



# OPTIMIZACIJA PARCIJALNIH METODA EKSTRAKCIJE ZA PROCENU BIODOSTUPNE FRAKCIJE TRIFLURALINA U SEDIMENTU

## OPTIMIZATION OF NON EXHAUSTIVE EXTRACTION METHODS FOR ASSESSMENT BIOAVAILABLE FRACTION OF TRIFLURALIN IN SEDIMENT

### REZIME

Trifluralin se široko primenjavao kao herbicid za borbu protiv korova u žitaricama i kukuruzu. Zbog svoje hidrofobnosti i perzistentnosti ima tendenciju da se u akvatičnim ekosistemima vezuje za sedimentnu fazu, gde se zadržavaju dugi niz godina i samim tim čini da kontaminiran sedimentna faza predstavlja izvor sekundarnog zagađenja. Opšte je poznato da se hidrofobna organska jedinjenja nakon dospevanja u sediment mogu relocirati u mikropore ili ireverzibilno vezati za čestice sedimenta. Ovo ukazuje na činjenicu da potencijal ispoljavanja toksičnosti ovih jedinjenja nije direktno vezan za ukupnu koncentraciju ovih jedinjenja u sedimentu. Zbog toga je procena biodostupne frakcije ovih jedinjenja ključni korak u proceni rizika zagađenih sedimenata. U cilju razvoja metoda za određivanje biodostupnosti trifluralina u sedimentu ispitivane su i optimizovane metode višestepene i jednostepene parcijalne ekstrakcije primenom sledećih hemijskih agenasa: Tenaks smole, XAD-4 smole i rastvora ciklodekstrina (2-hidroksipropil- $\beta$ -ciklodekstrina,  $\beta$ -ciklodekstrina i metil- $\beta$ -ciklodekstrina). Dobijeni rezultati pokazali su da je optimalni agens za procenu biodostupne frakcije trifluralina sa sedimenta XAD-4 smola, a optimalno vreme ekstrakcije primenom jednostepenih ekstrakcija je oko 8 h.

**Ključne reči:** biodostupnost, organski polutanti, sediment, procena rizika

### ABSTRACT

Trifluralin has been widely applied as a herbicide for control of weeds in cereals and corn. Due to its hydrophobicity and persistence, it tends to bind to sedimentary phase in the aquatic ecosystems, where can persist for many years and in this way contaminated sediment represent a source of secondary pollution. It is well known that after entrance of hydrophobic organic compounds into the sediment can be relocated into micropores or irreversibly bind to sediment particles. This points to the fact that the potential toxicity of these compounds is not directly related to the total concentration of these compounds in the sediment. Therefore, the estimation of the bioavailable fraction of these compounds is a crucial in risk assessment of the contaminated sediments. In order to develop and optimise methods for the bioavailability assessment of the selected organic pollutants, methods of multistep and single-step non exhaustive extraction were studied using the following chemical agents: Tenax resin, XAD-4 resin and a cyclodextrin solution (2-hydroxypropyl- $\beta$ -cyclodextrin,  $\beta$ -cyclodextrin and methyl- $\beta$ -cyclodextrin). Results showed that optimal agent for estimating the bioavailable fraction of selected organic pollutants from the sediment is XAD-4 resins, and that the optimum extraction time using single-step extraction is about 8 h.

**Keywords:** bioavailability, organic pollutants, sediment, risk assessment

### 1. UVOD

Akvatični ekosistemi u industrijalizovanim zemljama i zemljama u razvoju su često izloženi brojnim zagađujućim supstancama iz različitih izvora. Oni konstantno prihvataju zagađenje iz izvora kao što su komunalne i industrijske otpadne vode, bolnice, industrija, poljoprivreda i akcidenti (*Rabodonirina i sar., 2015*). Najproblematičnije zagađujuće supstance iz ovih izvora su perzistentne organske supstance koje pokazuju toksične karakteristike, perzistentnost u životnoj sredini, imaju osobinu biomagnifikacije i bioakumulacije u ekosistemima. Trifluralin se u poljoprivredi koristi od 1963. godine, kada je odobren u SAD kao herbicid za borbu protiv korova u žitaricama i kukuruzu (*Wallace, 2014*) i dalje je jedan

### 1. INTRODUCTION

Aquatic ecosystems in industrialized and developing countries are often exposed to numerous pollutants from different sources. They constantly accept pollution from sources such as municipal and industrial wastewater, hospital, industry, agriculture and accidents (*Rabodonirina et al., 2015*). The most problematic pollutants from these sources are persistent organic substances that show toxic characteristics, environmental persistence, biomagnification and bioaccumulation properties in ecosystems. Trifluralin has been used in agriculture since 1963, when it was approved in the United States as a herbicide to combat control weeds in cereals and corn (*Wallace, 2014*) and remains one of the most

<sup>1</sup> Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Trg Dositeja Obradovića 3, 21000 Novi Sad, Republika Srbija, e-mail: snezana.maletic@dh.uns.ac.rs



od najprimenljivijih herbicida u Sjedinjenim Državama (*Murschell i Farmer, 2019*). Po direktivi 2007/629/EC od 2007. godine upotreba, uvoz i promet trifluralina je zabranjena na teritoriji Evropske Unije. Zbog svoje hidrofobnosti trifluralin kao perzistentno jedinjenje ima tendenciju da se u akvatičnim ekosistemima vezuje za sedimentnu fazu, gde se zadržavaju dugi niz godina i samim tim čini da kontaminiran sedimentna faza predstavlja izvor sekundarnog zagađenja (*Ashraf, 2017*).

Sedimentna faza je zemljišna faza akvatičnih ekosistema koja se, iako poseduje većinu karakteristika zemljišta, mora posmatrati kao posebna celina sa svojim osobenostima koja je razlikuju od zemljišta. Sedimentna faza se ponaša i kao skladište i kao izvor organskog ugljenika i antropogenih zagađujućih supstanci u vodenim ekosistemima kroz mehanizme prihvatanja i otpuštanja velikih količina organske materije (*He i sar., 2015*). Ovi mehanizmi razmene uključuju biogeochemijsku transformaciju, adsorpciju, desorpciju, agregaciju i disoluciju (*von Wachenfeldt i Tranvik, 2008*). Poznato je da se hidrofobna organska jedinjenja nakon dospevanja na sediment mogu dislocirati u mikropore ili ireverzibilno vezivati za čestice sedimenta. Prema tome, biodostupnost ovih jedinjenja će se smanjivati tokom vremena, dok ukupna koncentracija u sedimentu ostaje ista (*Wong i Bidleman, 2010*). Smatra se da samo biodostupna frakcija ovih jedinjenja, tj., frakcija polutanta koja se može desorbovati sa sedimenta, lako podleže procesima bioakumulacije, biosorpcije i transformacije u prisustvu različitih organizama. Iz tog razloga je evaluacija biodostupne frakcije zagađujućih supstanci prisutnih u sedimentu od izuzetne važnosti (*Wang i sar., 2018, Zhou i sar., 2018*). Postoji veliki broj bioloških i hemijskih metoda za predviđanje potencijalno biodostupne frakcije zagađujućih materija. Za razliku od bioloških testova koji su pouzdani ali i veoma dugotrajni i komplikovani primenom hemijskih testova se veoma brzo dolazi do podataka da li je neki sediment potencijalno toksičan, kao i da li je njegova remedijacija potrebna i kada je ona završena. Međutim, jedinjenja na kojima su do sada najčešće vršena ispitivanja su policiklični aromatični ugljovodonici (*Cui i sar., 2013; Lydy i sar., 2014; Maletić i sar. 2015, 2018*). Iz ovih razloga je neophodan razvoj i optimizacija metoda za određivanje biodostupnosti šireg opsega jedinjenja.

