



Centrum pro výzkum
toxických látek
v prostředí

Bi5596

Moderní metody v ekotoxikologii

Moderní metody hodnocení expozice

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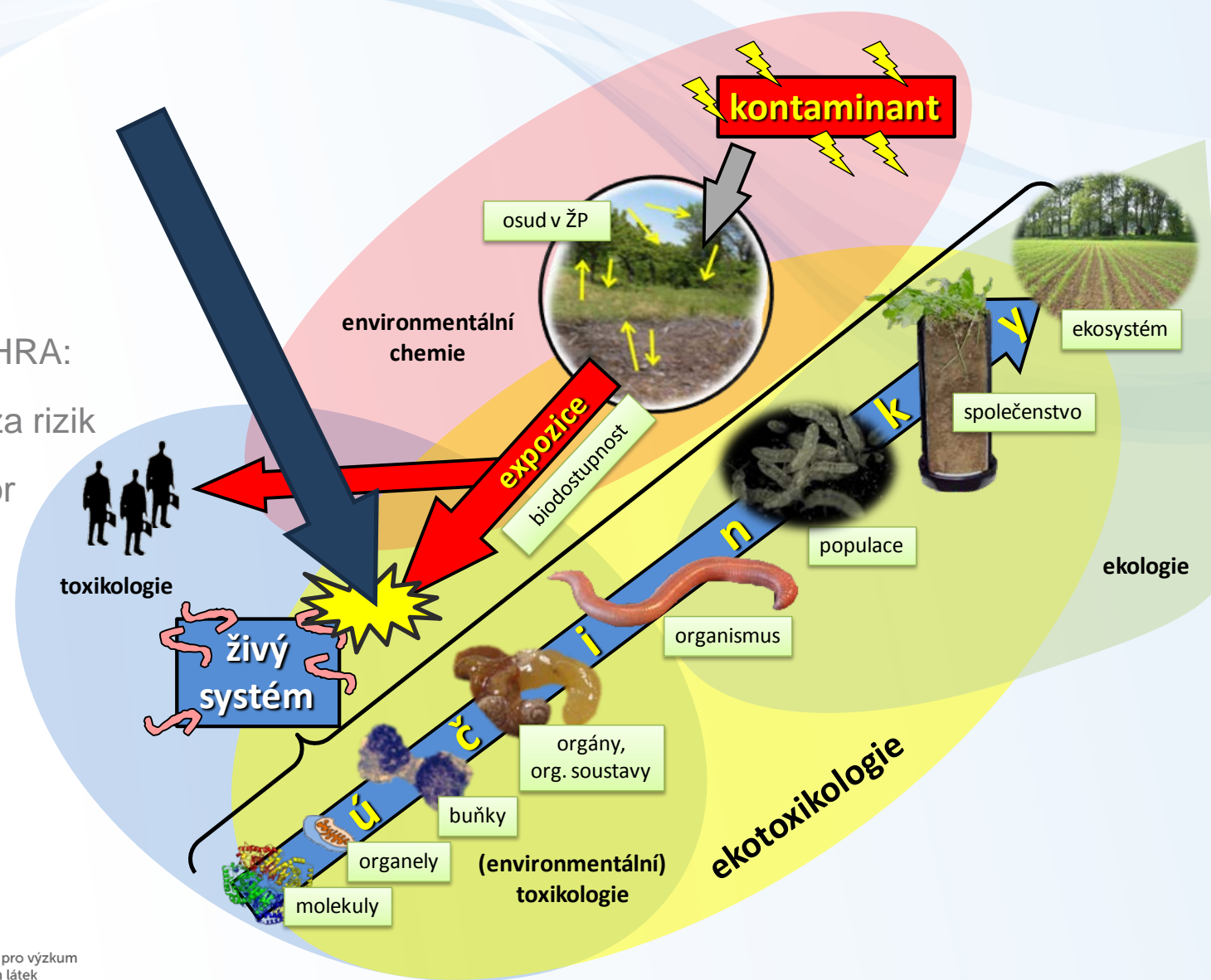
podzim 2014



Expozice v ekotoxikologii a v hodnocení ekologických rizik

Expozice v ekotoxikologii a v EcoRA

expoze v HHRA:
C8580 Analýza rizik
Dr. Pavel Čupr



Expozice v ekotoxikologii a v EcoRA

- hodnocení efektů bez znalosti expozice je téměř zbytečné

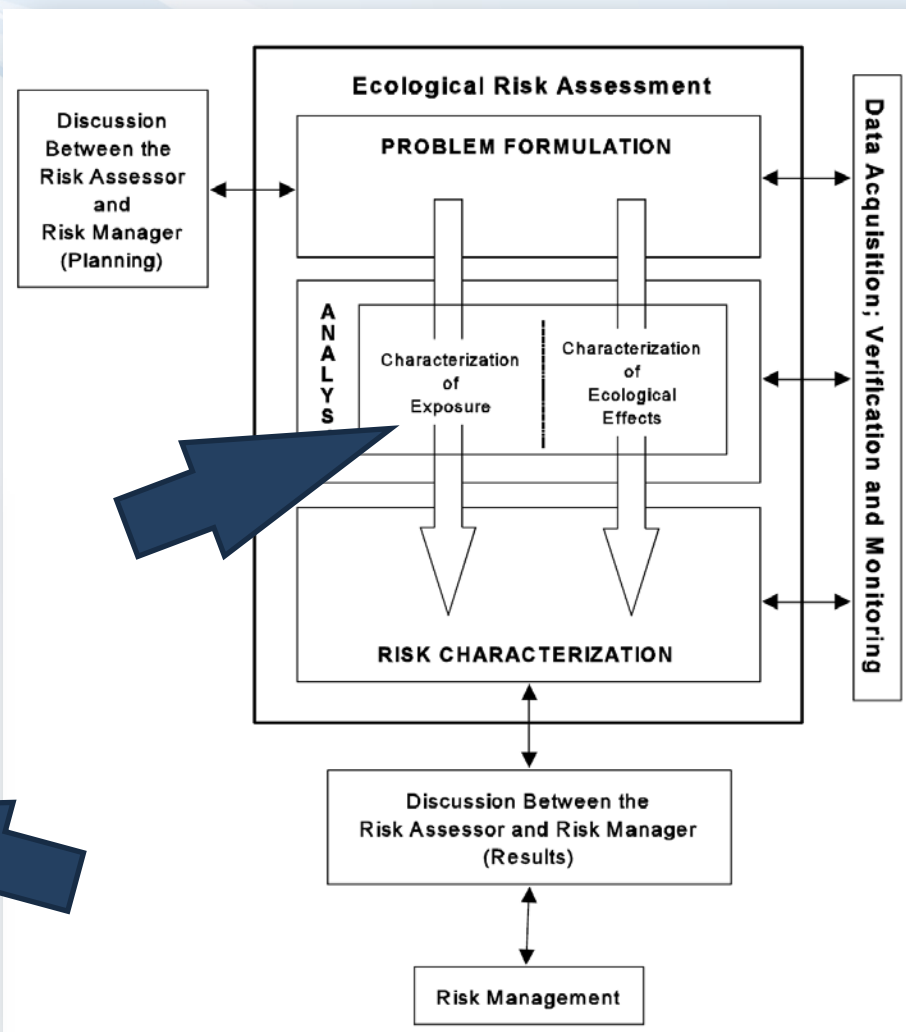
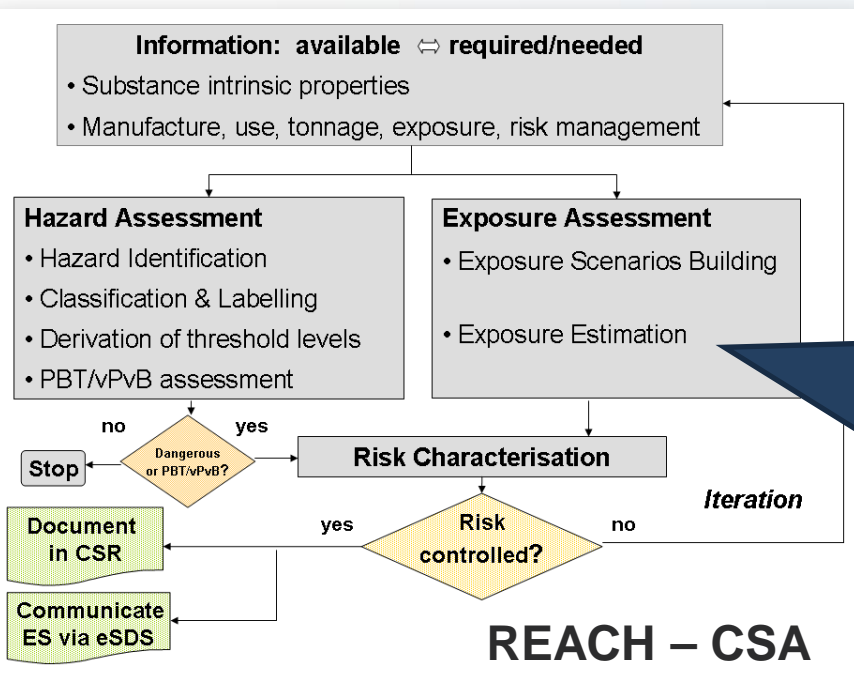
proč?

- **bez expozice není účinek, bez expozice je riziko = 0**
- z hlediska **poslání / cíle celé ekotoxikologie**: nejen řešit efekty, ale popsat celý problém, popsat riziko, odvodit opatření, chránit ŽP:
 - **predikce – hodnocení rizik** – pravděpodobnosti, že při dané koncentraci dojde k definovaným efektům
 - **kauzalita** – korelace intenzity stresoru (koncentrace chemické látky) a míry poškození biologického systému



Expozice v ekotoxikologii a v EcoRA

- **EcoRA** – ecological risk assessment
- **CSA** - chemical safety assessment (REACH)
- **ERA** – environmental risk assessment
- **HHRA** – human health risk assessment



US EPA (1999) Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments

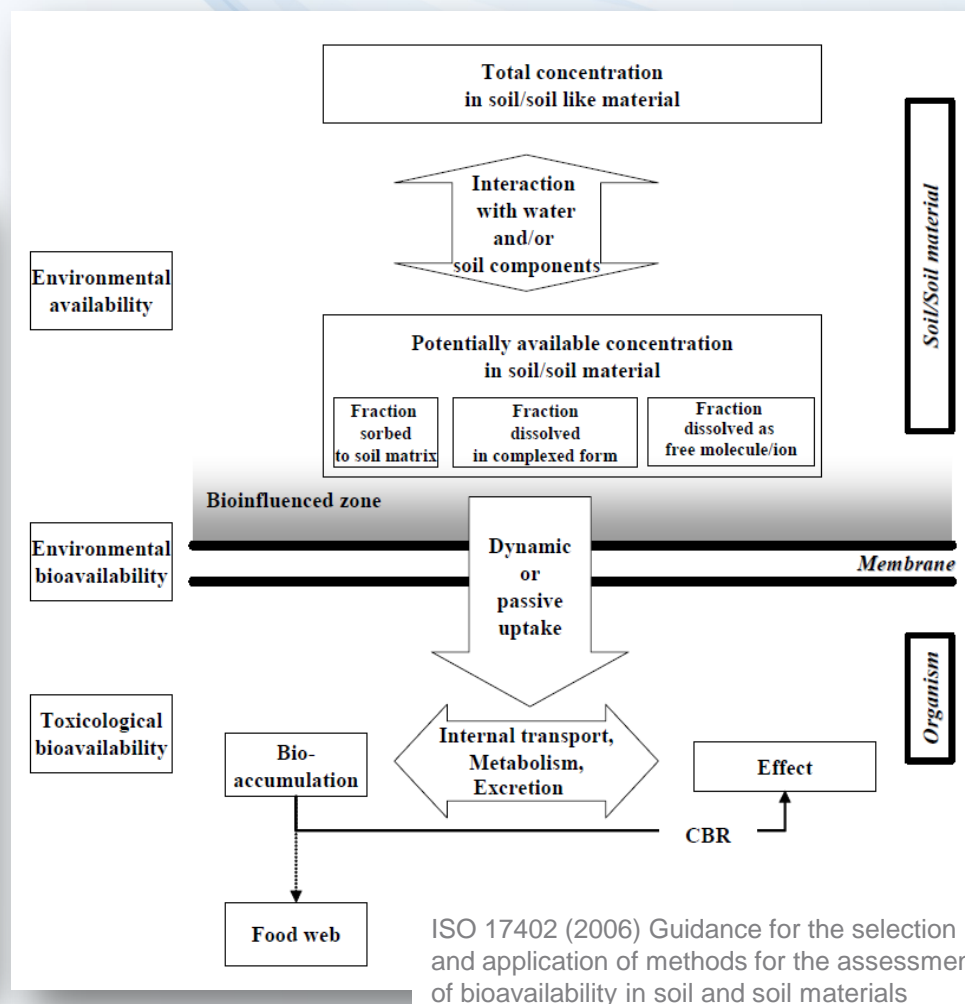
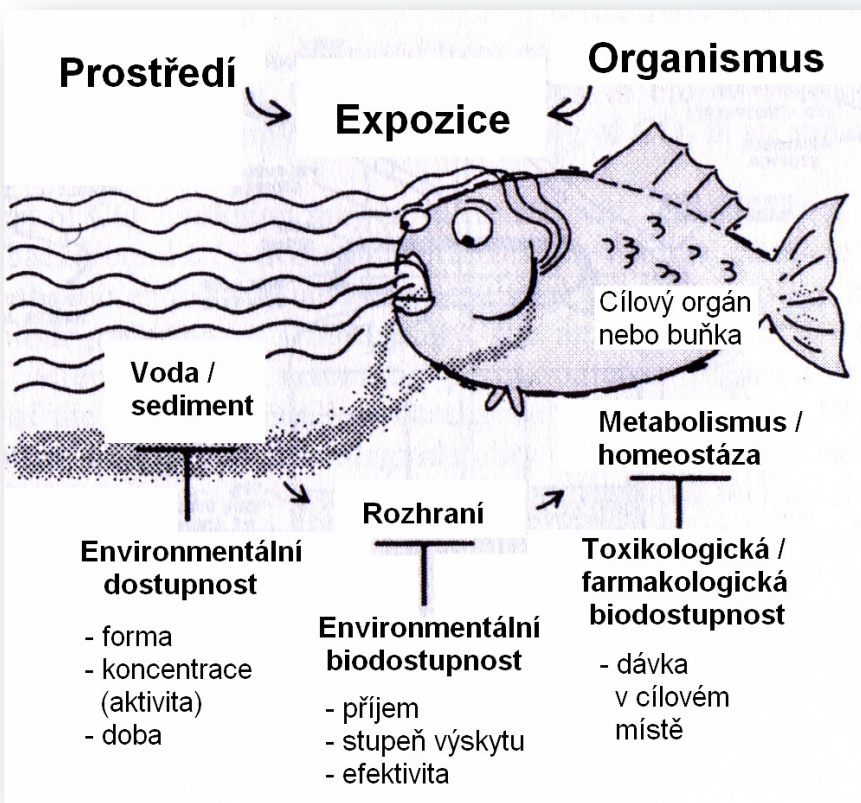
Expozice v ekotoxikologii a v EcoRA

- překryv s environmentální chemií
- expozici předchází **osud kontaminantu v prostředí**, který nemůže ekotoxikologie přehlížet, protože expozici klíčově ovlivňuje:
 - změna **environmentální dostupnosti**:
 - změna celkové koncentrace v prostředí
 - změna distribuce v různých částech prostředí
 - změna forem výskytu látky (např. kovy – speciace) a transformace
 - závisí zejména na vlastnostech látky a prostředí (uvedte konkrétní příklady)
 - změna **biodosažitelnosti a biodostupnosti**
 - vazba na složky prostředí
 - omezení příjmu organismy
 - závisí na vlastnostech látky, prostředí ale i organismů (uvedte konkrétní příklady)



Expozice v ekotoxikologii a v EcoRA

- všechny tyto procesy je potřeba popsat a vyhodnotit (= změřit/modelovat) pro kvalitní analýzu ekotoxikologického problému, protože v drtivé většině případů platí, že pro účinek musí látka vstoupit do organismu a reagovat s biol. receptorem
- expoziční cesta



Expozice v ekotoxikologii a v EcoRA

konstrukce expozičního scénáře – analýza situace

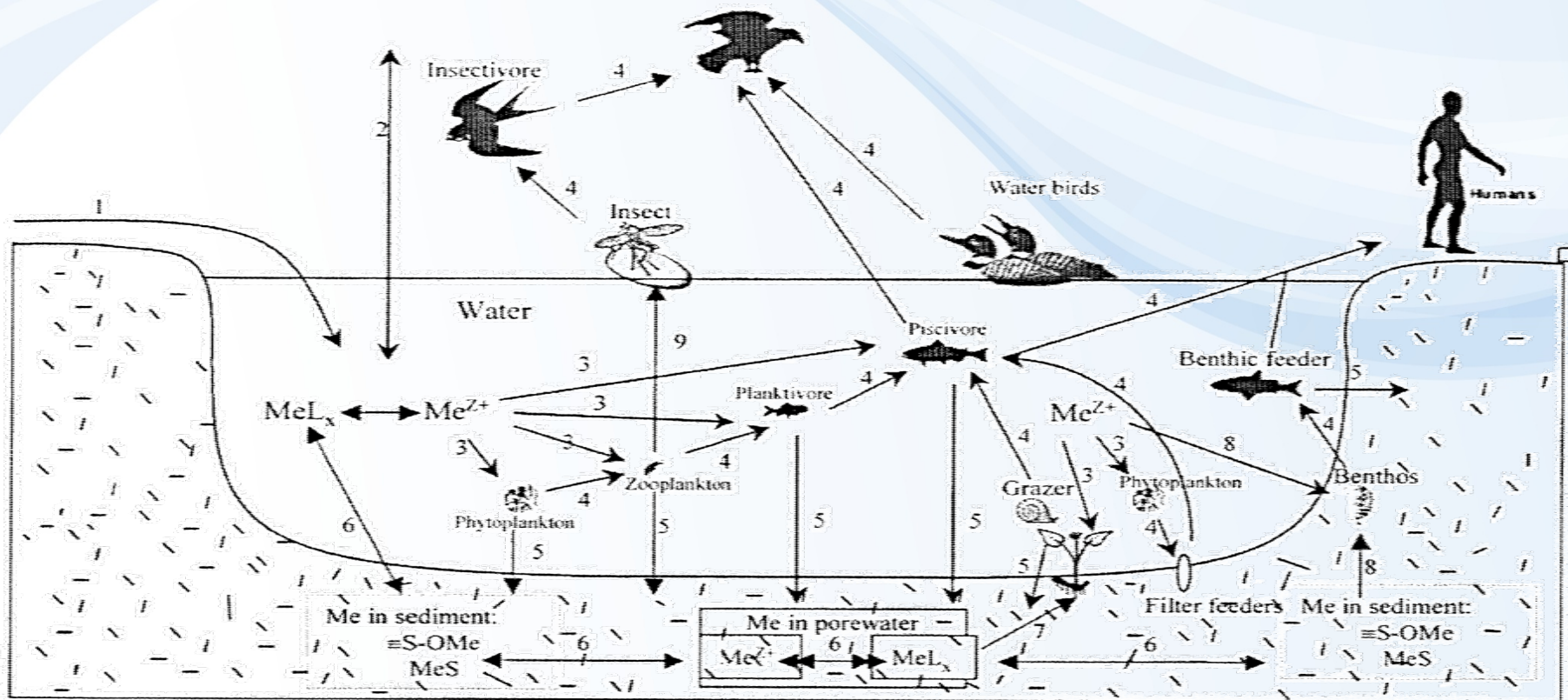


Figure 2. Conceptual model for metals in aquatic systems. (1) runoff and point sources; (2) atmospheric deposition (and volatilization for Hg); (3) uptake from dissolved phase; (4) trophic transfer; (5) deposition of detrital organic matter; (6) precipitation/dissolution and sorption/desorption; (7) uptake by rooted macrophytes; (8) benthic organisms may ingested sediment or irrigate their burrows and take up metals from water column; (9) emergence of insects. Me^{Z+} : free metal ions (metal aquo complexes); MeL_x : metal complexes with ligand L (charges are neglected for simplicity); MeS : metal precipitates; $\equiv S-OMe$: metal adsorbed on particles.



