic model (R^2=0.983) was much larger than that of other models.

Analyze: The results showed that the adsorption kinetic process in this experiment conformed to **the quasi-secondary kinetic model**, indicating that the **adsorption** process was mainly dominated by **chemisorption**.

Adsorption isothermal model fitting for PHE adsorption from sediment by rice straw biochar



Results: PHE adsorption by rice straw biochar increased with its initial concentration, and the **Langmuir** isothermal adsorption model (R^2=0.976) was better fitted for the PHE adsorption process by rice straw biochar compared to the Freundich isothermal adsorption model (R^2=0.943).

Analyze: It was shown that the adsorption mechanism of PHE by rice straw biochar was complex and dominated by **monomolecular layer adsorption.**

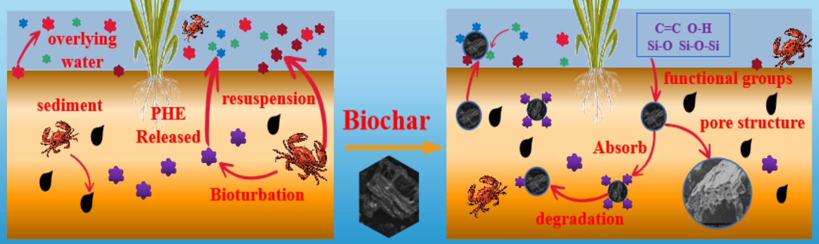
Research result 3: Changes in dissolved PHE content in overlying water

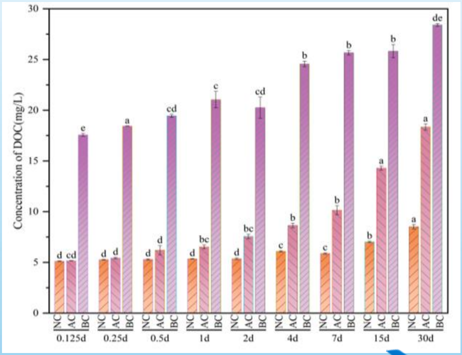
Explored changes in dissolved PHE content in overlying water

PHE (Sediments state) PHE (Particle state)

DOC TSS TOC PHE (Dissolved state)

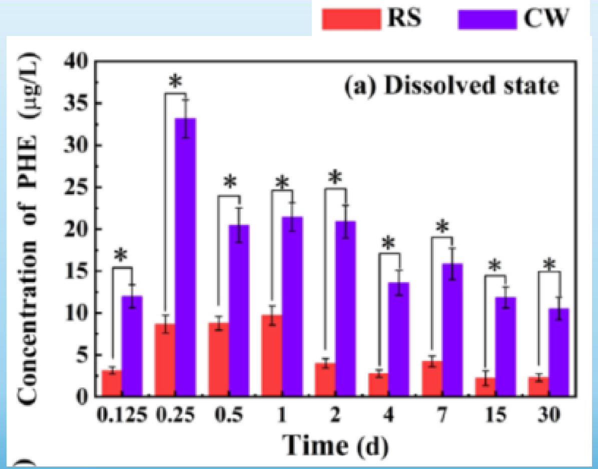
- Rice straw biochar (RSC) at a concentration of 0.5% (W/W) was added to all sediments and mixed uniformly (called RS)
- sediments were not spiked with any amount of biochar (called CW)





Change in DOC content in overlying water

significant correlation



Changes in dissolved PHE content in overlying water in biochar-added vs. biochar-free systems

The concentrations of dissolved PHE in the CW and RS ranged from 10.55 to 33.16 μg/L and 2.25–9.73 μg/L during the experimental period, respectively. **The addition of biochar caused a significant reduction in the dissolved PHE content ($P < 0.01$) compared with the CW treatment.**

The removal rate of dissolved PHE by biochar exceeded 50% throughout the experimental cycle, and the content of dissolved PHE decreased by 78.03% after 30 d of remediation.