Cilj ovog rada je optimizacija i odabir hemijskih testova koji daju brz odgovor na pitanje da li je neka organska zagađujuća supstanca biodostupna i u kojoj meri. U okviru ovoga ispitane su metode procene potencijalne biodostupnosti trifluralina testovima desorpcije primenom različitih čvrstih sorbenata (smola XAD-4 i Tenaks) kao i rastvora ciklodekstrina (2-hidroksipropil- $\beta$ -ciklodekstrin (HPCD)),  $\beta$ -ciklodekstrin (BCD) i metil- $\beta$ -ciklodekstrin (MCD)).

usable herbicides in the United States (*Murschell and Farmer, 2019*). According to Directive 2007/629 / EC since 2007, the use, import and trade of trifluralin is prohibited in the territory of the European Union. Because of its hydrophobicity, trifluralin as a persistent compound tends to bind to sedimentary phase in the aquatic ecosystems, where persist for many years and thus makes the contaminated sediment a source of secondary pollution (*Ashraf, 2017*).

The sedimentary phase is the soil phase of aquatic ecosystems, which, although it has most of the soil characteristics, must be regarded as a separate entity with its distinctive features that are different from the soil. The sediment phase also acts as a sink and source of organic carbon and anthropogenic pollutants in aquatic ecosystems through mechanisms of the acceptance and release of large amounts of organic matter (*He et al., 2015*). These exchange mechanisms include biogeochemical transformation, adsorption, desorption, aggregation and dissolution (*von Wachenfeldt and Tranvik, 2008*). It is well known that hydrophobic organic compounds can be dislocated into micropores or irreversibly bound to sediment particles after their entrance in the sediment. Accordingly, the bioavailability of these compounds will decrease over time, while the total concentration in the sediment remains the same (*Wong and Bidleman, 2010*). It is believed that only the bioavailable fraction of these compounds, i.e., the sediment-desorbable fraction of the pollutant, is easily subjected to bioaccumulation, biosorption and transformation processes in the presence of various organisms. For this reason, the evaluation of the bioavailable fraction of the pollutants present in the sediment is of great importance (*Wang et al., 2018; Zhou et al., 2018*). There are many biological and chemical methods for predicting potentially bioavailable fractions of pollutants. Unlike biological tests that are reliable but very time-consuming and complicated, the use of chemical tests quickly reveals whether the sediment is potentially toxic, and whether its remediation is needed and when it is completed. However, the most commonly tested compounds are polycyclic aromatic hydrocarbons (*Cui et al., 2013; Lydy et al., 2014*). For these reasons, the development and optimization of the methods for determination the bioavailability of a wider range of compounds is necessary.

The aim of this paper is the optimization and selection of chemical tests that give a quick answer to the question of whether an organic pollutant is bioavailable and to what extent. In this study, the methods for assessing the potential bioavailability of trifluralin with desorption tests using various solid sorbents (resin XAD-4 and Tenax) and cyclodextrin solutions (2-hydroxypropyl- $\beta$ -cyclodextrin (HPCD),  $\beta$ -cyclodextrin (BCD) and methyl-  $\beta$  -cyclodextrin (MCD)) were examined.



## 2. MATERIJALI I METODE

### *Sediment (priprema i karakterizacija)*

Sediment odabran za eksperiment je uzorkovan sa lokaliteta Jegričke. Vlažan sediment je sušen na vazduhu u mraku. Zatim je homogenizovan i prosejan kroz sito promera 2 mm. Spajkovan je metanolnim rastvorom trifluralina a zatim je ostavljen na vazduhu dve godine pre početka eksperimenta. Fizičko-hemijska karakterizacija sedimenta izvršena je i na sledeće parametre: sadržaj vlage (SRPS EN 12880:2007), sadržaj organske materije (SRPS EN 12879:2007), elektroprovodljivost (SRPS ISO 11265:2007), granulometrijski sastav ISO 11277:2009, ukupan organski ugljenik (*eng*, Total organic carbon).

Trifluralin je ekstrahovan iz 3 g sedimenta prema metodi EPA 3550B. Zatim je vršeno, frakcionisanje dobijenog ekstrakta hromatografijom na koloni silikagela na koju je na vrhu dodato 2 g aktiviranog bakra u cilju uklanjenja elementarnog sumpora iz ekstrakta (EPA 3660B, EPA 3630C). Nakon frakcionisanja ekstrakti su upareni do suva i rekonstituisani sa 1 ml heksana. Analiza dobijenih ekstrakata vršena je na gasnom hromatografu Hewlett Packard 5890 GC Series II na HP-5MS koloni (J&W Scientific), sa masenim detektorom 5971 MSD.

### *Parcijalne metode ekstrakcije za procenu biodostupne frakcije trifluralina*

U cilju razvoja metoda za određivanje biodostupnosti trifluralina ispitivane su i optimizovane metode parcijalne ekstrakcije primenom čvrstih sorbenata (smola XAD-4 i Tenaks) kao i rastvora ciklodekstrina ( $\beta$ -ciklodekstrin, 2-hidroksipropil- $\beta$ -ciklodekstrin i metil- $\beta$ -ciklodekstrin). Optimizacija metode obuhvatila je: (1) ispitivanje kinetike desorpcije trifluralina sa sedimenta primenom višestepene ekstrakcije sa navedenim hemijskim agenasima u toku 144 sata i (2) eksperimente jednostepenih ekstrakcija u cilju poređenja dobijenih rezultata sa podacima ispitivanja kinetike desorpcije. *Procedura višestepene ekstrakcije* detaljno je opisana od strane Spasojević i sar. (2015).

Na 1 g sedimenta, odmereno je 20 ml 5 mM  $\text{CaCl}_2$ , 1 ml  $\text{HgCl}_2$  (300 mg/l) i 0,2 g Tenaksa ili XAD-4 smole ili 25 ml ciklodekstrina (koncentracije svih ispitivanih ciklodekstrina su bile 50 mM). Probe su mučkane na 150 o/min  $25 \pm 2^\circ\text{C}$  u toku 144 h. Nakon 2 h, 4 h, 6 h, 24 h, 48 h, 96 h i 144 h probe su ostavljane, na tamno mesto, u cilju bistrenja tečne faze. U slučaju XAD4 i Tenaksa smola je odvajana iz supernatanta filtracijom, a na sediment je dodata sveža količina smole. U slučaju ciklodekstrina tečna faza je odvajana od sedimenta, a na sediment je nakon odvajanja tečne faze dodata nova količina ciklodekstrina i  $\text{HgCl}_2$ . U slučaju XAD-4 smole u uzorke je pre filtriranja dodavano oko 1,5 g  $\text{K}_2\text{CO}_3$  kako bi se povećala gustina vodene faze i smola isplivala na površinu.

## 2. MATERIALS AND METHODS

### *Sediment preparation*

For the purpose of this investigation, a sediment of the Jegrička river site in the Republic of Serbia was collected. Sediment was dried at room temperature in the dark, then ground and sieved through a 2 mm sieve. The prepared sediment was then spiked with a solution of trifluralin in methanol and left to age 2 years in the dark before the experiment began. The physicochemical characteristics of the sediment for total organic content and particle size distribution were determined using methods ISO 8245:1999 and ISO 11277:2009 respectively.