Expozice v ekotoxikologii a v EcoRA

- celá řada souvisejících procesů na překryvu ekotoxikologie a environmentální chemie
- definujte a rozlište, uveďte pro každý pojem příklad týkající se tématu vaší BP, DP, DisP):
 - bioakumulace
 - biokoncentrace
 - bioobohacování
 - biotransformace
 - biodegradace
 - toxokinetika
 - toxodynamika
- (DÚ do 1/10, soubory docx či pdf do odevzdáárny sam_prac_01)

Hodnocení expozice

Hodnocení expozice

- analýza intenzity, kvantifikace stresoru = chemické látky, toxikantu
- cíl = přesná a pravdivá koncentrace/dávka, které jsou biosystémy exponovány + případně četnost a doba trvání expozice a prostorové definování
- **měření versus modelování**
- nutno jasně definovat **KDE** (na jaké „vrstvě“) je stresor kvantifikován:
koncentrace v prostředí X koncentrace v organismu (dávka)
a **CO** vlastně vyjadřuje
- pro hodnocení rizika ($HI = PEC / PNEC$) je nutné, aby PEC a PNEC měly stejný kontext: musí být ve stejných jednotkách (např. celková koncentrace ve vodě / účinky při konkrétní celkové koncentraci ve vodě)
- u kauzality to nutné není (např. koncentrace ve vodě / počet buněk řas v ml) – ALE kvantifikace stresoru musí být co nejvíce relevantní k následným efektům (biodostupná koncentrace)



Metody hodnocení expozice

- „**klasické**“
 - stanovení **totální koncentrace v prostředí** (externí)
 - stanovení koncentrace **v organismu** (interní - body burden)
 - většinou **jednorázové stanovení aktuální koncentrace**
- „**moderní**“
 - stanovení „**biodostupných**“ koncentrací v prostředí – důraz na reálnou frakci – efektivní frakci toxikantu
 - stanovení reálné expozice z hlediska času – **dlouhodobé** zprůměrování koncentrace – time weighted average (TWA) – **pasivní vzorkování**
 - měření a modelování přestupu do organismu – **toxokinetika**
 - efektivní koncentrace **v organismu** (lethal body burden, incipient lethal level..) + **biomarkery expozice**
 - **modelování expozice** multisložkovými environmentálními modely



Celkové – totální – koncentrace

totální celkové koncentrace
silné, agresivní („harsh“) extrakce

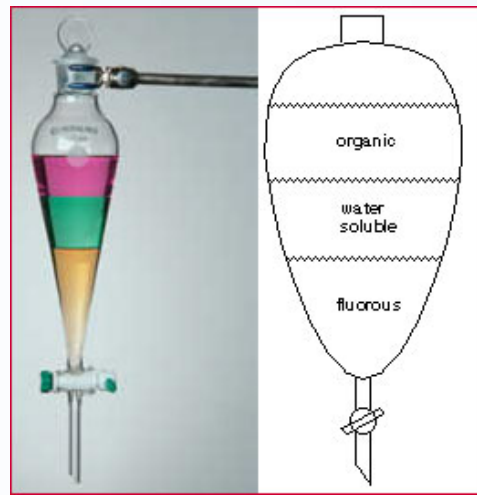
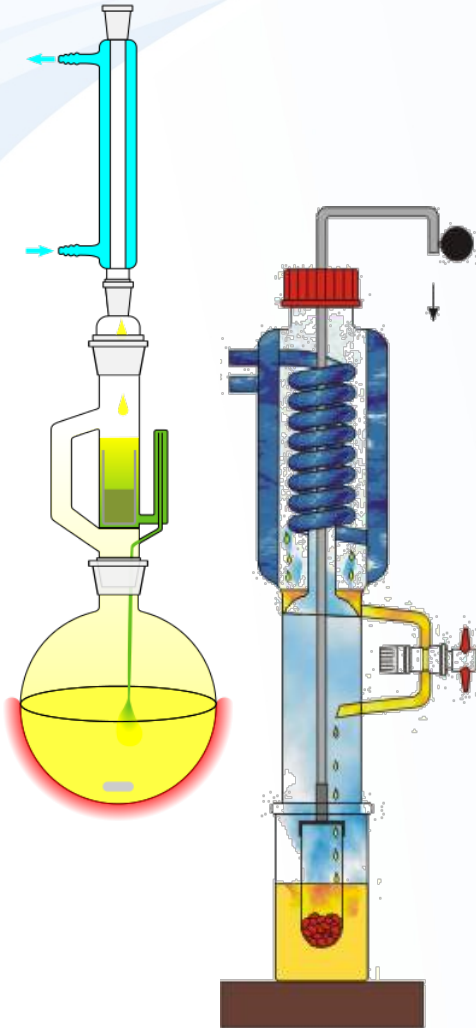
půda

sediment

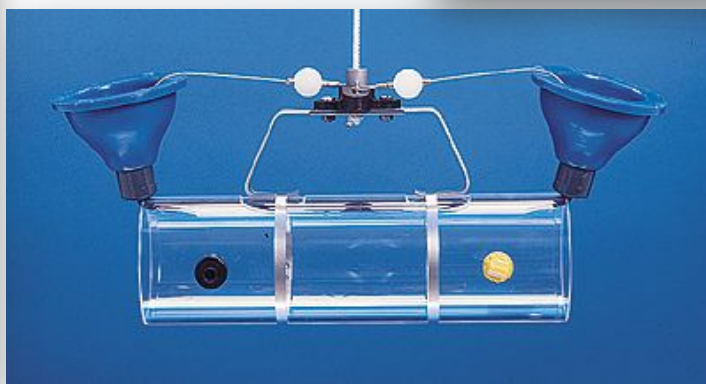
voda

vzduch (filtry)

biota



Aktuální koncentrace v médiu



Celkové – totální – koncentrace

Exposure Medium	Typical Tools for Measurement / Estimation	Typical Ancillary Parameters	Cautions / Key Issues
Soil	<ul style="list-style-type: none"> • Measurement of bulk soil chemistry, based on collection by trowel or auger 	<ul style="list-style-type: none"> • Site-specific, but may include organic matter content, pH, moisture content, soil texture, cation exchange capacity. 	<ul style="list-style-type: none"> • Sample depth • Differentiation of soil layers • Spatial design and resolution
Surface water	<ul style="list-style-type: none"> • Measurement of total or dissolved concentrations using typical water sampling gear 	<ul style="list-style-type: none"> • Site-specific, but may include hardness, pH, alkalinity, acidity, temperature, dissolved oxygen, anions, cations, nutrients, conductivity, salinity, TSS, DOC 	<ul style="list-style-type: none"> • Temporal variability including seasonality
Sediment and sediment porewater	<ul style="list-style-type: none"> • Measurement of bulk sediment chemistry using grabs, divers, or cores • Measurement of sediment porewater chemistry (dissolved) by extraction from sediments, or directly (e.g., using push-point samplers) 	<ul style="list-style-type: none"> • For sediment: organic carbon, particle size, pH, sulphides, SEM:AVS, possibly iron and manganese hydroxides • For porewater: redox, plus similar parameters to surface water 	<ul style="list-style-type: none"> • Understanding relevance of bulk sediment versus porewater for each receptor type • Sample depth • Spatial design and resolution • Understanding and addressing oxygenation of porewater samples during collection and transport
Air / Vapour	<ul style="list-style-type: none"> • Rare for ERA, but direct measurement and modeling are both used – see text. 		
Tissues	<ul style="list-style-type: none"> • Direct measurement preferred • Estimation using uptake factors or models 	<ul style="list-style-type: none"> • Lipid content • Moisture content 	<ul style="list-style-type: none"> • Consideration of whether to test whole organism or selected tissue types • Consideration of whether to depurate, depending on how tissue data will be used.

Měření biodostupnosti

Měření biodostupnosti

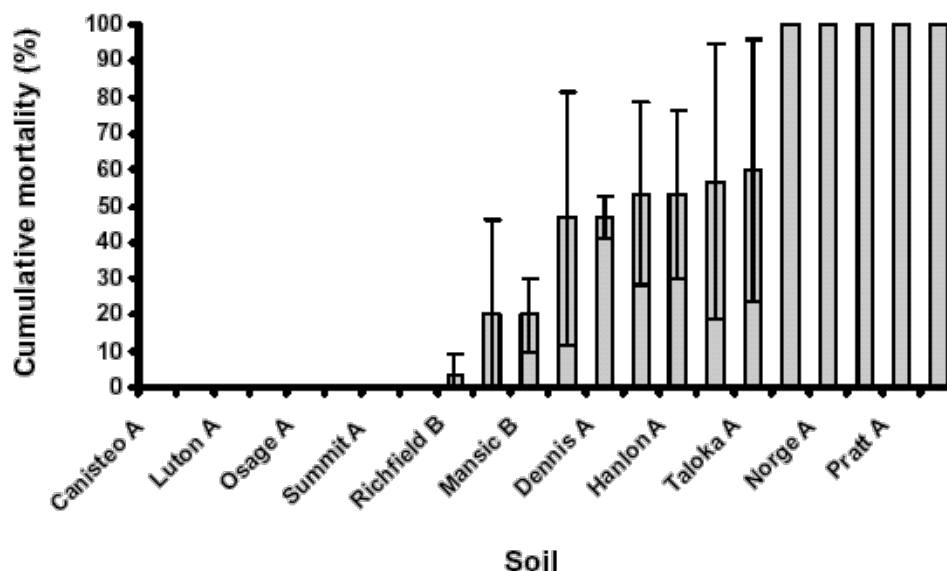
bioavailability

degree to which chemicals present in the soil may be absorbed or metabolised by human or ecological receptors or are available for interaction with biological systems

ISO 17402 (2006)

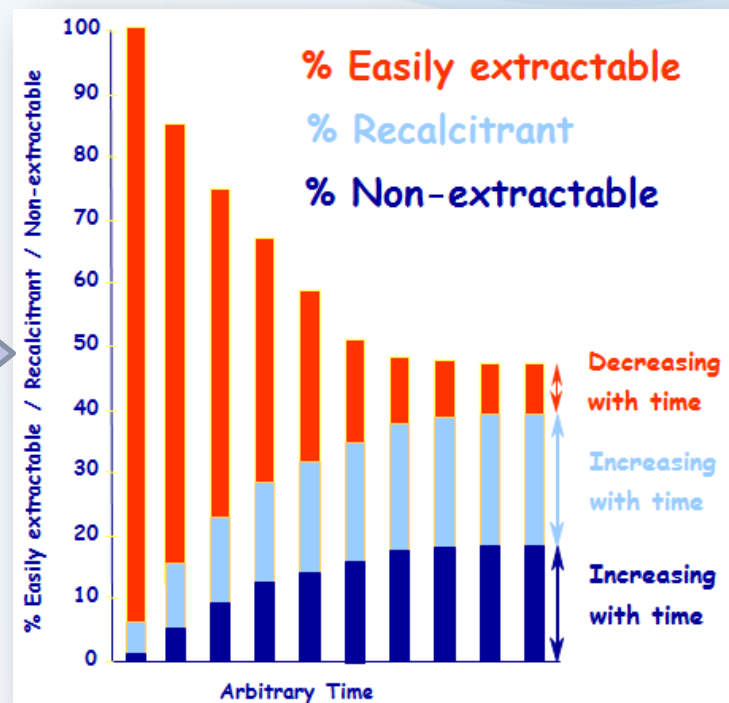
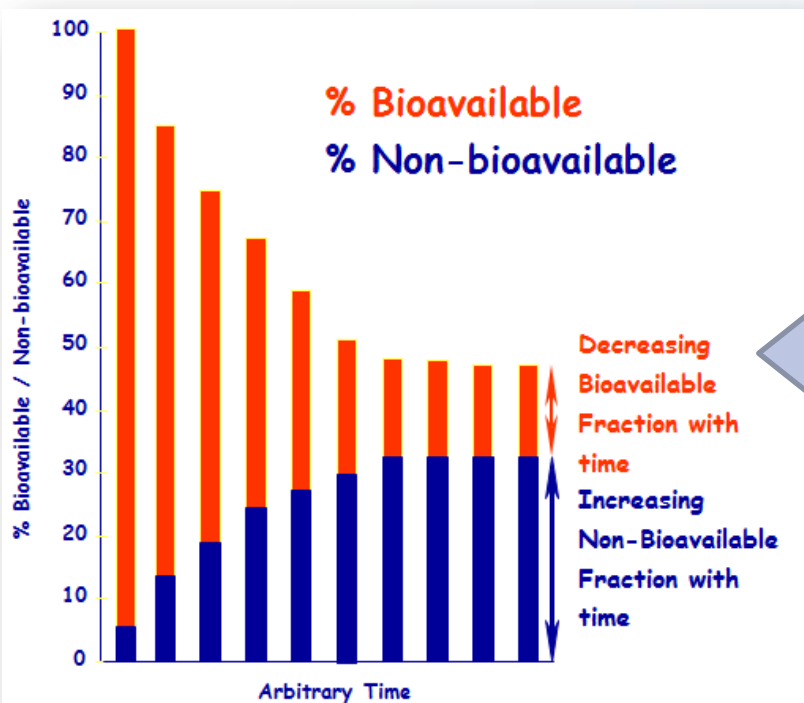
- je potřeba zejména při analýze **kauzality** mezi **expozicí** a **účinkem**
- je potřeba pro větší **mechanistické poznání** tohoto vztahu
- je potřeba pro možné **extrapolace** účinků mezi vzorky a kontaminanty

Eisenia andrei exponována olovu 2 g/kg (totalní koncentrace)



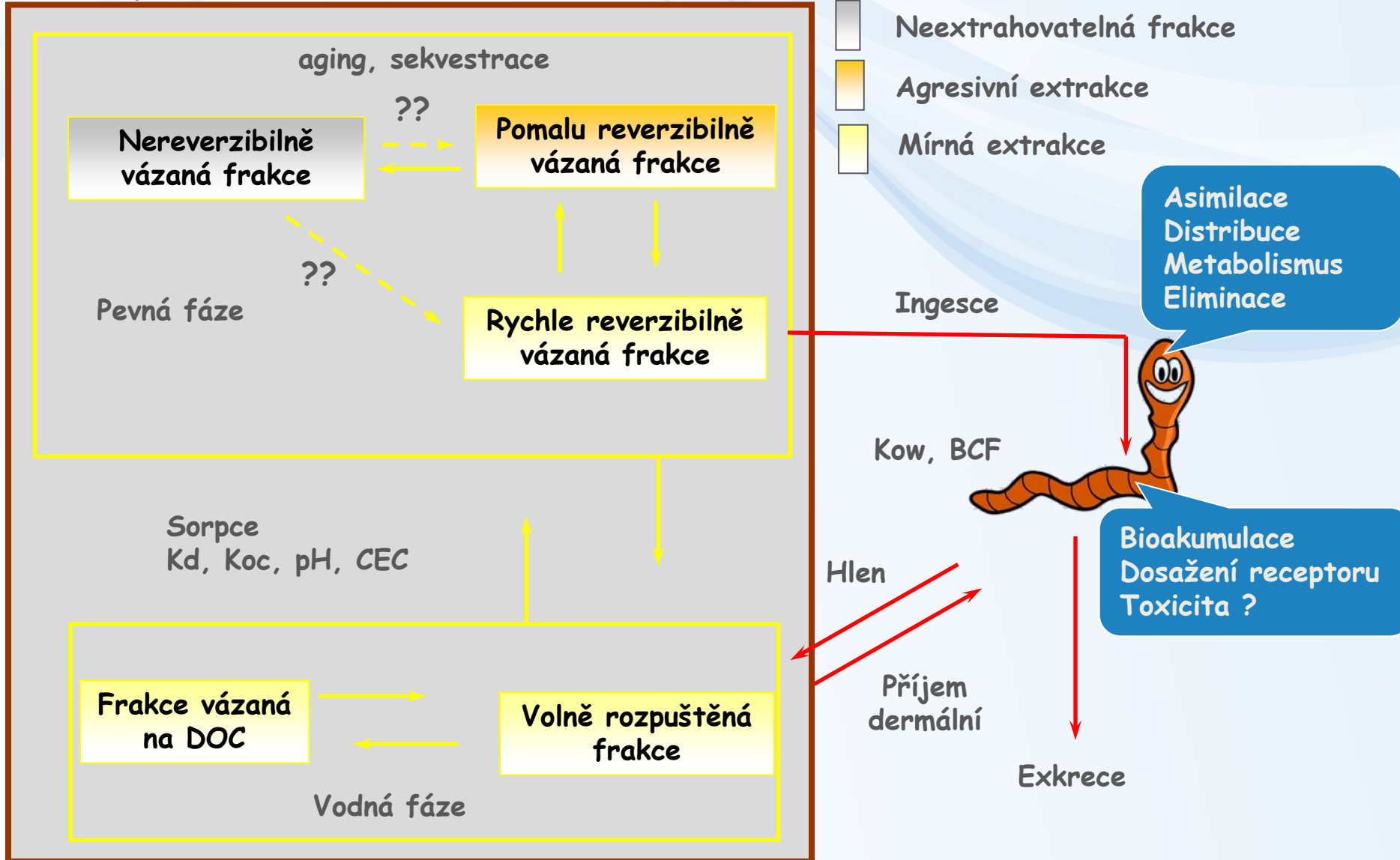
Jak změřit biodostupnost ?

- pravdivě **biodostupnou** koncentraci lze stanovit pouze analýzou organismu po jeho expozici případně analýzou efektů
- snaha vyvinout jednoduché chemické nástroje pro odhad biodostupné koncentrace / frakce kontaminantu
- pouze taková chemická metoda, která koreluje s biologickým příjmem či efekty je validní (**biomimetické metody / proxy for biota**)



Jak změřit biodostupnost ?

Celkový obsah



Jak změřit biodostupnost ?

MAYBE
AFTER

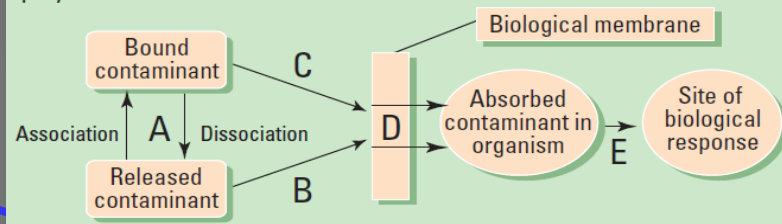
Biodosažitelná
=
Biodostupná
+
Potenciálně biodostupná

NOW

NEVER

Bioavailability processes

In both soil and sediment, processes that determine exposure to contamination include release of a solid-bound contaminant (A) and subsequent transport (B), transport of bound contaminants (C), uptake across a physiological membrane (D), and incorporation into a living system (E). Note that A, B, and C can occur internal to an organism, such as in the lumen of the gut. The NRC report defines A, B, C, and D to be bioavailability processes, but not E, because soil and sediment no longer play a role.

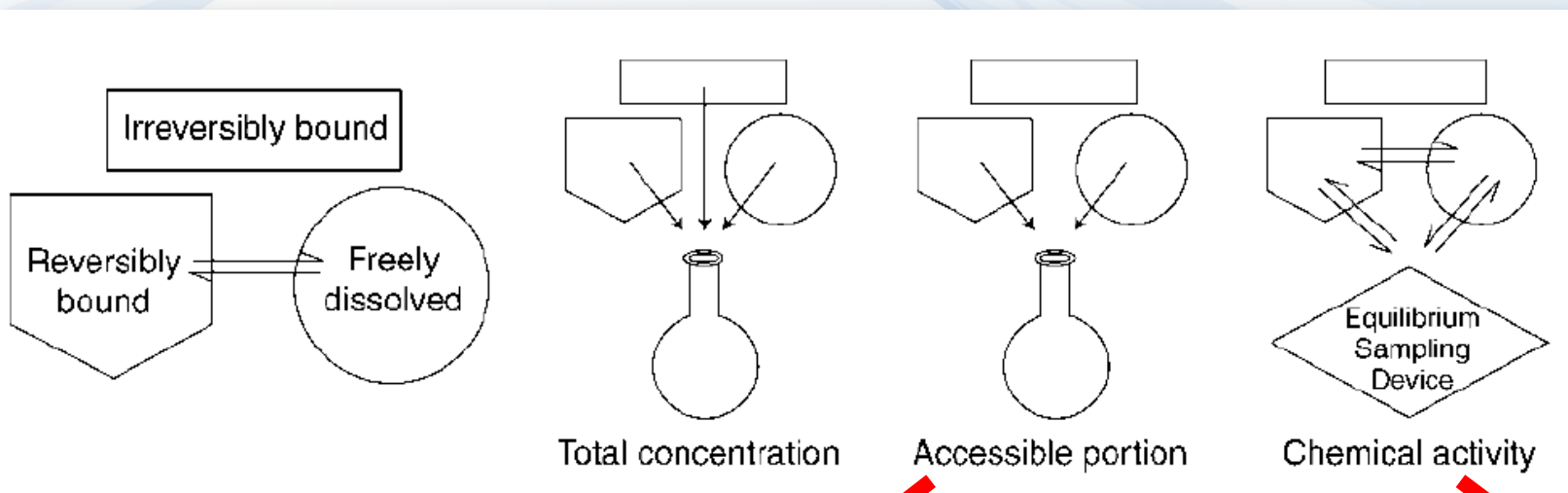


biodostupnost začíná
až přestupem přes
biomembránu



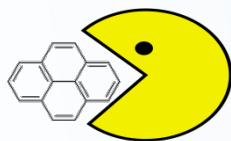
Jak změřit biodostupnost ?

- je to koncentrace/frakce či tendence/potenciál ?



Reichenberg and Mayer (2006) Environ Toxicol Chem 25, 1239

Kolik se může uvolnit PRO ..



**princip bude odstranění /
extrakce dostupné frakce**

Jaká je tendence pro vstup DO ...



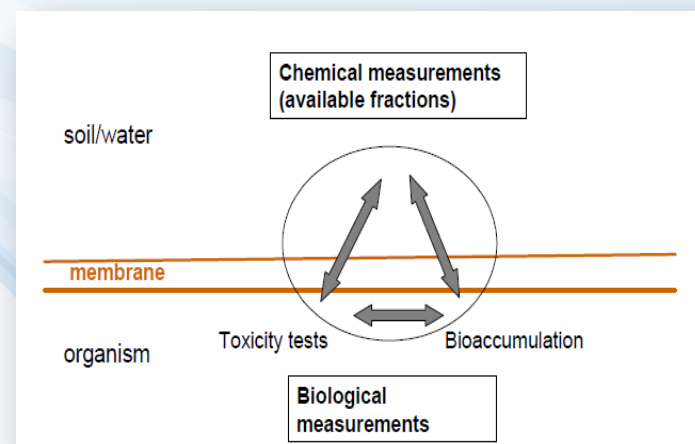
**princip bude rovnovážné
vzorkování (pasivní vzorkovače)**



Jak změřit biodostupnost ?

