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Variabilita rizik znečištění zemědělských půd v záplavových oblastech České republiky

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Doktorská disertační práce

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Poděkování

Ve své práci jsem navázal na výzkum svých mentorů a kolegů z Výzkumného ústavu meliorací a ochrany půdy, v.v.i., a České zemědělské univerzity v Praze. Rád bych poděkoval svému školiteli prof. Dr. Ing. Luboši Borůvkovi za odborné vedení, cenné rady a čas, který mi během studia věnoval. Dále bych chtěl poděkovat doc. Ing. Radimu Váchovi, Ph.D. za dlouholetou spolupráci a odborné vedení, díky kterému jsem měl možnost odborně růst a spolupracovat na zajímavých výzkumných tématech. Velmi si vážím spolupráce se všemi členy Oddělení hygieny půd Výzkumného ústavu meliorací a ochrany půdy, v.v.i. při řešení výzkumných úkolů. V neposlední řadě děkuji své rodině za trpělivost a podporu po celou dobu mého studia.

Prohlášení

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V Praze dne

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OBSAH

1 Úvod

Člověk a jeho hospodářská činnost se během historicky poměrně krátkého období (zejména za posledních 100 let) staly významným činitelem, který silně ovlivňuje chod biosféry i její celkovou dynamiku. Populační růst a technologický pokrok vedou v životním prostředí k významným změnám v koloběhu chemických látek a prvků na různých měřítkových úrovních. Činnost člověka významně ovlivňuje přirozené cykly prvků v biosféře, a zároveň do nich vstupují látky nové. Technologický pokrok přináší vyšší dynamiku vzniku nových chemických sloučenin, co do objemu, množství druhů i způsobu jejich uplatnění v ekonomické činnosti i každodenním životě člověka. Půdní prostředí hraje v koloběhu látek významnou roli, neboť významně ovlivňuje transport chemických látek mezi dílčími složkami životního prostředí. Vzhledem ke svým vlastnostem je významnou sorpční složkou, kde se chemické látky mohou nejen hromadit, ale také interagovat, transformovat či inaktivovat.

Údolní nivy patří k ekosystémům s přirozeně vysokou dynamikou transportu chemických látek mezi jednotlivými složkami životního prostředí a vysokou mírou ovlivnění hospodářskou činností. Dle Yu et al. (2007) jsou údolní nivy ústředním ekosystémem biogeochemických cyklů (tzv. biogeochemický hot spot) v souvislostech koloběhu živin a dynamiky znečištění. Procesy ovlivňující chemické, fyzikální či biologické vlastnosti se od ostatních půd liší z důvodu častých fluktuací hydrologických a hydraulických vlastností, a tím tedy z hlediska dostupnosti kyslíku v těchto půdách. Tato dynamika v závislosti na periodickém střídání záplavových a suchých období pak má klíčový význam pro vlastnosti těchto půd nejen z hlediska jejich schopnosti zadržovat znečišťující látky, ale také jejich imobilizace či přeměny. Vysoká úrodnost těchto půd byla známa našim předkům již v dávné historii, a proto byly tyto oblasti dlouhodobě využívány pro osidlování a rané zemědělské využití. Významné a dlouhodobě působící antropogenní činnosti v důsledcích vysoké populační hustoty v údolních nivách vedly k mnohým změnám tohoto ekosystému. Obecně právě zemědělské ekosystémy jsou spojeny se značnými změnami transportních cyklů prvků a látek v důsledku kombinace podstatných vstupů látek (hnojení, závlahy, pomocné půdní látky) a dynamiky odnosu látek (odnos sklizněmi, erozí aj.). Nivní pásma vodních toků jsou vysoce produkčními oblastmi, přitom však byla prokázána jejich zvýšená zátěž rizikovými prvky a perzistentními organickými polutanty. Lze tedy očekávat zvýšená rizika plynoucí z přítomnosti zvýšených koncentrací kontaminantů v těchto půdách.

Výše uvedené důvody naznačují, že citlivé a značně proměnlivé prostředí činí půdy údolních niv vhodným modelovým územím pro hodnocení významu rizik a kumulativních účinků chemických látek na různých měřítcích. Pro úspěšné řešení problematiky bylo potřeba získat v první fázi poznatky o obsahu vybraných stopových prvků a znečišťujících látek (zejména perzistentních organických polutantů) v nivních půdách. Hlavním cílem bylo ověření parametrů zátěže půd pomocí vhodně nastavených metod pro hodnocení diferencovaných rizik pro různé transferové cesty týkající se potravního řetězce, bezprostřední ochrany člověka či ekologických funkcí půdy. Výsledkem je pak hodnocení potenciálních rizik v záplavových územích v ČR, jejich prostorová regionalizace pomocí pokročilých statistických metod a interpretace těchto rizik v souvislostech potenciálních zdrojů kontaminace v povodích. Předkládaná disertační práce je souborem komentovaných publikovaných článků, které vznikly v průběhu řešení problematiky. V práci a publikačních výstupech je zároveň kladen důraz na prostorové souvislosti environmentálních dat, neboť metody prostorové analýzy dat umožňují sledovat a interpretovat vliv různých zdrojů na celkovou míru znečištění a zároveň profil zátěže a souvisejících rizik z hlediska kompoziční struktury. Vlastní prostorová analýza používá pro vizualizaci výsledků moderní nástroje z různých geovědních oblastí, jako je eostatistika, geografické informační systémy či statistická analýza dat. Publikační výstupy v praktické části práce detailněji popisují jednak několik případů úspěšné aplikace těchto nástrojů pro odhad rizik kontaminace půd rizikovými látkami, jednak výsledky experimentálního ověření dílčích rizik vyplývajících z kontaminace půd záplavových oblastí.

2 Literární přehled

2.1 Vymezení a vlastnosti údolních niv

Údolní nivy jsou komplexním, dynamickým ekosystémem s neustálou interakcí mezi terestrickým a vodním prostředím (Reddy & Patrick 1993). Systém údolních niv a nivních půd je součástí obecného transportně-akumulačního cyklu a globálních biogeochemických cyklů, zahrnujících procesy zvětrávání, eroze, říčního transportu, sedimentace, redistribuce sedimentů či pedogeneze. Z ekologického hlediska představuje říční krajina komplexní výsek krajiny charakterizovaný jako sled propojených biotopů s přirozenými ekologickými gradienty a významnými ekologickými funkcemi (Ward 1998; Luster et al. 2014). Ekologická diferenciace environmentálních gradientů a povrchových struktur říční nivy (půda, biota) odhaluje klíčový dynamický charakter a přirozenou heterogenitu projevující se v prostoru i v čase (Ward 1998). Vysoká úrodnost těchto půd byla známa našim předkům již v dávné historii, a proto byly tyto oblasti dlouhodobě využívány pro osidlování a zemědělské využití, což vedlo k mnohým změnám údolních niv (Vašků 2003). Jak uvádějí Tockner a Stanford (2002), 79 % břehových zón evropských řek je dnes intenzivně využíváno.