Results

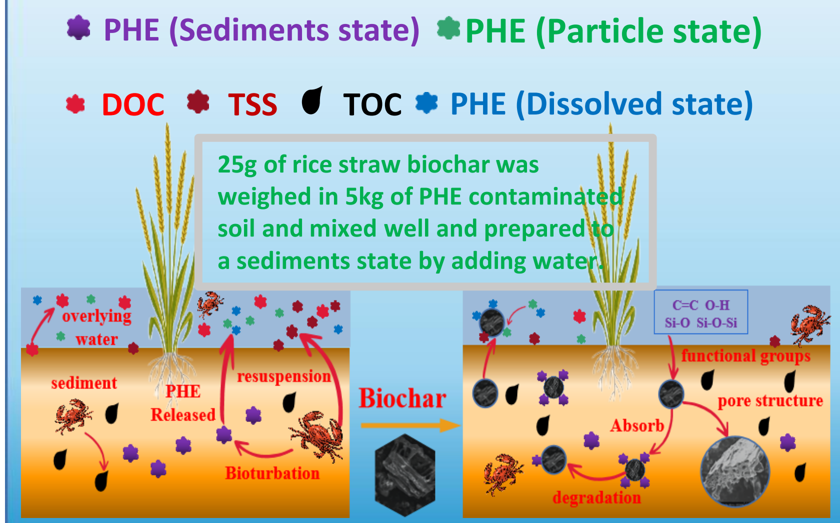
Bioturbation introduced a portion of the biochar particles from the sediments into the water column, and the freely dissolved PHE in the water was absorbed by the reactive sites provided by the large number of pore structures on the surface of the biochar, which reduced the level of contaminants in the overlying water.

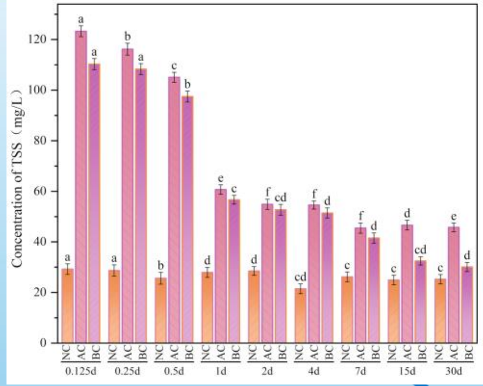
The activity of crabs can produce a large amount of dissolved organic matter (DOC), and the presence of DOC contributed to a reduction in the PHE content of water.

Analyze

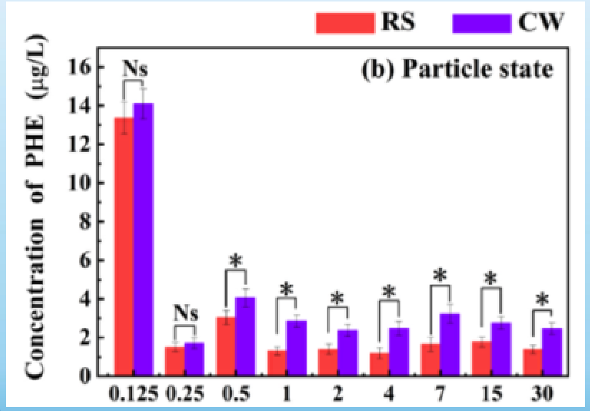
Research result 4: Changes in particulate PHE content in overlying water

Explored changes in particulate PHE content in overlying water





Change in TSS content in overlying water



significant correlation

Changes in particulate PHE content in overlying water in biochar-added vs. biochar-free systems

- The particulate PHE content in RS was significantly reduced compared to CW.（P<0.05） The particulate PHE in the overlying water of RS treatment was reduced by 43.72% compared to CW.
- RSC added to sediments can effectively inhibit the migration and release of PHE from the sediment to the overlying water.

Results

- Crab bioturbation caused an increase in TSS in the overlying water (P<0.05). the suspended particulate matter had a strong adsorbing effect on particulate PHE to reduce the content of PHE in the overlying water.
- RSC particles adsorbed on the sediment surface are also introduced into the overlying water by resuspension due to bioturbation, and the biochar separated from the sediment surface could adsorb particulate PHE to reduce the content of PHE in the overlying water.

