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Assessing the capacity of different organic amendments to reduce trifluralin bioavailability in a contaminated sediment

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ABSTRACT

This study provides new insights into the behavior, fate, and remediation of trifluralin (TFL), a persistent herbicide, in contaminated river sediments. By focusing on bioavailability, desorption, biodegradation, and immobilization, we evaluated the potential of combined bioremediation strategies. Desorption experiments identified XAD-4 resin as the most effective extraction agent, while β-cyclodextrin showed limited efficacy due to solubility constraints. Kinetic modeling confirmed the presence of both fast and slow desorption phases. To reduce TFL bioavailability, sediment amendments with activated carbon (AC), biochar (BC), and compost (CO) were investigated. AC at a rate of 0.5% reduced TFL bioavailability from 67.1% to <10 μg/kg within 90 days, outperforming BC and CO. Under anaerobic conditions, TFL degradation reached near-complete removal within 2 weeks, while XAD-4 enabled >95% extraction efficiency in 8 hours for accurate desorption assessment. Compost supported plant growth and enhanced phytoextraction potential. Phytotoxicity tests confirmed *Zea mays* as a resilient candidate for phytoremediation. Our findings suggest that integrating anaerobic biodegradation with carbon-rich amendments, particularly AC and BC, presents a promising in-situ remediation strategy. The application of compost offers a sustainable and locally available solution for pollutant sequestration, meriting further investigation for long-term and large-scale use.

1. Introduction

Trifluralin (TFL) is a widely used pre-emergence herbicide from the di-nitroaniline group, commonly applied in agricultural practices since the 1960s. Due to its high hydrophobicity, low water solubility, and strong affinity for organic matter (Wallace, 2014), TFL accumulates in soils and aquatic sediments where it persists for extended periods (Epp et al., 2017). Its classification as a ‘priority hazardous substance’ under the European Water Framework Directive reflects its ecotoxicological significance and the associated human health risks (Wexler et al., 2023). TFL’s persistence in sediments, with half-lives ranging from minutes under sunlight to several months in anaerobic conditions, exacerbates its ecotoxicity, including high acute toxicity to fish (LC50 in the sub-100 ppb range) and potential endocrine disruption (Grover et al., 1997). This underscores the need for targeted remediation strategies beyond traditional approaches. Given its frequent detection in sediment environments and potential for partial bioavailability, TFL serves as a representative model compound for studying the behavior of persistent organic pollutants (POPs) in contaminated sediments.

Traditional risk assessments of polluted sites have relied on measuring total pollutant concentrations (Chen et al., 2023; Klimkowicz-Pawlas et al., 2023). This method often overestimates risks because only the bioavailable fraction—determined by desorption kinetics—drives toxicity and mobility (Zhou et al., 2018). Challenges include accurately measuring bioavailability in complex sediment matrices, where aging processes reduce accessibility over time, complicating bioremediation (Wang et al., 2018a, 2018b). Integrating bioavailability into risk assessment and remediation planning has become essential (Semple et al., 2004; Muz et al., 2020). Desorption kinetics, which reflect the equilibrium between pollutants bound to sediment and those dissolved in pore water, are particularly important for evaluating environmental exposure and bioremediation potential (Semple et al., 2004; Pignatello and Xing, 1996).

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Nomenclature section - list of abbreviations or acronyms

TFL	Trifluralin
AC	Activated carbon
BC	Biochar
CO	Compost
POPs	Persistent Organic Pollutants
PAHs	Polycyclic Aromatic Hydrocarbons
PGPB	Plant Growth-Promoting Bacteria
OPPs	Organophosphorus Pesticides
HPCD	2-hydroxypropyl β-cyclodextrin
BCD	β-cyclodextrin
MCD	Methyl-β-cyclodextrin
MDL	Method Detection Limit
PQL	Practical Quantitation Limit
MEF	Maximum Extractable Fraction

The application of organic amendments (carbon-rich sorption agents) enhances the sorption and sequestration of organic pollutants in soils (Valizadeh et al., 2022; Sharma et al., 2025) and sediments (Spasojevic et al., 2015). When pollutants become more strongly trapped, their levels in surrounding water decrease, reducing uptake by organisms (Rämö et al., 2022). Prior studies have demonstrated that black carbons (e.g., BC) facilitate abiotic reduction of TFL by sulfides in anoxic sediments, enhancing degradation rates up to 4-fold at 2 % dosage (Gong et al., 2016). AC has reduced bioavailability of hydrophobic organic contaminants (HOCs) like TFL analogs by 60–90 % in sediments, as seen in field trials (Janssen et al., 2013). CO and other organic waste have shown variable effects, sometimes repressing biodegradation by limiting microbial access due to strong sorption (Kanisser and Sims, 2011; Boutasknit et al., 2024). Comparative evaluations of AC, BC and CO for TFL in sediments are scarce, with most research focused on soils or other pesticides (Gong et al., 2016; Rasool et al., 2022). Key difficulties include site-specific variability (e.g., pH, organic matter content) and long-term efficacy, as amendments may degrade or release pollutants over time (Hatzisymeon, et al., 2021). These studies provide a strong foundation for our approach, supporting the hypothesis that carbon-based amendments can reduce pollutant mobility and bioavailability, aiding risk mitigation and environmental recovery. To enhance soil sorption capacity, various carbon materials have been tested, including sustainable, low-cost options like biochar derived from waste biomass (Fang et al., 2017; Kah et al., 2017; Gryta et al., 2024; Grgić et al., 2019a, 2019b) and advanced materials like carbon nanotubes (Zhang et al., 2017; Alazaiza et al., 2021).

Despite promising lab-scale results, challenges persist in scaling these amendments for field use, including incomplete knowledge of their interactions under real environmental conditions and potential for unintended effects like microbial inhibition (Mukherjee et al., 2022; Tamma et al., 2025; Barthod, 2018). The key problems and difficulties in using different organic amendments to reduce TFL bioavailability in contaminated sediments includes variability in amendment properties (e.g. surface area, porosity, functional groups, and chemical composition) (Maletić et al., 2022); standardization challenges (e.g. differences in feedstock, pyrolysis conditions, and post-treatmen) (Ghorbani et al., 2024); dosage optimization (Spasojevic et al., 2015); sediment-specific effects (e.g. organic matter content, pH, texture, and hydrodynamics) (Sharma et al., 2025); bioavailability vs. ecological impact (Maletić et al., 2022); sediment dynamics (e.g. sorption, desorption, and degradation processes can vary over time) (Čučak et al., 2017) and integration with phytoremediation or biota (Arayal, 2024). Recent innovations, such as biochar-PGPB composites for phytoremediation (Kamyab et al., 2025) or nanocomposites for pesticide delivery (Ly et al., 2023; (Sotoudehnia Korrani et al., 2023), highlight the need for integrated approaches but rarely address TFL immobilization in sediments. To assess the bioavailability of TFL and explore the potential for its remediation, this study seeks to advance our understanding of the behavior and persistence of TFL within the sediment–water system. The novelty of the work, to the best of our knowledge, lies in the fact that AC, BC and CO have not previously been comparatively evaluated within the framework of our defined objectives. Specifically, the research aims to: (1) develop optimized chemical tests for rapid detection of TFL bioavailability; (2) assess the biodegradation potential of TFL in sediments to investigate the potential use of selected materials as a bioremediation technique, taking into account which is the most efficient and cost-effective method; and (3) investigate the possibility of using carbon-rich agents to locally alter the geochemical properties of sediment to immobilize and sequester TFL in the sediment.

2. Materials and methods

In this study, we evaluated the bioavailability, biodegradation potential, and immobilization of TFL in river sediments, both unamended and amended with selected organic materials (Fig. 1*; see Chapter 2.2*). TFL was chosen as a model pollutant to simulate contamination scenarios and test remediation strategies under controlled conditions. The experiments were conducted using a predefined spiked concentration of TFL, relevant for assessing bioavailability and treatment efficiency, rather than measuring background levels.

Step 1: Sediment samples were collected with an Eijkelkamp core sampler from a depth of 0 – 0.5 m.

Step 2: The sediment was spiked with TFL at approximately 4000 μg/kg and aged for two years before further testing. Initial TFL concentration was confirmed after this aging period.

Step 3: Potential bioavailability was assessed through desorption experiments using different extraction agents (e.g., Tenax, XAD-4, and three types of cyclodextrins). A multistage extraction approach was applied, followed by modeling to estimate the bioavailable fraction of TFL.

Step 4: The biodegradation potential of TFL was evaluated under both aerobic and anaerobic conditions using an inoculum derived from channel sediments and wastewater sludge (*see Chapter 2.4*).