Z hlediska geomorfologického vymezení údolních niv je zásadní otázkou evoluce říčních niv v interakci změn říčního koryta a sedimentace říčních aluvií. Výsledkem vývoje je geomorfologický útvar říčních niv – tj. nejnižší terasa nad korytem vodního toku, která mívá nejčastěji podobu akumulačního plochého rovinatého území, mírně ukloněného ve směru toku určující vodoteče, které je, nebo dříve bylo, během povodní zaplavováno (Vašků 2003). Nicméně, jak uvádí Vašků (2003), detailní tvářnost reliéfu niv nebývá vždy úplně jednotvárná a v nivách lze rozlišit z hlediska podrobnější amplitudy reliéfu řadu dílčích geomorfologicky odlišných útvarů vzniklých dynamikou koryta (ramena vodních toků) a dynamikou akumulačních procesů (tzv. hrudy jako vyvýšená místa v nivě, zrnitostně a fytocenologicky vystupující z nivních sedimentů, či tzv. kolky jako konkávní terénní útvary v nivách, které zůstávají vlhčí než okolní polohy nivy). Z geomorfologického hlediska je klíčové pochopení množství sedimentovaného materiálu a prostorových vzorců sedimentace v údolní nivě. Změna sedimentační rychlosti či prostorových trendů sedimentace je zapříčiněna různými změnami, přičemž řada z nich má antropogenní charakter s úzkým vztahem k historickým změnám krajiny (de Moor et al. 2008). S tím souvisejí i vztahy mezi depozicí sedimentů a vázaných kontaminantů v nivách, sledované v řadě regionálních geochemických studií (např. Hudson-

Edwards et al. 1999; Macklin et al. 1994; Hren et al. 2001; Walling et al. 2003), což vyústilo v dřívější využití břehových sedimentů pro geochemické mapování prvků v regionálních měřítcích (Otesen et al. 1989; Bølviken et al. 1996) či nově ve využití prvků pro geochemické datování fluviálních sedimentů (Bábek et al. 2015; Grygar et al. 2010; 2014).

Z pedologického hlediska bývají oblasti, které jsou pravidelně zasahovány povodněmi, obvykle vymezeny pásmem výskytu fluvizemí na aluviálních sedimentech. Jak ukázali Novák et al. (1998) na příkladu Moravy, velké recentní povodně svým rozlivem dobře korelovaly s areály fluvizemí. Nicméně lze předpokládat, že pedogeografická situace se v různých povodích liší jednak pod vlivem charakteristických půdotvorných faktorů v povodí, jednak pod vlivem antropogenních zásahů, které ovlivňovaly erozně-depoziční podmínky v povodí a přirozenou dynamiku vodních toků (změny vedení trasy koryta, úpravy podélného a příčného profilu toku, změny hydrického režimu nivy). Nivní polohy se zpravidla vyznačují složitými katénami synlitogenních fluvizemí, ale i černic, (pseudo)glejů a také svéráznou vegetací, ovlivňovanou jednak zátopami za povodní, hladinou podzemní vody a různorodostí zrnitostního složení půdně-litologického prostředí (Vašků 2003; Němeček & Tomášek 1983). Pokud budeme hovořit o přirozené variabilitě půd v záplavových zónách, lze vyjít z diferenciace říčních gradientů dle Warda (1998) na longitudinální, vertikální a laterální. Z hlediska půdní diverzity se longitudinální gradient projevuje diferenciací či kontinuitou zastoupení půdních typů v nivě odrážející ve svém pořadí změnu půdotvorných činitelů podél toku. Jurča (1974) prokázal zákonitý sled vlastností fluvizemí v korelaci s klimatickými podmínkami a charakterem sedimentace od horního po dolní tok. Vertikální gradient vyjadřuje podle Stanforda a Warda (1993) interakce mezi tekoucí vodou v říčním toku a zdroji podzemní vody a souvisejícími procesy, které z hlediska pedogeografie mají úzkou vazbu na hydromorfní režim půd navazujících niv. Z pedogeografického hlediska lze nivu chápat jako část komplexního systému pedogeomorfní katény, kde se laterální heterogenita projevuje toposekvencí půd rozvodí-svah-niva-vodní tok, přičemž vymezení fluvizemí vůči půdám navazujících svahů je nejednoznačné z důvodů rozostřené hranice fluviálních, deluviofluviálních a deluviálních sedimentů a pedogenetické příbuznosti půdních typů (Šefrna 2008; Zádorová et al. 2008).

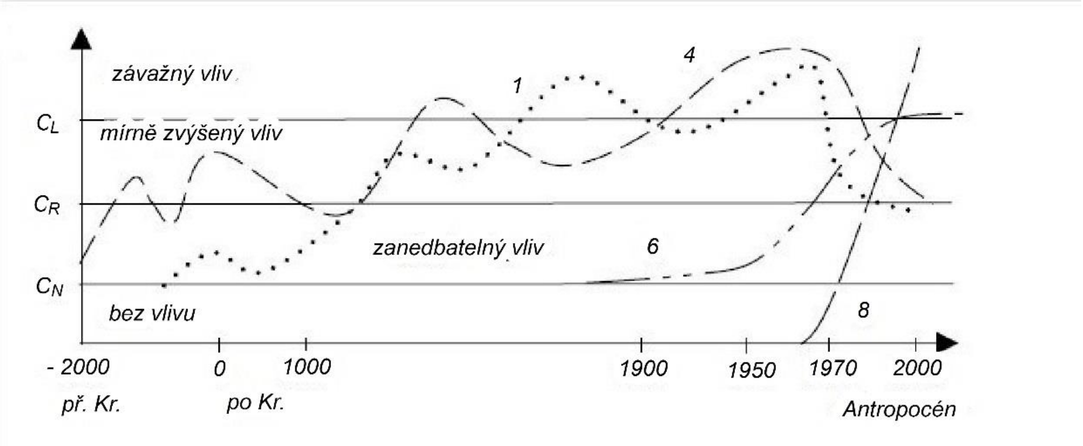
Z hlediska pochopení dynamiky znečištění údolních niv a hodnocení rizik znečištění jsou klíčové čtyři faktory – zdroje, (re)distribuční mechanismy, vlastnosti kontaminantů a sorpční vlastnosti půdy.