Řešení:

- nemůže existovat jedna univerzální metoda
- různé organismy, látky, situace:
 - toxicita pro organismy žijící v médiu ☹️
 - biodegradace kontaminantu 😊
 - přestup kontaminantu do potravních řetězců ☹️
- nutné se ptát: **biodostupnost PRO** jakou látku ?
 - jaký organismus ?
 - jakou situaci ?
 - jaký cíl ochrany ?
 - ... ?
- specifické okolnosti definovat a pro danou situaci hledat vhodnou metodu



Metody hodnocení biodostupnosti

půda / sediment	hydrofóbní polutanty	polární polutanty	kovy
koncentrace v pórové vodě		✓	✓
extrakce vodnými roztoky H ₂ O, CaCl ₂ , NH ₄ NO ₃		✓	✓
vzorkování volných kovů diffusive gradient in thin film (DGT), Donnan membrane technique (DMT)			✓
slabé kyseliny či komplexující činidla CH ₃ COOH, EDTA			✓
roztok v kombinaci se sorbenty Tenax, XAD či hydroxypropyl-β-cyclodextrin (HPCD)	✓	✓	
slabá organická rozpouštědla butanol, metanol, etanol, směsi s vodou	✓	✓	
superkritická fluidní extrakce (SFE) nastavitelná síla / polarita extrakce	✓	✓	
biomimetické sorbenty / pasivní vzorkovače polyoxymethylene (POM), polydimethylsiloxane (PDMS), solid phase microextraction (SPME), semi-permeable membrane devices (SPMD)	✓	✓	

voda / vzduch	hydrofóbní polutanty	polární polutanty	kovy
biomimetické sorbenty / pasivní vzorkovače POM, PDMS, SPME, SPMD, Polar organic compounds integrative sampler (POCIS), Chemcatcher,	✓	✓	
vzorkování volných iontů kovů diffusive gradient in thin film (DGT), Donnan membrane technique (DMT)			✓

Metody hodnocení biodostupnosti – půda / sediment

- **ISO 17402 (2006)**
Guidance for the selection and application of methods for the assessment of bioavailability in soil and soil materials
- výběr metod dle mnoha kritérií – nejen prostá korelace s biologií (empirické metody), ale důraz na **mechanistický / fyziologický princip** = logicky souvisí s biologickými efekty / příjmem
- **validace na více látkách, více půdách/sedimentech**

Mechanism	Simulates	Pathway	Method	Calibrated		Recommended	Limitations
				Contaminant	Target		
Neutral extract	Pore water concentration	Direct contact with water	Neutral water extract (NaNO ₃ ; KNO ₃ /NH ₄ NO ₃ ; CaCl ₂)	Cd/Zn/Ni	Soil organisms, plant uptake	+	NH ₄ NO ₃ may reduce pH in low buffered soils. CaCl ₂ may reduce DOC concentrations Poorly soluble compounds Depends on
Separation by diffusion	Free metal concentration	Direct contact with water	Extraction of pore water	Cd/Zn/Ni	Soil organisms, plant uptake	+	Pore water not available in dry soil Equilibration time if water is added
		Transport	Leaching test	Inorganic/organic	Ground-water	+	Poorly soluble compounds
		Uptake	DMT, DGT	inorganic	Soil organisms, plant uptake	+	Specialized equipment
Acid extraction	Potential soluble in water	Uptake	Acid extract (HNO ₃)	Cd/Zn/Ni	Plant uptake after including soil characteristics	+	
		Transport	Leaching test	Inorganic	Ground-water	+	
		Uptake	Acid extract (pH of stomach or lower)	Pb	Screening, human ingestion	+	Gives a maximum of bioavailability, because pH in the intestine system is higher
Complexing agent	Potential soluble in water, competitive	Uptake, Transport	EDTA extract	Heavy metals	Plant uptake, groundwater		
Simulation of digestion	Oral uptake	Human uptake	Stomach and intestine system	Pb/Cd/Zn/Ni/Hg/PCB/PAH method comparison	Human	+	
Adsorption to competitive adsorbant	Amount in equilibrium with pore water	Contact with pore water	Adsorption to solid phase (TENAX, XAD, cyclodextrines)	PAH	Degrading organisms	+	
			Adsorption to solid phase (SPME, TENAX)	PAH/PCB/OCP	Uptake invertebrates	+	
Increasing solubility	Amount in equilibrium with pore water	Contact with pore water	Mild (water + organic) solvent	PAHs	Degrading organisms		
Partial oxidation of organic matter	Amount of weakly bounded organic contaminants	Easy attainable by micro-organisms	Oxidation with persulphate	PAHs	Degrading organisms	+	



Metody hodnocení biodostupnosti – půda / sediment

organické polutanty:

A. stanovení biodosažitelné frakce pomocí extrakce rozpouštědly či pomocí vodných roztoků s přidanými sorbenty

Method	Working principle	Strengths	Weaknesses
Mild solvent extraction (Kelsey et al., 1997; Liste and Alexander, 2002)	<ul style="list-style-type: none">Analyze HOC in mild solvent after extractionPartial extraction measuring rapid desorption fraction	<ul style="list-style-type: none">Easy operation	<ul style="list-style-type: none">Results vary with solvent, matrix and organismsNot applicable for <i>in situ</i> measurement
HPCD extraction (Cuypers et al., 2002; Reid et al., 2000)	<ul style="list-style-type: none">Analyze HOC in HPCD after extractionPartial extraction measuring rapid desorption fraction	<ul style="list-style-type: none">Fast and easy operation	<ul style="list-style-type: none">Species-dependent performance and limited extraction capacityNot applicable for <i>in situ</i> measurement
Sequential Tenax extraction (Cornelissen et al., 1997; Xu et al., 2008)	<ul style="list-style-type: none">Consecutive desorption with Tenax as HOC trapUse regression model to estimate various desorption fractionsUse F_{rapid} to indicate bioaccessibility	<ul style="list-style-type: none">Tenax reused and economicalUnderstanding of desorption kinetics	<ul style="list-style-type: none">Time consuming and laboriousNot applicable for <i>in situ</i> measurement
6-h Tenax extraction (Cornelissen et al., 2001)	<ul style="list-style-type: none">Single-step desorption with Tenax as HOC trapUse F_{6h} to approximate bioaccessibility	<ul style="list-style-type: none">Fast and easy operation	<ul style="list-style-type: none">F_{6h} may not equal to F_{rapid}Not applicable for <i>in situ</i> measurement

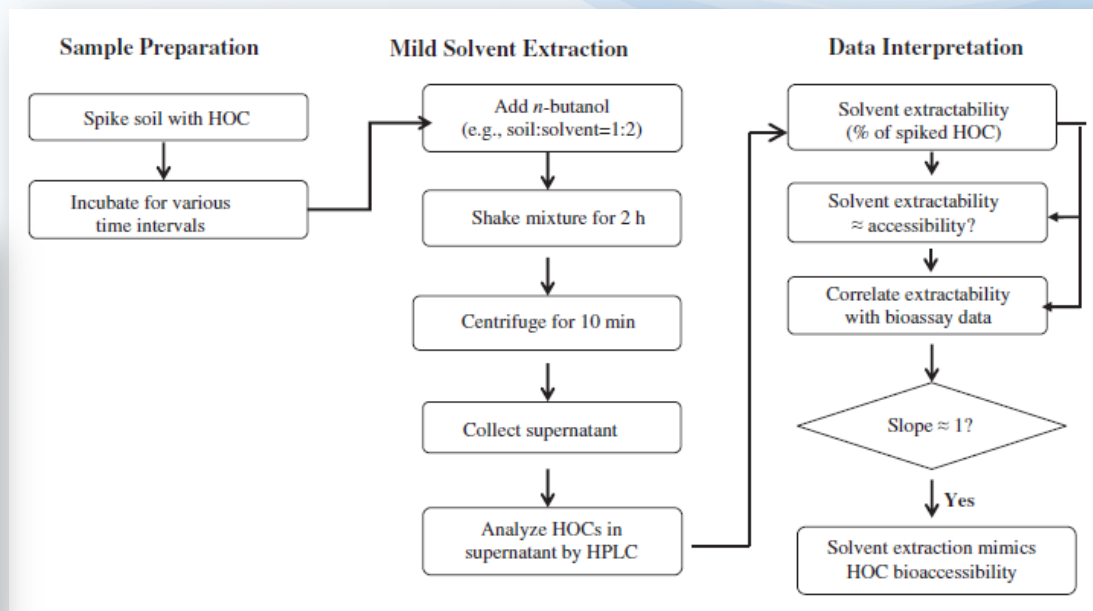
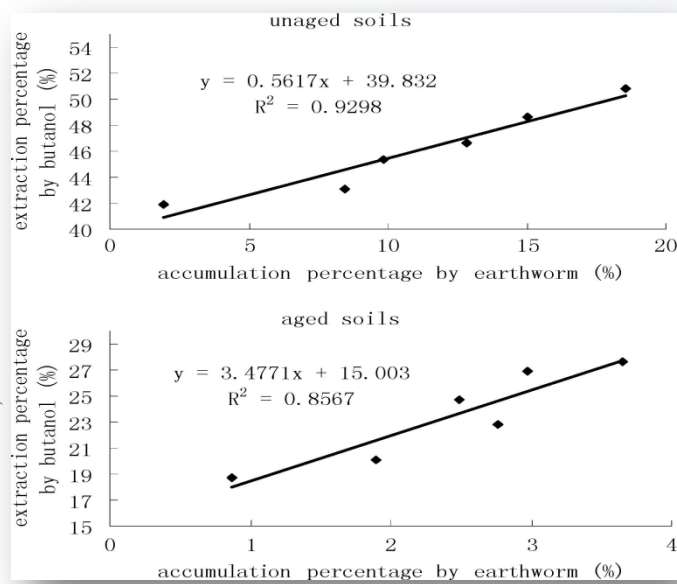
Cui et al. (2013) Environmental Pollution 172: 223-234



Metody hodnocení biodostupnosti – půda / sediment

slabá rozpouštědla

- polárnější organická rozpouštědla (BuOH, MeOH, EtOH) / směsi rozpouštědel a vody / případně sekvenční extrakce – zvyšující se síla extrakce
- nízká mechanistická / fyziologická obhajitelnost
- nutnost korelace s biologickými endpointy je klíčová

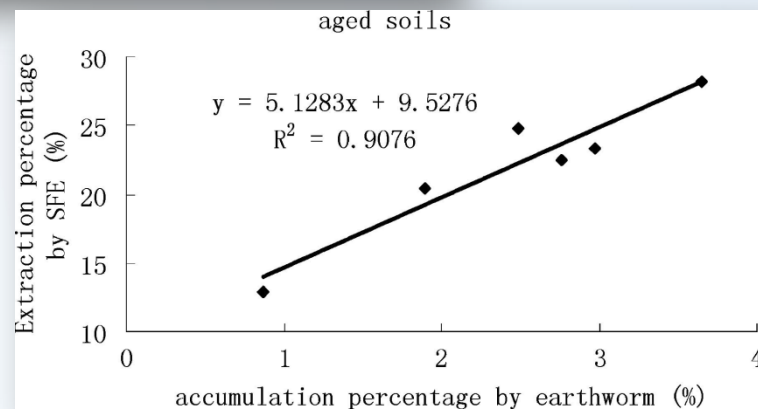
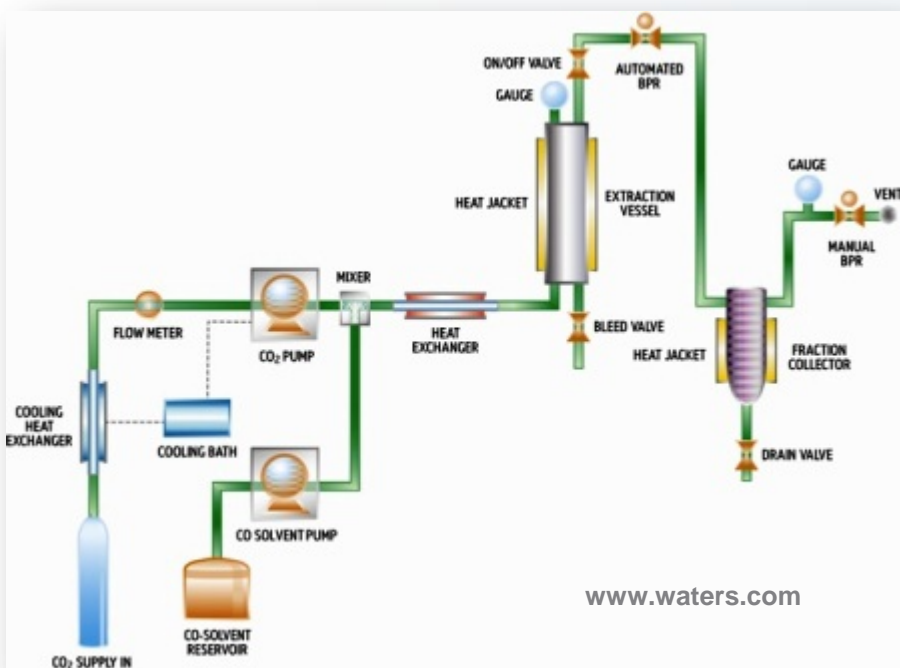


Cui et al. (2013) Environmental Pollution 172: 223-234

Metody hodnocení biodostupnosti – půda / sediment

superkritická fluidní extrakce (SFE)

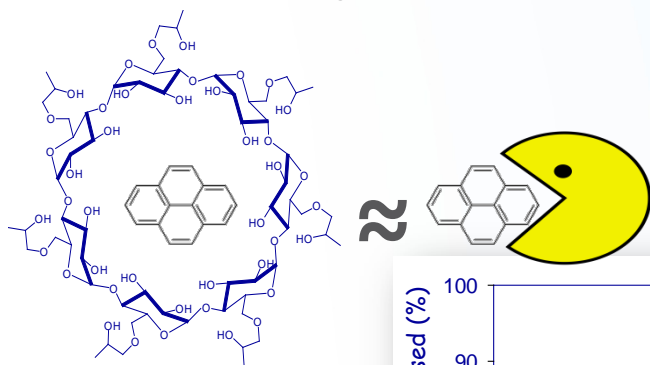
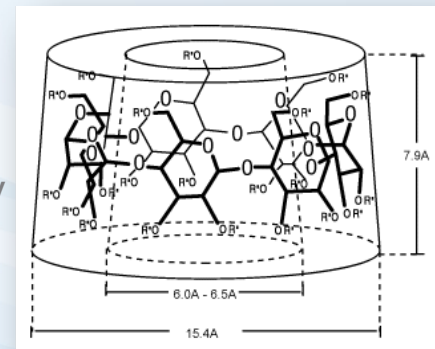
- CO₂ v superkritickém stavu
- možnost měnit tlak a teplotu a tím sílu / polaritu extrakce, např.:
 - **mild extraction:** 12 MPa + extrakční teplota 50°C + teplota restriktoru 120°C + extrakční čas 30 min
 - **harsh extraction:** 40 MPa + extrakční teplota 150°C + teplota restriktoru 120°C + extrakční čas 45 min
- nutnost korelace s biologickými endpointy je klíčová



Metody hodnocení biodostupnosti – půda / sediment

hydroxypropyl- β -cyclodextrin (HPCD)

- oligosacharidový cyklus s hydrofóbní kavitou a hydrofilním exteriérem
- obrovská kapacita roztoku HPCD připomíná degradaci (úbytek) látky díky biodegradaci – měří vlastně **mass transfer**, který je limitujícím faktorem biodegradace
- perfektní korelace s **biodegradací** pro PAHs, PCBs, OCPs, alkany napříč různými půdami a látkami !! (pro jiné organismy nevhodný !!)



Sample Preparation

Soil or sediment with HOC

HPCD Extraction

Add 25 ml HPCD solution (50 mM) to 1.25 g soil

Shake mixture for 20 h

Centrifuge for 10 min

Collect supernatant

Analyze HOCs in supernatant by HPLC

Data Interpretation

HPCD extractability (% of spiked HOC)

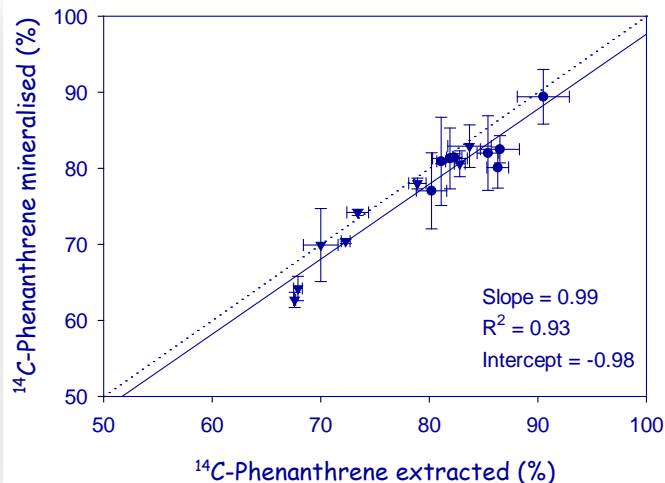
HPCD extractability \approx accessibility?

Correlate extractability with bioassay data

Slope \approx 1

Yes

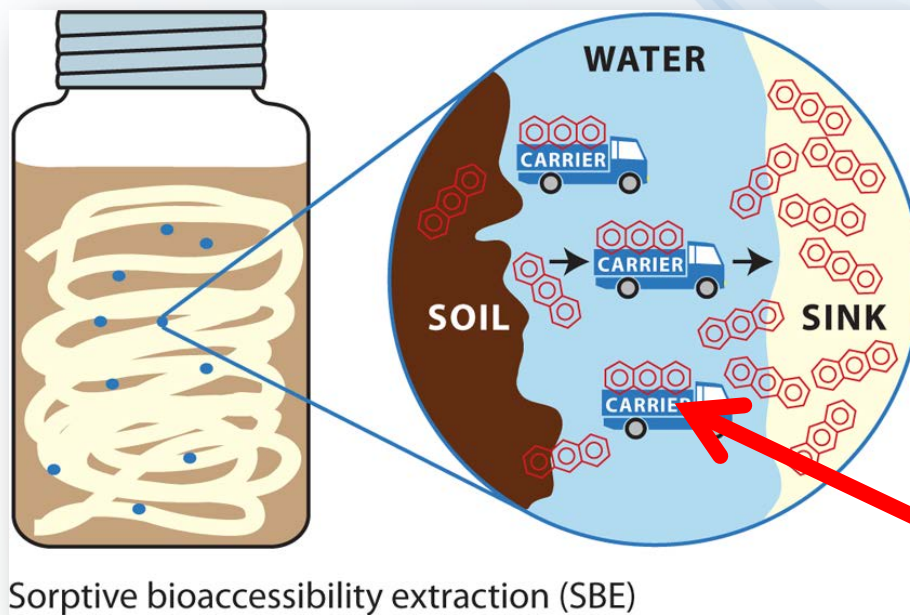
HPCD extraction mimics HOC bioaccessibility



Metody hodnocení biodostupnosti – půda / sediment

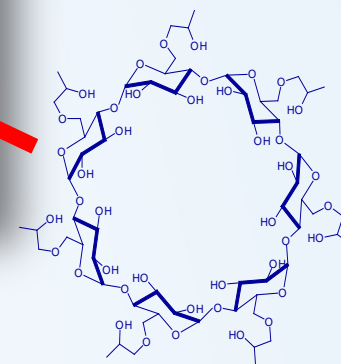
hydroxypropyl- β -cyclodextrin (HPCD)

- omezená kapacita HPCD vyřešená pomocí PDMS „infinite sink“



Sorptive bioaccessibility extraction (SBE)

Gouliarmou and Mayer (2012) Environ Sci Technol 46, 10682–10689



Metody hodnocení biodostupnosti – půda / sediment

Tenax

- vysoce porézní polymer (2,6-diphenyl-p-phenyleneoxide), lehčí než voda - lze odfiltrovat
- většinou jako sekvenční extrakce v několika opakovaných extrakcích stejného vzorku – desorpční kinetika s rychlou (F_{rapid}), pomalou a velmi pomalou desorpcí
- dlouhá metoda – existuje 6h varianta

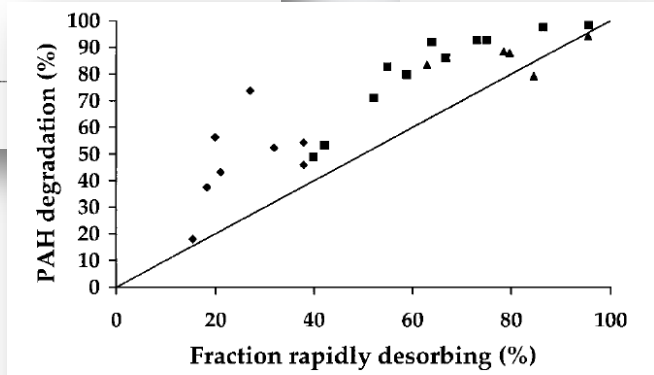
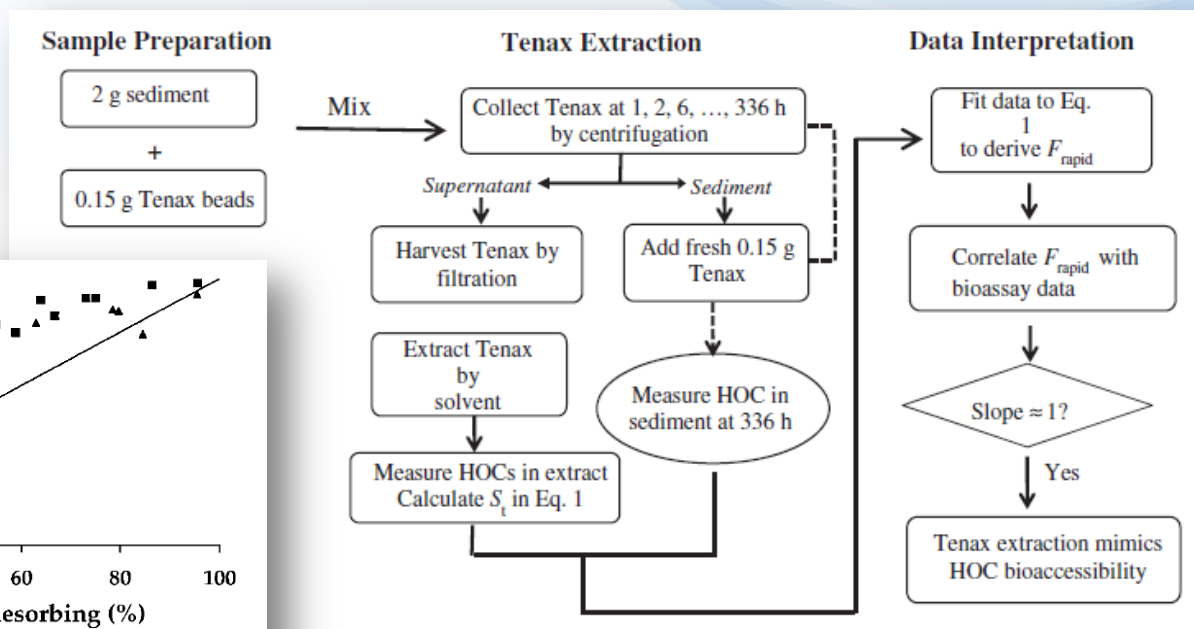
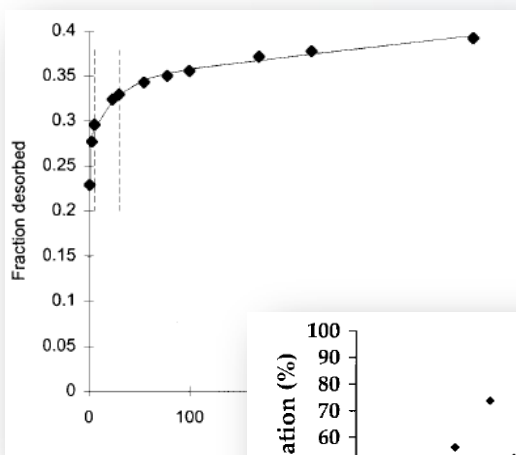
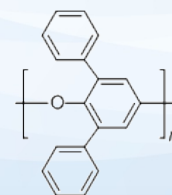


Fig. 3. Estimation of polycyclic aromatic hydrocarbon (PAH) bioavailability using Tenax. Amount degraded (%) versus rapidly desorbed (%). Degradation in a bioreactor (■ and ▲) or by landfarming (◆) (Cornelissen et al., 1998a, b).