Analyze

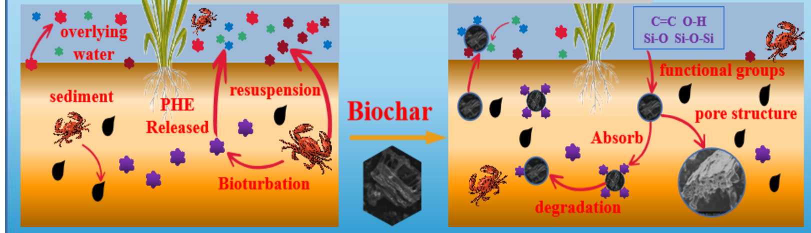
Research result 5: Changes in PHE content in the sediments

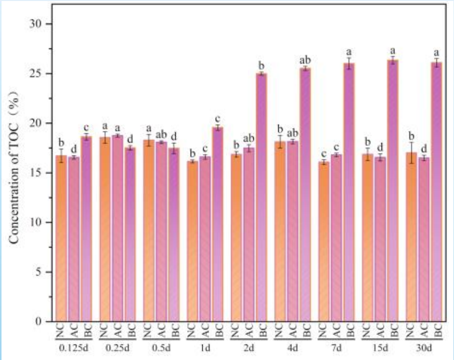
Explored changes in PHE content in the sediments

PHE (Sediments state) PHE (Particle state)

DOC TSS TOC PHE (Dissolved state)

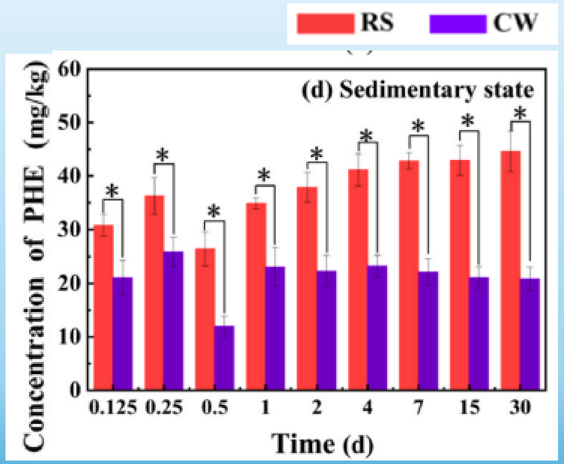
25g of rice straw biochar was weighed in 5kg of PHE contaminated soil and mixed well and prepared to a sediments state by adding water.





Changes in TOC content in the sediments

Significant negative correlation



Changes in PHE content in the sediments of rice straw biochar-added versus no biochar system

- No statistically significant difference in PHE content in the sediments of CW was found at the beginning and after 30 d, indicating a relatively slow decay process for PHE in the sediments in the microcosm system.
- The content of PHE in the RS sediments increased by 40.41%–119.62% within 30 d compared with the CW sediments, indicating that the addition of biochar had a significant fixation effect on the PHE in the sediments.

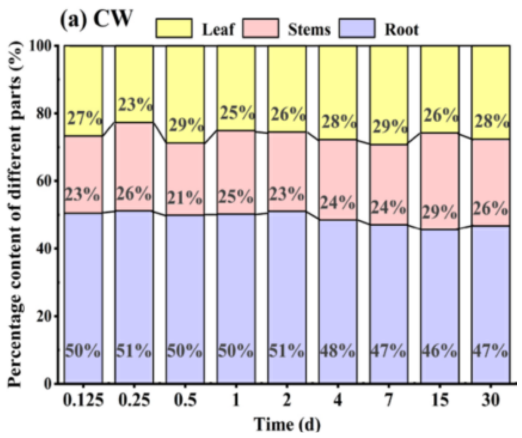
Results

- RSC in the sediment adsorbed the PHE in the sediment through its complex pore structure and developed specific surface area.
- The PHE content in the sediment was significantly negatively correlated with the TOC content in the sediment, showing that rice biochar can be used as a metabolic carbon source for microorganisms, promote the growth of PAH-degrading strains, and accelerate PHE degradation in sediment.