2.1.1 Zdroje a distribuční mechanismy znečištění v záplavových oblastech

V případě kontaminace rizikovými prvky (RP) se doplňují zdroje přirozené (tj. geologicky podmíněné) se zdroji antropogenními. Jinak je tomu u perzistentních organických polutantů (POP), kde je z hlediska kvantitativních vstupů otázka přirozených koncentrací spíše marginální (Alcock et al. 1998). V případě odlehlých povodí s minimálním antropogenním vlivem jsou hydrologické procesy eroze půdních částic hlavními mechanismy vstupu rizikových prvků do říčního systému. Jak uvádějí Janeček et al. (2005), erozní splaveniny jsou výsledkem selektivního procesu, při němž jsou jemnější částice přednostně odnášeny odtékající vodou, a sedimenty tím obsahují obecně více jílovitých, prachovitých a organických látek než zdrojové půdy. Tyto půdní frakce lze obecně charakterizovat velkou schopností vazby kontaminantů. Quinton a Catt (2007) či Jiao et al. (2012) sledovali významné obohacení erozního sedimentu RP spolu s obsahem jílové a organické složky, přičemž výsledné trendy odnosu půdních prvků kopírují trendy ztráty půdy, ale příliš nekorespondují s obsahy RP ve zdrojové půdě, což ukazuje na významný vliv celkové produkce sedimentu na difúzní cesty RP z půdy vlivem eroze.

V mnoha oblastech světa je dnes patrné, že říční systémy mohou být ovlivněny mnohem více antropogenními tlaky než přirozenými přírodními vlivy (Messerli et al. 2000). Meybeck (2003) charakterizuje současné změny říční krajiny jako soubor antropocenních syndromů (regulace, fragmentace, změny sedimentace, chemická a mikrobiální kontaminace, eutrofizace, acidifikace) s popsanými příznaky a příčinami stavu. Jednotlivé antropogenní činnosti mají specifické distribuční mechanismy kontaminace v povodích a jejich nivách. Zemědělství ovlivňuje distribuční mechanismy přímou aplikací rizikových látek do půd prostřednictvím závlahy znečištěnou vodou, dotací hnojiv a pomocných půdních látek se zvýšenými obsahy rizikových látek (hnojiva, komposty, čistírenské kaly, sedimenty) či ošetřením produkce v záplavových oblastech přípravky na ochranu rostlin. Průmysl je odpovědný za přímé distribuční mechanismy v podobě vypouštění nečištěných či znečištěných vod do hydrologického recipientu, kde mohou následně vlivem hydrologických redistribučních mechanismů migrovat ve vodním toku (v sedimentech) či mimo vodní tok (do nivních půd).

Druhým přímým mechanismem vstupu rizikových látek je atmosférický vstup z imisních spadů z průmyslových podniků uvnitř či vně povodí. Třetí možností jsou nahodilé vstupy ve formě havárií či jednorázových úniků rizikových látek z průmyslových zdrojů či starých ekologických zátěží. Z hlediska vlivu na chemické vlastnosti říčních systémů má významné postavení těžba a zpracování nerostů, kde hlavními distribučními mechanismy jsou eroze materiálu z pozůstatků důlní činnosti a přímý vstup důlních vod do vodotečí. Další zdroj úzce souvisí s urbanizací niv – tj. koncentrací obyvatel a dopravy, kdy lze sledovat významné přímé distribuční mechanismy znečištění do říčních systémů v podobě splachu vod nasycených znečištěním z městského prostředí vlivem zvýšené zátěže dopravními kontaminanty (dopravní cesty, parkovací plochy) či vlivem splachu z budov (zejména střech).



Obr 1 Historický vývoj znečištění říčních systémů a jejich ovlivnění člověkem v západní Evropě dle Meybecka (2003) - (*1 – organické znečišťující látky, 4 – rizikové prvky, 6 – dusíkaté znečištění, 8 – pesticidy*)

Význam jednotlivých zdrojů kontaminace se v průběhu historie mění, přičemž tyto změny probíhají odlišně v různých částech světa s důsledky pro pohyb znečišťujících látek (Lohman et al. 2007). Na Obr. 1 lze sledovat vývoj chemické kontaminace v Evropě od prvotních lokálních vlivů úpravy rud (Hong et al. 1996; Macklin et al. 1997) přes masivní růst kontaminace v 19. stol. v souvislostech se spotřebou kovů během průmyslové revoluce (Middlekoop 2000) až po vrchol kontaminace kovy mezi roky 1950–1970 vlivem emisí ze spalování uhlí. Nárůst POP je spojen dominantně s industriálním obdobím i s intenzifikací zemědělství a širokým využitím pesticidů od 40. let 20 století. Emise POP do prostředí jsou od 70. let 20. století v Evropě a Severní Americe snižovány díky zákazům a kontrole emisí některých POP (Jones & Vogt 1999), zároveň dochází ke geografickému posunu produkce POP vlivem řady faktorů, jako jsou globální přesuny výrobních kapacit do Asie, spalování biomasy a lesní požáry v tropických oblastech či nárůst využití pesticidů v zemědělství a regulace rozšíření tropických nemocí (Lohman et al. 2007). V ČR lze od 90. let 20. století sledovat významné zlepšení kvality povrchových vod vlivem politicko-ekonomických změn, které přinesly snížení intenzity průmyslové a zemědělské výroby i rozvoj legislativní ochrany životního prostředí (Langhammer 2010).

2.1.2 Redistribuční mechanismy kontaminace půdy v záplavových oblastech

Výslednicí zdrojů a distribuce jsou obsahy rizikových látek v říčních systémech. Tyto obsahy jsou veličinou s významnou dynamikou, přičemž v nivních oblastech může tato dynamika vzrůstat vlivem změn interakce s říční vodou. Baborowski et al. (2007) či Zonta et al. (2005) prokázali, že očekávané kontaminace povodňových sedimentů RP jsou úměrné obsahu jejich forem vázaných na suspendované částice ve vodním prostředí během povodňové vlny. Následky povodňové redistribuce znečištění lze sledovat v říčních systémech pod silným vlivem jedinečného zdroje – například v případech odnosu a sedimentace toxických důlních odpadů v důsledku extrémních hydrologických událostí (Borůvka et al. 1996; Cabrera et al. 1999; Diaz-Barrientos et al. 1999). Podobně Žák et al. (2009) sledovali toky RP v silně kontaminované nivě řeky Litavky a potvrdili povodňovou redistribuci RP do dolních částí toku ve vazbě na obsahy suspendovaných částic vzniklých erozí kontaminovaných břehových sedimentů. Navrátil et al. (2008) pak sledují vlivy redistribuce kontaminace horní Litavky v navazujícím povodí Berounky. Podobný posun znečištění byl sledován v navazujících říčních systémech řeky Mulde (oblast soutoku Mulde a její zdrojnice Spittelwasser), kde v regionu Bittefeld (Německo) byly v návaznosti na chemickou výrobu sledovány anomální obsahy POP i RP v nivních půdách a sedimentech (Brack et al. 1999; Schwartz et al. 2006; Götz et al. 2007). Podobně je dlouhodobě sledován vliv hot spotu kontaminace POP na říční systémy v industrializovaném povodí řeky Passiac ve státě New Jersey (USA) (Bopp et al. 1991; Wenning et al. 1994; Barabas et al. 2004).