The total amounts of trifluralin in the sediment and resins were determined according to EPA3550B by ultrasound extraction technique with acetone-hexane mixture (1:1, v/v). Elemental sulfur was removed with copper powder according to EPA3660B method. The samples were fractionated according to the procedure EPA3620B. Trifluralin was analyzed using gas chromatography with mass detection (Agilent Technologies 7890A GC System / 5975C VL MSD) with Agilent J&W Scientific HP-5MS column according to the EPA method 8270C.

### *Non exhaustive extraction methods for assessment of trifluralin bioavailable fraction*

In order to develop the methods for assessment the bioavailability of trifluralin, optimized partial extraction methods were investigated using solid sorbents (resin XAD-4 and Tenax) as well as cyclodextrin solutions ( $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin and methyl- $\beta$ -cyclodextrin). Optimization of the method involved: (1) investigation the desorption of trifluralin from the sediment using multistep extraction with defined chemical agents during 144 hours, and (2) single-step extraction experiments in order to compare the obtained results with the desorption kinetics test data. The procedure of multistep extraction is described in detail by Spasojević et al. (2015).

In glass vial with 1 g of sediment, 20 mL of 5 mM  $\text{CaCl}_2$ , 1 ml of  $\text{HgCl}_2$  (300 mg/L) and 0.2 g of Tenax or XAD-4 resins or 25 mL of cyclodextrin were measured (concentrations of all tested cyclodextrins were 50 mM). The probes were shaken at 150 rpm  $25 \pm 2^\circ\text{C}$  for 144 h. After 2 h, 4 h, 6 h, 24 h, 48 h, 96 h and 144 h the vials were left, in a dark place, in order to clarify the liquid phase. In the case of XAD4 and Tenax, the resin was separated from the supernatant by filtration, and a fresh amount of resin was added to the sediment. In the case of cyclodextrins, the liquid phase is separated from the sediment, and a new amount of cyclodextrin and  $\text{HgCl}_2$  was added to the sediment after separation of the liquid phase. In the case of XAD-4 resins, about 1.5 g of  $\text{K}_2\text{CO}_3$  was added to the samples before filtration to increase the aqueous phase density and the resin poured onto the surface. The content of trifluralin was



Sadržaj trifluralina je određivan u smolama i rastvoru ciklodekstrina nakon svakog odvajanja trostepenom ekstrakcijom smešom aceton:heksan, a nakon 144 h, određena je i rezidualna koncentracija u sedimentu. Istovremeno je rađena i slepa proba, bez dodatka sorbenta ili ciklodekstrina.

*Modelovanje desorpcije.* U cilju određivanja potencijalno biodostupne frakcije trifluralina u sedimentu dobijeni podaci višestepene parcijalne ekstrakcije su modelovani primenom dvočlanog i tročlanog kinetičkog modela predloženog od strane Cornelissen i saradnika (1997):

$$\frac{S_t}{S_0} = F_{brzi} \cdot e^{-k_{brzi} \cdot t} + F_{spori+veoma\ spori} \cdot e^{-k_{spori+veoma\ spori} \cdot t} \quad 1)$$

$$\frac{S_t}{S_0} = F_{brzi} \cdot e^{-k_{brzi} \cdot t} + F_{spori} \cdot e^{-k_{spori} \cdot t} + F_{veoma\ spori} \cdot e^{-k_{veoma\ spori} \cdot t} \quad 2)$$

gde su:

- $S_t$  i  $S_0$  količina organskog jedinjenja koja je sorbovana u početnom trenutku ( $t=0$ ) i vremenu  $t$ ,
- $k_{brzi}$ ,  $k_{spori}$  i  $k_{veoma\ spori}$  predstavljaju konstante brzina prvog reda za brzu, sporu i veoma sporu fazu desorpcije,
- $F_{brzi}$ ,  $F_{spori}$  i  $F_{veoma\ spori}$  predstavljaju brzo-, sporo- i veoma sporo-desorbujuće frakcije (Cornelissen i sar., 1997).

*Procedura jednostepene ekstrakcije* detaljno je opisana od strane Spasojević i saradnika (2015). Ukratko: na 1 g spajkovanog suvog sedimenta (na višem i nižem koncentracionom nivou) odmereno je 20 ml 5 mM  $CaCl_2$ , 1 ml rastvora  $HgCl_2$  (300 mg/l) i 1 g Tenax ili XAD-4 smole ili 25 ml rastvora ciklodekstrina (koncentracije ciklodekstrina su iznosile 7,16 mM BCD, 42,7 mM MCD i 50 mM HPCD respektivno). Ovako pripremljene probe su obložene aluminijumskom folijom i postavljane na mešanje. Prvih deset vijala je uklonjeno sa mešalice nakon 6 h, zatim sledeći nakon 8 h i nakon 24 h. Probe su ostavljane na tamno mesto radi bistrenja tečne faze i nakon odvajanja smole i rastvora ciklodekstrina od sedimenta rađene su ekstrakcije po ranije opisanim procedurama.

### 3. REZULTATI I DISKUSIJA

Sadržaj organske materije, izražen kao gubitak žarenjem, iznosio je 16,0%, dok je sadržaj gline iznosio 31,6%. Relativno visok sadržaj organske materije u sedimentu ukazuje na visok potencijal sedimenta za kompleksiranje dok relativno visok sadržaj gline ukazuje na potencijal sorbovanja zagađujućih materija koje dospevaju u sediment. Posledica toga je smanjenje biodostupne frakcije zagađujućih materija (Spasojević i sar., 2015; 2018). Neophodno je istaći da 83,0% sedimenta predstavljaju frakcije manje od 63  $\mu m$  koje imaju veliki afinitet za sorpciju različitih zagađujućih materija. Poređenjem dobijenih

determined in resins and a solution of cyclodextrin after each separation by three-step extraction with acetone:hexane, and after 144 h, residual concentration in sediment was also determined. At the same time, a blank test was performed without the addition of sorbent or cyclodextrin

*Desorption modeling.* In order to determine the potentially bioavailable fraction of trifluraline in the sediment, the obtained multistep extraction data were modeled using the two-compartment and three-compartment kinetic model proposed by Cornelissen et al. (1997):

Where:

- $S_t$  and  $S_0$  - the sediment-sorbed amounts at time  $t$  (h) and at the start of the experiment, respectively;
- $k_{fast}$ ,  $k_{slow}$  and  $k_{very\ slow}$  - the rate constant of the rapidly, slow and very slowly contaminant desorbing fraction;
- $F_{rap}$ ,  $F_{slow}$  and  $F_{slow+very\ slow}$  - the fractions of contaminant present in the aqueous phase and in the rapidly, slow and very slowly desorbing compartment in sediment at time zero (Cornelissen i sar., 1997).

*The single-step extraction procedure* is described in detail by Spasojević et al., (2015). In brief: 20 g of 5 mM  $CaCl_2$ , 1 ml of  $HgCl_2$  (300 mg/L) solution and 1 g of Tenax or XAD-4 resin or 25 mL of a cyclodextrin solution (concentrations of cyclodextrin amounted to 7.16 mM BCD, 42.7 mM MCD and 50 mM HPCD, respectively). The prepared vials are coated with aluminum foil and placed on shaker. The vials were removed from the shaker after 6 h, then after 8 h and after 24 h. The probes were left in a dark place for the clarification of the liquid phase, and after extraction of the resin and the cyclodextrin solution from the sediment, extractions were carried out according to the procedures described earlier.