Cui et al. (2013) Environmental Pollution 172: 223-234

Cornelissen et al. (2001) Environmental Toxicology and Chemistry 20: 706-711

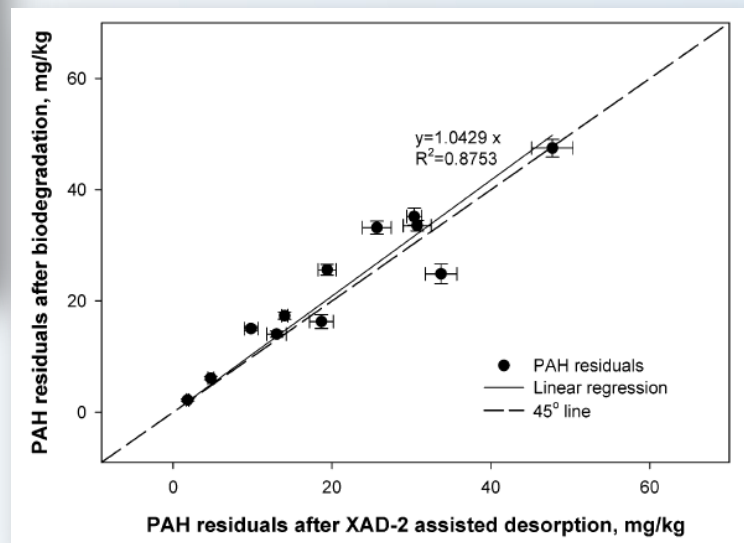
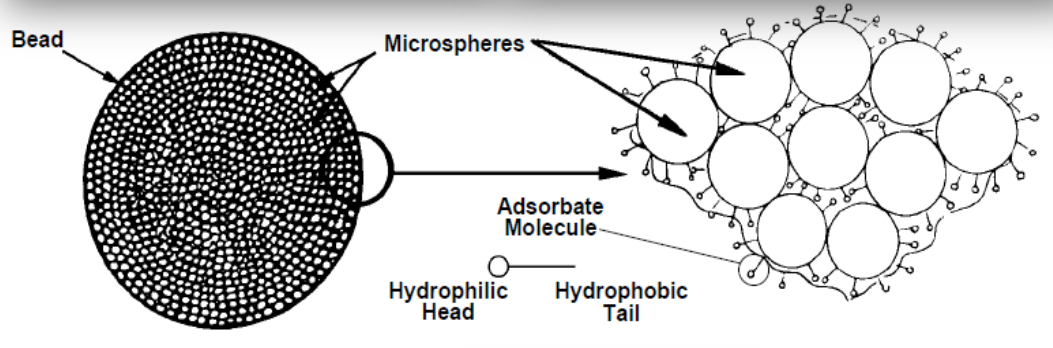
Metody hodnocení biodostupnosti – půda / sediment

XAD

- XAD-2, XAD-4 (amberlite) kopolymer polystyrenu
- výhoda – stabilita do 200°C – lze použít termální desorpci
- postup podobný jako u Tenax

SUPELCO

Porosity: 0.41 mL pore/mL bead
Surface Area (Min.): 300 m²/g
Mean Pore Diameter: 90 Å



Metody hodnocení biodostupnosti – půda / sediment

organické polutanty

B. stanovení volně rozpuštěné koncentrace s využitím sorbentů – pasivních vzorkovačů

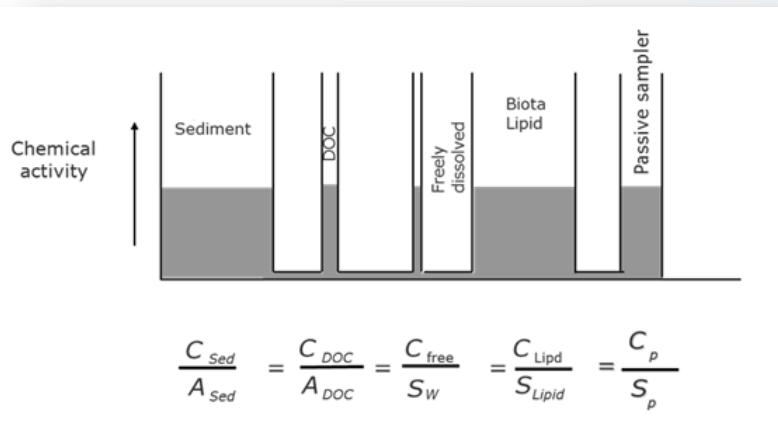
(vlastně velice podobné postupy jako pasivní vzorkování vody)

Method	Working principle	Strengths	Weaknesses
SPMD (Semi-permeable membrane device) (Huckins et al., 1990; Zimmerman et al., 2004)	<ul style="list-style-type: none">• Expose sampler in sample matrix• Analysis of HOC in sampler after solvent extraction• Derive C_{free} and use C_{free} to indicate bioavailability	<ul style="list-style-type: none">• Good sensitivity due to large sampler volume• Commercially available• Applicable for <i>in situ</i> measurement	<ul style="list-style-type: none">• Extensive post-sample processing• Require large sample size• Very long equilibration times• Not compatible with bench-scale bioassays
PED (Polyethylene device) (Cho et al., 2009)	<ul style="list-style-type: none">• Expose sampler in sample matrix• Analysis of HOC in sampler after solvent extraction• Derive C_{free} and use C_{free} to indicate bioavailability	<ul style="list-style-type: none">• Good sensitivity due to large sampler volume• Inexpensive• Applicable for <i>in situ</i> measurement	<ul style="list-style-type: none">• Require large sample size• Very long equilibration times• Not compatible with bench-scale bioassays
Injector-type SPME (Arthur and Pawliszyn, 1990; Xu et al., 2007)	<ul style="list-style-type: none">• Expose sampler in sample matrix• Analyze HOC on fiber by direct injection• Derive C_{free} via external calibration and use C_{free} to indicate bioavailability	<ul style="list-style-type: none">• Good sensitivity due to analysis of whole fiber• Less time consuming and solvent-free• Automation possible• Applicable for <i>in situ</i> measurement	<ul style="list-style-type: none">• Non-equilibrium sampling• Matrix effect• Not compatible with bench-scale bioassays
Disposable SPME (Mayer et al., 2000; Hunter et al., 2008)	<ul style="list-style-type: none">• Expose fiber in sample matrix• Analyze HOC at equilibrium• Derive C_{free} via K_{SPME} and use C_{free} to indicate bioavailability	<ul style="list-style-type: none">• Inexpensive and easy operation• Compatible with bench-scale bioassays and co-exposure• Applicable for <i>in situ</i> measurements	<ul style="list-style-type: none">• Sensitivity may be low• Long equilibrium times for HOCs with large K_{ow}

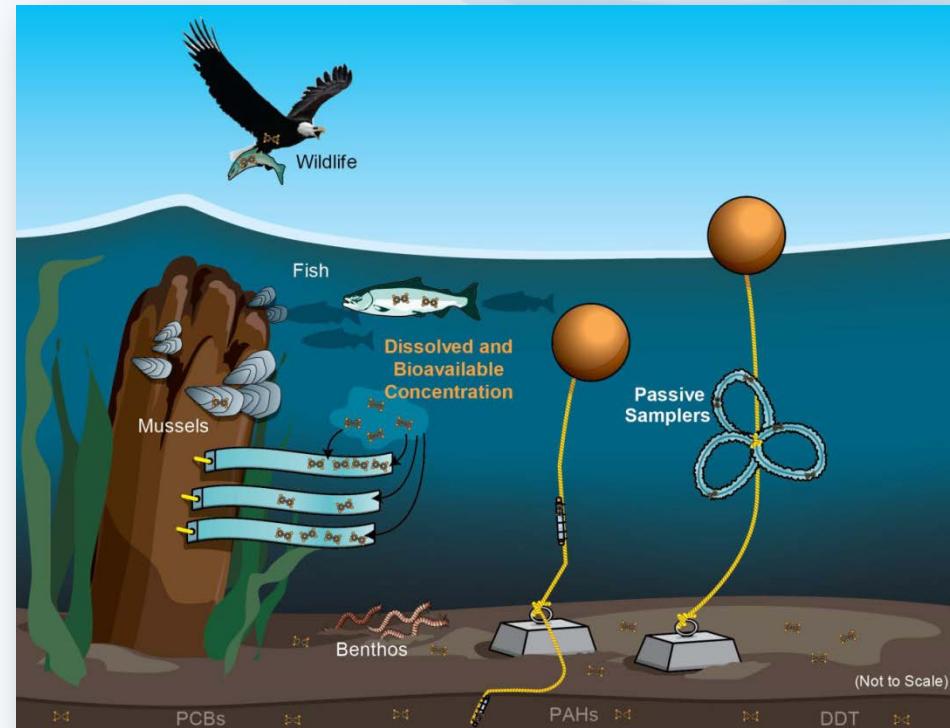


Passive sampling - teorie

- několik zásadních výhod oproti klasickému vzorkování:
 - vzorkovač – sorbent je vystaven v mediu většinou delší dobu podobně jako organismus – time weighted average (TWA) concentration
 - je snaha, aby rozdělovací koeficienty mezi médiem a vzorkovačem připomínaly přestup do bioty – „biomimetic“, „proxy to biota“
 - vzorkuje relevantní koncentraci – „free dissolved concentration“ (C_{free})
- <http://youtu.be/xZnQt0IKIRE> od 1:38
- <http://youtu.be/4zIQQbnxxR0>



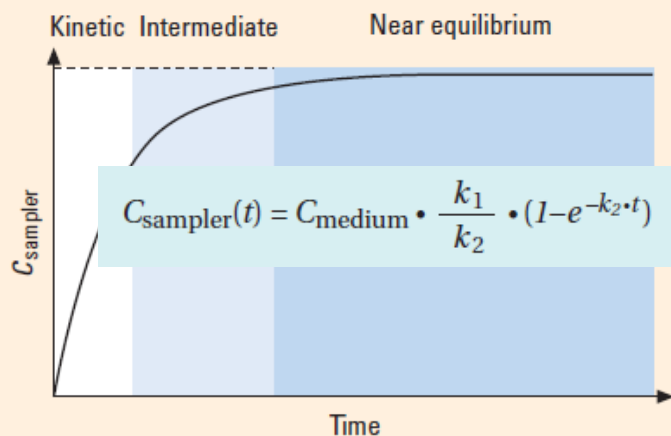
US EPA (2012) Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites



Passive sampling - teorie

Generalized uptake profile for a passive sampling device

The passive sampler operates in three regimes: kinetic (white), intermediate (light blue), and near equilibrium (blue). A first-order one-compartment model (Equation 1) is often used to fit experimental measurements.



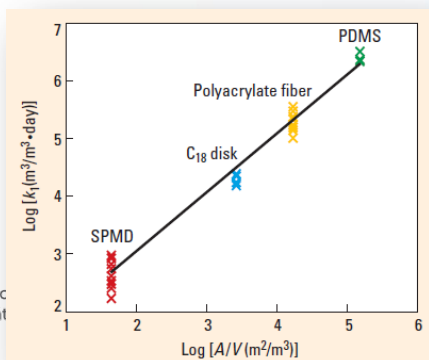
Mayer et al (2003) Environ Sci Technol 37: 184A–191A

- kinetika 1. řádu, jednosložkový model – vstupní proměnné k_1 a k_2 (rychlost příjmu a výdeje)
- v monitoringu ŽP je upřednostněno **nerovnovážné vzorkování** – lineární příjem látky vzorkovačem – pro dosažení TWA, zatímco při stanovení biodostupnosti je častější **rovnovážné vzorkování**
- v rovnováze nejsou $k_{1,2}$ potřeba a C_{free} a fugacita mohou být spočítány ze vztahu

$$C_{\text{free}} = C_{\text{sampler}} / K_s$$

kde K_s je rozdělovací koeficient vzorkovač-vzorek

- čím vyšší je poměr povrch / objem, tím rychleji je dosaženo rovnováhy



Passive sampling - teorie

- **základní předpoklad** = volně rozpuštěná koncentrace (C_{free}) je hlavní determinant příjmu látky biotou a následných efektů a rizik
- platí zejména u malých organismů přijímajících látky pasivní difúzí
- **jakmile hraje významnou roli potrava, nemusí být již tento přístup validní !!**
- vzorkování by nemělo ovlivňovat vzorkovaný systém:
tzv. **negligible depletion**
- depleci lze využít pro stanovení dosažitelné frakce

$$\frac{V_{\text{sampler}} \cdot K_{\text{sampler, medium}}}{V_{\text{medium}}} < 0.05$$

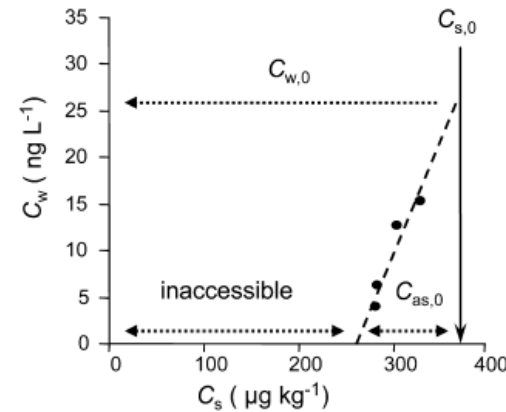
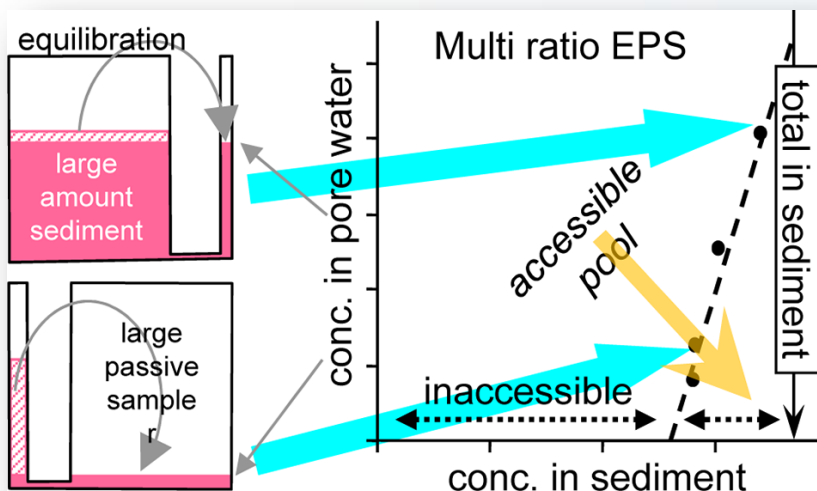
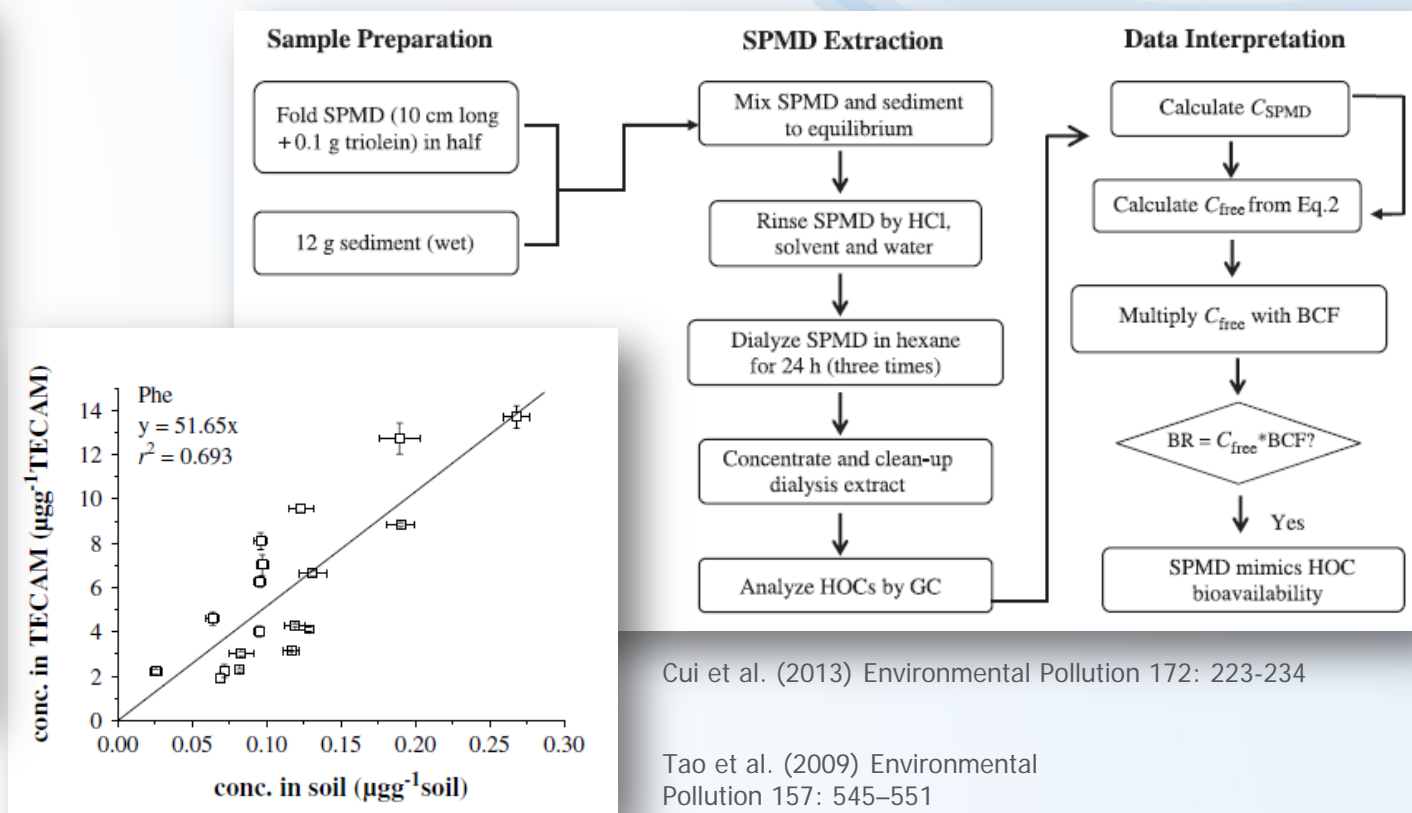
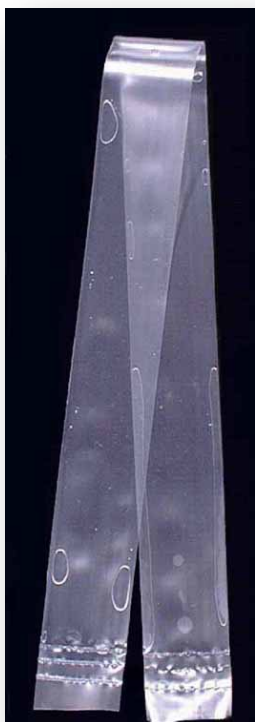
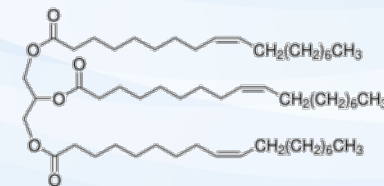


Figure 3. Fluoranthene concentrations in the water (C_w) versus the residual concentration in the sediment (C_s) as calculated by eq 5. The arrow on the right indicates the original concentration in the sediment ($C_{s,0}$).

Metody hodnocení biodostupnosti – půda / sediment / voda

SPMD – semipermeable – membrane devices

- membrána („obal“) - LDPE (low-density polyethylene) či acetát celulózy (TECAM)
- náplň dle sledovaných látek - pro HOCs nejčastěji lipid triolein
- rozpuštěné molekuly se difúzí dostávají do pórů LDPE (max 10 Å) a kumulují se v trioleinu



Cui et al. (2013) Environmental Pollution 172: 223-234

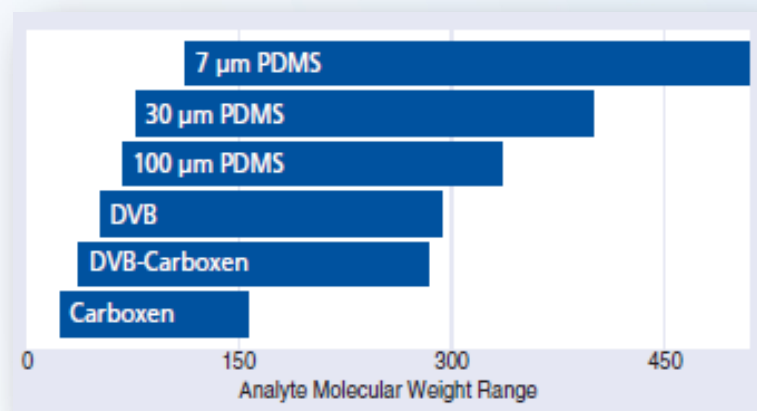
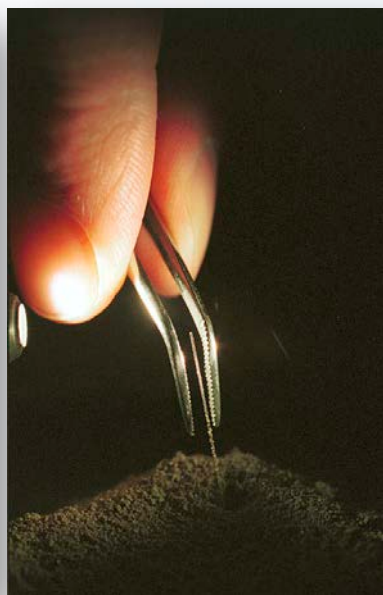
Tao et al. (2009) Environmental Pollution 157: 545-551



Metody hodnocení biodostupnosti – půda / sediment / voda

SPME

- tzv. **matrix SPME** nebo **disposable SPME** - odvozeno od injekční SPME
- vlákno s tenkou vrstvou PDMS či jiných sorbentů (divinylbenzen - DVB, polyakrylát – PA, carboxen. carbowax ...)
- velká praktičnost, rychlost, prostorová nenáročnost
- pro použití je nutné předem determinovat K_{PDMS}



www.sigma-aldrich.com



Metody hodnocení biodostupnosti – půda / sediment / voda

SPME

- použití pro vodu

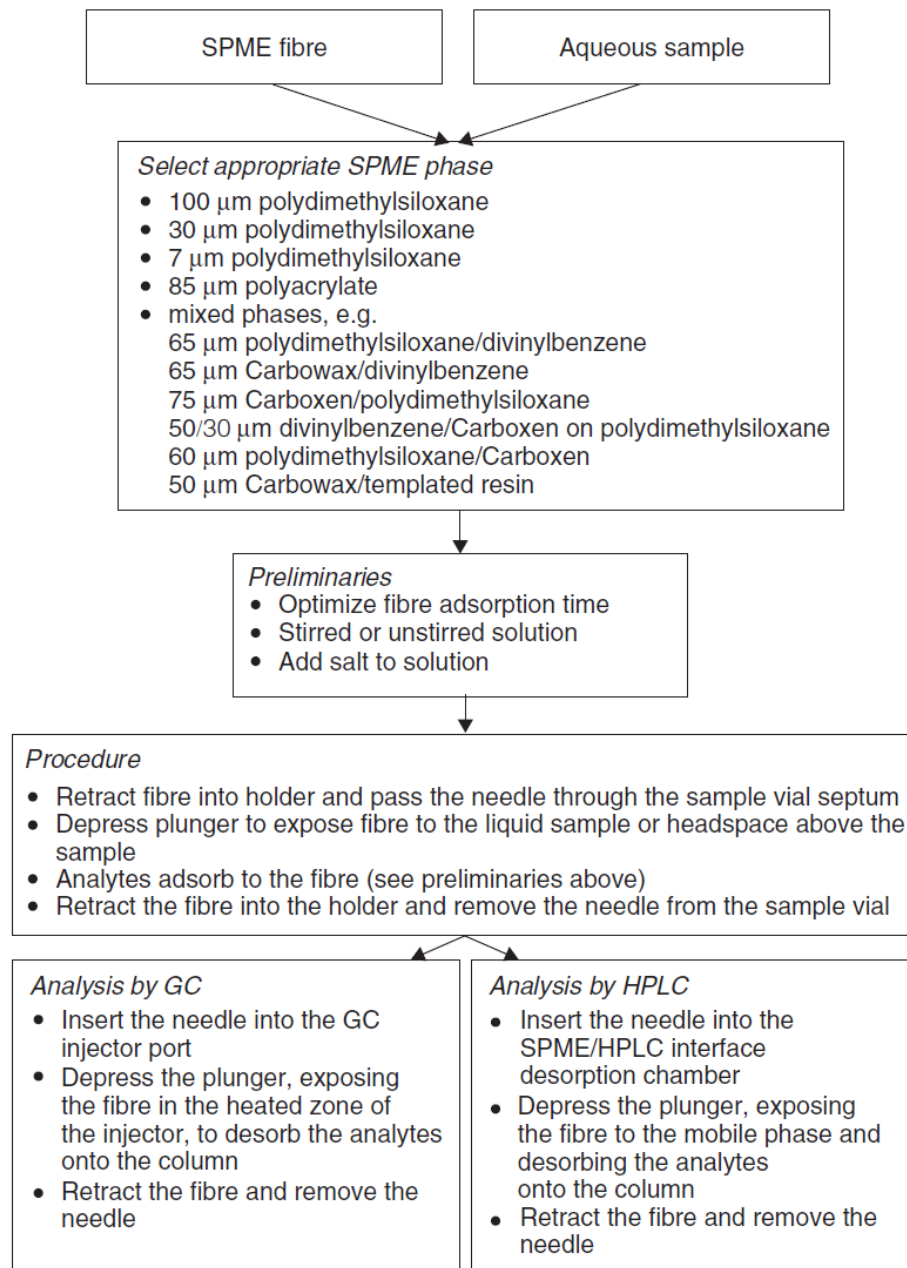


Figure 3.10 Typical procedure used for the solid-phase microextraction of liquids. From Dean, J. R., *Methods for Environmental Trace Analysis*, AnTS Series. Copyright 2003. © John Wiley & Sons, Limited. Reproduced with permission.