Složitost procesu povodňové redistribuce kontaminace byla prokázána celou řadou srovnávacích studií, kdy byly sledovány koncentrační změny polutantů vlivem povodňových událostí. Cebula et al. (2005) dokumentovali zvýšení obsahu RP v povodí Odry vlivem povodně v roce 1997. Elhotová et al. (2006) či Pulkrabová et al. (2008) sledovali nárůst znečištění rizikovými látkami na lokalitách v povodí Vltavy a Labe po povodni v roce 2002. Naopak Vácha et al. (2003) nesledovali signifikantní nárůst obsahu rizikových látek v povodí dolního Labe po povodni v roce 2002, podobně Maliszewska-Kordybach et al. (2011) prokázali na příkladu povodí Vistuly, že v oblastech bez významnějších urbánních a průmyslových zdrojů znečištění nedošlo vlivem povodňové události v roce 2010 k významnějším změnám hygienického stavu půdy. Podobné závěry potvrdila ekotoxikologická srovnávací studie Mullera et al. (2003), která neprokázala nárůst toxicity povodňových sedimentů v důsledku povodně. Řada studií na druhou stranu potvrdila, že v důsledku extrémních hydrologických událostí se mohou sedimenty (dnové či deponované na půdách) dočasně stát zdrojem kontaminace kvůli remobilizaci a redistribuci zakonzervovaného znečištění (Förstner 2004; Krueger et al. 2005; Hilscherová et al. 2007). Říční systémy (koryta, povodňové plošiny, příbřežní mokřiny) jsou tedy dle řady autorů dočasným úložištěm kontaminantů, které v případě změn podmínek mohou představovat „chemickou časovanou bombu“ (Stigliani et al. 1991; Japenga a Salomons 1993; Cappuyns et al. 2006). Schwartz (2006) analyzoval stabilitu dnových sedimentů na středním Labi se závěry, že zvýšené povodňové průtoky v roce 2002 vedly k remobilizaci starších pohřbených sedimentů s významně vyšší zátěží a rizikem jejich redepozice do říčních niv. Podobně Kaiglová et al. (2015) popsali rizika případné mobilizace dnových sedimentů na příkladu Bíliny a Labe. Umlauf et al. (2005) pozorovali, že půdy za povodňovými valy, které nebyly při povodni v roce 2002 na dolním Labi zaplaveny, byly zanedbatelně kontaminované látkami POP ve srovnání s pravidelně zaplavovanými půdami říční nivy. Autoři zároveň konstatovali, že se kontaminační toky v době této extrémní události posunuly od vnosu kontaminace povodňovou vlnou spíše k vyplavování historicky zakonzervované kontaminace. Jak ukazují Macklin (1992) či Hudson-Edwards et al. (1998) na příkladu olova a zinku v silně kontaminovaném aluviu řeky Tyne v severovýchodní Anglii, k redepozici sedimentárně pohřbené kontaminace může docházet po relativně dlouhé době od primárního vstupu.

V případě POP a rtuti je třeba uvažovat o i dalších mechanismech redistribuce, kdy semivolatilní kontaminanty mají tendenci vstupovat do plynné fáze s potenciálem k přenosu a redepozici. Kruh volatilizace a depozice může být mnohokrát opakován, a tak může docházet k jejich akumulaci v oblastech vzdálených od oblasti jejich použití (Koblížková et al. 2009). Dálkový přenos znečištění jako důležitý mechanismus globální distribuce POP (Lunde & Bjorseth 1977) je dnes intenzivně zkoumán, dochází neustále k rozšiřování znalostí o globálních tocích látek na základě globálních modelů distribuce (Wania & Mackay 1999). Otázce rtuti v kontaminovaných fluviálních půdách a možné redistribuci s ohledem na volatilní charakter dílčích sloučenin rtuti (Lindberg et al. 2002) je věnována velká pozornost v oblasti středního Labe – Wallschläger et al. (2000); Devai et al. (2005); Rinklebe et al. (2010). V neposlední řadě lze za dílčí proces redistribuce látek v záplavových zónách považovat přestup rizikových látek do rostlin (a odnos sklizní v zemědělsky využívaných půdách), což je zásadní i z hlediska rizik vstupů do potravního řetězce (viz kapitola 2.2.1).

2.1.3 Půdní vlastnosti jako faktory sorpce znečišťujících látek

Z hlediska klíčových faktorů bude odděleně diskutována dynamika rizikových prvků a perzistentních organických polutantů, přičemž diskuze poznatků z odborné literatury je směrována k vlivu těchto faktorů v nivních půdách. Skupina RP zahrnuje stopové prvky, které se přirozeně vyskytují v půdách v nízkých koncentracích, nicméně překročení vazebné kapacity půd může vést k závažným environmentálním důsledkům (toxicita, zvýšení mobility, přestup do rostlin) (Alloway 1990). POP jsou širokou skupinou chemických sloučenin organické povahy a jejich hlavním rysem je perzistence v prostředí a rizika pozdních účinků kvůli jejich dlouhodobému biologickému působení v organismech s potenciálními účinky genotoxickými, karcinogenními a mutagenními (Jones & de Voogt 1999) či s potenciálním narušením fyziologických funkcí endogenních hormonů (Kavloc 1996; Kelce et al. 1995).

Hlavními charakteristikami půdy, které ovlivňují mobilitu RP a jejich transport, jsou pH, redox potenciál, kationtová výměnná kapacita, množství a kvalita organické hmoty, oxidů a jílových minerálů, stupeň provzdušnění půdy či mikrobiální aktivita (Alloway 1990). Celý tento provázaný komplex vlastností se mění s hydrickými vlastnostmi půdy a dostupností kyslíku v půdě, které se v nivách mění pod vlivem střídání suchých podmínek podobných terestrickým půdám s podmínkami zaplavených (mokřadních) půd. Dynamiku RP určují interakce mezi procesy sedimentace, adsorpce, srážení, kationtové výměny, tvorby komplexů, mikrobiální aktivity a příjmu rostlinami (Matagi et al. 1999). Výsledkem interakce je ustanovení rovnováhy pro jednotlivé RP mezi jílovými minerály, půdní organickou hmotou a hydratovanými oxidy, přičemž půdní pH a redoxní podmínky mají klíčový význam pro ustanovení rovnovážných stavů (Zunkel & Krueger 2009; van Griethuysen et al. 2005).