Step 5: The immobilization of TFL in sediment was tested by applying carbon-based amendments—biochar (BC), activated carbon (AC), and compost (CO). Different amendment doses and aging periods were assessed to determine the most effective conditions for reducing TFL mobility. Germination tests were also performed to evaluate potential phytotoxic effects.

2.1. Chemicals

For the experiments, the following chemicals and reagents were used: amberlite XAD-4 resin (Fluka, Buchs, Germany), silica gel (Fluka, Buchs, Germany), $CaCl_2$ (Sigma, Darmstadt, Germany), K_2CO_3 (Merck, Darmstadt, Germany), and $HgCl_2$ (Centrochem, Stara Pazova, Serbia). Organic solvents (p.a.) used in this study were acetone, hexane, pentane, and dichloromethane. The standard of TFL was of analytical purity (Sigma, Darmstadt, Germany). Carbon-rich sorption agents were activated carbon (Norit, Marshall, USA), biochar (Maxigrill, Kaona, Serbia) and commercially available compost (Savacoop, Novi Sad, Serbia). Tenax is produced by Sigma-Aldrich (Missouri, USA) and three cyclodextrins (2-hydroxypropyl β-cyclodextrin (HPCD), β-cyclodextrin (BCD), and methyl-β-cyclodextrin (MCD)) were obtained from Wacker, Munich, Germany. Physico-chemical properties of selected chemical are given in Table 1.

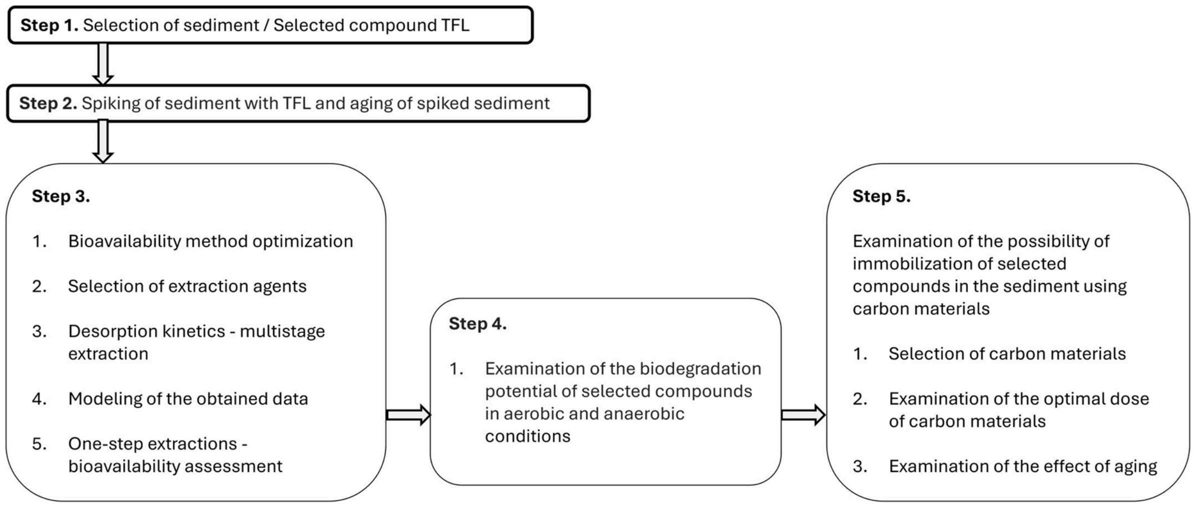

Fig. 1. Flow diagram of experiment setup.

Table 1
Physico-chemical properties of selected chemical agents.

	Size particle (mesh)	Density (g/cm^3)	Pore volume (ml/g)	Pore size (nm)	Surface area (m^2/g)
XAD-4	20–60	1.02	0.980	10	750
Tenax	60–80	0.25	2.40	200	35
	n[1]	**$R = H$ or**	**Subst.**[1]	**M**[2] **(Yes)**	**Solubility in water (mg/l)**[3]
*****BCD**	1	-H	0	1135	18.5
******MCD**	1	$-CH_3$	1.80	1312	> 500
*******HPCD**	1	$-CH_2CHOHCH_3$	0.65	1400	> 600

* BCD = β-cyclodextrin ** MCD = methyl-β-cyclodextrin, and *** HPCD = 2-hydroxypropyl β-cyclodextrin,.

[1] - the average number of substituents per repeating unit of glucose units.

[2] - molecular mass.

[3] - solubility at 25 °C.

2.2. Sediment samples characterization

The sediment selected for the experiments was sampled from the Jegrička, a 64 km long river in Vojvodina (Republic in of Serbia). This sediment was selected based on its geochemical properties and the sorption potential of selected organic compounds. Previous research (Grgić et al., 2019a, 2019b) showed, that this sediment had no history of contamination with the TFL, which is important for the selected tests due to interactions in the sediment. Surface samples were taken using Eijkelkamp's core sampler, from 0 to 0.5 m depth according to the standard sediment method (SRPS ISO 5667–12:1995). The 2-year aging period was designed to simulate real-world environmental conditions, enhancing the relevance of our findings for long-term pollutant behavior. The sediment was air dried, stored under control conditions to mimic natural aging processes. It was kept at a constant temperature of 20 °C in a dark, humidity-controlled environment (relative humidity ~60 %) to prevent microbial activity and ensure consistent aging, homogenized, and sieved through a 2 mm sieve. The sediment was spiked at concentration range around 4000 μg/kg with TFL dissolved in methanol and left for two years to age. After aging, the initial TFL concentration was determined using GC/MS (Agilent Technologies 7890B GC System/5977A, USA) and it was 3780 μg/kg. Additional characterization is given in Table S1 in Supplementary Material. TFL concentration is measured by the method described in Supplementary material with method detection limit (MDL) of 10 μg/kg and practical quantitation limit (PQL) of 25 μg/kg.

2.3. Optimization of partial extraction methods to assess the bioavailability of TFL

Chemical extraction methods, although not fully representative of biological processes, are widely employed in sediment studies as an initial tool to estimate the potentially bioavailable fraction of organic contaminants. They allow for rapid, reproducible, and cost-effective screening of pollutant lability in complex environmental matrices.

To optimize methods for assessing TFL bioavailability in sediments, five extraction agents were tested: Tenax, XAD-4 resin, and three cyclodextrins (HPCD, BCD, MCD), selected for their physicochemical properties (Table 1) and ability to represent different bioavailability aspects.

Tenax, widely applied for hydrophobic organic compounds, offers high sorption capacity and inertness, effectively simulating desorption from sediments under benthic-like conditions. Its reliability for compounds such as PAHs (Cornelissen et al., 2011; Bernhardt et al., 2013) and POPs are well documented (Cui et al., 2013; Lydy et al., 2014).

Cyclodextrins (HPCD, BCD, MCD) are cyclic oligosaccharides forming inclusion complexes with non-polar molecules, enhancing solubility and mobilization. They have proven effective for extracting PAHs and similar contaminants from soils (Bernhardt et al., 2013) and sediments (Spasojević et al., 2015). However, their application for TFL remains largely unexplored, underscoring the novelty of this study.

XAD-4 resin, an aromatic polymer with a high surface area, shows strong sorptive and desorptive properties. Although primarily used for PAHs in sediments (Spasojević et al., 2015; Rončević et al., 2016), its high efficiency and low cost make it a promising option for scalable, routine monitoring.

Together, these agents cover diverse desorption behaviors, enabling a comparative evaluation of their effectiveness in estimating the bioavailable TFL fraction in sediments.

Method optimization followed Spasojević et al. (2015) and involved multistep extraction over 144 h at intervals of 2, 6, 12, 24, 48, 96, and 144 h. For BCD, HPCD, and MCD extractions, 1 g of TFL-spiked sediment was placed in 500 ml flasks (triplicates), treated with 1 ml $HgCl_2$ (300 mg/l) to inhibit microbial activity, and mixed with 25 ml of 50 mM cyclodextrin solution. Flasks were shaken horizontally, and samples were collected at predefined contact times. Each liquid sample was sonicated with 10 ml methanol for 1 h, extracted with 3 ml hexane, and analyzed by GC–MS (see Supplementary material). For XAD-4 resin extractions, the resin was purified by Soxhlet extraction using ultra-pure water, methanol, hexane/acetone (1:1), methanol, and water, each for six hours. Then, 0.2 g resin, 1 g sediment, 1 ml $HgCl_2$ (300 mg/l), and 0.8 g K_2CO_3 (to promote flocculation) were combined. After extraction, the supernatant was decanted and analyzed for TFL. From the multistep tests, equilibrium desorption time was determined and applied in subsequent single-step extractions. In sediment-water systems, equilibrium is achieved when TFL exchange between phases is balanced, with no net concentration change despite molecular-level interactions.