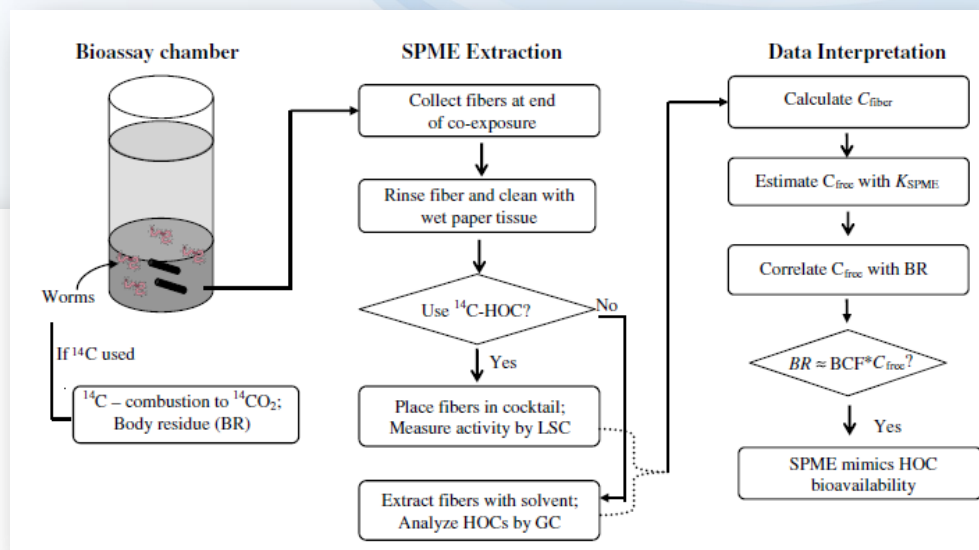
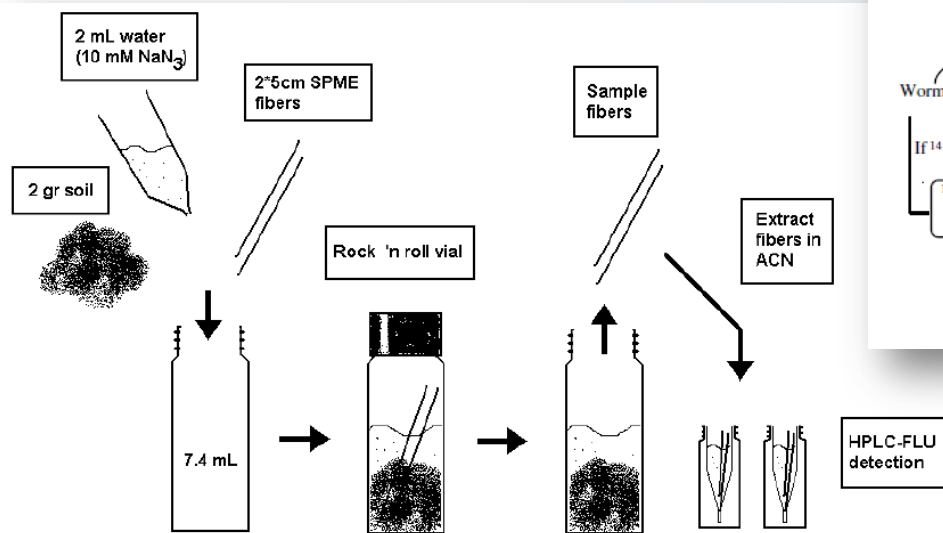


Metody hodnocení biodostupnosti – půda / sediment / voda

SPME

- použití pro půdy / sedimenty
- varianta se suspenzí – třepání do dosažení rovnováhy (nutno stanovit předem dostatečný čas – řešit kinetiku a poměr vlákno / vzorek – **nedepletivní !!**)
- varianta vláken přímo exponovaných ve vzorku

Ter Laak (2005) Sorption to soil of hydrophobic and ionic organic compounds: measurement and modeling



Cui et al. (2013) Environmental Pollution 172: 223-234

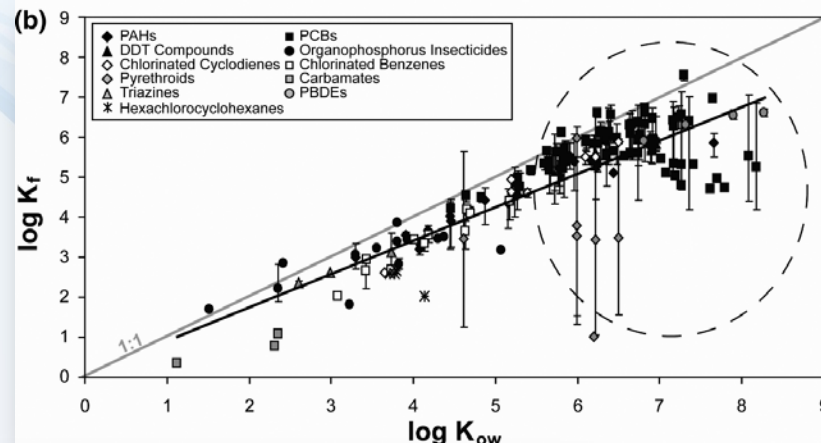
Figure 1: A schematic picture of negligible depletion passive samplers to measure freely dissolved aqueous concentrations of contaminants in soil.

Metody hodnocení biodostupnosti – půda / sediment / voda

SPME

- velice dobré korelace s příjmem biotou
- mechanistické / fyziologické opodstatnění
- aplikovatelnost pro fugacitní modelování

DiFilippo (2010) Environ Sci Technol 44, 6917–6925



van der Wal (2004) Environ Sci Technol 38: 4842-4848

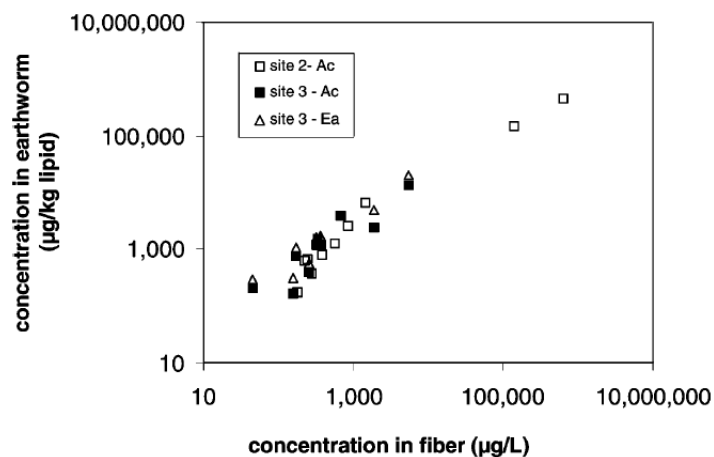


FIGURE 3. Relationship between steady-state concentrations of different contaminants (HCB, telodrin, dieldrin, and PCBs) in earthworms (*Aporrectodea caliginosa* (Ac) and *Eisenia andrei* (Ea); see Table 4) and in 30- μ m PDMS fibers (see Table 3) exposed to site 2 and site 3 soil.

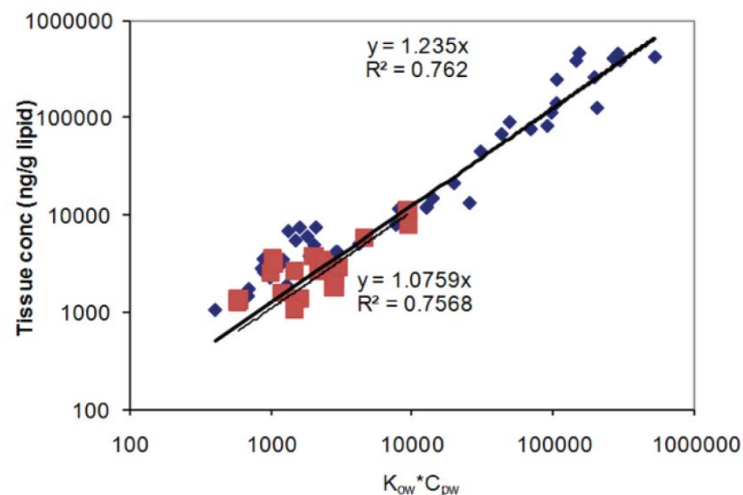
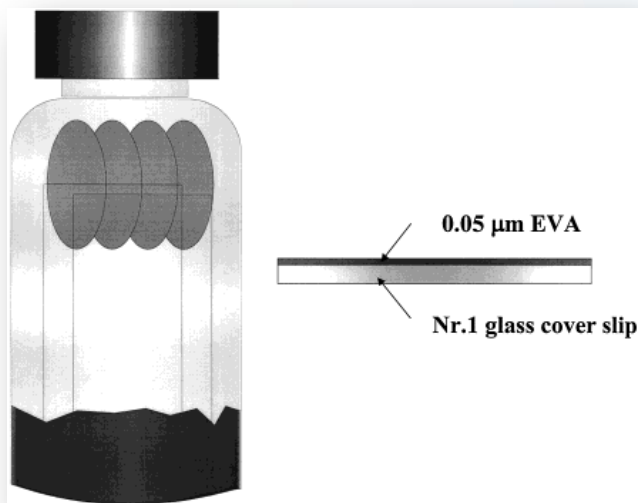
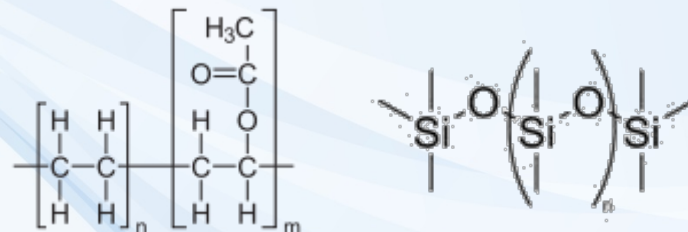


Figure 1. Comparison of predicted tissue concentrations in oligochaetes derived using passive samplers with measured data. Symbols denote river (squares) and diluted river (diamonds) sediments. K_{ow} = octanol-water partition coefficient; $C_{pw} = C_{free}$. (Source: Lu X, Skwarski A, Drake B, Reible DD. 2011. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. Environ Toxicol Chem. 30(5):1109–1116. Reprinted with permission.)

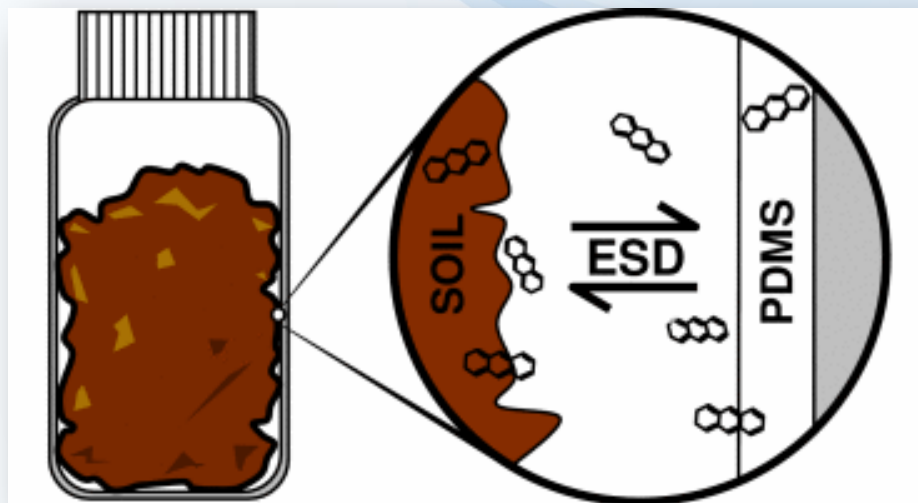
Metody hodnocení biodostupnosti – půda / sediment / voda

„coated vials“

- vialky s tenkou (μm) vrstvou sorbentu:
 - ethylene vinyl acetate (EVA)
 - polydimethylsiloxane (PDMS)
- čím tenčí (vyšší poměr povrch / objem), tím rychlejší dosažení rovnováhy



Wilcockson and Gobas (2001) Environ Sci Technol 35: 1425-1431

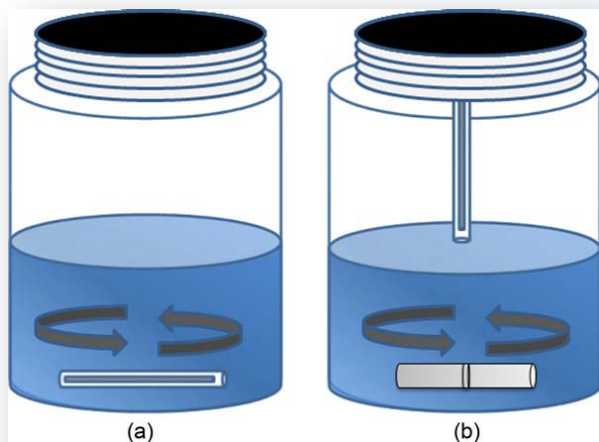


Reichenberg et al. (2008) Chemistry Central Journal 2

Metody hodnocení biodostupnosti – půda / sediment / voda

stir bar sorptive extraction (SBSE)

- míchadélko potažené PDMS



Prieto (2010) *Journal of Chromatography A*, 1217: 2642–2666



Metody hodnocení biodostupnosti – půda / sediment / voda

proužky PDMS či POM

- malé proužky silikonové gumy či polyoxymethylenu (POM) přímo v půdní suspensi – exponované do dosažení rovnováhy, extrakce

Environ. Sci. Technol. 2001, 35, 3742–3748

Polyoxymethylene Solid Phase Extraction as a Partitioning Method for Hydrophobic Organic Chemicals in Sediment and Soot

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*Aquatic Ecology and Water Quality Management Group,
Department of Environmental Sciences,
Wageningen University, P.O. Box 8080,
6700 DD Wageningen, The Netherlands*

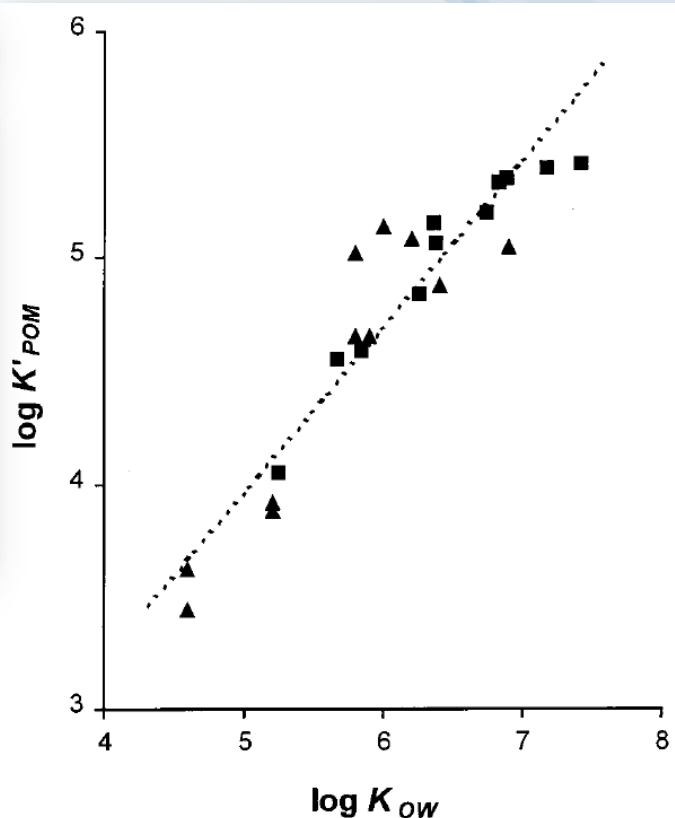
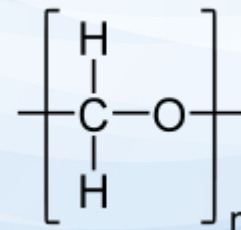


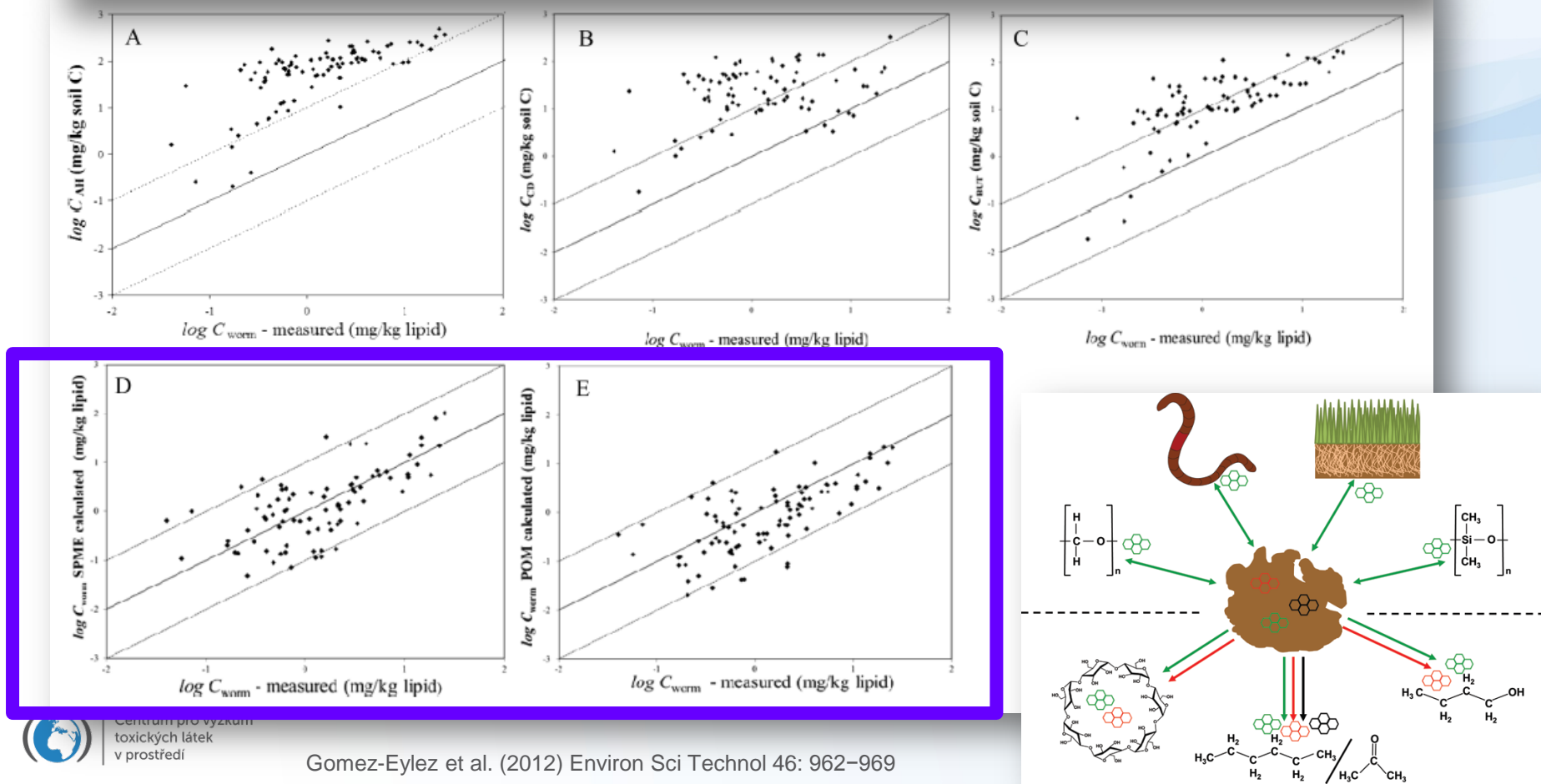
FIGURE 4. Relationship between $\log K'_{POM}$ and $\log K_{OW}$ (both in L/L) for PAHs (triangles) and PCBs (squares).



Metody hodnocení biodostupnosti – půda / sediment / voda

PDMS a POM - pro bezobratlé a rostliny mnohem lepší predikce biodostupnosti než u rozpouštědel a HPCD !!!