Cyklické změny režimu hrají klíčovou úlohu ve změnách redoxního potenciálu s vlivem na mobilitu prvků, což bylo potvrzeno jak v terénních studiích (Shiller 1997), tak v laboratorních experimentech (Chuan et al. 1996). Schwartz (2001, cit. v Zunkel & Krueger 2009) popsal redoxní změny v různých fázích povodně na středním Labi a zaznamenal významné rozvolnění vazeb Fe a Mn vlivem rozpouštění oxidů v době snížení redoxního potenciálu, což vede jednak ke ztrátě adsorpčních míst pro RP, a jednak ke zvýšené kompetici mezi kationty při výměnné sorpci s výsledkem potenciální mobilizace RP. Obecně přítomnost ostatních iontů významně ovlivňuje speciaci RP v půdách (Sims 1986), kdy vlivem různé vytěsňovací síly různých iontů dochází ke kompetici při obsazování adsorpčních míst (Hoins et al. 1993). Shaheen et al. (2013) prokázali, že silněji vázané prvky v půdě (Pb, Cu) jsou méně ovlivněny kompeticí než mobilní prvky (Cd, Ni, Zn). Proti procesu rozpuštění oxo-hydroxidů působí tvorba sulfidů a karbonátů Fe či Mn či sulfidických precipitátů s imobilizačním efektem, přičemž v běžných půdách převažuje spíše efekt imobilizace (Förstner 1992). Vliv jednotlivých faktorů je složitý a mnohdy antagonistický, což v případě zaplavovaných půd umocňuje dynamika půdních vlastností. Například Schwartz (2001, cit. v Zunkel & Krueger 2009) zjistil, že k významným změnám redoxních podmínek dochází v případě příznivých podmínek z hlediska obsahu organické hmoty a teploty, což vede dle autorů jednak k významnějším fluktuacím redoxního potenciálu v půdách bohatých na humus (depresní půdy niv), jednak k sezónním rozdílům mobilizace prvků mezi povodněmi v letním a zimním období, což lze přisoudit zejména vlivu vyšší teploty na mikrobiální aktivitu s následným nárůstem obsahu RP v půdním roztoku v důsledku komplexace s organickými ligandy. Vlivu organické hmoty na sorpci RP v půdách je věnována řada studií a např. Carrillo-Gonzalez et al. (2006) nabízejí ucelené zpracování tématu. Obecně lze říci, že půdní organická hmota má přímý význam pro sorpci RP díky tvorbě organokovových komplexů a zároveň jako adsorpční povrch, na druhou stranu se podílí na tvorbě rozpustných organických komplexů, které naopak mohou chránit prvky před adsorpcí nebo vysrážením (Carrillo-Gonzalez et al. 2006). Sedimentace a postdepoziční degradace organické hmoty povodňových sedimentů jsou významnými biogeochemický procesy s možnými dopady na RP (Zunkel & Krueger 2009). Krueger et al. (2005) sledovali vztah obsahu organické hmoty, elevace terénu a četnosti záplav a zjistili vyšší obsahy organické hmoty a RP v nižších partiích záplavové oblasti středního Labe. Eisenmann (2002) či Albering et al. (1999) na příkladu Labe resp. Meuse determinovali lineární korelační vztah mezi obsahem organické hmoty a RP. V laboratorní studii byl tento korelační vztah vysvětlován spíše významem organické hmoty pro zvyšování vazebné kapacity povrchu jílových minerálů (Zunkel & Krueger 2009). Nicméně jak uvádějí Kalbitz a Wennrich (1998), vliv organické hmoty na mobilizaci v záplavových půdách se liší u jednotlivých RP a významně závisí na kvalitě organické hmoty a vlastnostech půdního roztoku. Například význam organické hmoty signifikantně klesal při poklesu pH pod 4,5 (Kalbitz & Wennrich 1998). Obecně snížení pH půdy vede u většiny RP ke zvýšení mobility (Alloway 1990), neboť pH patří ke klíčovým faktorům rozpustnosti RP v půdě (Brallier et al. 1996). Významný vliv pH souvisí s velkou senzitivitou jílových minerálů, hydratovaných oxidů Fe a Al či půdní organické hmoty ke změnám pH (Harter & Naidu 2001). Dynamika pH ve vazbě na redox potenciál se pak projevuje signifikantním vztahem změn pH a mobility RP v záplavových zónách (Krueger & Groengroeft 2004). Geller et al. (2004, cit. v Zunkel & Krueger 2009) sledovali ve většině vzorků záplavových půd v povodí Labe pH < 6, kdy lze očekávat relativně vysokou mobilitu Cd, Ni, Zn, méně Cr a relativně nízké obsahy mobilních forem Pb a Cu (Adriano 2001).

Sorpce prvků na oxo-hydroxidy Fe a Mn je významným faktorem speciace RP nejen v záplavových půdách (Jenne 1968; Triverdi & Axe 2000). Ve vazbě na dynamiku režimu půd je klíčové střídání tvorby jejich stabilních krystalických forem během oxidačních podmínek v suchých obdobích s příslušným imobilizačním efektem na RP (Tack et al. 2006) a jejich reduktivního rozpouštění vlivem inundace (Davranche & Bollinger 2000; Grybos et al. 2007). Afinita jednotlivých RP na hydratované oxidy se významně liší při současné existenci vazebných preferencí jednotlivých oxidů k jejich adsorpci (Triverdi & Axe 2000). Obecně větší význam pro sorpci RP mají dominantně zastoupené oxidy Fe (ferihydrit > goethit > hematit) oproti minoritním oxidům Mn, které však mají vyšší vazebnou kapacitu (Zunkel & Krueger 2009). Podobně jílové minerály mají z hlediska sorpčního potenciálu RP menší význam oproti hydratovaným oxidům či organické hmotě, nicméně jejich množství v půdách zvyšuje jejich vazebný potenciál (Kabata-Pendias & Pendias 2001). Jak ukazují Rinklebe et al. (2007)

či Zunkel a Krueger (2009) na příkladu dolního Labe, obsah jílových a prachových částic výrazně dominuje ve fluviálních půdách v nivních depresích, zatímco obsah písku roste na akumulačních rovinách. Zunkel a Krueger (2009) uvádějí, že ve fluviálních půdách dolního Labe byl dominantním jílovým minerálem illit, méně pak kaolinit, což ukazuje spíše na střední vazebnou kapacitu fluviálních půd z hlediska obsahů jílových minerálů. Eisemann (2002) popsal lineární vztah obsahu jílu a RP v záplavových půdách středního Labe, zatímco Albering et al. (1999) v záplavových půdách řeky Meuse tento vztah neprokázali.

Chemické vlastnosti POP, především pak hydrofobní a lipofilní charakter, determinují jejich výskyt a transferové cesty v ekosystému směrem k silnější vazbě na půdy a organické matrice a k omezenému vstupu do vodní fáze (Jones & de Voogt 1999). Jejich vlastnosti umožňují cirkulaci mezi jednotlivými ekosystémy, přičemž ovzduší je hlavní složkou, v níž k přenosu dochází. Osud a chování POP v půdách se odvíjejí od jejich chemické struktury, fyzikálně-chemických vlastností a environmentálních podmínek, přičemž rozhodující jsou následující vlastnosti a procesy:

- vlastnosti důležité pro transport ve složkách prostředí – perzistence, bioakumulace, sorpce;
- chování v jednotlivých složkách prostředí a jejich fázích – tj. mezifázová distribuce v jednotlivých složkách prostředí (tuhá–plynná, tuhá–kapalná, kapalná–plynná fáze);
- abiotické degradační postupy – hydrolýza, oxidace, fotodegradace v jednotlivých fázích;
- biodegradace.