2.4. Desorption modeling

To assess the bioavailable fraction of TFL in the sediment from the multistep partial extraction a two-compartment kinetic model according to Cornelissen et al. (1997) was fitted to the measured data:

$$\frac{S_t}{S_0} = F_{fast} \times e^{-k_{fast} \times t} + F_{slow+veryslow} \times e^{-k_{slow+veryslow} \times t} \qquad \text{(Eq.1)}$$

where S_t and S_o (μg/kg) represent the amount of TFL sorbed at initial time ($t = 0$) and after time t (h), while k_{fast} and $k_{slow+very\ slow}$ (t^{-1}) represent the first-order rate constants for the fast and slow+very slow phases of desorption, whereas F_{fast} and $F_{slow+very\ slow}$ (%) represent the fast- and slow+very slow- desorbing fractions. Data processing was done in OriginPro 8, Origin Systems, Inc. Statistical analysis was conducted using one-way ANOVA on the original (untransformed) data. A significance threshold of $p < 0.05$ was applied to determine statistically meaningful differences.

2.5. Biodegradation potential of TFL in the sediment

The biodegradation potential of TFL in the sediment was assessed to explore the feasibility of utilizing bioremediation as a cost-effective and environmentally friendly treatment method. This assessment involved testing various aerobic and anaerobic conditions, with optimization achieved through biostimulation and bioaugmentation strategies.

2.5.1. Examination of the aerobic degradation potential of TFL in sediments

For evaluating the aerobic conditions for degradation, 3 g of dry sediment was weighed into 40 ml vials. After, 3 ml of different inoculums described in Table 2 and 0.1 ml of mineral medium (MM) ($K_2HPO_4 \times 3H_2O$, $NaH_2PO_4 \times 3H_2O$, NH_4Cl_2, $MgSO_4 \times 7H_2O$, $FeSO_4 \times 7H_2O$, $MnSO_4 \times 7H_2O$, $ZnSO_4 \times 7H_2O$, $CoSO_4 \times 7H_2O$, and yeast extract) were added. The introduction of different inoculums aimed to assess their potential to enhance the biodegradation of TFL by promoting microbial activity and metabolic diversity. All procedures that include addition of mineral medium and degradation monitoring are conducted following previous studies published by Yuan et al. (2001) and Čučak et al. (2017).

Microcosms were aerated daily by briefly opening each vial for three minutes to allow controlled oxygen exchange while minimizing sediment disturbance. After aeration, vials were resealed and placed on a thermostatic shaker (30 °C, 20 rpm) to maintain gentle agitation and simulate natural conditions. Aerobic degradation was monitored for three weeks. At the end of this period, samples were dried with anhydrous sodium sulfate, and TFL concentrations were determined after preparation (see Supplementary Table S1 for methods). An abiotic control, containing no inoculum and 3 ml of $HgCl_2$ solution (300 mg/l) as a biological inhibitor, was included to separate physical and chemical losses from biological activity. Bacterial consortia capable of degrading TFL were isolated via selective enrichment in mineral medium, prepared following Yuan et al. (2001) with the addition of 0.1 g/l yeast extract.

Table 2
Labels and origin of inoculum for aerobic and anaerobic biodegradation.

Label consortium	Place of origin
I-1	Pre-final sludge of the wastewater treatment plant
I-2	Sediment from the canal that receives wastewater industry
I-3	Sediment 1
I-4	Sediment 2
I-5	Sludge from the anaerobic digester from the plant for treatment of municipal wastewater

2.5.2. Examination of the anaerobic degradation potential of TFL in sediment

To investigate the anaerobic degradation potential of TFL in the sediment, 3 g of spiked sediment was added in vials of 40 ml, whereby triplicates were used, 3 ml of sediment suspensions I-2, I-3 and I-4 (origin and labels given in Table 2), 3 ml of stabilized sludge I-5 and 0.1 ml of the mineral medium. Sewage sludge was added for the anaerobic degradation processes of TFL in the sediment to enhance microbial activity and provide nutrients facilitating the breakdown of the persistent TFL, which should potentially increase the degradation rates, reduce its environmental impact. The vials with the sediment mixtures were blown with a gentle stream of nitrogen for 3 min to remove any oxygen, and the samples were then sealed and placed in a thermostatic shaker (30 °C and 20 rpm). Anaerobic degradation potential was monitored for 10 weeks. After 10 weeks, all samples were removed from the shaker, dried with anhydrous sodium sulfate, and TFL in the sediments was measured using the GC/MS method given in Supplementary material. As done for the aerobic system, abiotic loss was determined by including a blank test.

2.6. Immobilization of TFL in sediment using organic amendments

To reduce the bioavailability of the TFL in the sediment, three different organic amendments (AC, BC and CO) were added to the sediment. TFL concentration was measured at the beginning of the experiment without the addition of amendments and after 14, 30, 90, and 180 days of contact time. Weighted masses of added amendments materials are given in Table 3. The mass of added AC, BC, and CO was determined based on their carbon content to ensure consistent carbon levels across all samples (SRPS EN 12879:2007). For the experiment 1 g of dry sediment was placed in 40 ml glass vials, along with organic amendments in specific ratios (Table 3). To avoid biodegradation 20 ml of 300 mg/l $HgCl_2$ solution was added.

The samples were stored in the dark for 14, 30, 90, and 180 days. After the four different contact times the bioavailability was determined using desorption with XAD-4 resin, and a germination test as well as a test for toxicity using *Vibrio fischeri* were determined in samples without $HgCl_2$ addition.

Table 3
Weighed masses of activated charcoal, biochar, and compost.

Time	Sample name	Mass AC (g)	Mass BC (g)	Mass CO (g)
Day 0	0	/	/	/
Day 14	05_SP	/	/	/
	05_5	0.005	0.005	0.020
	05_10	0.01	0.01	0.039
	05_50	0.05	0.05	0.196
	05_100	0.1	0.1	0.392
Day 30	1_SP	/	/	/
	1_5	0.005	0.005	0.020
	1_10	0.01	0.01	0.039
	1_50	0.05	0.05	0.196
	1_100	0.1	0.1	0.392
Day 90	3_SP	/	/	/
	3_5	0.005	0.005	0.020
	3_10	0.01	0.01	0.039
	3_50	0.05	0.05	0.196
	3_100	0.1	0.1	0.392
Day 180	6_SP	/	/	/
	6_5	0.005	0.005	0.020
	6_10	0.01	0.01	0.039
	6_50	0.05	0.05	0.196
	6_100	0.1	0.1	0.392

2.7. Evaluation of the TFL bioavailability

After 14, 30, 90, and 180 days after the start of the experiment, solid $CaCl_2$ (0.5 g) and 0.2 g of XAD-4 microporous resin were added to the vials. TFL concentrations in sediment and XAD-4 resins samples were determined after sample preparation by GC/MS technique (Supplementary material, table S1).

The test of germination and phytotoxicity of TFL in spiked, but unamended sediment was determined in the presence of four types of plants: two types of pumpkin (*Cucurbita pepo*), lettuce (*Lactuca sativa L.*), and corn (*Zea mays*) according to the methodology described by Coulon et al. (2010). The mentioned plants were previously intensively used in phytoremediation studies and germination tests (Rončević et al., 2016). For germination tests, 15 g of dry sediment was placed in 100 ml jars, and five seeds of each test plant species were sown. Samples were kept under daylight at 25 °C for 10 days and watered regularly. After 10 days, germinated seeds were counted, and aboveground biomass was measured. A control without seeds was included to account for abiotic TFL loss. Residual TFL in sediment and plant uptake were analyzed using GC–MS. Parallel tests were conducted with sediments amended with activated carbon and compost at varying ratios (Table 3). Biochar was excluded from germination and phytotoxicity tests due to limited material, although immobilization experiments indicated efficiency similar to compost. For these amended samples, germination tests were repeated after 50 days using corn (*Zea mays*), previously shown to tolerate TFL without negative effects on germination or biomass. Ecotoxicity was assessed using the *Vibrio fischeri* luminescence inhibition test following ISO 21338:2010 on a *LUMIStox* instrument (Hach Lange, Germany). Tests were performed in duplicate with strain NRRL-B-11, 177, measuring luminescence after 30 min, corrected for changes in control sample intensity.