Figure 1. Relationships between PAH concentrations measured in *E. fetida* and concentrations in soil measured by (A) acetone/hexane extractions, (B) cyclodextrin extractions, and (C) butanol extractions; and concentrations in earthworms predicted (based on equilibrium partitioning calculations) by (D) solid phase micro extraction, and (E) polyoxymethylene solid phase extraction. The solid black lines represent the 1:1 relationships, whereas the dotted black lines delimit the 1 order of magnitude deviation intervals.



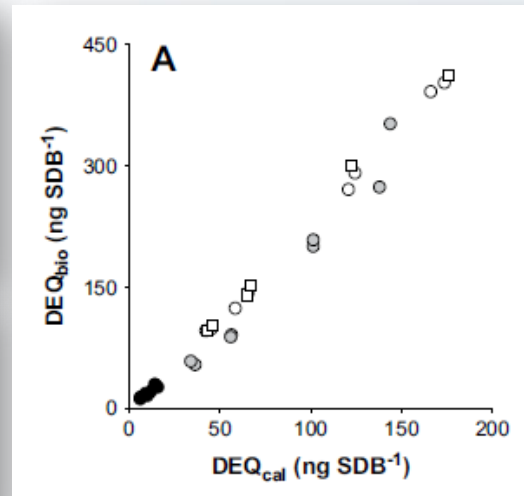
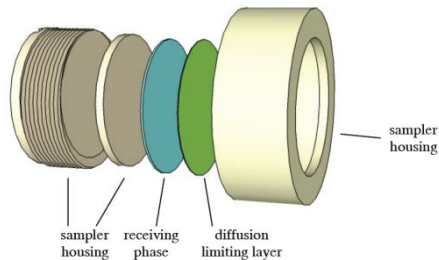
Metody hodnocení biodostupnosti – voda

POCIS

- polar organic compounds integrative sampler

Chemcatcher

- Empore disks
- styrene-divinylbenzene (SDB)
- <http://youtu.be/f7Xzr4FIJmg>



Vermeirssen et al (2009) Water Research 43, 903-914



Fig. 1. Differences in polar organic chemical integrative samplers (POCIS) fouling from different deployment environments. Very lightly fouled POCIS (upper picture) deployed in the Norwegian Sea (~200 km offshore) for 42 d and moderately fouled POCIS (bottom picture) from wastewater treatment works after 14 d exposure. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com.]

Metody hodnocení biodostupnosti – voda

různé sorbenty (PDMS, PE, POM ...)

<http://youtu.be/xZnQt0IKIRE>

https://www.youtube.com/watch?feature=player_detailpage&v=

výhoda je zejména cena a jednoduchost



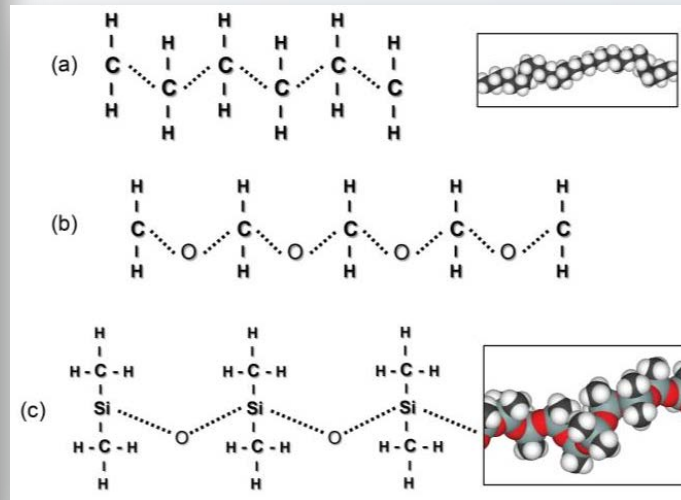
Polyethylene



Polyoxymethylene



Solid Phase Micro-Extraction



US EPA (2012) Guidelines for Using Passive Samplers to Monitor Organic Contaminants at Superfund Sediment Sites

Metody hodnocení biodostupnosti – půda / sediment

kovy:

A. stanovení pomocí extrakce včetně sekvenční extrakce

- (Weak) salt extractions (e.g., CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, NH_4Ac , NaNO_3 , Mg salts, BaCl_2 , in concentrations from as low as 0.001 M and up to 1 M salt solutions).
- Reductive extractions (e.g., sodium ascorbate, hydroxylamine HCl, sodium dithionite).
- Weak acid extractions (e.g., acetic acid, citric acid).
- Strong complexation methods (e.g., DTPA-TEA, EDTA, NTA).
- Dilute strong acids (e.g., HNO_3 , HCl, “double acid” (HCl + H_2SO_4)).
- Combined extractants (e.g., Ammonium oxalate–oxalic acid, Mehlich III (dilute acid, salt, and EDTA)).

Peijnenburg and Jager (2003) *Ecotoxicology and Environmental Safety* 56 : 63–77

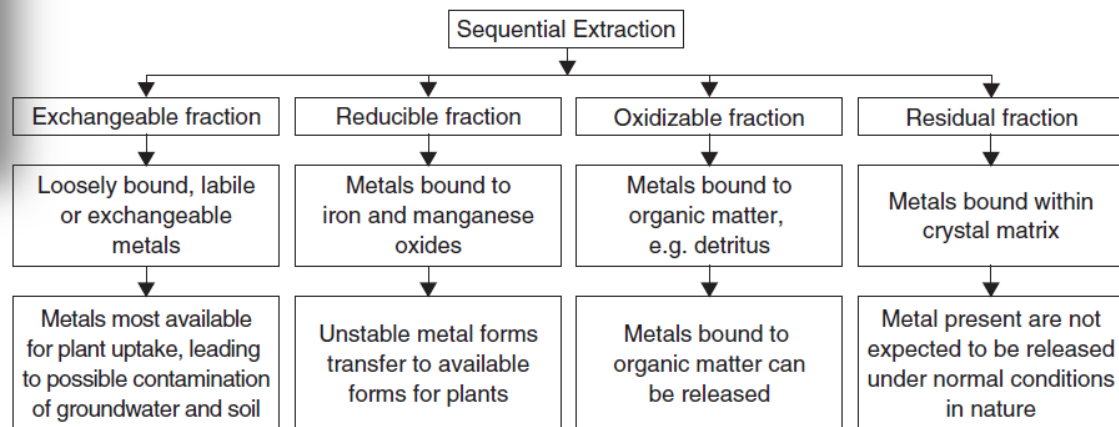


Figure 4.7 Overview of the sequential extraction method for metals, as applied to the analysis of soils and sediments [45]. From Dean, J. R., *Methods for Environmental Trace Analysis*, AnTS Series. Copyright 2003. © John Wiley & Sons, Limited. Reproduced with permission.



Metody hodnocení biodostupnosti – půda / sediment

extrakce kovů

Extraction agent	Type of binding						
	ion exchange	surface adsorption	precipitate (carbonates, sulphides or hydroxides)	Coprecipitate (amorphous hydroxides)	organic complexes	occlusion (crystalline hydroxides)	mineral crystal lattice
electrolytes	MgCl ₂						
acetic acid (buffer)	CH ₃ COOH + CH ₃ COOH / CH ₃ COONa						
acetic acid (reducing)	CH ₃ COOH + NH ₂ OH						
oxalic acid (buffer)	(COOH) ₂ + (COONH ₄) ₂						
diluted mineral acid	HNO ₃						
digestion: acid mixture + HF	HCB + HNO ₃ + HF						
aqua regia	HCB +						
alkaline fusion (extracts + acid)	Na ₂ CO ₃						
basic solution				NaOH			
complex formers	EDTA, DTPA						
complex formers	citric acid (hot)						

Dean (2007) Bioavailability, Bioaccessibility and Mobility of Environmental Contaminants.

Table 4.1 Extraction procedures used to isolate nominal soil/sediment phases [1]

Phase	Reagent or method of isolation	Comments
Water-soluble, soil solution, sediment pore water	Water, centrifugation, displacement, filtration, dialysis	Contains the most mobile and hence potentially available metal species
Exchangeable	MgCl ₂ , NH ₄ OAc, HOAc	Contains weakly bound (electrostatically) metal species that can be released by ion-exchange with cations such as Ca ²⁺ , Mg ²⁺ or NH ₄ ⁺ . Ammonium acetate is the preferred extractant as the complexing power of acetate prevents re-adsorption or precipitation of released metal ions. In addition, acetic acid dissolves the exchangeable species, as well as more tightly bound exchangeable forms
Organically bound	Na ₄ P ₂ O ₇ , H ₂ O ₂ at pH 3/NaOAc	Contains metals bound to the humic material of soils. Sodium hypochlorite is used to oxidize the soil organic matter and release the bound metals. An alternative approach is to oxidize the organic matter with 30% hydrogen peroxide, acidified to pH 3, followed by extraction with ammonium acetate to prevent metal ion re-adsorption or precipitation
Carbonate	NaOAc at pH 5 (HOAc)	Contains metals that are dissolved by sodium acetate acidified to pH 5 with acetic acid
Mn oxide-bound	NH ₂ OH.HCl	Acidified hydroxylamine hydrochloride releases metals from the manganese oxide phase with minimal attack on the iron oxide phases
Fe (amorphous) oxide	(NH ₄) ₂ C ₂ O ₄ in the dark	Amorphous forms of iron oxides can be discriminated between by extracting with acid ammonium oxalate in the dark
Fe (crystalline) oxide	(NH ₄) ₂ C ₂ O ₄ under UV light	Crystalline forms of iron oxides can be discriminated between by extracting with acid ammonium oxalate under UV light

Metody hodnocení biodostupnosti – půda / sediment

extrakce (nejen) kovů napodobující pórovou vodu

Salt solution	Concentration (M)	Reference
Calcium chloride (CaCl ₂)	0.01	Smith <i>et al</i> (2010) Krishnamurti (2008) Peijnenburg <i>et al</i> (2007) Barriuso <i>et al</i> (2004) Houba <i>et al</i> (2000)
	0.05	Krishnamurti (2008) Cheng (1990)
	0.1	Peijnenburg <i>et al</i> (2007)
Calcium nitrate (Ca(NO ₃) ₂)	0.1	Peijnenburg <i>et al</i> (2007) Lanno <i>et al</i> (2004)
Ammonium acetate (NH ₄ Ac)	1.0	Peijnenburg <i>et al</i> (2007)
Mg-salts	n/a ¹	Peijnenburg <i>et al</i> (2007)
Barium chloride (BaCl ₂)	n/a ¹	Peijnenburg <i>et al</i> (2007)
Sodium nitrate (NaNO ₃)	0.01	Yin <i>et al</i> (2002)
	0.1	Peijnenburg <i>et al</i> (2007)
Ammonium nitrate (NH ₄ NO ₃)	0.1	Peijnenburg <i>et al</i> (2007)

¹ n/a: not available

A 0.01M CaCl₂ solution has been documented as the preferential extraction solution because the concentration of Ca²⁺ ions is similar to that measured in soil pore water solutions (Peijnenburg *et al*, 2007) and a similar ionic strength (Houba *et al*, 2000).



Metody hodnocení biodostupnosti – půda / sediment

extrakce kovů

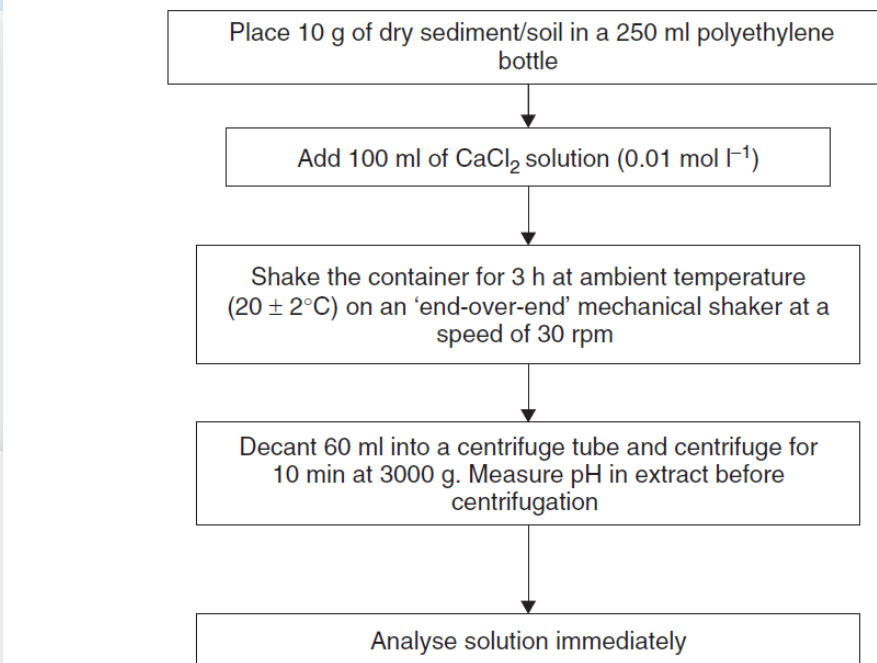
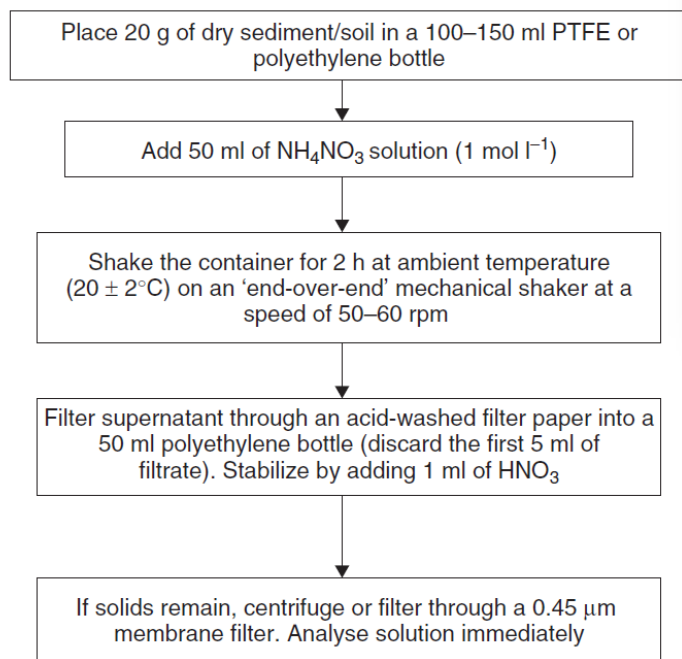


Figure 4.5 Procedure adopted in the single extraction method for metals (employing calcium chloride (CaCl_2)), as applied to the analysis of soils and sediments [2].

Figure 4.4 Procedure adopted in the single extraction method for metals (employing ammonium nitrate (NH_4NO_3)), as applied to the analysis of soils and sediments [2].

Metody hodnocení biodostupnosti – půda / sediment

extrakce kovů

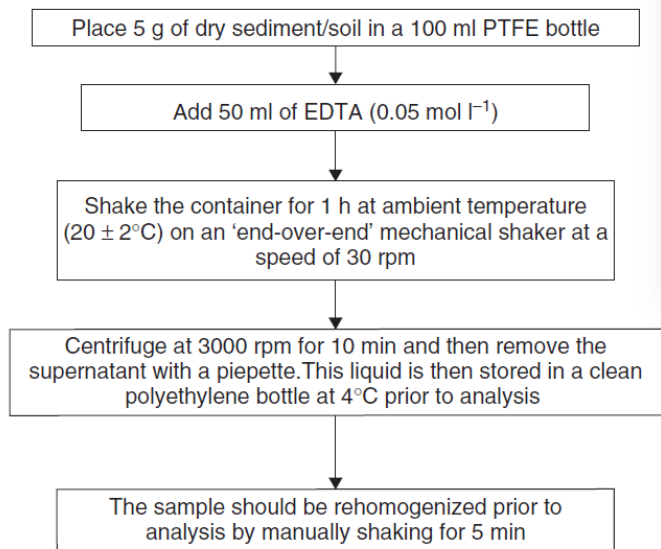


Figure 4.1 Procedure adopted in the single extraction method for metals (employing ethylenediamine tetraacetic acid (EDTA)), as applied to the analysis of soils and sediments [45]. From Dean, J. R., *Methods for Environmental Trace Analysis*, AnTS Series. Copyright 2003. © John Wiley & Sons, Limited. Reproduced with permission.

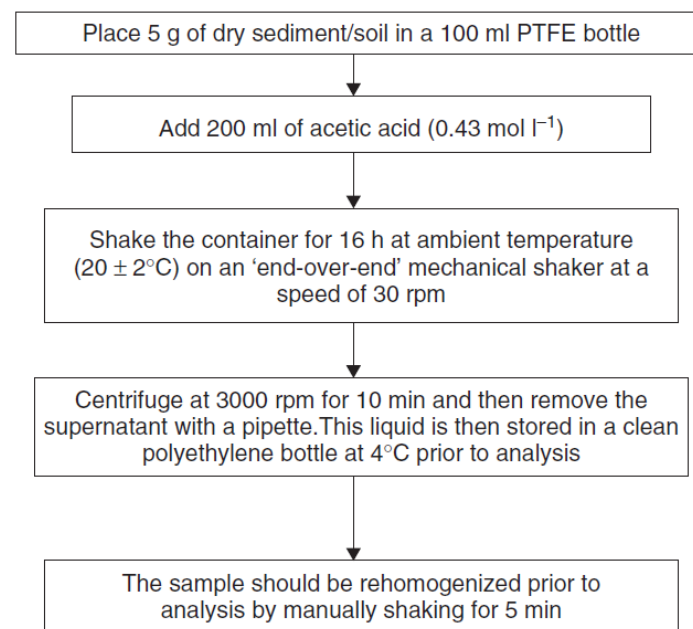


Figure 4.2 Procedure adopted in the single extraction method for metals (employing acetic acid), as applied to the analysis of soils and sediments [45]. From Dean, J. R., *Methods for Environmental Trace Analysis*, AnTS Series. Copyright 2003. © John Wiley & Sons, Limited. Reproduced with permission.

Metody hodnocení biodostupnosti – půda / sediment

kovy:

B. Separační techniky založené na iontové výměně (IE), sorbentech, či mikroseparačních metodách jako Donnan membrane technique (DMT) či diffusive gradients in thin-film gels (DGT)

Knutsson (2013) Passive sampling for monitoring of inorganic pollutants in water. ISBN 978-91-7385-854-0

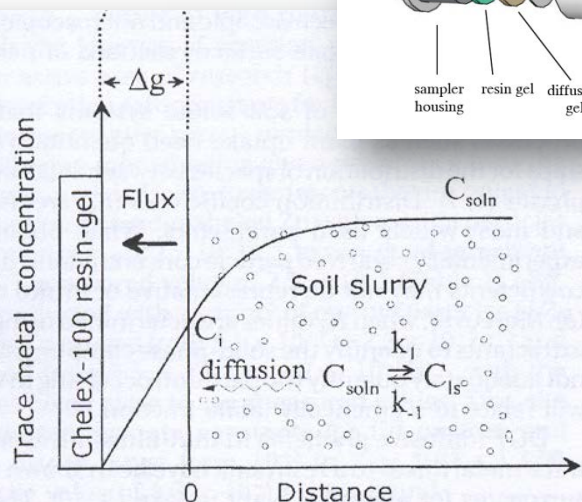
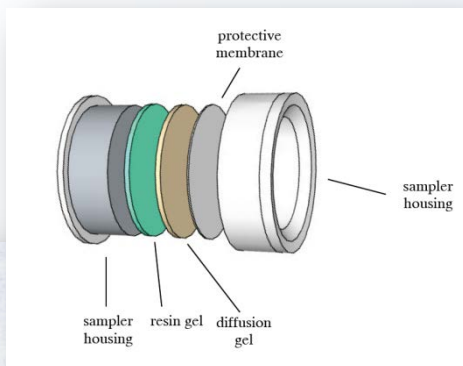


FIGURE 1. Processes induced by deployment of a DGT probe (exploded view) in a soil slurry. The mass (M) of metal is accumulated by diffusion across the diffusion layer of exposed interfacial area (A). Further explanations are given in the text.

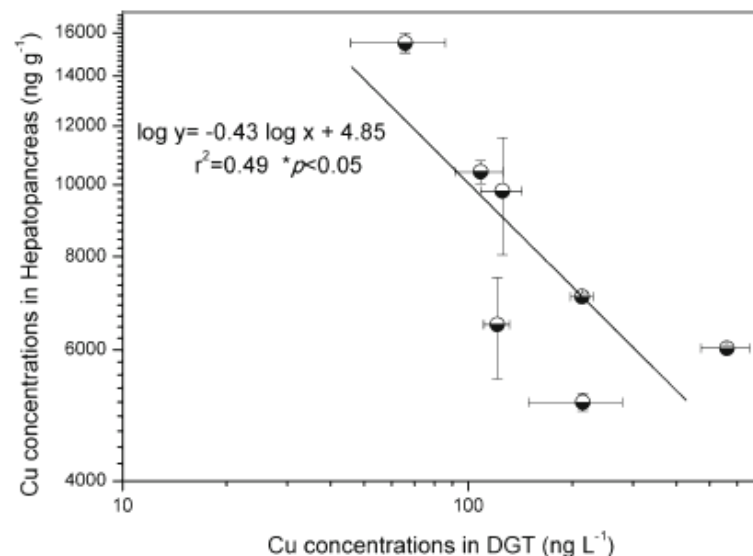
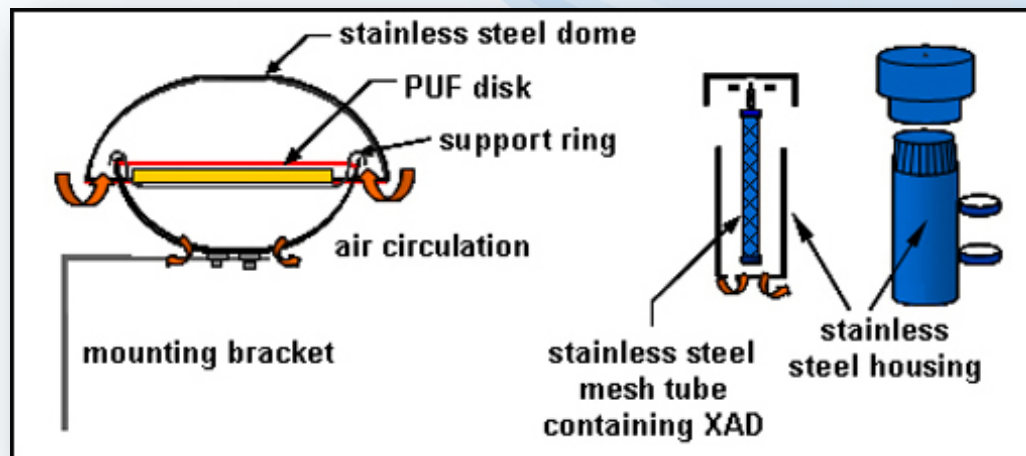


Fig. 4 Logarithmic representation of Cu concentrations measured directly in hepatopancreas of *L. vannamei* versus the DGT-measured concentrations. Both DGT measurements and Cu burdens were natural log transformed. Error bars are the standard deviations of replicates ($n=3$). Regression equation and correlations coefficient (significant r^2 value) shown are calculated from all pooled data points

Passive sampling - ovzduší

- často je kladen více důraz na TWA, biomimetické schopnosti jsou v pozadí
- <http://youtu.be/w-Cn8LzB21c>
- Global Atmospheric Passive Sampling (GAPS) Network



<http://www.ec.gc.ca/rs-mn/default.asp?lang=En&n=6AA18234-1>



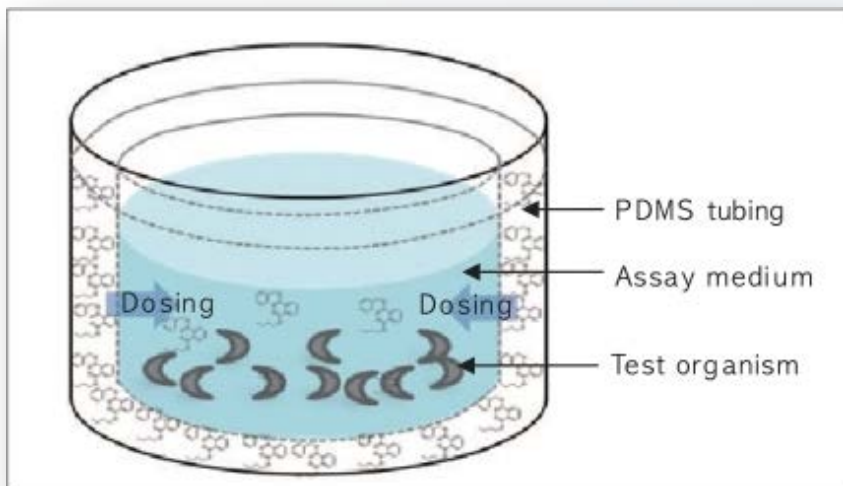
The background features several overlapping, wavy blue lines that create a sense of motion and depth. A semi-transparent grey rectangular box is centered horizontally, containing the text 'Passive dosing' in a white, bold, sans-serif font.