### 3. RESULTS AND DISCUSION

The content of organic matter, expressed as an loss of ignition, was 16.0%, while the clay content was 31.6%. The relatively high content of organic matter in the sediment indicates the high potential of sediment for complexing, while the relatively high content of clay indicates the potential for sorption of contaminants into the sediment. As a consequence, the reduction of the bioavailable fraction of pollutants can occur (Spasojević et al., 2015; 2018). It is necessary to point out that 83.0% of sediments are fractions of less than 63  $\mu m$  which have a high affinity for the sorption of various pollutants. Comparing the obtained

vrednosti za granulometrijski sastav sa teksturnim trouglom za zemljište, sediment na kom je rađena ova teza je okarakterisan kao srednje fina praškasto glinovita ilovača.

### Optimizacija parcijalnih metoda ekstrakcije u cilju procene biodostupnosti trifluralina

Koncentracije trifluralina u sedimentu za eksperiment višestepenih i jednostepenih ekstrakcija su iznosila je 3780 µg/kg. Ukupna količina desorbovanih ispitivanih jedinjenja sa sedimenta primenom parcijalnih metoda ekstrakcije nakon 144 h je prikazana na slici 1. Primećuje se širok raspon desorbovanog trifluralina primenom različitih agenasa, pri čemu su se vrednosti kretale od 30,0% do čak 96,1%. Na osnovu prikazanih rezultata primećuje se da je najveća količina desorbovana primenom XAD-4 smole. Ovi rezultati indikuju da se i nakon dve godine starenja primenom XAD-4 smole sa sedimenta može desorbovati skoro celokupna količina prisutnog trifluralina. Primljeni ekstrakcioni agensi održavaju koncentracioni gradijent između vodene faze i čvrstog matriksa smola ili šupljina ciklodekstrina, čime se obezbeđuje desorpcija ispitivanih jedinjenja sa sedimenta (Hua i sar., 2017) and 75% reduction for HCH, and 93% and 59% decrease for DDTs in aqueous equilibrium concentration, respectively. Similarly, the reduction efficiencies of DDT and HCH uptake by semipermeable membrane devices (SPMDs). U slučaju XAD-4 kao posledica velike specifične površine granula smole (750 m<sup>2</sup>/g) i njihovog velikog sorpcionog kapaciteta prema hidrofobnim organskim jedinjenjima desorbovana količina trifluralina je skoro 100%. S druge strane ostali primljeni ekstrakcioni agensi su desorbovali manje trifluralina sa sedimenta. Tenaks je jedno od najčešće korišćenih agenasa za procenu biodostupne frakcije jedinjenja kao što su policiklični aromatični ugljovodoni (Cui i sar., 2013; Lydy i sar., 2014). U slučaju trifluralina desorbovao je manje količine u poređenju sa XAD-4, što može biti posledica nedovoljnog afiniteta prema trifluralinu i značajno manje specifične površine (35 m<sup>2</sup>/g).

Primljeni ciklodekstrini su desorbovali značajno manje trifluralina sa sedimenta u odnosu na smole. Prema Hartnik i sar. (2008) količina jedinjenja koja može da se ekstrahuje ciklodekstrinima zavisi od ravnotežnog stanja sediment-voda-ciklodekstrin. Ciklodekstrini će izekstrahovati slabo vezanu frakciju ako njihov ekstrakcioni kapacitet prevaziđe sorpcioni kapacitet sedimenta. U suprotnom, sistem dostiže ravnotežno stanje i ciklodekstrini neće izekstrahovati švu slabo vezanu frakciju jedinjenja. Efikasnost ekstrakcije ciklodekstrinima procenjena je izračunavanjem maksimalne ekstraktivne frakcije (MEF) na osnovu metodologije date od strane Wong i Bidleman, (2010), jednačina 3:

$$MEF = \frac{EC}{EC + SC}$$

gde je:

values for the particulate size composition with the textural triangle for the soil, the used sediment is characterized as a medium fine powdered clay loam.

### Optimization of non exhaustive extraction methods for the trifluralin bioavailability assessment

The concentrations of trifluralin in the sediment used for the experiment of multistep and single-step extractions were 3780 µg/kg. The total amount of desorbed trifluralin from the sediment using non exhaustive extraction methods after 144 h is shown in Figure 1. A wide range of desorbed trifluralin is observed with the use of various agents, the values ranging from 30.0% to as much as 96.1%. Based on the results presented, it is revealed that the greatest amount is desorbed using XAD-4 resin. These results indicate that even after two years of sediment aging, almost the entire amount of trifluralin can be desorbed from sediment using XAD-4 resin. The applied extraction agents maintain a concentration gradient between the aqueous phase and the solid matrix of the resin or the cyclodextrine cavity, which ensures the desorption of the compounds from the sediment (Hua et al., 2017). In the case of XAD-4 as a result of the large specific surface area of the resin grain (750 m<sup>2</sup>/g) and their high sorption capacity towards hydrophobic organic compounds, the desorbed amount of trifluralin is almost 100%. On the other hand, the other extraction agents used desorbed lower amount of trifluralin from the sediment. Tenax is one of the most commonly used agents for bioavailable fraction assessment for the compounds such as polycyclic aromatic hydrocarbons (Cui et al., 2013; Lydy et al., 2014; Maletić et al. 2015, 2018). In the case of trifluralin it desorbed smaller amounts compared to XAD-4, which may be due to insufficient affinity for trifluralin and significantly less specific surface area (35 m<sup>2</sup>/g).

Applied cyclodextrins desorbed significantly less trifluraline from sediment than resins. According to Hartnik et al. (2008), the amount of a compound that can be extracted with cyclodextrins depends on the sediment-water-cyclodextrin equilibrium state. Cyclodextrins will extract a weakly bound fraction if their extraction capacity exceeds the sorption capacity of the sediment. Otherwise, the system reaches an equilibrium state and the cyclodextrins will not eliminate this poorly bound fraction of the compound. The efficiency of extraction with cyclodextrins was estimated by calculating the maximum extractive fraction (MEF) based on the methodology given by Wong and Bidleman, (2010), equation 3:

3)

where:



- EC – ekstrakcioni kapacitet ciklodekstrina ( $EC=M_{CD} * K_{CD}$ ),
- SC – sorpcioni kapacitet sedimenta ( $SC=M_{sed} * f_{oc} * K_{oc}$ ),
- $M_{CD}$  i  $M_{sed}$  – masa ciklodekstrina i sedimenta,
- $K_{CD}$  – koeficijent raspodele između ciklodekstrina i vode,
- $K_{oc}$  – koeficijent raspodele između organskog ugljenika u sedimentu i vode,
- $f_{oc}$  – frakcija organskog ugljenika u sedimentu.

$K_{CD}$  je izračunat na osnovu linearne korelacije predložene od strane Wang i Brusseau, (1993),  $\log K_{CD}=0,62 * \log K_{ow} + 0,34$ , uz napomenu da je ova jednačina izvedena za eksperimente u kojima je korišćen 2-hidroksipropil- $\beta$ -ciklodekstrin.