Vztahy mezi těmito vlastnostmi a procesy pak určují toky mezi složkami prostředí, přičemž během tohoto transportu mohou být jednotlivé látky abioticky i bioticky přeměňovány. Z hlediska potenciálu k pohybu v půdním prostředí jsou určující faktory distribuce sloučenin mezi pevnou, kapalnou a plynnou půdní fází (Jones & de Voogt 1999). Toto rozdělování látek lze popsat pomocí distribučních koeficientů, které vyjadřují sumu molekulárních interakcí (zahrnující iontové interakce, van der Waalsovy síly, vodíkové můstky) mezi látkou a dvěma fázemi (Ehlers & Loibner 2006). Rovnovážné rozdělení hmoty mezi vodnou a plynnou fázi lze charakterizovat pomocí Henryho konstanty. Rozdělovací koeficient mezi oktanolem a vodou (K_{OW}) je dnes považován za indikátor rozdělení mezi pevnou a kapalnou fází a společně s obsahem organické hmoty v půdě slouží k odhadu sorpce POP na půdu (Jones & de Voogt 1999). Obsah organické hmoty je považován za klíčový pro obsahy POP (Sweetman et al. 2005; Dalla Valle et al. 2005), nicméně většinou nelze tento obsah snadno využít pro predikci POP v půdě lineárními modely, neboť variabilita POP ve vztahu k obsahu organické hmoty je silně maskována dalšími faktory – především blízkostí zdroje (Meijer et al. 2003) či vlivem teplotní diferenciace (Ribes et al. 2002). Avšak obecně lze konstatovat, že v přirozeném půdním profilu dochází vlivem vyšších organických obsahů ke kumulaci POP ve svrchní vrstvě půdy (Cousins et al., 1999; Krauss et al. 2000; Moeckel et al. 2008), nicméně v orných půdách dochází vlivem kultivace k posunu i do hlubších vrstev (Armitage et al. 2006). Fikarová et al. (2018) sledovali odlišné vertikální distribuce vybraných POP v profilech nivních půd, což ukazuje na význam ovlivnění distribuce POP procesy evoluce nivy a sedimentace, především pak jemných a organických frakcí v níže položených částech nivy. Vliv těchto frakcí potvrzuje také vysoká lokální variabilita POP v nivních půdách se signifikantní korelací POP s obsahem jílových a prachových částic i obsahem organického uhlíku (Witter et al. 1998; Kiersch et al. 2010). Obecný význam půdní organické hmoty potvrzují také často sledované zvýšené obsahy POP v lesních půdách (Tremolada et al. 2008). Půdní organická hmota je z hlediska chemického složení velmi variabilní a význam frakcionace organické hmoty na specifické vazby POP byl sledován pro vybrané pesticidy (Piccolo et al. 1998; Ahmad et al. 2001), ale také pro polychlorované bifenyly (PCB) a polyaromatické uhlovodíky (PAU) (Doick et al. 2005; Pan et al. 2006), kdy byl dokumentován dominantní vliv huminu na obsahy hydrofobních POP. Na podkladě terénních výsledků obsahu PCB v půdách Švýcarska navrhují Tremolada et al. (2012) obsah uhlíku v huminu půdní organické hmoty jako vhodný ukazatel pro odhad akumulační schopnosti půdy pro POP. Ačkoliv u fluvizemí lze obecně očekávat střední obsah humusu s převahou fulvokyselin ve frakčním složení, budou zde pravděpodobně významné rozdíly způsobené variabilitou půdního složení záplavových oblastí.

2.1.4 Variabilita znečištění v záplavových půdách

Depozice polutantů v nivních oblastech je dána především ukládáním sedimentu a má tedy přímou souvislost s geomorfologickými procesy probíhajícími na povodňové plošině. U přirozených, laterálně meandrujících říčních koryt tak dochází k agradaci kontaminovaného sedimentu na povodňové plošině, přičemž míra kontaminace se pak liší v závislosti na vývoji sedimentace, zejména staří a celkového úhrnu (Perry & Taylor 2007). Často lze tedy sledovat vyšší míry kontaminace v bezprostřední blízkosti vodního toku s následným poklesem směrem do distálních částí údolní nivy (Leigh 1997). Tento gradient není však pravidlem a byly sledovány i vyrovnané obsahy v celém rozsahu plošiny (Bradley & Cox 1990; Martin 1994). Popsané rozdíly jsou s největší pravděpodobností ovlivněny zrnitostí sedimentu (Ladd et al. 1998; Walling et al. 2003). Kontaminanty vázané na jemnozrnné sedimenty se ukládají v topograficky níže položených oblastech povodňových plošin (Bradley & Cox 1990). Leenaers a Rang (1989) popsali rozdíly mezi obsahy Cd, Zn a Pb v závislosti na frekvenci záplav v povodí řeky Geul, kde byl s vyšší četností záplav pozorován významný nárůst obsahu těchto prvků v příslušných půdách. Zapojení podrobné amplitudy reliéfu v modelu koregionalizace a vzájemného krigingu pak umožnilo lepší odhad RP v aluviální půdě (Leenaers et al. 1990). Potvrzuje se tedy, že půdy nejnižších říčních teras jsou více zatíženy rizikovými látkami v důsledku sedimentace organických látek a jemných jílovitých částic během zaplavování (Devai et al. 2005; Overesch et al. 2007; Rinklebe et al. 2007). Podobné výsledky byly sledovány také ve studii malého měřítka na středním Labi, kde byla sledována vysoká variabilita obsahů 29 různých POP pod vlivem půdních vlastností (textura, organická hmota) (Kiersch et al. 2010). Rinklebe et al. (2007) prokázali na dolním Labi, že obsahy Cd, Zn a Cu byly vyšší v silně jílovitých půdách odpovídajících terasovým černicím, dále v terasových glejích a až následně v hlinitých fluvizemích. Autoři pak využili znalosti půdních typů a substrátů k odhadu obsahu RP v záplavových oblastech na příkladu dolního Labe. Podobně Middelkoop (2000) prokázal na případové studii Rýnu a Meuse, že nejnižší obsahy RP byly v distálních částech údolní nivy s nízkou četností záplavových událostí a nižší průměrnou sedimentací (~ 5 mm za rok), zatímco nejvyšší obsahy byly sledovány v nejnižších terasách s vysokou frekvencí záplav a vyšší roční sedimentací (> 10 mm za rok). V regionálně zaměřené studii fluviálních půd Labe byla potvrzena vysoká zátěž nivních půd na aluviálních sedimentech celou škálou RP a POP (Podlešáková et al. 1994; Vácha et al. 2003). Na základě porovnání obsahů vybraných rizikových látek v geomorfologicky vymezených částech údolní nivy bylo prokázáno, že intenzita zátěže půd nivních oblastí je statisticky významně vyšší ve srovnání s ostatními zemědělsky využívanými půdami ČR.