3. Results and discussion

3.1. Physical and chemical characterization of the sediment

The organic matter content of the sediment was quite high with16.0 ± 0.23 % at moderate clay content of 31.6 ± 0.21 %. The high organic matter content suggests an exciting potential for complexation of organic pollutants in the sediment, while the high clay content will favor sorption of pollutants. Both mechanisms will reduce the bioavailable fraction of pollutants as suggested by Spasojević et al. (2015) or Spasojević et al. (2018). 83.0 % of the sediment is smaller than 63 µm (clay and silt) (Table S2), which will increase the sorbing potential of the sediment for pollutants. Based on the *t*-test and method proposed by Horvath and Kawazoe (HK method) it can be concluded that the sediment consists mainly of mesopores (Supplementary material, table S2). Additional information on the sediment surface characteristics was obtained by SEM analysis (Figure S1, Supplementary material). The measurements of background pollution revealed that the sediment was free of organochlorine pesticides and polychlorinated biphenyls. By correcting the measured PAHs concentrations by the organic matter content, the sediment was classified as slightly polluted according to the Official Gazette No. 50/2012 classification.

The additional physico-chemical characterization and background contents of selected organic pollutants of the sediment used in this study are provided in the Supplementary material (Table S2 and S3).

3.2. Optimization of the partial extraction methods to assess the bioavailability of TFL

The total amount of desorbed TFL from the sediment using the different partial extraction methods after 144 h were 2738, 3630, 1130, 2240, and 1470 µg/kg for Tenax, XAD-4, HPCD, MCD, and BCD, indicating that the XAD-4 resin desorbed the highest proportion of all tested compounds (96.0 %) and HPCD the lowest (34.4 %). BCD also showed relative low desorption (38.9 %), whereas MCD and Tenax lie in the range between 59–72 %. Fig. 2 shows the desorption of the different tested compounds after each selected equilibration time revealing again the difference in the desorption potential. As can be seen from the figure, both resins (XAD-4 and Tenax) showed slower desorption rates compared to cyclodextrins. The smaller desorption of the Tenax compared to XAD-4 can be explained by its lower affinity for TFL and significantly smaller specific surface area (Tenax 35 m^2/g versus XAD-4 750 m^2/g, see Table 1). In contrast, the cyclodextrins desorbed TFL from the sediment to a smaller extent than the resins. According to Hartnik et al. (2008), the efficiency of the extraction of pollutants by cyclodextrins depends on how the equilibrium between the sediment, water, and cyclodextrins is achieved. In general, cyclodextrins will extract a weakly bound fraction of the pollutants if their capacity exceeds the sediment's sorption capacity. Otherwise, an equilibrium state will be reached, where the cyclodextrins do not extract all the fraction of weakly bound pollutants.

The efficiency of the extraction based on the different cyclodextrins was assessed by calculating the maximum extractable fraction (MEF) following the methodology for cyclodextrins outlined by Wong and Bidleman (2010) given in Supplementary material (Eq. S1). MEF value represents a maximum amount of compound in soil or sediment that can be extracted with a certain amount of cyclodextrins. Obtained MEF values for TFL are given in Table 4. As can be seen, calculated MEF values are higher than those values obtained experimentally for K_{ow}. The finding that the MEF is always higher than the experimental extractability, and that there are enough cyclodextrins to remove all the loosely bound chemicals from the soils or sediments, is consistent with the findings of Wong and Bidleman (2010).

These results obtained suggest that the selected concentration of these extraction agents was adequate to release the weakly bound fraction of TFL. In contrast, BCD exhibited much lower MEF values compared to the other cyclodextrin extraction agents and to the experimental results, indicating a possible insufficiency of the agent to extract all the weakly bound TFL. This limitation is likely due to the low solubility of BCD, leading to its less frequent practical use compared to its more soluble derivatives such as HPCD (Wong and Bidleman, 2010) and MCD (Liu et al., 2013).

3.3. Desorption kinetics

Desorption kinetics are influenced by two main factors: (1) the release of sorbate (here TFL) from sorption sites of the sorbent (here sediment) (Spasojević et al., 2015), and (2) the diffusion of sorbate through the sorbent into the water (Sinčić Modrić et al., 2023) (Table 5).

The values of k_{fast} and $k_{slow+very\ slow}$ from the two-compartment model showed some variability in the rate constant and sorption times between 1.7 to 8.9 hours for k_{fast} and 66 to 2128 hours for $k_{slow+very\ slow}$. Greenberg et al. (2005) used three compartment model and gained values for k_{fast}, k_{slow}, and $k_{veryslow}$ in the order of 10^{-1}, 10^{-3}, and 10^{-4} h^{-1}, using Tenax as extraxtion agent for TFL extraction, which is line what was found in our study with a k_{slow} of 0.114 and $k_{slow+very\ slow}$ of 0.0015 h^{-1}. The variability in the sorption times k_{fast} and $k_{slow+very\ slow}$ reflects the differences in the kinetics of TFL desorption across the different sorbents. The sorbents tested differ in physicochemical properties (Table 1), influencing TFL accessibility and interaction strength. Cyclodextrin-based sorbents can form inclusion complexes with TFL (Gilevska et al., 2022; Yin et al., 2025), while Tenax and XAD-4 interact through simpler mechanisms, leading to faster desorption (Rojas et al., 2022). According to the two-compartment model, heterogeneous sorption sites cause variable diffusion rates: simple structures (e.g., Tenax) enable rapid diffusion and shorter sorption times, whereas complex structures (e.g., HPCD) slow diffusion, prolonging sorption.

Experiments on TFL desorption kinetics are limited, but data on other organic pollutants offer comparisons. Spasojevic et al. (2015) reported k_{fast} values of 0.19–0.34 h^{-1} for PAHs using XAD-4 resin and

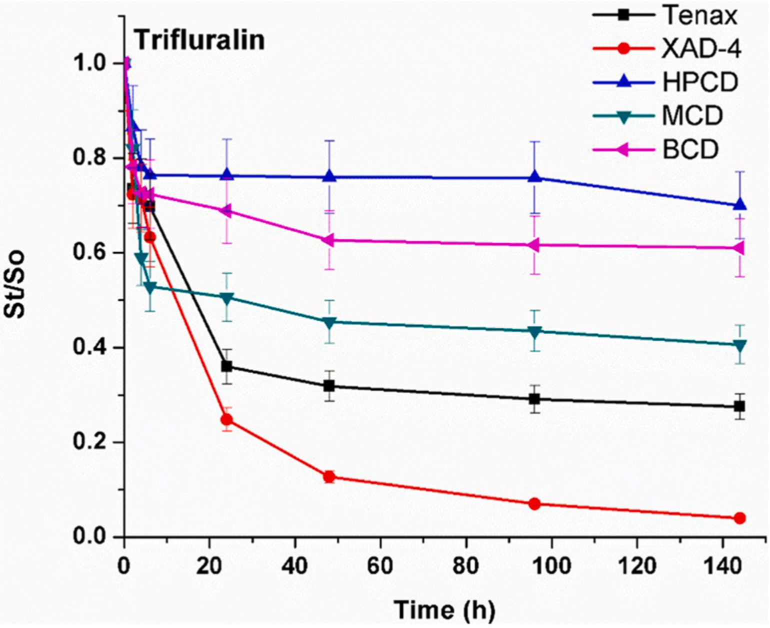

Fig. 2. Desorption of TFL from sediment over time using different chemical agents. The X-axis shows desorption time (h). The Y-axis represents the relative concentration of TFL remaining in the sediment at time *t* (St) normalized to the initial concentration at time zero (S₀), expressed as a dimensionless ratio (St/S₀). Error bars indicate the standard deviation of triplicate measurements.

Table 4
Values of logK_{ow}, logK_{oc}, and maximum extractable fraction (MEF) of cyclodextrin for trifluralin (TFL).

Parameters	Value	Parameters	Value
logK_{ow}	5.34	MEF_{BCD}	12.1 – 51.1
logK_{oc}	4.48 – 5.34	MEF_{MCD}	48.7 – 87.8
logK_{CD}	3.65	MEF_{HPCD}	54.3 – 90.0

Table 5
Fitted kinetic parameters for the two compartments kinetic model fitted to trifluralin (TFL) desorption data using Tenax, XAD-4, HPCD, MCD, and BCD.