$K_{oc}$  je izračunat prema Seth i saradnicima (1999) bur most notably the octanol/water partition coefficient K-OW and water solubility. From an analysis of the theory underlying in this partitioning and an examination of the existing database, it is suggested that The preferred approach is to correlate the quantity  $\log(K-OC/K-OW, K_{oc}=0,35 * K_{ow}$  uz faktor varijacije od 2,5 u oba pravca. Na osnovu dobijenih rezultata može se zaključiti da je MEF vrednost u slučaju 2-hidroksipropil- $\beta$ -ciklodekstrina i metil- $\beta$ -ciklodekstrina bliska ili veća od eksperimentalno dobijenih vrednosti ukazujući na činjenicu da je koncentracija ekstrakcionih agenasa bila dovoljna za oslobađanje slabo vezane frakcije trifluralina. S druge strane u slučaju  $\beta$ -ciklodekstrina, za donji opseg MEF (kada je  $K_{oc}=0,35 * K_{ow} * 2,5$ ) dobijene su značajno niže vrednosti od eksperimentalno dobijenih, indikujući mogućnost nedovoljne količine agensa za ekstrakciju slabo vezane frakcije trifluralina (tabela 1). Ovo je posledica male rastvorljivosti  $\beta$ -ciklodekstrina, zbog čega se u praksi najčešće primenjuju njegovi rastvorljiviji derivati kao što su 2-hidroksipropil- $\beta$ -ciklodekstrin i metil- $\beta$ -ciklodekstrin (Wong i Bidleman, 2010; Liu i sar., 2013) Međutim, svakako je bitno napomenuti i da su kako izračunati, tako i eksperimentalno dobijeni ekstrakcioni kapaciteti značajno niži od onih dobijenih primenom smola.

- EC – extraction capacity of cyclodextrines ( $EC=M_{CD} * K_{CD}$ ),
- SC – sedimen sorption capacity ( $SC=M_{sed} * f_{oc} * K_{oc}$ ),
- $M_{CD}$  and  $M_{sed}$  – mass of cyclodextrine and sediment,
- $K_{CD}$  – cyclodextrin water distribution coefficient,
- $K_{oc}$  – prganic carbon water distribution coefficient,
- $f_{oc}$  – organic carbon fraction in sediment.

$K_{CD}$  was calculated on the basis of the linear correlation proposed by Wang and Brusseau, (1993),  $\log K_{CD} = 0.62 * \log K_{ow} + 0.34$ , with the notation that this equation was performed for experiments in which HPCD was used.

$K_{oc}$  was calculated according to Seth and Associates (1999),  $K_{oc} = 0.35 * K_{ow}$  with a variation factor of 2.5 in both directions. Based on the results obtained, it can be concluded that the MEF value in the case of 2-hydroxypropyl- $\beta$ -cyclodextrin and methyl- $\beta$ -cyclodextrin is close or greater than the experimentally obtained values, indicating that the concentration of the extraction agents was sufficient to release the weakly bound fraction of trifluralin. On the other hand, in the case of  $\beta$ -cyclodextrin, for the lower level (when  $K_{oc} = 0.35 * K_{ow} * 2.5$ ) the MEF was significantly lower than the experimentally obtained, indicating the possibility of an insufficient amount of the extraction agent of the weakly bound fraction of trifluralin (Table 1). This is due to the low solubility of  $\beta$ -cyclodextrin, for this reason in practice its soluble derivatives such as 2-hydroxypropyl- $\beta$ -cyclodextrin and methyl- $\beta$ -cyclodextrin are most frequently used (Wong and Bidleman, 2010; Liu et al., 2013). However, it is worth mentioning that both the calculated and the experimentally obtained extraction capacities are considerably lower than those obtained by using the resin.

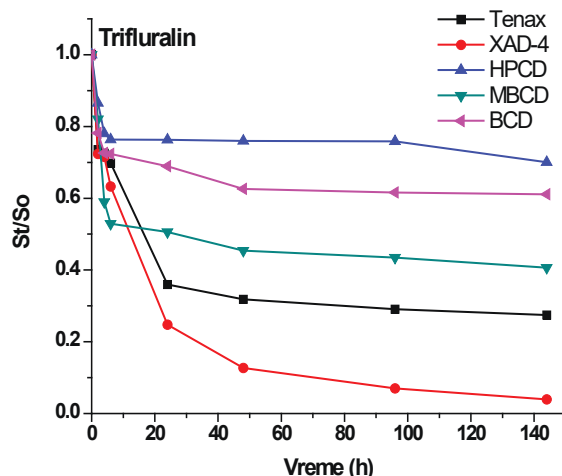
**Tabela 1.** Maksimalni ekstrakcioni kapacitet ciklodekstrina

$\log K_{ow}$	$\log K_{oc}$	$\log K_{CD}$	MEF <sub>BCD</sub>	MEF <sub>MCD</sub>	MEF <sub>HPCD</sub>
5,34	4,48 – 5,34	3,65	12,1 – 51,1	48,7 – 87,8	54,3 – 90,0

**Table 1.** Maximal extraction capacity of cyclodextrines

Manja ekstraktabilnost primenom ciklodekstrina može biti posledica: veličine i strukture molekula (Voncina i Vivod, 2013), visoke hidrofobnosti i jačeg afiniteta sorpcije odabranih organskih jedinjenja u organskoj materiji sedimenta od afiniteta prema formiranju inkluzionih kompleksa (Wong i Bidleman, 2010), adsorpcije ciklodekstrina i inkluzionih kompleksa ciklodekstrina na česticama sedimenta, čime se pospešuje sekvestracija hidrofobnih jedinjenja u sedimentu (Liu i sar., 2013) the choice of cyclodextrin (CD).

Smaller extractability with the use of cyclodextrin can be due to: the size and structure of the molecules (Voncina and Vivod, 2013), high hydrophobicity and a stronger affinity of the selected organic compounds in the organic matter of the sediment from affinity to the formation of inclusion complexes (Wong and Bidleman, 2010), adsorption of cyclodextrin and inclusion complexes of cyclodextrin on sediment particles, which promotes the sequestration of hydrophobic compounds in sediment (Liu et al., 2013).



**Slika 1.** Desorpcija trifluralina sa sedimenta primenom smola i ciklodekstrina u toku različitog vremena uravnoteženja

**Figure 1.** Trifluralin desorption from the sediment by resins and cyclodextrines during the selected equilibrium time

Desorpciona kinetika je generalno bifazna sa inicijalnom fazom brze desorpcije odabranih jedinjenja, koja je praćena dužom sporom fazom desorpcije preostale količine jedinjenja, reflektujući na ovaj način frakcije odabranih jedinjenja sorbovanih na sediment različitom jačinom (Cornelissen *et al.*, 1997; Spasojević *et al.*, 2015) pyrene, chrysene and benzo(a). Desorpciona kinetika je ograničena sa dva faktora: (1) oslobađanja sorbata (odabranog jedinjenja) sa sorpcionih mesta sorbenta (sedimenta) i (2) difuzije sorbata kroz sorbent do vode (Cornelissen *et al.*, 1998).

Desorption kinetics is generally biphasic with the initial phase of rapid desorption of the selected compounds, which is followed by a slower phase of desorption of the remaining amount of the compound, reflecting in this way fractions of selected compounds sorbed to sediment by variable intensity (Cornelissen *et al.*, 1997; Spasojević *et al.*, 2015). Desorption kinetics is limited by two factors: (1) the release of sorbate (selected compound) from sorption sites of sorbent (sediment) and (2) sorbate diffusion through sorbent to water (Cornelissen *et al.*, 1998).

U cilju dalje procene metode za određivanje biodostupne frakcije dobijeni podaci su modelovani primenom jednačina 1 i 2. Modelovanjem dobijenih podataka desorpcije se dobijaju podaci za biodostupnu frakciju jedinjenja. Generalno, desorpcija trifluralina za sve odabrane ekstrakcione agense je pokazala da se ravnoteža brzo postiže u toku 1 dana (slika 1). Prihvaćeno je da je ona frakcija jedinjenja koja se nalazi u domenu brzo-desorbujuće organske frakcije ( $F_{brzi}$ ) u stvari biodostupna frakcija. Primenom ranije opisanih jednačina dobijene su visoke vrednosti za koeficijente korelacije za oba primenjena modela (tabela 2). Primećuje se da postoji značajna razlika u dobijenim vrednostima za brzo-desorbujuću frakciju trifluralina, gde je značajno niža vrednost za  $F_{brzi}$  dobijena primenom tročlanog kinetičkog modela, osim u slučaju primene 2-hidroksipropil- $\beta$ -ciklodekstrina i metil- $\beta$ -ciklodekstrina, dok su u slučaju dvočlanog kinetičkog modela dobijene vrednosti bliske ukupno desorbovanoj količini jedinjenja primenom svih agenasa.