Ukazuje se, že distribuce rizikových látek v údolní nivě závisí na vzdálenosti od říčního koryta, frekvenci záplav, geomorfologii nivy a jejím vývoji, půdních vlastnostech, ale také na existenci a pozici umělých bariér (přehradní nádrže, protipovodňové hráze) omezujících kontinuitu říčního systému a jeho interakce s nivou (Japenga & Salomons 1993; Borůvka et al. 1996; Martin 2000; Middelkoop 2000; Du Laing et al. 2009; Majerová et al. 2018).

2.2 Rizika znečištění v nivních půdách a metody jejich hodnocení

Narušení přirozeného biogeochemického cyklu prvků a vnášení obtížně degradovatelných, perzistentních cizorodých látek do prostředí vede ke změnám distribuce těchto látek směrem k selektivní akumulaci v prostředí. Rizika spojená s touto postupující akumulací byla globálně identifikována jako významná jak pro ekosystémy, tak pro člověka. Laboratorní i terénní experimenty publikované v odborné literatuře potvrzují skutečnost, že řada rizikových prvků a perzistentních organických polutantů má škodlivé účinky na lidské zdraví, přičemž z humanotoxikologického hlediska jsou za nejzávažnější považovány pozdní účinky v souvislostech dlouhodobého biologického působení polutantu v organismech s potenciálními genotoxickými, karcinogenními a mutagenními účinky (Jones & de Voogt 1999). Kombinace vysoké intenzity zemědělství, populační hustoty a zvýšené environmentální zátěže v nivních oblastech ukazují na potřebu odborného hodnocení rizik a vývoj vědecky odvozených kritérií pro posouzení těchto rizik. S tím je spojeno hodnocení potenciálu přestupu do potravního řetězce přes transferovou cestu půda-rostlina, hodnocení účinku na zdraví člověka (přímé zdravotní účinky zvýšených koncentrací toxických prvků a látek), hodnocení ekologických rizik (ekotoxikologických účinků) a stanovení rizikového profilu z pohledu zdravotních i ekologických rizik.

2.2.1 Rizika znečištění pro potravinové řetězce

Z hlediska přestupu kontaminace z půdy do rostlin lze v záplavových oblastech uvažovat několik kritických cest (upraveno dle Trapp & Mc Farlene 1999; Mikeš et al. 2009):

a) příjem z půdního roztoku kořenem,
b) absorpce kontaminantu na povrch kořene,
c) foliární příjem látek odpařených z půdního povrchu,
d) absorpce kontaminace na listovou plochu.

Pokud se podíváme na jednotlivé cesty pro potenciální příjem rizikových látek v rostlinách, je patrné, že prakticky všechny cesty mohou být silně ovlivněny v době povodňové události vlivem přímého kontaktu s kontaminovanými vodami a sedimenty. Absorpce kořenovým systémem je hlavním transportním mechanismem příjmu rizikových prvků (Kabata-Pendias & Pendias 2001), nicméně bilance kořenového a mimokořenového (převážně foliárního) příjmu se mezi jednotlivými prvky liší. Harrison a Chirgawi (1989) sestavili pořadí prvků podle jejich příjmu z atmosféry: Pb > Cr > Ni > Zn = Cd. Pro příjem rizikových prvků kořeny rostlin je nezbytné, aby byly nejdříve uvolněny do půdního roztoku jako volné disociované ionty nebo rozpustné anorganické a organické komplexy (Adriano 2001), proto klíčové půdní faktory pro příjem látek korespondují s faktory mobility těchto prvků v půdě (Brümmer et al. 1986). Z literárních údajů lze určit obecné pořadí rizikových prvků podle přístupnosti prvků pro rostliny – např. Harrison a Chirgawi (1989): Zn > Cd > Ni > Cr > Pb (někdy Cd > Zn). Němeček et al. (2010) uvádějí řadu: Cd > Zn, Tl > Cu > Mn > Ni, Co > Pb, As, Be > Cr > Hg a při zohlednění mobility prvku jako klíčového faktoru transferové cesty půda-rostlina lze řadu modifikovat na Cd, Tl > Mn > Zn > Co, Cu > Ni, Pb > As > Be > Cr, Hg. Přestup z půdy také ovlivňují rostliny (druh rostliny, velikost, vývojové fáze, charakter kořenového systému, kořenové exudáty, mykorhiza) (Kabata-Pendias & Pendias 2001). Na podkladě terénních a simulačních dat prokázali Podlešáková a Němeček (2001) pomocí faktorové analýzy významnou rozdílnost vztahů přestupu jednotlivých prvků do rostliny a půdních vlastností a následně vícenásobnou regresní analýzou navrhli transferové rovnice, vyjadřující interakcí půdních složek vyvolané přestupy jednotlivých RP do rostlin. Právě lineární modely byly dříve nejčastěji vyvíjeny a testovány pro jednotlivé rizikové prvky a jejich sorpci v půdě (Elzinga et al. 1999; Streck & Richter 1997) a pro modelování přestupu rizikových látek z půdy do rostlin (Efroymson et al. 2001; Němeček et al. 2001; Rodrigues et al. 2012). V současnosti se nově uplatňují také pokročilejší metody strojového učení pro parametrizaci sorpce prvků v půdě. Covelo et al. (2008) využili metody regresních a klasifikačních stromů pro tvorbu modelu sorpce RP v půdě, kdy využili celou řadu vysvětlujících proměnných (zrnitostní složení půdy, obsahy hydratovaných oxidů Fe a Mn, mineralogické složení půd – jílové minerály apod.) a na podkladě výsledků definovali klíčové prediktory sorpce prvků v půdách.