Passive dosing

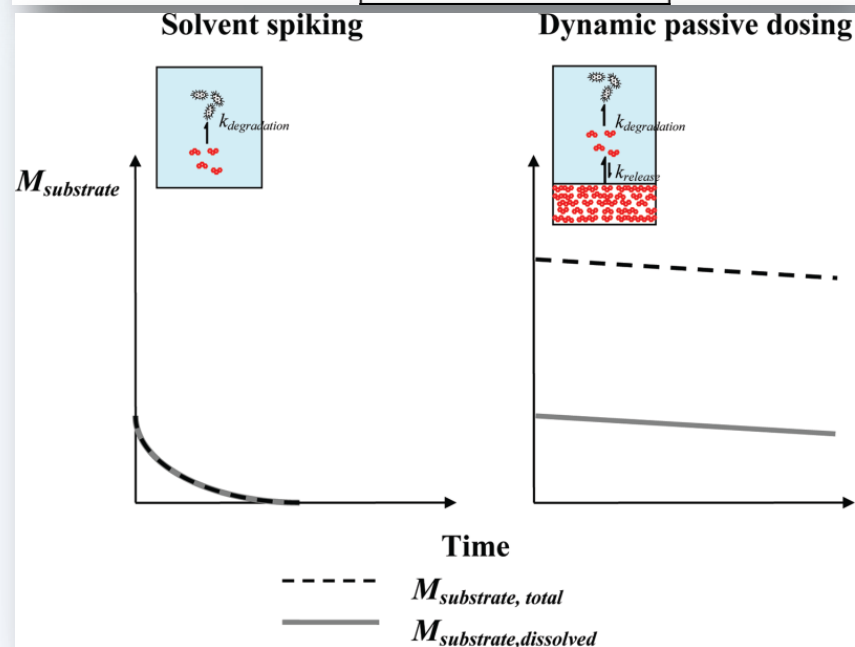
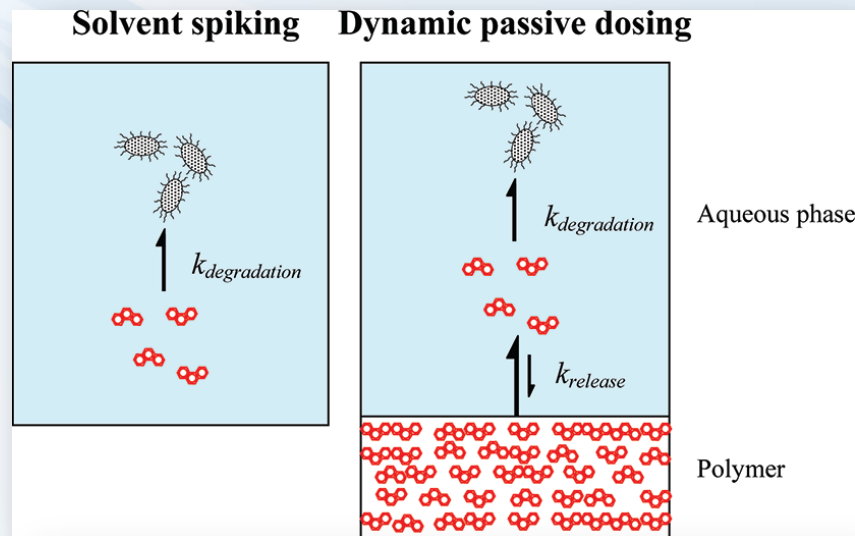
Passive dosing

- PDMS potažené nádoby či O-kroužky

Smith (2012) Environ Sci Technol 46: 4852–4860



Kwon et al. (2011) Environ Health Toxicol



Passive dosing

Butler et al. (2013) Sci Total Environ 463-464: 952-8



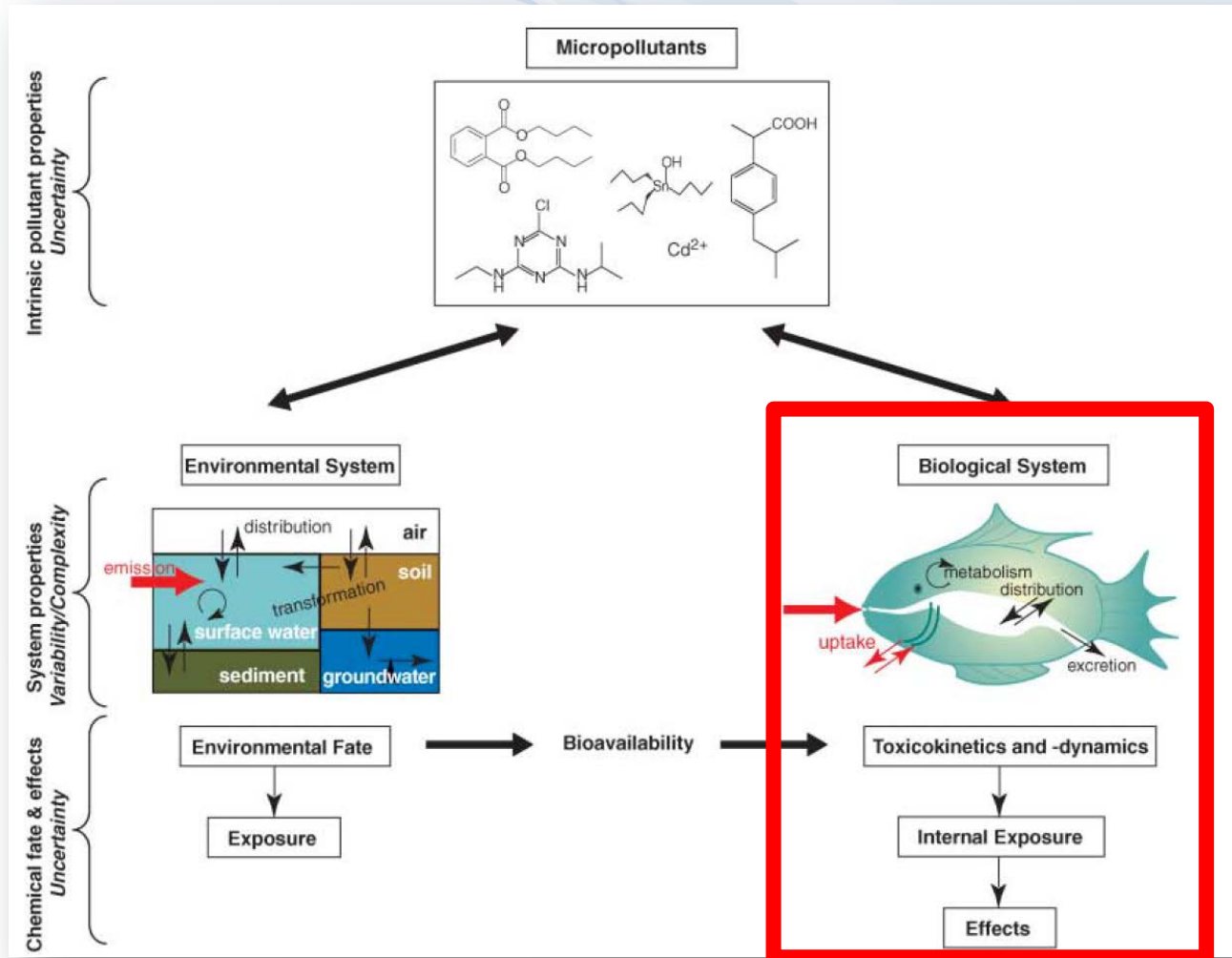
Fig. 1. The passive dosing unit showing the inlet (lower left) and outlet (lower right) ports for the perfusion of the lumen. The other three ports are for the perfusion of the shell space.

Adolfsson-Erici et al. (2012) Chemosphere 86: 593–599



Měření a modelování příjmu kontaminantů organismy

Měření a modelování toxikokinetiky



Schwarzenbach et al. (2006) The challenge of micropollutants in aquatic systems. Science 313, 1072-1077



Měření a modelování toxikokinetiky

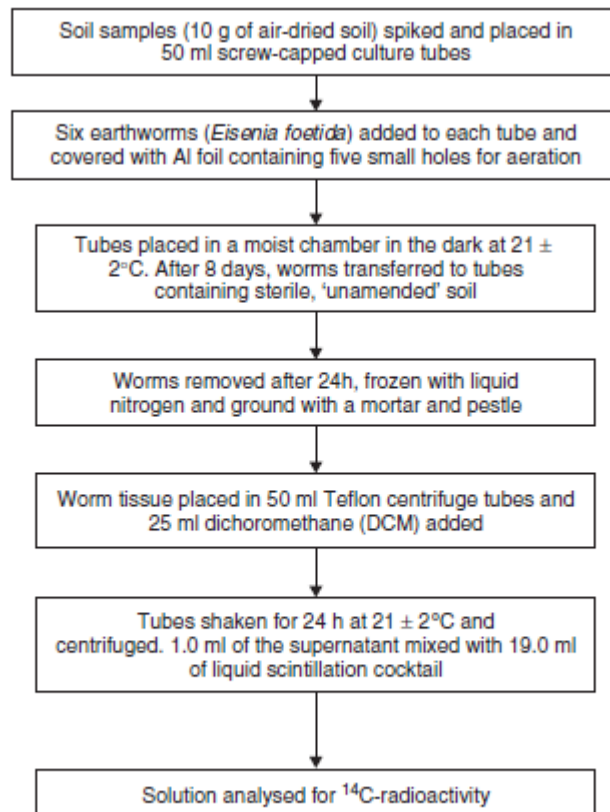


Figure 5.3 Procedure adopted in the earthworm uptake studies used by Kelsey *et al.* [3].

$$\text{BSAF} = \frac{C_{\text{org}} \cdot F_{\text{om}}}{C_{\text{s}} \cdot F_{\text{lip}}}$$

where

BSAF= biota–soil accumulation factor

C_{org} = concentration in the worm

C_{s} = concentration in soil solid phase

F_{lip} = weight fraction of lipid in the organism

F_{om} = weight fraction of OM.

critical Body Residues (CBR)

internal concentration accumulated in a tissue, organ or all body that is correlated with an adverse effect



Equilibrium sampling of biota



Fig. 1. Circular PDMS thin-films were inserted into intact fish tissue for equilibrium sampling of PCBs. The samplers were retrieved after time periods of 1 h up to 7 d. Picture: U. Berger.

Jahnke (2009) *Chemosphere* 77: 764–770

Exhaustive extraction	Equilibrium sampling
$C_{\text{Fish,lipid-normalized}} = \frac{C_{\text{Fish,wetweight}}}{f_{\text{Lipid}}}$	$C_{\text{Fish,lipid,equilibrium}} = C_{\text{PDMS}} \cdot D_{\text{Lipid,PDMS}}$
<p>What is done: All measured analyte is assigned to the lipid phase.</p>	<p>What is done: C_{Lipid} is calculated based on equilibrium partitioning.</p>
<p>Assumption: All analyte is present in lipids.</p>	<p>Assumption: The partitioning into the lipids of the sample is well represented by the applied $D_{\text{Lipid,PDMS}}$ value.</p>
<p>Applicability domain: The assumption is best met for lipophilic analytes in lipid-rich tissue.</p>	<p>Applicability domain: The sampling works best in lipid-rich tissue.</p>
<p>Strengths: Well-established procedure.</p>	<p>Strengths: Well-defined partitioning phase. Results can be directly compared to equilibrium sampling in the exposure medium that is relevant for the organism.</p>
<p>Limitations: Results do not give a measure of the fugacity of the chemical in the tissue, and hence do not allow comparison of the chemical's thermodynamic status in the tissue with other tissues or organisms.</p>	<p>Limitations: $D_{\text{Lipid,PDMS}}$ values have only been determined for a limited range of HOCs. Equilibrium sampling in lean tissue has been found to be challenging.</p>

Fig. 1. Overview of two different approaches to estimating the concentrations of hydrophobic organic chemicals (HOCs) in the lipid fraction of biota: lipid normalization of total extract concentrations obtained from exhaustive extraction; converting equilibrium partitioning concentrations in polydimethylsiloxane (PDMS) to concentrations in biota lipids. [Color figure can be seen in the online version of this article, available at wileyonlinelibrary.com]

PBET – napodobování trávicího procesu

Sorptive Physiologically Based Extraction of Contaminated Solid Matrices: Incorporating Silicone Rod As Absorption Sink for Hydrophobic Organic Contaminants

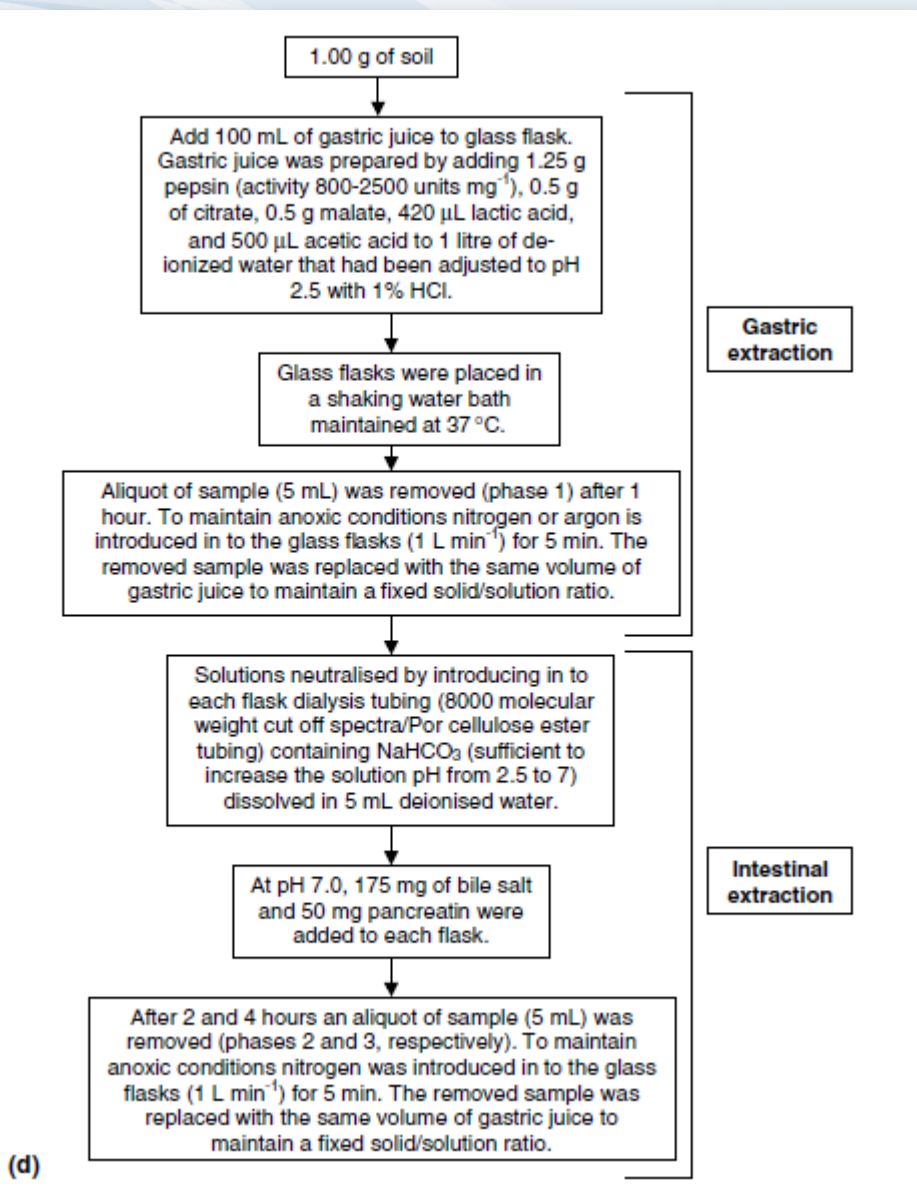
Gouliarmou et al. 2013, Environ Sci Technol 47: 941–948



Stomach	0.50 g	sodium malate
pH 2.5	0.50 g	tri-sodium citrate
	420 µL	lactic acid
	500 µL	glacial acetic acid
	1.25 g	pepsin (porcine)
Small intestine	1.78 g	bile salts
(added to stomach medium)	0.5 g	pancreatin (porcine)
pH 7.0		
Colon	4.0 g	type II mucin (porcine stomach)
pH 6.5	4.5 g	sodium chloride
	4.5 g	potassium chloride
	1.5 g	sodium bicarbonate
	1.25 g	magnesium sulphate hexahydrate
	800 mg	cysteine hydrochloride
	500 mg	potassium phosphate
	500 mg	di-potassium phosphate
	400 mg	bile salts
	189.0 mg	calcium chloride
	50.0 mg	haemin (≥ 80%, bovine)
	5.0 mg	iron (II) sulphate heptahydrate



PBET – napodobování trávicího procesu



Dean (2004) Trends in Analytical Chemistry 23, 609-618



PBET – napodobování trávicího procesu

- simulated earthworm gut (SEG) test

Table 2. Composition of tested simulated earthworm gut fluids

Treatment	Cellulase (g) ^a	Volume added (ml)					Total
		Media ^b	Culture ^c	Water ^d	0.2 M CaCl ₂ ^e	Amylase ^f	
Control (media)	0	3.8	0	0.2	0	0	4
0.01 M CaCl ₂	0	3.8	0	0	0.2	0	4
Enzyme	0.29	3.8	0	0.062	0	0.108	4
Culture	0	0	3.8	0.2	0	0	4
Enzyme and culture	0.29	0	3.8	0.062	0	0.108	4

^a On the basis of stock enzyme containing 0.64 U/mg protein and the target cellulase activity of 400 µg glucose produced/mg enzyme/h.

^b Filter-sterilized earthworm gut culture from chemostat.

^c Unsterilized earthworm gut culture from chemostat.

^d Sterile deionized water.

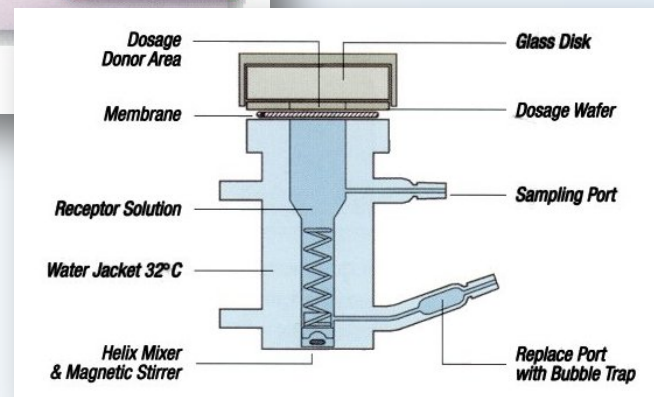
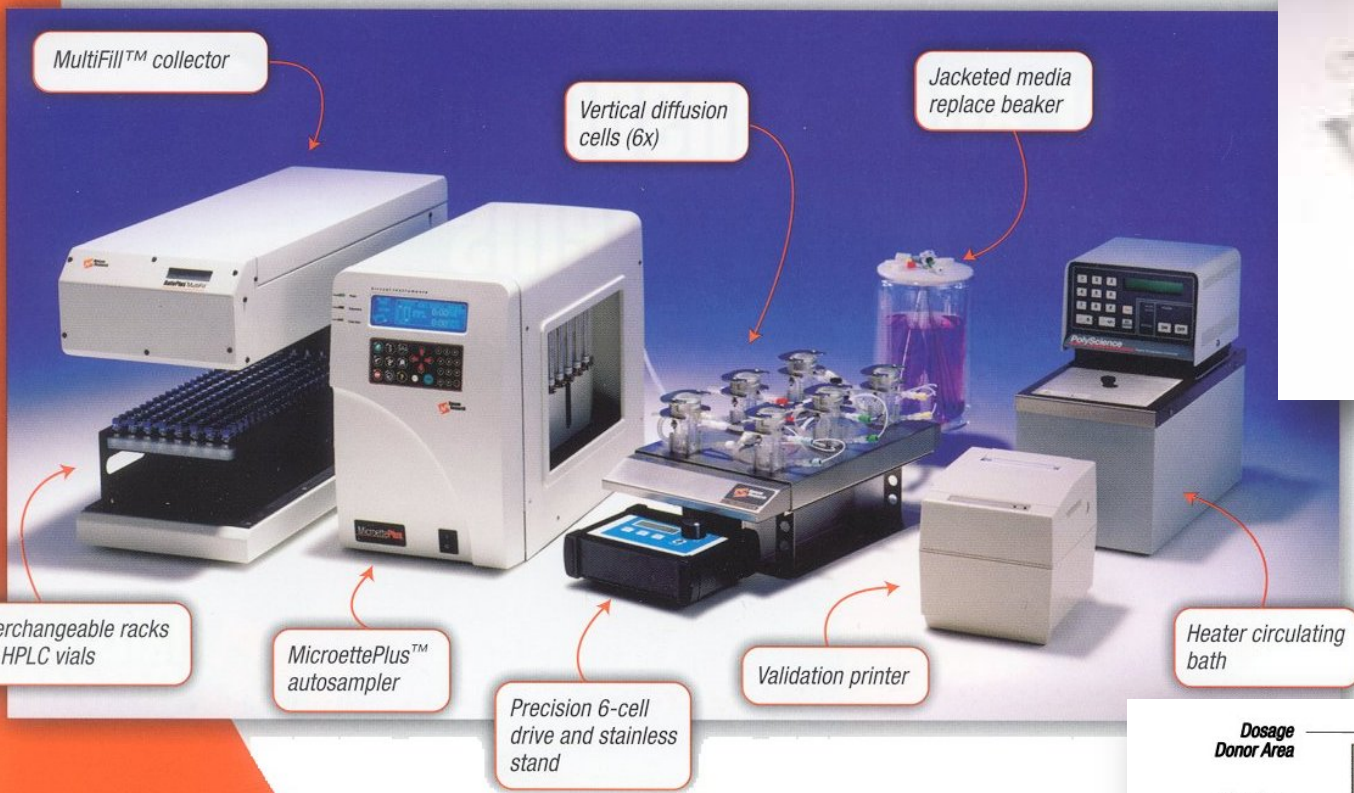
^e Made in deionized water and then filter-sterilized.