In order to further assess the method for bioavailable fraction assessment, the obtained data were modeled using equations 1 and 2. By modeling the obtained desorption data, data for the bioavailable fraction of the compound are obtained. In general, trifluralin desorption for all selected extraction agents has shown that the equilibrium is rapidly achieved within 1 day (Figure 1). It is accepted that the fraction of the compound located in the domain of rapidly desorbing organic fractions ( $F_{fast}$ ) represent bioavailable fraction. Using the previously described equations, high values for correlation coefficients were obtained for both models applied (Table 2). It is noticeable that there is a significant difference in the values obtained for the rapidly desorbing fraction of trifluralin, where there is a significantly lower value for  $F_{slow}$  obtained by the application of the three-compartment kinetic model, except in the case of the use of 2-hydroxypropyl- $\beta$ -cyclodextrin and methyl- $\beta$ -cyclodextrin. Hence, in the case of a two-compartment kinetic model the obtained value were close to the total desorbed amount of the compound using all agents.

Vrednosti  $k_{brzi}$  i  $k_{spori+veoma\ spori}$  za primenjeni dvočlani kinetički model su relativno bliske između primenjenih ekstrakcionih agenasa i u skladu sa literaturnim podacima za desorpciju trifluralina (Lydy *et al.*, 2014).

The values of the  $k_{fast}$  and  $k_{slow+very\ slow}$  for the applied two-compartment kinetic model are relatively similar between the applied extraction agents and in accordance with the literature data for the desorption of trifluralin (Lydy *et al.*, 2014).

Generalno, na osnovu svih prikazanih rezultata

In general, based on all the results of desorption



**Tabela 2. Kinetički parametri desorpcije trifluralina**  
**Table 2. Kinetic parameters for the trifluralin desorption**

		Tenaks Tenax	XAD-4	HPCD	MBCD	BCD
<b>Dvočlani model</b> <b>Two-compartment model</b>						
$F_{brzi}$	$F_{fast}$	61,3	67,1	23,4	51,1	30,3
$F_{spori+veoma\ spori}$	$F_{slow+very\ slow}$	38,7	28,5	76,9	48,9	69,7
$k_{brzi} (h^{-1})$	$K_{fast} (h^{-1})$	0,114	0,112	0,525	0,332	0,584
$k_{spori+veoma\ spori} (h^{-1})$	$K_{slow+very\ slow} (h^{-1})$	0,00153	0,0151	0,00047	0,00125	0,00112
$R^2$	$R^2$	0,955	0,979	0,953	0,960	0,966
<b>Tročlani model</b> <b>Three-compartment model</b>						
$F_{brzi}$	$F_{fast}$	15,9	15,9	23,4	51,1	25,8
$F_{spori}$	$F_{slow}$	56	74,5	16,4	48,8	13,6
$F_{veoma\ spori}$	$F_{very\ slow}$	28,1	9,6	60,2	0,1	60,6
$k_{brzi} (h^{-1})$	$K_{fast} (h^{-1})$	$4,8 \times 10^3$	$2,18 \times 10^{10}$	0,524	0,332	0,881
$k_{spori} (h^{-1})$	$K_{slow} (h^{-1})$	0,0663	0,0583	$4,72 \times 10^{-04}$	0,00125	0,0285
$k_{veoma\ spori} (h^{-1})$	$K_{very\ slow} (h^{-1})$	$1,76 \times 10^{-19}$	0,00516	$4,66 \times 10^{-04}$	0,00112	0
$R^2$	$R^2$	0,968	0,989	0,906	0,919	0,985

modelovanja kinetike desorpcije može se zaključiti da je dvočlani kinetički model primenljiviji. Naime, i pored dobijenih visokih koeficijenata korelacije, tročlani kinetički model se nije pokazao kao konzistentan u pogledu dobijenih vrednosti za  $F_{brzi}$  naročito prilikom primene smola koje su se generalno pokazale značajno efikasnijim u pogledu desorpcije odabranih jedinjenja. S druge strane, pored toga što je dvočlani kinetički model bio uporediv sa ukupno desorbovanom količinom odabranih jedinjenja, dobijene vrednosti za  $k_{brzi}$  su bile u opsegu od  $10^{-1}$  do  $10^1$  što je u skladu sa literaturnim podacima (Cornelissen i sar., 1997; Lydy i sar., 2014) while growing on maize root exudates (REs).

Dalja optimizacija metode za procenu biodostupnosti podrazumevala je određivanje vremena potrebnog za jednostepenu ekstrakciju. U cilju ovoga, poređene su vrednosti dobijene dvočlanim kinetičkim modelom za brzo-desorbujuće frakcije organskih jedinjenja sa frakcijom trifluralina desorbovane nakon određenog vremena  $F_{brzi}/F_{Xh}$  (gde X predstavlja 2, 4, 6, 24, 48, 96 i 144 h) (tabela 3). Kada je vrednost odnosa  $F_{brzi}/F_{Xh}$  bliska jedinici smatra se da je izekstrahovana brzo-desorbujuća frakcija datog jedinjenja i da je dato  $F_{Xh}$  potrebno vreme za jednostepenu ekstrakciju.

**Tabela 3. Odnosi  $F_{brzi}$  u određenom vremenskom periodu**

	Tenaks	XAD-4	HPCD	MBCD	BCD
$F_{brzi}/F_{2h}$	2,32	2,43	3,43	2,94	1,38
$F_{brzi}/F_{4h}$	2,23	2,36	1,68	1,29	1,10
$F_{brzi}/F_{6h}$	2,03	1,83	1,11	1,12	1,09

kinetics modeling, it can be concluded that the two-compartment kinetic model is more applicable. Namely, in spite of the high correlation coefficients obtained, the three-compartment kinetic model did not prove to be consistent with the obtained values for  $F_{fast}$ , especially when using resins which in general proved to be significantly more effective in desorption of the selected compound. On the other hand, in addition to the fact that the two-compartment kinetic model was comparable to the total desorbed amount of the selected compound, the obtained values for the  $k_{fast}$  were in the range of  $10^{-1}$  to  $10^1$  which is in accordance with the literature data (Cornelissen et al., 1997; Lydy and sar., 2014).

Further optimization of the bioavailability assessment method involved determining the time required for single-step extraction. For this purpose, the values obtained by a two-compartment kinetic model for fast-desorbing fractions of organic compounds with the fraction of trifluraline desorbed after a certain time  $F_{fast}/F_{Xh}$  (where X represents 2, 4, 6, 24, 48, 96 and 144 h) are compared (Table 3). When the value of the  $F_{fast}/F_{Xh}$  ratio is a close to unit, it is considered that a rapidly desorbing fraction of the given compound is extracted and that the given  $F_{Xh}$  represents the time for single-step extraction.