	Tenax	XAD-4	HPCD	MCD	BCD
F_{fast} (%)	61.3	69.4	23.3	51.1	30.3
$F_{slow+very\ slow}$ (%)	38.7	30.6	76.7	48.9	69.7
k_{fast} (h^{-1})	0.114	0.102	0.525	0.332	0.584
$k_{slow+very\ slow}$ (h^{-1})	0.00153	0.0150	0.00047	0.00125	0.00112
R^2	0.96	0.98	0.95	0.96	0.97

0.16–0.42 h^{-1} with MCD, highlighting the importance of sediment and pollutant properties in sorption behavior. The two-compartment kinetic model, though not mechanistic, describes binding sites with varying desorption rates, requiring activation enthalpies from near zero (fast) to 60–100 kJ/mol (slow) (Cornelissen et al., 1997). Pignatello and Xing (1996) noted slower desorption at lower initial concentrations, suggesting delayed desorption dominates as pollutant levels drop. Fast-desorbing TFL fractions (F_{fast}/F_{Xh}, $X = 2, 4, 6, 24, 48, 96, 144$ hours) were compared, showing that after 24 hours with Tenax, XAD-4, or cyclodextrins, F_{fast}/F_{24h} values near 1 indicate 24 hours is sufficient for effective desorption (Table 6).

In summary, XAD-4 and Tenax exhibit faster TFL desorption due to simpler interactions, while cyclodextrins' complex structures result in slower kinetics, highlighting the impact of sorbent properties on desorption behavior.

Table 6
Ratios of TFL to fractions at a specific time in function of F_{fast}/F_x.

	Tenax	XAD-4	HPCD	MBCD	BCD
F_{fast}/F_{2h}	2.32	2.43	3.43	2.94	1.38
$F_{fast}/F4_{h}$	2.23	2.36	1.68	1.29	1.10
F_{fast}/F_{6h}	2.03	1.83	1.11	1.12	1.09
F_{fast}/F_{24h}	0.96	0.89	1.07	1.07	0.97
F_{fast}/F_{48h}	0.90	0.77	1.03	0.97	0.81
F_{fast}/F_{96h}	0.86	0.72	0.96	0.93	0.78
F_{fast}/F_{144h}	0.85	0.70	0.94	0.89	0.77

3.4. Examination of one-step desorption of TFL by partial extraction methods

To validate the results obtained from multistage extraction of TFL from contaminated sediment, additional single-stage extraction experiments were carried out at three different contact times (6, 8, and 24 h). This enabled a direct comparison between the total and bioavailable fractions of TFL obtained through multistage extraction and those extracted in a single step. Alongside the extractions with different agents, a blank control was prepared using spiked soil and deionized water. As shown in Fig. 3, single-stage extractions with BCD released higher fractions of desorbed TFL than the total fraction obtained during multistage extraction with the same sorbent, regardless of contact time. This outcome is somewhat unexpected, given that the single-stage extractions involved much shorter contact times compared to the cumulative 144 h of the multistage procedure. A plausible explanation lies in the limited solubility of BCD and the formation of inclusion complexes, as previously reported (Charumanee et al., 2016).

On the other hand, the one-step extractions with HPCD and MCD yielded desorbed fractions and F_{fast} fraction comparable to those obtained by multistage extraction, because F_{fast} is considered as bioavailable fraction. It was found that this comparable extraction efficiency to multistage extraction of TFL was independent on contact time (6 to 24 h of contact time) as also during multistage extraction high (and more or less constant) desorption was also detected after relatively short contact times as shown in Fig. 2. On the other hand, the extraction based on the resins (Tenas and XAD-4) yielded in general higher desorption

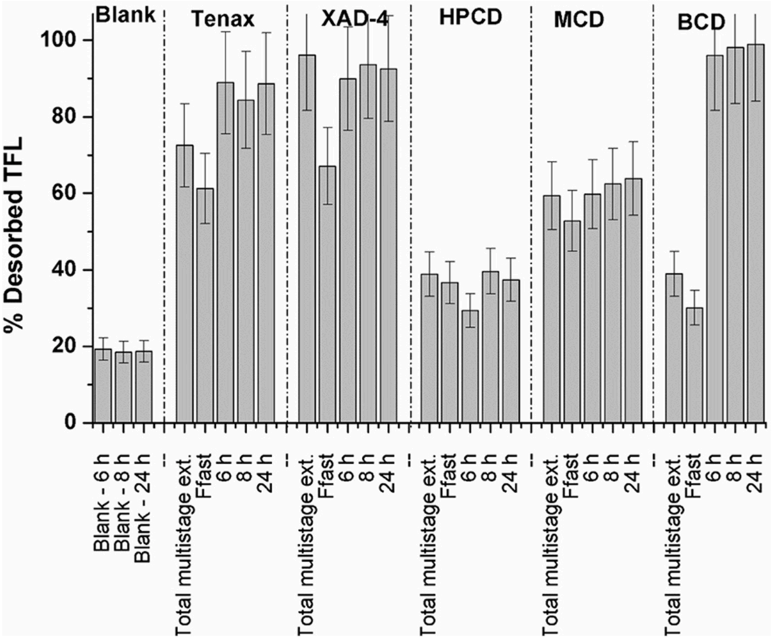

Fig. 3. Comparison of the results of multistage extraction, F_{fast} and single-stage extraction after three contact times for TFL. Error bars represent the standard deviation of the measured triplicates.

efficiencies compared to HPCD and MCD not only for the already discussed multistage approach but also for the one-step desorption. Looking at the contact times, one can also see that the resins require a slightly longer contact time (8 + *h*) to reach optimal efficiency compared to the use of the cyclodextrins. The XAD-4 was slightly more efficient in desorption compared to the Tenax resins. All used extraction agents showed for multi- and single-step extraction good efficiencies and comparable results for even short contact times 8 h, except in case of BCD, which can be explained by its limited solubility in water (Table 1).

Summary: Single-stage extraction experiments with contact times of 6, 8, and 24 hours were conducted to validate multistage extraction results for TFL from contaminated sediment, allowing direct comparison of total and bioavailable TFL fractions. A blank with spiked soil and deionized water was included. Fig. 3 shows that single-stage extractions with BCD yielded higher desorbed TFL fractions than multistage extractions (144 hours total), likely due to BCD's limited solubility and formation of inclusion complexes. In contrast, HPCD and MCD single-stage extractions produced desorbed fractions and F_{fast} (bioavailable) fractions comparable to multistage results, independent of contact time (6–24 hours), as high desorption was observed even at short times (Fig. 2). Resins (Tenax, XAD-4) showed higher desorption efficiencies than cyclodextrins in both single- and multistage extractions, with XAD-4 slightly outperforming Tenax, though requiring longer contact times (8+ hours) for optimal efficiency. In summary, all extraction agents demonstrated good efficiencies in both single- and multistage approaches, with comparable results at short contact times (8 hours), except for BCD, where solubility limitations likely enhanced single-stage desorption.

3.5. *Biodegradation potential of TFL in the sediment*

With an extraction efficiency near 100 % using XAD-4 and an 8-hour contact time, XAD-4 can estimate TFL degradation in sediments. Fig. 4a shows aerobic degradation, while Fig. 4b presents cumulative percentages after 3 weeks. Degradation was highest (40–60 %) with inoculum I-1, I-2, and I-3, while I-4 showed low degradation, like the abiotic control treated with $HgCl_2$. A significant portion of TFL remained after 3 weeks, likely due to the short experiment duration and sorption reducing TFL

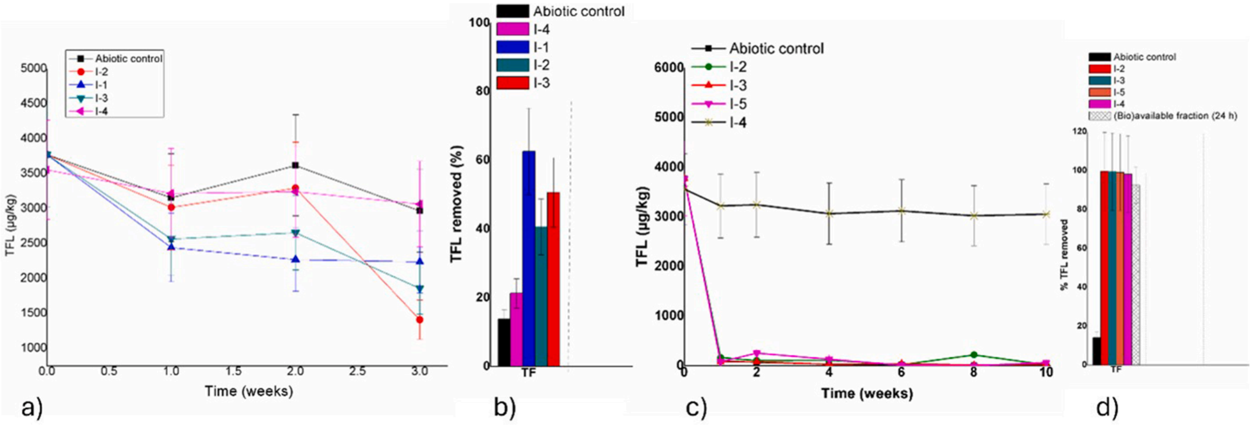

Fig. 4. a) Degradation of TFL in the sediment under aerobic conditions over a time course of 3I weeks, b) cumulative percentage of degraded TFL from the sediment under aerobic conditions after 3 weeks, c) degradation of TFL in the sediment under anaerobic conditions over a time course of 10 weeks, and d) cumulative percentage of degraded TFL from the sediment under anaerobic conditions after 10 weeks. Error bars represent the standard deviation of the triplicates.

bioavailability. Degradation plateaued after 2 weeks with some inoculum, possibly influenced by sorption processes. Aging over 2 years may have further reduced biodegradability by stabilizing residues, making them less accessible (Carpio et al., 2021).