Analyze

Research result 6: changes in PHE content in plants

Explored changes in PHE content in plants

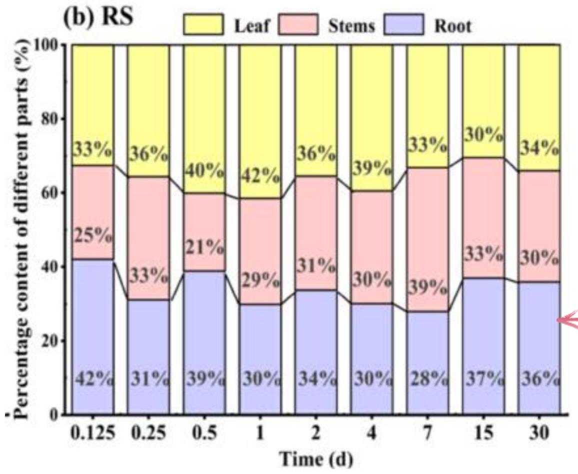


Percentage of PHE in each part of rice in CW treatments

1. After rice growth entered the **tillering stage**, rice plants with straight stalks and rapid growth were selected as experimental rice.
2. Sampling times were **3h, 6h, 12h, 24h, 2d, 4d, 7d, 15d and 30d** after the start of the experiment, and **three** sets of parallel samples were set for each treatment at each sampling point.

Ultrasonic water bath extraction

Measurement of PHE content by liquid chromatography



Percentage of PHE in various parts of rice in RS treatments

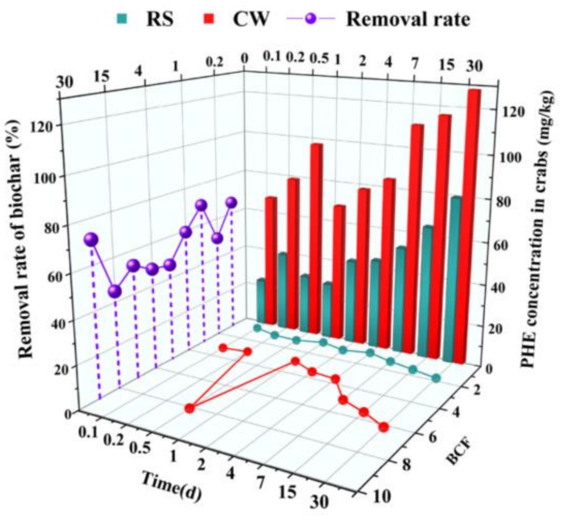
1. However, there was a **large difference** between the contents of PHE in rice from the two treatment groups. The proportion of PHE in the stems and leaves of rice in RS increased by **2%–15%** and **4%–17%**, respectively, while the proportion in the roots showed a significant decrease ($P < 0.01$).

2.The inhibitory effect of biochar on plant uptake of organic pollutants may be due, on the one hand, to the fact that the biochar reduced the concentration of **bioavailable PHE** in the soil, and on the other hand, the loose and porous structure of biochar provided a suitable living environment and shelter for a variety of **PAHs-degrading bacteria** in the soil.

3. The result confirmed that the transfer of PHE from sediments to plant roots was **greatly limited** due to the addition of **biochar**. it was still unknown how biochar interfered with and inhibited the uptake and **translocation of PAHs** in different parts of the plant, but the effect of biochar addition on the alteration of soil properties and the signaling between interroot microorganisms cannot be excluded.

Research result 7: Changes in PHE levels in crabs

Explored changes in PHE levels in crabs



The crabs were destructively sampled at 3 h, 6 h, 12 h, 24 h, 2 d, 4 d, 7 d, 15 d and 30 d in the system.