**Table 3. Ratio of  $F_{fast}$  in the defined time**

	Tenaks	XAD-4	HPCD	MBCD	BCD
$F_{fast}/F_{2h}$	2.32	2.43	3.43	2.94	1.38
$F_{fast}/F_{4h}$	2.23	2.36	1.68	1.29	1.10
$F_{fast}/F_{6h}$	2.03	1.83	1.11	1.12	1.09



$F_{brzi}/F_{24h}$	0,96	0,89	1,07	1,07	0,97
$F_{brzi}/F_{48h}$	0,90	0,77	1,03	0,97	0,81
$F_{brzi}/F_{96h}$	0,86	0,72	0,96	0,93	0,78
$F_{brzi}/F_{144h}$	0,85	0,70	0,94	0,89	0,77

Na osnovu prikazanih rezultata može se zaključiti da je desorpcija trifluralina u prisustvu Tenaksa i XAD-4 i ciklodeksrina nakon 24 h dovoljna da ukloni frakciju organskog jedinjenja u brzo-desorbujućem domenu organske materije, jer je  $F_{24h}$  slično vrednosti  $F_{brzi}$ , pa su dobijeni odnosi oko 1. Desorpcija nakon 24 h uklanja ne samo frakciju organskog jedinjenja u brzo desorbujućem domenu organske materije, već i deo frakcije koji se nalazi u sporo-desorbujućem domenu, jer su  $F_{48h} - F_{144h}$  veći u poređenju od  $F_{brzi}$ , pa su dobijeni odnosi manji od 1.

### Ispitivanje jednostepene desorpcije trifluralina parcijalnim ekstrakcionim metodama

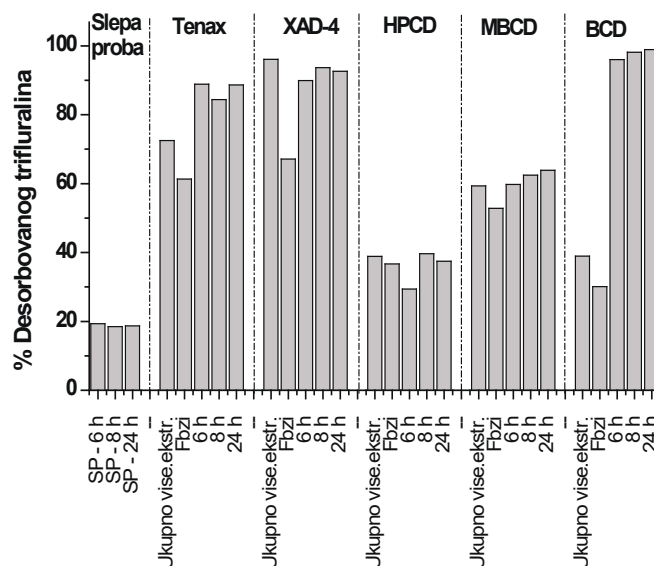
U cilju potvrde dobijenih rezultata primenom višestepene ekstrakcije trifluralina sa sedimenta urađeni su eksperimenti jednostepenih ekstrakcija na tri različita vremena (slika 2). Ovo je omogućilo direktno poređenje dobijene ukupne i biodostupne frakcije trifluralina nakon višestepene ekstrakcije sa frakcijom jedinjenja iz ekstrahovane jednostepenom ekstrakcijom.

$F_{fast}/F_{24h}$	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

Based on the results shown, it can be concluded that the desorption of trifluralin in the presence of Tenax and XAD-4 and cyclodextrin after 24 hours is sufficient to remove the fraction of the organic compound in the fast-desorbing domain of organic matter, because  $F_{24h}$  is similar to  $F_{fast}$ , so the obtained ratio are about 1. Desorption after 24 hours removes not only the fraction of the organic compound into the rapidly desorbing domain of organic matter, but also the fraction of the slow-desorbing domain, because  $F_{48h} - F_{144h}$  is larger compared to  $F_{fast}$ , so the obtained ratio are less than 1.

### Single-step desorption of trifluralin by non exhaustive extraction methods

In order to confirm the results obtained by using a multistep extraction of trifluralin from sediment, experiments of one-step extractions were performed at three different times (Figure 2). This allowed direct comparison of the obtained total and bioavailable fraction of trifluralin after multistep extraction with the fraction of the compound extracted by single-step extraction.



**Slika 2.** Desorbovane količine trifluralina nakon tri odabrana vremena uravnoteženjana

**Figure 2.** Desorbed amount of trifluralin in three selected equilibrium times

Na osnovu prikazanih rezultata može se uočiti da je primenom jednostepenih ekstrakcija sa  $\beta$ -ciklodeksrinom i metil- $\beta$ -ciklodeksrinom udeo desorbovane frakcije značajno veći od ukupne desorbovane količine dobijene prilikom višestepene ekstrakcije. S druge strane primena jednostepenih ekstrakcija sa sva tri ciklodeksrina udeo desorbovane frakcije je sličan ukupno desorbovanoj i  $F_{brzo}$  frakciji

Based on the results shown, it can be observed that by using single-step extractions with  $\beta$ -cyclodextrin and methyl- $\beta$ -cyclodextrin the fraction of the desorbed fraction is significantly higher than the total desorbed amount obtained in the multistep extraction. On the other hand, by the application of single-step extractions for all three cyclodextrins obtained desorbable fraction was similar to the total desorbed and  $F_{fast}$  fraction



dobijenoj višestepenoj ekstrakciji. Za postizanje navedenih efikasnosti desorpcija trifluralina za sve ciklodekstrine je bilo potrebno vreme od 6 h - 8 h.

S druge strane primena smola (Tenaks i XAD-4) omogućila je postizanje desorpcije trifluralina na nivou koji odgovara ukupnoj i  $F_{brzo}$  frakciji desorbovane količine dobijene prilikom višestepene ekstrakcije. Međutim, u slučaju Tenaksa za postizanje navedenih efikasnosti desorpcije je bilo potrebno vreme od 8 h - 24 h. U slučaju XAD-4 je bilo potrebno vreme od 6 h - 8 h, ukazujući na neznatno bolje performanse XAD-4 smole u odnosu na Tenaks. Na osnovu svih prikazanih rezultata može se zaključiti da je optimalni agens za procenu biodostupne frakcije trifluralina sa sedimenta XAD-4, a da je optimalno vreme ekstrakcije primenom jednostepenih ekstrakcija oko 8 h.

#### 4. ZAKLJUČAK

Na osnovu prikazanih rezultata procene biodostupnosti može se zaključiti sledeće: (1) Efikasnost primenjenih agenasa za desorpciju trifluralina sa sedimenta tokom višestepene ekstrakcije opada sledećim redom XAD-4 > Tenaks > ciklodekstrini. (2) Modelovanje kinetike desorpcije pokazalo je da dvočlani kinetički model bolje opisuje desorpciju trifluralina sa sedimenta. (3) Dvočlani kinetički model pokazao je da je optimalno vreme ekstrakcije 24 h, kada je vrednost odnosa  $F_{brzi}$  i  $F_{24h}$  najbliža vrednosti 1. (4) Jednostepene parcijalne ekstrakcije potvrdile su rezultate dobijene višestepenim ekstrakcijama i modelovanja u slučaju primene smola (Tenaks i XAD-4), gde je postignuta desorpcija odabranih jedinjenja na nivou koji odgovara ukupno desorbovanoj i  $F_{brzo}$  frakciji organskih jedinjenja. Generalno, optimalni agens za procenu biodostupne frakcije trifluralina sa sedimenta je XAD-4 smola, a optimalno vreme ekstrakcije primenom jednostepenih ekstrakcija je oko 8 h.

**Zahvalnost.** Istraživanja su finansirana od strane Ministarstva za nauku i tehnološki razvoj (Projekti TR37004 i III43005).

obtained by the multistep extraction. To achieve the mentioned trifluralin desorption efficacy for all cyclodextrins a time of 6 to 8 h was required.