Fig. 4c shows anaerobic TFL degradation, with cumulative percentages in Fig. 4d after 10 weeks. TFL degraded rapidly, nearly fully breaking down within 2 weeks. This may be due to the inoculum sourced from anaerobic environments, fostering microbes with specialized metabolic pathways for TFL breakdown (Li et al., 2022; Gryta et al., 2024). Anaerobic conditions and TFL's chemical properties may further promote degradation through specific enzymes or redox reactions (Lara-Moreno et al., 2022).

Lara-Moreno et al. (2022) demonstrated effective TFL bioremediation, showing 34 % degradation in 100 days with nutrient biostimulation. Inoculation with microbial consortia boosted degradation to 62–74 % (DT50 of 5.9–11 days), while individual strains varied from 2.3 % to 55 %. Bioaugmentation with *Arthrobacter aurescens* CTFL7 alongside RAMEB (randomly methylated-β-CD) achieved 88 % degradation, with a DT50 of just 19 days.

Summary: The biodegradation potential of TFL in sediment was assessed, with XAD-4 achieving near-100 % extraction efficiency at an 8-hour contact time, enabling accurate degradation estimates. Under aerobic conditions (Fig. 4a, 4b), degradation after 3 weeks ranged from 40 to 60 % with inocula I-1, I-2, and I-3, while I-4 showed low degradation, similar to the abiotic control ($HgCl_2$-treated). A significant TFL fraction persisted, likely due to the short experiment duration and sorption reducing bioavailability, with degradation plateauing after 2 weeks in some cases, possibly due to 2-year sediment aging stabilizing residues. Anaerobic degradation (Fig. 4c, 4d) was rapid, with near-complete TFL breakdown within 2 weeks, attributed to inoculum from anaerobic environments with specialized metabolic pathways and TFL's chemical properties promoting enzymatic or redox reactions. In summary, anaerobic conditions facilitated faster and more complete TFL degradation than aerobic conditions, driven by specialized microbial activity and reduced sorption constraints.

3.6. *Immobilization and bioavailable fraction of TFL after amendments with different carbon rich materials*

The physico-chemical properties of the carbon-rich amendments (AC, BC and CO) used for TFL immobilization are listed in Table S4. AC had the highest total organic carbon content (83.3 %) compared to BC (75.4 %) and CO (18.5 %), indicating BC and CO were more polar. AC also had greater surface area and porosity, with a microporous structure, while BC and CO were mainly mesoporous (Figure S2). TFL immobilization efficiency was assessed through multistep desorption with XAD-4 resin, bioavailability tests, germination tests, and *Vibrio fischeri* toxicity. Four contact times (14, 30, 90, and 180 days) and four amendment dosages (0.5, 1, 5, and 10 % w/w) were tested. Longer contact times provided insights into TFL bioavailability in aged soil and sorption mechanisms. Fig. 5 illustrates the bioavailable fraction of TFL in sediment treated with AC, BC and CO at dosages of 0.5 %, 1 %, 5 %, and 10 % (w/w) over contact times of 14, 30, 90, and 180 days. A decrease in bioavailability is the desired outcome, indicating effective immobilization of TFL to reduce its environmental mobility and toxicity. Compared to untreated sediment, where TFL bioavailability is 67.1 %, all amendments significantly reduced bioavailability to below 15 % within 14 days and to below 10 µg/kg (effectively negligible) by 90 days, as shown in subfigures (a), (b), and (c) for AC, BC, and CO. Error bars represent the standard deviation of triplicates, and any variability (e.g., higher values at 30 days for some treatments) reflects experimental desorption kinetics, discussed further with Table 7.

The consistent decrease in bioavailability across all treatments demonstrates effective TFL immobilization, with all amendments achieving concentrations below 10 µg/kg by 90 days. Note that some treatments (e.g., 0.5 % AC at 30 days) show higher variability, likely due to desorption kinetics, as detailed in Table 7. All amendments significantly reduced TFL bioavailability compared to the untreated sediment (67.1 %). By 90 days, all treatments achieved bioavailable TFL concentrations below 10 µg/kg, indicating near-complete stabilization. Even low dosages (e.g., 1 % AC, BC, or CO) and shorter contact times (30 days) were sufficient to achieve substantial reductions in bioavailability,

Table 7
Amounts of desorbed (bioavailable) TFL after application of the three different carbon rich amendments at different dosages and for different contact times.

Treatment	Unit	14 days	30 days	90 days	180 days
0.5 % AC	µg/kg	256 ± 55.3	526 ± 103.1	<10.0	<10.0
	%	6.77 ± 2.14	13.9 ± 5.15	/	/
1 % AC	µg/kg	464 ± 35.4	<10.0	<10.0	<10.0
	%	12.3 ± 4.21	/	/	/
5 % AC	µg/kg	153 ± 11.1	67.7 ± 16.4	<10.0	<10.0
	%	4.05 ± 0.44	1.79 ± 0.47	/	/
10 % AC	µg/kg	35.7 ± 2.27	191 ± 5.58	<10.0	<10.0
	%	0.95 ± 0.05	5.06 ± 0.99	/	/
0.5 % BC	µg/kg	183 ± 4.86	83.9 ± 5.36	<10.0	<10.0
	%	4.93 ± 0.96	2.22 ± 0.69	/	/
1 % BC	µg/kg	144 ± 10.8	33.3 ± 7.72	<10.0	<10.0
	%	3.81 ± 0.75	0.88 ± 0.06	/	/
5 % BC	µg/kg	542 ± 31.4	<10.0	<10.0	<10.0
	%	6.41 ± 0.52	/	/	/
10 % BC	µg/kg	431 ± 11.2	<10.0	<10.0	<10.0
	%	11.4 ± 1.15	/	/	/
0.5 % CO	µg/kg	361 ± 16.9	302 ± 21.5	<10.0	<10.0
	%	9.55 ± 2.04	8.0 ± 0.83	/	/
1 % CO	µg/kg	316 ± 15.4	68.5 ± 8.84	<10.0	<10.0
	%	8.35 ± 1.21	1.81 ± 0.85	/	/
5 % CO	µg/kg	271 ± 24.5	52.9 ± 14.4	<10.0	<10.0
	%	7.17 ± 0.96	1.40 ± 0.08	/	/
10 % CO	µg/kg	288 ± 24.7	<10.0	<10.0	<10.0
	%	7.63 ± 0.64	/	/	/

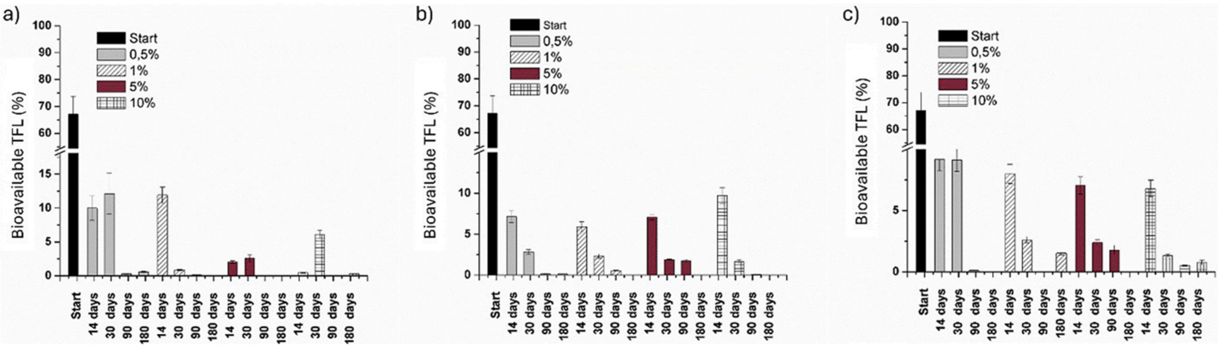

Fig. 5. Bioavailable fraction of TFL in sediment treated with (a) AC, (b) BC and (c) CO at dosages of 0.5 %, 1 %, 5 %, and 10 % (w/w) over 14, 30, 90, and 180 days, compared to untreated sediment (67.1 % bioavailability). Error bars represent the standard deviation of triplicates.

with AC showing the fastest stabilization, followed by BC and CO. Table 7 provides detailed measurements, including percentage bioavailability and anomalies observed at 30 days for certain treatments. It quantifies the bioavailable TFL (in µg/kg and percentage relative to initial TFL) in sediment treated with AC, BC and CO at dosages of 0.5 %, 1 %, 5 %, and 10 % (w/w) over 14, 30, 90, and 180 days. Compared to untreated sediment (67.1 % bioavailability), all amendments reduced bioavailability to below 15 % within 14 days and below the detection limit. (<10 µg/kg) by 90 days. Some treatments (e.g., 0.5 % AC and 10 % AC at 30 days) show higher bioavailability than at 14 days, likely due to variable desorption rates or experimental artifacts during XAD-4 resin extraction. These anomalies do not affect the overall trend of effective TFL immobilization, as confirmed by the negligible bioavailability at 90 and 180 days.