cryogenic freezing

Ultrasonic water bath extraction

concentrate

Measurement of PHE content by liquid chromatography

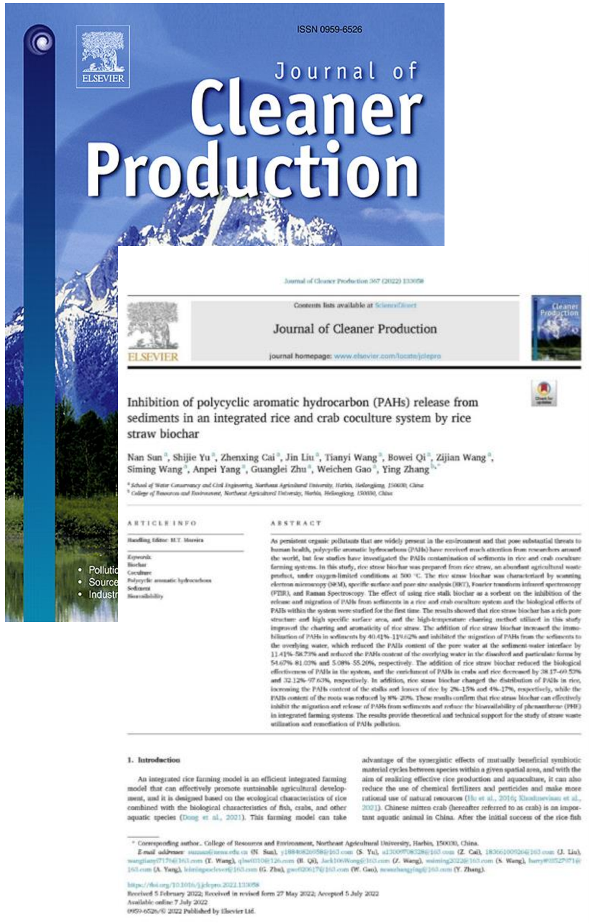
Crab enrichment factor

$$BCF = \frac{C_{PHE(cral}}{C_{PHE(mud)}}$$

1. Although the PHE concentration in the artificially polluted sediments in this study was high, the crabs exposed to the sediments showed a high survival rate (>86%), which may be because crabs in the larval stage were more tolerant to PAHs. However, a significant decrease was observed in the biological activity of the crabs in both CW and RS after 30 d of being exposed to PHE in the sediments.

2. The total uptake of PHE and the BCF in crabs in RS was significantly lower ($P < 0.01$). After 30 d of biochar amendment, the enrichment of PHE by crabs in RS was 38.17% lower compared with CW, indicating that the addition of straw biochar effectively inhibited the uptake of PHE from the sediment by crabs.

3. The process of PHE immobilization by biochar in the sediments also reduced the ability of PHE to be released into the water in a bioavailable state, which blocked the uptake of PHE from the water and sediments by crabs during respiration and feeding activities.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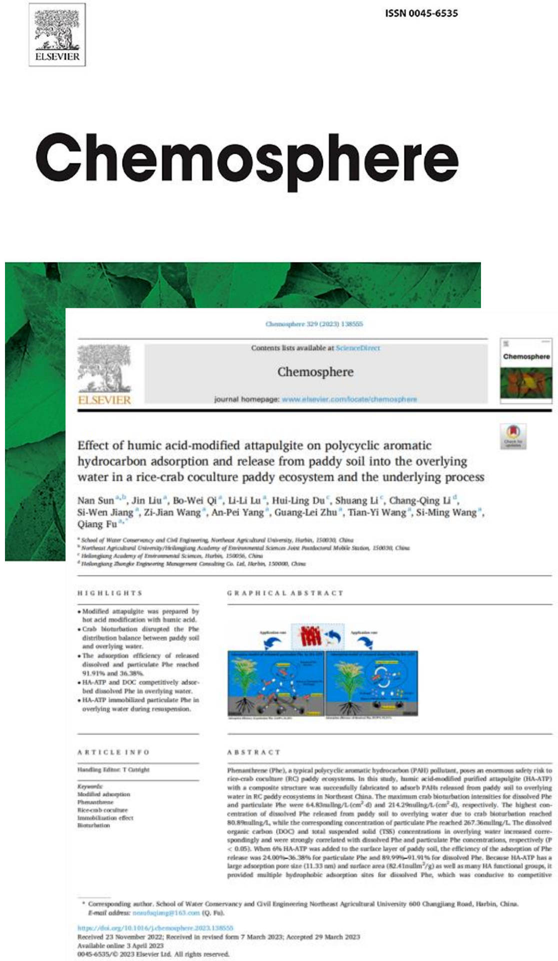
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Thank you!