^f On the basis of stock enzyme solution made to 6.25 U/µl (filter-sterilized) and the target amylase activity of 300 µg starch consumed/mg enzyme/h.

Ma et al. (2009) Environmental Toxicology and Chemistry 28: 1439–1446



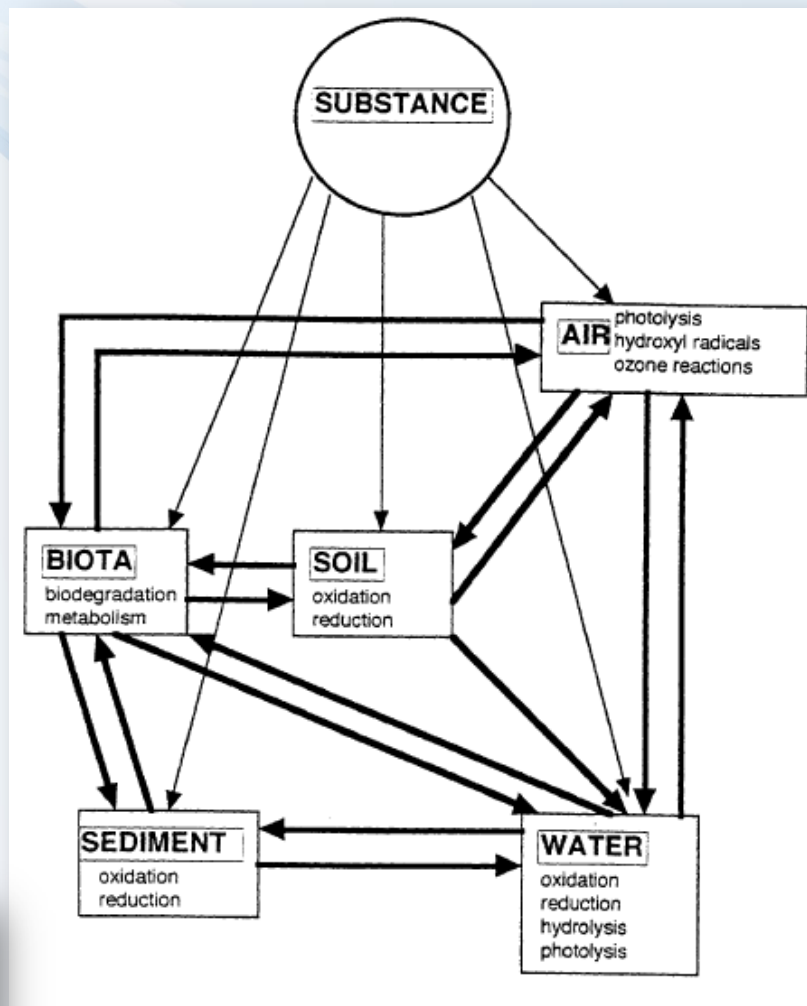
Měření přestupu přes biologické membrány



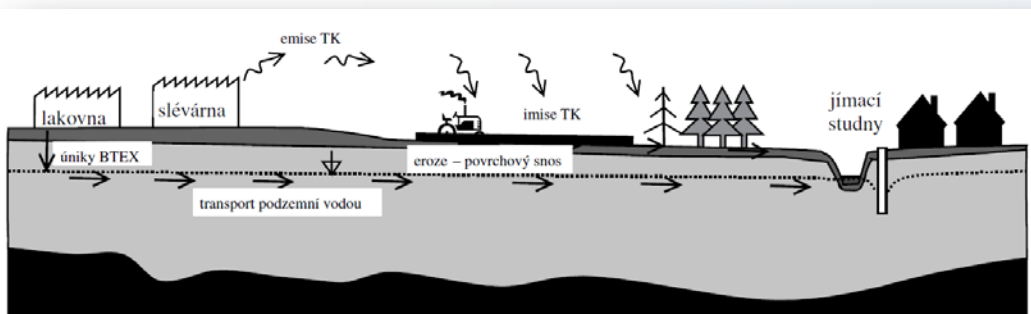
Modelování expozice

Modelování expozice

- scénáře („worst case scenario“ či jiné)
- modelování:
 - transportu od zdroje
 - změny koncentrace
 - degradace a vzniku transformačních produktů
 - distribuce v ŽP
 - distribuce v rámci dané složky prostředí (např. v půdě)
- zdrojem jsou data o zdrojích + data vlastnostech látek a prostředí



The Edinburgh Centre for Toxicology. UNEP/IPCS Training Module No. 3, Section B, Environmental Risk Assessment.



Modelování expozice

The following assumptions are made:

a) Sludge produced	0.085 kg /head /day
b) Population served by water treatment plant	100 000
c) Application rate to land	1 kg / m ²
d) Depth of soil penetration	20 cm.

$$\begin{aligned}\text{Concentration in sludge} &= \frac{(i) \times (ii) \times (iii) \times (v)}{(a) \times (b)} \\ &= \frac{5 \times 10^9 \times 0.13 \times 0.03 \times 0.9}{0.085 \times 100\,000} \quad \text{mg / kg}\end{aligned}$$

$$= 2.06 \times 10^3 \text{ mg / kg}$$

$$\begin{aligned}\text{Concentration in receiving soil} &= \frac{2.06 \times 10^3 \times (c)}{(d)} \quad \text{mg / kg} \\ &= \frac{2.06 \times 10^3 \times 1}{200} \quad \text{mg / kg}\end{aligned}$$

$$= 10.3 \text{ mg / kg}$$

This assumes a soil density of 1 tonne / m³. Given a low water solubility, and high log Kow, it is anticipated that leaching will be minimal. This assessment takes no account of the potential effects of repeat applications of sludge.

Of course, the assumptions made above must be justified (see below).

modelování zátěže
jednotlivých složek ŽP – od
zdroje do okolí organismu

The Edinburgh Centre for Toxicology. UNEP/IPCS
Training Module No. 3, Section B, Environmental
Risk Assessment.



Modelování expozice

- multimedia fate models (Mackay)
- fugacitní modely I až IV
- fugacita = tendence utíkat/prchat z příslušné fáze

$$C = f \cdot Z$$

C - koncentrace v dané fázi

f – fugacita

Z - konstanta fugacity

- v rovnováze platí:

$$f_{\text{soil}} = f_{\text{air}} = f_{\text{sediment}} = f_{\text{biota}}$$

Affinity	Water S in g / L	Air H in Pa m ³ /mol	Soil log Koc	Animal biota log Kow	Plant biota log Koa
high	>1	>10	>5	>5	>8
medium high	1 - 10 ⁻²	10 - 10 ⁻¹	5 - 4	5 - 3.5	8 - 7
medium	10 ⁻² - 10 ⁻³	10 ⁻¹ - 10 ⁻²	4 - 2	3.5 - 3	7 - 5
medium low	10 ⁻³ - 10 ⁻⁵	10 ⁻² - 10 ⁻⁴	2 - 1	3 - 1	> 4
low	<10 ⁻⁵	<10 ⁻⁴	<1	<1	<4

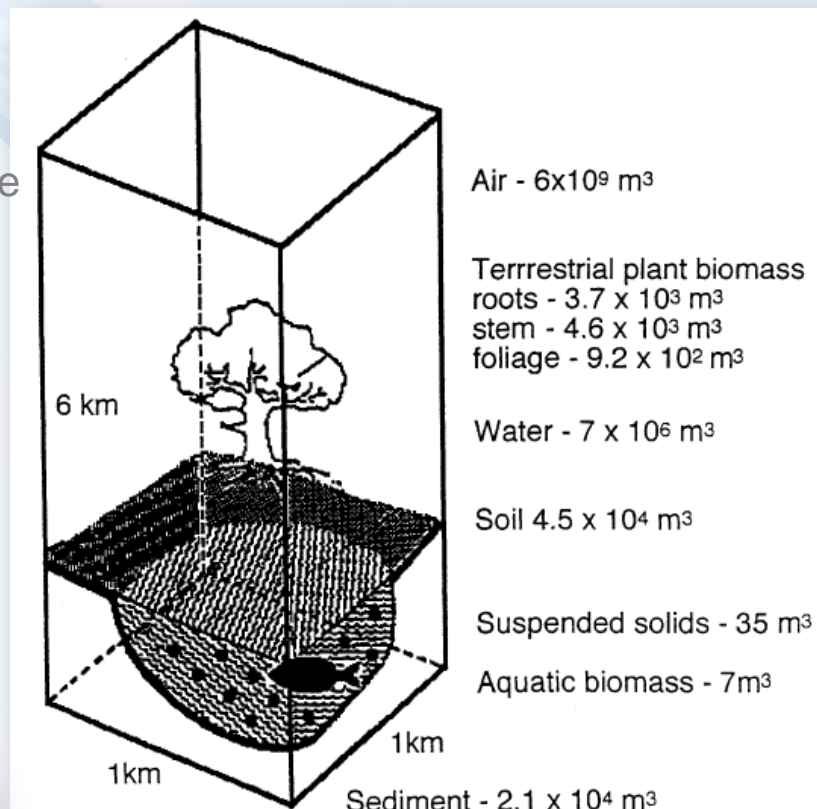


FIGURE A4.2 The "unit of world" in Mackay's fugacity model with the inclusion of terrestrial plant biomass

The Edinburgh Centre for Toxicology. UNEP/IPCS Training Module No. 3, Section B, Environmental Risk Assessment.

Modelování expozice

Table R.16-9: Characterisation of environmental compartments

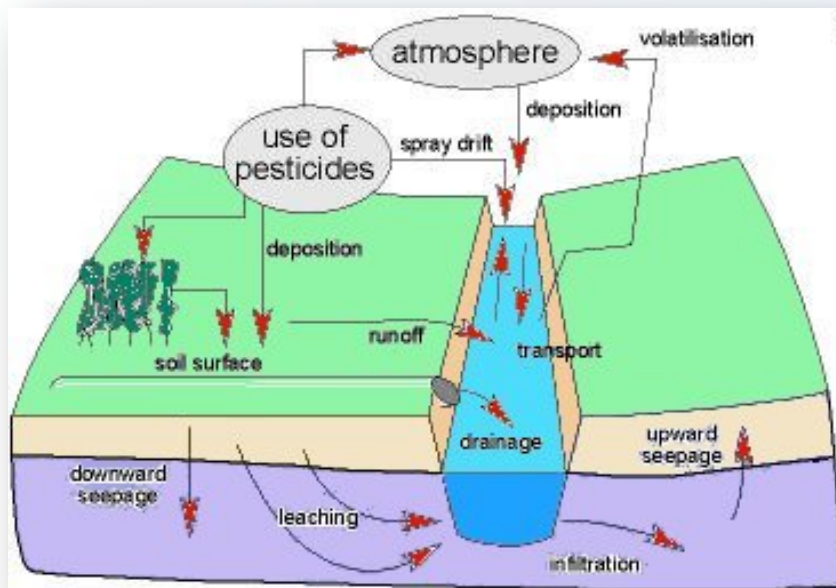
Parameter	Symbol	Unit	Value
General			
Density of the solid phase	RHOSolid	$[\text{kg}_{\text{solid}} \cdot \text{m}_{\text{solid}}^{-3}]$	2,500
Density of the water phase	RHOWater	$[\text{kg}_{\text{water}} \cdot \text{m}_{\text{water}}^{-3}]$	1000
Density of air	RHOair	$[\text{kg}_{\text{air}} \cdot \text{m}_{\text{air}}^{-3}]$	1.3
Temperature (12°C)	TEMP	[K]	285
Surface water			
Concentration of suspended matter (dry weight)	SUSP _{water}	$[\text{mg}_{\text{solid}} \cdot \text{l}_{\text{water}}^{-1}]$	15
Suspended matter			
Volume fraction solids in susp. Matter	Fsolid _{susp}	$[\text{m}_{\text{solid}}^3 \cdot \text{m}_{\text{susp}}^{-3}]$	0.1
Volume fraction water in susp. Matter	Fwater _{susp}	$[\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{susp}}^{-3}]$	0.9
Weight fraction organic carbon in susp. solids	Foc _{susp}	$[\text{kg}_{\text{oc}} \cdot \text{kg}_{\text{solid}}^{-1}]$	0.1
Sediment			
Volume fraction solids in sediment	Fsolid _{sed}	$[\text{m}_{\text{solid}}^3 \cdot \text{m}_{\text{sed}}^{-3}]$	0.2
Volume fraction water in sediment	Fwater _{sed}	$[\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{sed}}^{-3}]$	0.8
Weight fraction organic carbon sediment solids	Foc _{sed}	$[\text{kg}_{\text{oc}} \cdot \text{kg}_{\text{solid}}^{-1}]$	0.05
Soil			
Volume fraction solids in soil	Fsolid _{soil}	$[\text{m}_{\text{solid}}^3 \cdot \text{m}_{\text{soil}}^{-3}]$	0.6
Volume fraction water in soil	Fwater _{soil}	$[\text{m}_{\text{water}}^3 \cdot \text{m}_{\text{soil}}^{-3}]$	0.2
Volume fraction air in soil	Fair _{soil}	$[\text{m}_{\text{air}}^3 \cdot \text{m}_{\text{soil}}^{-3}]$	0.2
Weight fraction organic carbon in soil solids	Foc _{soil}	$[\text{kg}_{\text{oc}} \cdot \text{kg}_{\text{solid}}^{-1}]$	0.02
Weight fraction organic matter in soil solids	Fom _{soil}	$[\text{kg}_{\text{om}} \cdot \text{kg}_{\text{solid}}^{-1}]$	0.034

modelové ŽP
(modelování pro
potřeby REACH)

ECHA (2012): Guidance on information requirements and chemical safety assessment. Chapter R.16: Environmental Exposure Estimation. ECHA-10-G-06-EN

Modelování expozice

- Plant protection products (PPP) – pesticides
- **FOCUS** modely EU - <http://focus.jrc.ec.europa.eu/>
- PELMO, PEARL, MACRO, PRZM – podzemní voda
- STEP 1 a 2, SWASH, TOXWA, SWAN – povrchová voda
- EVA – ovzduší
- cílem jsou hodnoty PEC_s , PEC_{sw} , PEC_{sed} , PEC_{gw}



<http://www.pesticidemodels.eu/home>



Modelování expozice

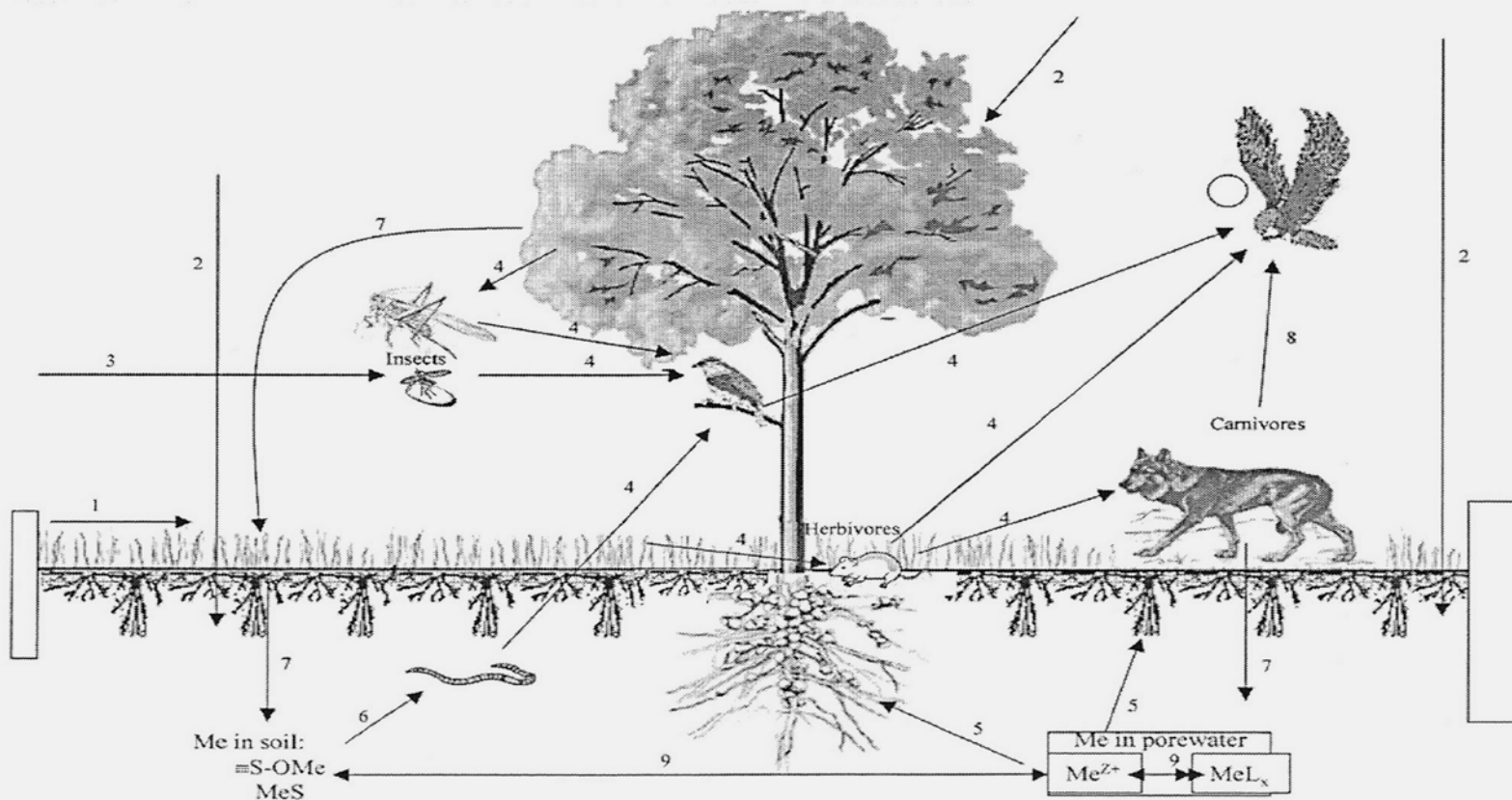


Figure 3. Conceptual model for metals in terrestrial systems. (1) surface runoff/erosion; (2) atmospheric deposition; (3) insect emergence from aquatic systems; (4) trophic transfer; (5) metal uptake from soil pore water; (6) soil ingestion; (7) organic matter decay; (8) scavenging of dead organic matter; (9) precipitation/dissolution and sorption/desorption. Me^{Z+} : free metal ions (metal aquo complexes); MeL_x : metal complexes with ligand L (charges are neglected for simplicity); MeS : metal precipitates; $\bar{S}-OMe$: metal adsorbed on particles.



Equilibrium Partitioning Theory (EqP)

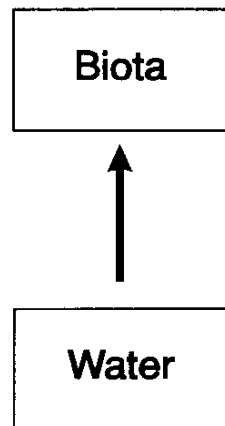
Environmental Toxicology and Chemistry, Vol. 10, pp. 1541–1583, 1991
Printed in the USA. Pergamon Press plc

Annual Review

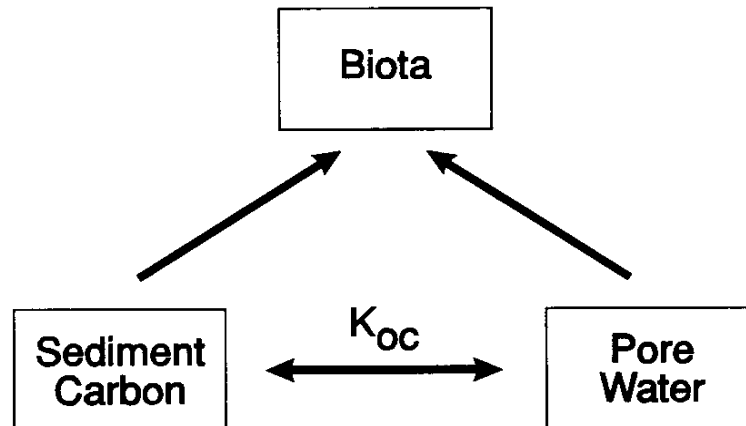
TECHNICAL BASIS FOR ESTABLISHING SEDIMENT
QUALITY CRITERIA FOR NONIONIC ORGANIC
CHEMICALS USING EQUILIBRIUM PARTITIONING

DOMINIC M. DI TORO*

**Water Only
Exposure**



**Sediment - Pore Water
Exposure**



Equilibrium Partitioning

- v rovnováze lze namodelovat pomocí K_d koncentrace v pórové vodě a půdě / sedimentu a pomocí BCF potom koncentrace v organismu
- následně lze použít k extrapolacím mezi různými látkami (QSAR) či mezi různými půdami/sedimenty
- předpokládá, že klíčovou koncentrací pro následný vstup do organismu a efekty je rozpuštěná koncentrace C_{free}

Biotic Ligand Model – BLM

- **Ligandy** – hlavní ovlivnění biodostupnosti – anionty nebo molekuly, jež vedou ke vzniku koordinačních sloučenin nebo komplexů s kovy
- Rozpustné ligandy mohou modifikovat transport kovů přes membrány několika mechanismy:
 - soupeření o povrchová ligandová místa
 - změnu rozpustnosti v tucích
 - srážení komplexů
 - tím jsou modifikovány biologické procesy – osmoregulace, respirace, vylučování