On the other hand, the application of resins (Tenax and XAD-4) achieved trifluralin desorption at a level corresponding to the total and  $F_{fast}$  trifluralin fraction obtained in the multistep extraction. However, in the case of Tenax time needed to achieve the mentioned efficiency of the desorption were in range 8 to 24 h. In the case of XAD-4, needed time were in range of 6 to 8 h, indicating a slightly better performance of the XAD-4 resin compared to Tenax. Based on all of the results shown, it can be concluded that the optimal agent for estimating the bioavailable fraction of trifluralin from the sediment was XAD-4, and that the optimum extraction time using single-step extractions is about 8 h.

#### 4. CONCLUSION

Based on the presented results of bioavailability assessment, the following conclusion can be made: (1) The effectiveness of the applied desorption agents during the multi-step extraction decreases with the following order XAD-4 > Tenaks > cyclodextrins. (2) Desorption kinetics modeling showed that the two-compartment kinetic model better describes the desorption of the trifluralin from the sediment. (3) The two-compartment kinetic model showed that the optimal extraction time was 24 h, when the ratio of the  $F_{fast}$  and  $F_{24h}$  was approximately 1. (4) Single-step extractions have confirmed the results obtained by multistep extractions and modeling in the case of resins (Tenaks and XAD-4), where the desorption of the trifluralin was at a level corresponding to the total desorbed and  $F_{fast}$  fraction. In general, the optimum agent for assessing the bioavailable fraction of trifluralin from the sediment was XAD-4 resin, and the optimal extraction time using single-step extractions was about 8 hours.

**Acknowledgement.** The research was funded by the Ministry of Education, Science and Technological Development of Republic of Serbia through projects III43005 and TR37004.



## 5. LITERATURA / LITERATURE

1. Ashraf, M.A., 2017. Persistent organic pollutants (POPs): a global issue, a global challenge. *Environmental Science and Pollution Research* **24**, 4223-4227.
2. Cornelissen, G., Govers, H.A.J., van Noort, Paul C.M., 1997. Desorption kinetics of chlorobenzenes, PAHs and PCBs: sediment extraction with Tenax and effects of contact time and solute hydrophobicity. *Environmental Toxicology and Chemistry* **16**, 1351-1357.
3. Cornelissen, G., Van Noort, P.C.M., Govers, H.A.J., 1998. Mechanism of slow desorption of organic compounds from sediments: A study using model sorbents. *Environmental Science & Technology* **32**, 3124-3131.
4. Cui, X., Mayer, P., Gan, J., 2013. Methods to assess bioavailability of hydrophobic organic contaminants: Principles, operations, and limitations. *Environmental Pollution* **172**, 223-234.
5. Hartnik, T., Jensen, J., Hermens, J.L.M., 2008. Nonexhaustive  $\beta$ -cyclodextrin extraction as a chemical tool to estimate bioavailability of hydrophobic pesticides for earthworms. *Environmental Science & Technology* **42**, 8419-8425.
6. He, W., Jung, H., Lee, J., Hur, J., 2015. Differences in spectroscopic characteristics between dissolved and particulate organic matters in sediments: Insight into distribution behavior of sediment organic matter. *Science of The Total Environment* **547**, 1-8
7. Hua, S., Gong, J.-L., Zeng, G.-M., Yao, F.-B., Guo, M., Ou, X.-M., 2017. Remediation of organochlorine pesticides contaminated lake sediment using activated carbon and carbon nanotubes. *Chemosphere* **177**, 65-76. <https://doi.org/10.1016/j.chemosphere.2017.02.133>.
8. Liu, H., Cai, X., Chen, J., 2013. Mathematical Model for Cyclodextrin Alteration of Bioavailability of Organic Pollutants. *Environmental Science & Technology* **47**, 5835-5842.
9. Lydy, M.J., Harwood, A.D., Nuttle, S.A., Landrum, P.F., 2014. Tenax Extraction of Sediments to Estimate Desorption and Bioavailability of Hydrophobic Contaminants: A Literature Review. *Integrated Environmental Assessment and Management* **11**, 208-220.
10. Maletić, S., Rončević, S., Agbaba, J., Molnar Jazić, J., Kragulj Isakovski, M., Spasojević, J., Dalmacija, B. (2015) Značaj procene biodostupnosti perzistentnih organskih materija, *Voda i sanitarna tehnika*, 5-6, str. 5-11.
11. Maletić S., Grgić M., Kragulj Isakovski M., Beljin J., Tubić A., Rončević S., Agbaba J. (2018) Sekvestracija odabranih organskih polutanata u aluvijalnom nanosu Dunava primenom ugljeničnih materijala. *Voda i sanitarna tehnika*, 3-4, 13-20. Izdavač: Udruženje za tehnologiju vode i sanitarno inženjstvo.
12. Murschell, T., and Farmer D.K., 2019. Atmospheric OH oxidation chemistry of trifluralin and acetochlor, *Environmental Science: Processes & Impacts* **21**, 650-658.
13. Rabodonirina, S., Net, S., Ouddane, B., Merhaby, D., Dumoulin, D., Popescu, T., Ravelonandro, P., 2015. Distribution of persistent organic pollutants (PAHs, Me-PAHs, PCBs) in dissolved, particulate and sedimentary phases in freshwater systems, *Environmental Pollution* **206**, 38-48.
14. Seth, R., Mackay, D., Muncke, J., 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environmental Science & Technology* **33**, 2390-2394.
15. Spasojević, J., Maletić, S., Rončević, S., Grgić, M., Krčmar, D., Varga, N., Dalmacija, B., 2018. The role of organic matter and clay content in sediments for bioavailability of pyrene. *Water Science and Technology* **77**, 439-447.
16. Spasojević, J.M., Maletić, S.P., Rončević, S.D., Radnović, D. V., Čučak, D.I., Tričković, J.S., Dalmacija, B.D., 2015. Using chemical desorption of PAHs from sediment to model biodegradation during bioavailability assessment. *Journal of Hazardous Materials* **283**, 60-69.
17. Von Wachenfeldt, E., Tranvik, L.J., 2008. Sedimentation in boreal lakes - the role of flocculation of allochthonous dissolved organic matter in the water column. *Ecosystems* **11**, 803-814.
18. Voncina, B., Vivod, V., 2013. Cyclodextrins in Textile Finishing.
19. Wallace, D.R., 2014. Trifluralin in encyclopedia of toxicology. In: Wexler, P. (Ed.), *Encyclopedia of Toxicology*, 3<sup>rd</sup> ed. Academic Press, Oxford, 388-389.
20. Wang, J., Taylor, A., Xu, C., Schlenk D., Gan, J., 2018. Evaluation of different methods for assessing bioavailability of DDT residues during soil remediation. *Environmental Pollution* **238**, 462-470.
21. Wang, X., Brusseau, M.L., 1993. Solubilization of Some Low-Polarity Organic Compounds by Hydroxypropyl- $\beta$ -cyclodextrin. *Environmental Science & Technology* **27**, 2821-2825.
22. Wong, F., Bidleman, T.F., 2010. Hydroxypropyl- $\beta$ -cyclodextrin as non-exhaustive extractant for organochlorine pesticides and polychlorinated biphenyls in muck soil. *Environmental Pollution* **158**, 1303-1310.
23. Zhou, W., Lu, Y., Jiang, S., Xiao, Y., Zheng, G., Zhou, L., 2018. Impact of sludge conditioning treatment on the bioavailability of pyrene in sewage sludge. *Ecotoxicology and Environmental Safety* **163**, 196-204.