BC is still emerging in remediation research and has proved less effective than activated AC for TFL sorption. Stabilization occurred with 5–10 % BC after 30 days, while CO showed no significant bioavailability difference between 0.5 %, 1 %, and 5 % doses. All amendments stabilized TFL bioavailability after 90 days, but real-world use depends on cost and availability — CO is cheapest and locally available, though highly variable, while AC and BC are pricier and less accessible. In untreated sediment, TFL bioavailability was 67.1 %, but all amendments reduced it to below 15 % within 14 days, demonstrating their effectiveness in immobilizing TFL to minimize environmental risks. This reduction is considered a positive outcome in the context of remediation, as it limits TFL's mobility and potential toxicity. As shown in Fig. 5 and Table 7, bioavailability further decreased to below 10 µg/kg by 90 days across all treatments, with AC generally outperforming BC and CO due to its higher surface area and microporous structure. Some treatments exhibited higher bioavailability at 30 days compared to 14 days (e.g., 0.5 % AC: 13.9 % at 30 days vs. 6.77 % at 14 days), possibly due to variable desorption kinetics or experimental variability during multistep desorption tests. These anomalies are transient, as all treatments achieve near-complete stabilization by 90 days. This reduction links to TFL's structure — a tertiary amino group, nitro groups, and a trifluoromethyl group — promoting strong sorption to organic matter (Coleman et al., 2020). Sorption depends on surface area, organic carbon content, and carbon structure: biochar (Gomez-Eyles et al., 2013; Oleszczuk et al., 2012; Josko et al., 2013; Chi and Liu, 2016) and compost (Ghosh et al., 2019) provide soft, amorphous carbon with diverse functional groups, while AC offers hard, non-graphitizable carbon (Gomez-Eyles et al., 2013; Ghosh et al., 2019; Oleszczuk et al., 2012; Josko et al., 2013). TFL binds differently to each amendment: it penetrates biochar and compost's polyaromatic organic matter, while AC traps TFL in micropores through irreversible π–π bonds (Cornelissen et al., 2005; Vasilyeva et al., 2010). Overall, biochar shows equal — if not better — potential for TFL immobilization compared to AC and compost.

Dorner et al. (2022) explored the potential of designer biochars for targeted organohalide remediation, highlighting that their effectiveness in abiotic and biotic dehalogenation depends on physicochemical and electrochemical properties—such as surface area, porosity, redox capacity, and functional groups or metal oxides—determined by feedstock, pyrolysis conditions, and post-treatment. The variability in biochar composition, however, complicates standardization and cross-study comparisons. Similarly, Gong et al. (2016) demonstrated that biochar addition to contaminated coastal sediments can enhance abiotic reduction of dinitroaniline herbicides without increasing erosion, though success depends on biochar type, dosage, sediment characteristics, temperature, and hydrodynamics.

TFL immobilization was tested using carbon-rich amendments—activated carbon (AC, 83.3 % TOC, microporous), biochar (BC, 75.4 %, mesoporous), and coke (CO, 18.5 %, mesoporous)—with properties in Table S4 and Figure S2. Desorption (XAD-4), bioavailability, germination, and Vibrio fischeri assays assessed efficiency at 0.5–10 % w/w and 14–180 days. Compared to untreated sediment (67.1 % bioavailability), all amendments reduced bioavailability below 15 % in 14 days and under 10 µg/kg by 90 days (Fig. 5, Table 7). AC stabilized TFL fastest due to high surface area and microporosity, followed by BC and CO, with binding via π–π interactions and polyaromatic domains (*Cornelissen* et al.*, 2005;* Vasilyeva et al., 2010). Some treatments showed transient variability, likely from desorption dynamics, but near-complete stabilization occurred by 90 days. Overall, AC, BC, and CO effectively immobilized TFL, with AC providing the most rapid and consistent reduction.

3.7. Germination and phytoextraction test

Phytotoxicity of unamended TFL-contaminated sediment was tested using Zea mays, Lactuca sativa, and Cucurbita pepo. After 10 days, TFL concentrations in biomass were 481, <25, and 134 µg/kg dry biomass, showing Zea mays had the highest uptake and Lactuca sativa the lowest. Germination rates were 100 % for Zea mays, 80 % for Lactuca sativa, and 40 % for Cucurbita pepo, indicating high resistance in Zea mays (Alvarez et al., 2012) and toxicity for the others (Alvarez et al., 2015).

Amended sediments with AC and CO showed no adverse effects on Zea mays germination. Biomass increased with AC dosage, aligning with reduced TFL bioavailability, while CO showed no dosage effect but yielded slightly more biomass (Fig. 6). CO, acting as an organic fertilizer, improved soil quality and supported plant growth, while AC's high sorption capacity may also trap essential nutrients, potentially limiting growth.

The *Vibrio fischeri* assay showed decreased toxicity with higher CO dosages, especially at 10 %, whereas 10 % AC increased bacterial inhibition, likely due to nutrient depletion from AC's strong sorption capacity. Bioluminescence can be influenced by nutrient availability, specific substances, environmental factors, and bacterial physiology (Abbas et al., 2018).

Phytoextraction potential using *Zea mays* was also assessed. After 10 days of growth in unamended and amended sediments, residual TFL in sediment and plant biomass was measured (Fig. 5b). Low CO dosage (0.5 %) left a higher bioavailable TFL fraction and low plant uptake, while higher dosages reduced bioavailability and slightly increased uptake. Greater uptake with CO is attributed to its role as an organic fertilizer enhancing root growth and water uptake, indirectly increasing TFL absorption. The unexpectedly low bioavailable fraction at 1 % CO, despite higher plant uptake and dissipation, remains unclear. For AC, low dosages (0.5–1 %) yielded high bioavailable TFL and intermediate uptake, whereas higher dosages promoted strong sorption, reducing both bioavailability and plant uptake.

Centofanti et al. (2016) found that compost amendments (aged dairy manure and biosolids) reduced the bioavailability of aged pesticides (DDT, DDE, dieldrin) in orchard soils by 18–39 % in planted microcosms, while unplanted soils showed unchanged or increased values. Pine chip BC was ineffective. According to the US EPA Soil Screening Level method, adding 10 % aged dairy compost lowered hazard quotients below 1.0, indicating reduced ecological risk. These results suggest compost amendment as a sustainable and globally applicable approach for mitigating pesticide contamination.

Summary: Phytotoxicity and phytoextraction of TFL were tested using *Zea mays, Lactuca sativa*, and *Cucurbita pepo* in unamended and amended sediments (AC and CO). In unamended sediment, TFL concentrations in biomass after 10 days were 481, <25, and 134 µg/kg dry biomass for *Zea mays, Lactuca sativa, and Cucurbita pepo*, with germination rates of 100 %, 80 %, and 40 %, indicating *Zea mays'* high resistance. AC and CO amendments eliminated adverse germination effects for *Zea mays*, with AC increasing biomass with higher dosages due to reduced TFL bioavailability, while CO, acting as an organic fertilizer, slightly enhanced biomass without dosage effects. Vibrio fischeri tests showed reduced toxicity with increasing CO dosage (especially at 10 %), but 10 % AC increased inhibition, likely due to nutrient sorption. Fig. 5b shows that low CO dosage (0.5 %) resulted in higher bioavailable TFL and lower plant uptake, while higher CO dosages and AC (0.5–1 %)

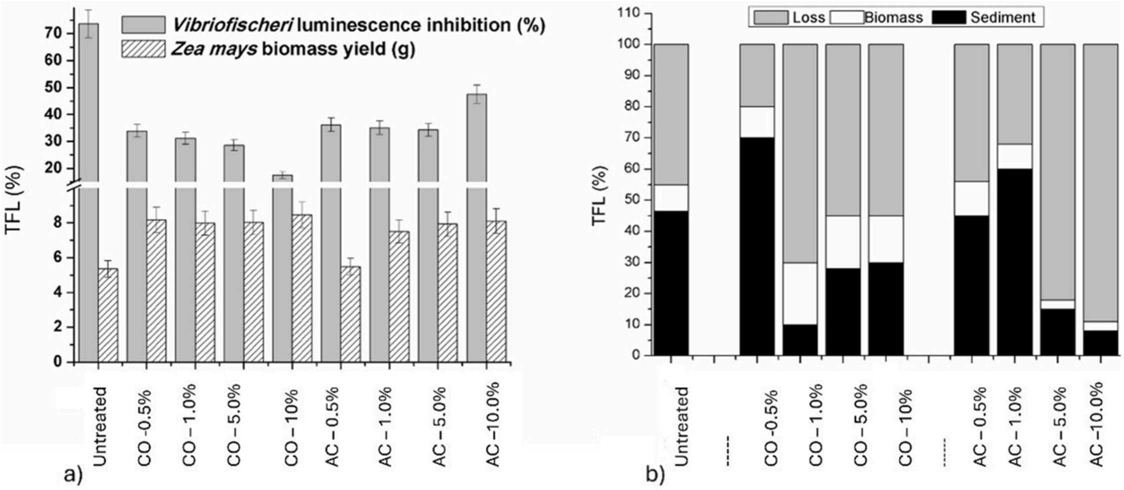

Fig. 6. a) Biomass yield of *Zea mays* after 10 days and percentage of luminescence inhibition of *Vibrio fisheri* bacteria b) distribution of TFL in the amended sediments, expressed as % in sediment, biomass, and loss (expressed as 100 % minus % in sediment and in biomass). Error bars represent the standard deviation of the triplicates.

reduced bioavailability, with AC's higher dosages (5–10 %) promoting strong sorption and minimal uptake. In summary, AC and CO amendments effectively reduced TFL phytotoxicity and bioavailability, with *Zea mays* showing strong potential for phytoextraction, particularly with CO enhancing plant growth.

3.8. Scaling up BC, AC and CO applications: field feasibility, economic considerations and feasibility in field applications

The large-scale application of BC, AC and CO presents significant variability in terms of cost, environmental sustainability, and field feasibility. Each material offers unique benefits and limitations that must be weighed carefully when considering their use in agricultural or contaminated land remediation settings.

Economic considerations. Among these amendments, BC has gained attention for its potential in long-term carbon storage and enhancement of soil health. However, its production and application costs are highly variable, depending on feedstock type, pyrolysis conditions, and regional regulations. In the UK, for example, the estimated cost of biochar applications ranges from £148 to £389 per ton, with the most economical outcomes linked to waste-based feedstocks and optimized processing strategies (Shackley et al., 2011, 2015).

AC is widely used for its high sorption capacity, particularly for organic pollutants and heavy metals, considerably more expensive due to its high energy input requirements (approximately 97 MJ/kg) and associated greenhouse gas emissions. These factors reduce it's overall environmental favorability, especially when compared to BC (Alhashimi and Aktas, 2017). Thus, while AC is effective, its use in large-scale field applications is economically and ecologically less attractive.

CO is often more affordable and widely available, especially when derived from municipal or agricultural organic waste streams. Despite its benefits in enhancing microbial activity and improving soil organic matter content, compost typically offers lower nutrient density and incurs higher transportation and application costs due to its bulkiness (Bergman et al., 2022).

Feasibility in field applications. BC has shown strong potential in field trials, particularly in improving soil health, water retention, and crop productivity on degraded lands (Vijay et al., 2021). Its stability in soil makes it a promising tool for long-term soil management and carbon sequestration strategies. AC, while highly effective in contaminant immobilization, is rarely used at large scales due to logistical and financial constraints. Its application remains limited to high-priority or localized remediation projects where performance outweighs cost. CO continues to be a staple in sustainable farming practices and is favored for its ease of production and integration into existing agricultural systems. However, its shorter persistence in soil and lower capacity for pollutant adsorption make it less effective than BC or AC in certain remediation contexts.

The application of AC, BC and CO, offers significant potential for reducing trifluralin bioavailability in contaminated sediments, providing opportunities for industrial-scale remediation. AC is highly effective due to its rapid and strong sorption capacity, though its high energy requirements and cost can limit large-scale use (Mishra et al., 2024). BC provides longer-term immobilization of contaminants, along with additional benefits such as soil health improvement and carbon sequestration (Antonangelo et al., 2025). CO, while less efficient in sorbing contaminants, is widely available and promotes microbial activity, enhancing natural degradation processes (Hadibarata et al., 2025). Integrating these amendments with advanced detection and monitoring tools, such as high-resolution mass spectrometry, biosensors, or bioassays, allows real-time assessment of trifluralin bioavailability, degradation, and ecological impacts (Pathiraja et al., 2023; Zheng et al., 2022). This combination of remediation strategies with modern analytical approaches provides a pathway for optimizing industrial applications, informing amendment selection and dosage, and improving risk assessment frameworks.

4. Summary and conclusions

This study provides a comprehensive and novel approach to assessing the fate and remediation of TFL in contaminated sediments by combining chemical extraction, biodegradation, and immobilization strategies. A key innovation lies in the integration of multiple assessment techniques (e.g., XAD-4 resin desorption, cyclodextrin screening, kinetic modeling, and phytotoxicity testing) to quantify bioavailable fractions of TFL and evaluate the performance of organic amendments under both aerobic and anaerobic conditions. This represents the first step toward establishing effective strategies for the remediation of TFL in contaminated sediments and soils. Moreover, the findings provide valuable insights into the mechanisms governing herbicide bioavailability, highlighting the potential of organic amendments as sustainable tools for mitigating environmental risks associated with persistent organic pollutants.

Quantitatively, the study demonstrates that XAD-4 resin achieved over 95 % desorption efficiency of TFL within 8 hours, outperforming commonly used Tenax and cyclodextrins (e.g., HPCD: 34.4 %

efficiency). The application of anaerobic consortia resulted in near-complete TFL degradation within 14 days, in contrast to a maximum of 60 % degradation under aerobic conditions after 21 days, indicating a significantly faster and more effective bioremediation pathway under anoxic environments.

Regarding immobilization, activated carbon (AC) reduced TFL bioavailability from an initial 67.1 % to below 10 μg/kg after 90 days at a 1 % dosage. Biochar and compost showed comparable performance, though with more gradual kinetics. These results exceed commonly reported TFL reductions in similar studies, where immobilization efficiencies often plateau below 80 % (e.g., Lara-Moreno et al., 2022). Moreover, the study quantitatively benchmarks amendment effectiveness using multiple dosages (0.5–10 %) and confirms that even low doses of AC and BC can achieve >90 % reduction in bioavailability after 3 months.

In terms of novelty, this work uniquely compares short- and long-term immobilization kinetics across amendments while introducing field-relevant desorption kinetics modeling. The dual consideration of pollutant behavior and ecological interactions, particularly phytotoxicity and Vibrio fischeri inhibition, adds significant depth to the risk assessment framework.

These findings provide strong scientific value for advancing sediment remediation strategies, particularly for persistent herbicides. They also offer practical implications for selecting low-cost, effective amendments (e.g., compost or biochar from local biomass) for in situ remediation, highlighting their potential applicability in real-world scenarios based on demonstrated efficacy, cost feasibility, and environmental sustainability. Future studies should incorporate biological assays, such as bioaccumulation tests in model organisms, to validate and support chemical extraction data, thereby offering a more holistic view of pollutant bioavailability. Including background concentrations of contaminants in natural sediments would also improve ecological relevance by establishing a comparative baseline. To enhance the applicability of findings, future research should combine controlled laboratory conditions with more realistic environmental settings. Special attention should be given to the use of CO as an affordable and locally accessible amendment for TFL immobilization, given its beneficial impact on both pollutant sequestration and plant development.

CRediT authorship contribution statement

Jelena Beljin: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marijana Kragulj Isakovski:** Methodology, Investigation, Formal analysis, Data curation. **Srđan Rončević:** Writing – review & editing, Supervision, Resources, Methodology. **Lutz Weihermüller:** Writing – review & editing, Methodology, Data curation. **Snežana Maletić:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

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

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2025.100874.

Data availability

Data will be made available on request.

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