Z hlediska přestupu POP z půdy do rostlin jsou podobně jako pro sorpci v půdách určující faktory distribuce sloučenin mezi pevnou, kapalnou a plynnou půdní fázi. Cousin a Mackay (2001) se pokusili zahrnout terestrickou vegetaci do již vytvořeného multifázového modelu a definovali základní procesy příjmu POP vegetací, přičemž pro jednotlivé procesy jsou klíčové rozdělovací koeficienty (distribuční koeficient půda-voda - K_d , rozdělovací koeficient oktanol-voda - K_{ow}, bezrozměrná Henryho konstanta - K_{aw}, rozdělovací koeficient organický uhlík-voda - K_{oc}) (Briggs 1984; Trapp 2003). Potenciál přechodu látek z atmosféry do prýtu mají především látky s nižším K_{aw}, kdy, jak uvádí Trapp a Mathies (1999), se přestup vzduchem týká látek s K_{aw} do 10^{-4}, které budou spíše volatilizovat z půdy a dále interagovat s nadzemní částí rostlin. Pro příjem ze vzduchu jsou pak kromě fyzikálních vlastností látky dalšími determinanty hlavně lipidická složka povrchu rostlin (kutikulární vosk) a fyziologická specifika rostlinných druhů (Kylin & Bouwman 2012). Duarte Davidson et al. (1996) rozdělili organické chemikálie do tří tříd dle intenzity sorpce v závislosti na $\log K_{ow}$, kdy látky s vyššími hodnotami $\log K_{ow}$ (< 4,0) mají silnou tendenci k sorpci na povrchu kořenů, zatímco látky s velmi nízkým $\log K_{ow}$ (< 2,0) se mohu snadno transportovat dále. Z výsledků Mikeše et al. (2009) plyne, že přestup z kontaminované zeminy do plodin významně ovlivňují také resuspendované půdní částice, které mohou ulpívat na listech plodin. Existuje také přímá přestupová cesta půda-nadzemní část při kontaktu prýtu s kontaminovanou půdou, která může v důsledku povodňových událostí nabývat většího významu.

Groengroeft et al. (2005) sledovali významně zvýšené obsahy rizikových prvků v rostlinách ihned po povodni v roce 2002 v německé části Labe vlivem depozice kontaminovaných sedimentů na rostlinný povrch, přičemž i přes významné snížení obsahů přibližně po 1 měsíci hodnoty stále překračovaly relevantní limity dle EU. Jak uvádějí Krueger a Groengroeft (2004) či Overesch et al. (2007) na příkladu výsledků z Labe, nelze většinou nalézt přímou vazbu mezi obsahy prvků v půdě a obsahy v rostlině kvůli komplexní podmíněnosti procesu přestupu do rostlin vlivem půdních podmínek (velká prostorová variabilita a dynamika půdních podmínek) a variability rostlinných společenstev (druh rostliny, období odběru, stadium vývoje rostliny). Umluaf et al. (2005) také neprokázali signifikantní přestup půda-rostlina pro látky ze skupiny polychlorovaných dibenzo-p-dioxinů a furanů (PCDD/F). Autoři sledovali vysoké obsahy v rostlinách na půdách mimo záplavová území, zatímco na půdách s nejvyššími obsahy byly naměřené koncentrace v rostlinných vzorcích velmi nízké. Podobně Stachel et al. (2006) při sledování obsahů vybraných POP v nivách prokázali jejich zvýšené obsahy v půdách i rostlinách, avšak bez jasných signifikantních korelačních vztahů mezi obsahy v půdě a příslušných plodinách. Nicméně vlivem povodňové události v roce 2002 bylo prokázáno zvýšení obsahů POP, které se projevilo zvýšeným obsahem POP v rostlinách a následně v potravním řetězci (kravské mléko) (Stachel et al. 2005). K jednoznačným závěrům došli také autoři, kteří sledovali na pastvinách s vysokou četností záplav významně zvýšené obsahy POP v mléku či hovězím mase ve srovnání s kontrolními stanovišti nepostiženými záplavami

(Alcock et al. 2002; Hendriks et al. 1996; Stachel et al. 2005; Lake et al. 2005; 2014), kdy částečný vliv lze přisoudit ingesci půdy společně s přijímanou potravou.

2.2.2 Zdravotní a ekosystémová rizika znečištění v nivních oblastech

Rizika environmentálních koncentrací chemických látek pro zdraví člověka či ekosystém vyplývají z potenciálních možností přestupu těchto látek z prostředí do živého (včetně lidského) organismu (Holoubek 2003). Z hlediska cílového organismu tedy rozlišujeme hodnocení rizik humanotoxikologikých a ekotoxikologických. Principiálně lze obě metody založit na principu hazard indexu (HI) – tj. na srovnání environmentálních koncentrací mezi skutečnou zátěží matrice (c) a na účincích založených referenčních hodnot (SSL) pro dílčí polutanty z i toxikologicky významných chemických látek pro sledovaný vztah stresor – receptor[1]. Formálně lze tento vztah vyjádřit rovnicí:

$$HI_{RISK} = \frac{c_1}{SSL_1} + \frac{c_2}{SSL_2} + \cdots + \frac{c_i}{SSL_i} \qquad (-1-)$$

V případě rizik pro zdraví člověka vyžaduje jejich hodnocení exaktní přístupy pro popis podmínek pro expoziční transport – tj. kdy a jak je člověk vystaven kontaktu s chemickými látkami. Klíčovou otázkou je množství, forma a toxicita chemických látek v environmentálních matricích. Proto je monitoring výskytu toxikologicky významných chemických látek v půdním prostředí jednou z cest pro získávání užitečných podkladů pro hodnocení a interpretaci dat o předpokladech expozičního transportu do lidského organismu, a z něho plynoucích rizik pro zdraví člověka (Holoubek 2003). Cílem hodnocení rizik je tedy získat maximálně spolehlivé a úplné informace o uvažovaných chemických látkách a podmínkách expozice. Získání všech podkladů je ideální situace, a proto je velmi důležité zohlednit či zahrnout nejistoty postupu odvození zdravotních rizik (Holoubek 2003). Spolehlivé informace pro nastavení podmínek expozice přináší především experimentální stanovení dané látky v tkáních sledovaných

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[1] *Specifickým problémem je skutečnost, že analyticky stanovujeme omezené spektrum látek , zatímco v reálném prostředí jsou chemické látky přítomny v podobě různě komplikovaných směsí a dosud není dostatek informací o vzájemných interakcích mezi jednotlivými komponentami směsi (Holoubek 2003). Proto kromě chemických analýz polutantů v environmentálních vzorcích lze k indikaci rizikových procesů v půdách či sedimentech využít biologické metody založené na laboratorním sledování vlivu znečištěného půdního prostředí na modelové půdní organismy (živočichové, rostliny, mikroorganismy) či biologické (nejčastěji mikrobiální) parametry půdy (Hofman et al. 2003; Vašíčková et al. 2013) Ekotoxikologická hodnocení mají celou řadu výhod ve srovnání s chemickou analýzou, neboť integrují výsledné působení celé směsi přítomných polutantů a jejich funkční stav v půdě (biodostupnost), avšak zároveň přinášejí rizika vyšších nejistot z důvodů vysoké variability výsledků, vlivu dalších faktorů a nedostatku srovnávacích (referenčních) hodnot (Hofman et al. 2003; Sáňka et al. 2015; Sochová et al. 2006; Vašíčková et al. 2013).*

organismů. V případě, že empirická měření nejsou z nejrůznějších důvodů k dispozici, využívají se expoziční modely, které parametrizují příjem chemických kontaminantů prostřednictvím přímé expozice z abiotických medií (Holoubek 2003). Pro tyto potřeby se využívají screeningové predikční výpočty expozice, kdy do výpočtu samotného rizika vstupují hodnoty environmentálních koncentrací chemických látek a také parametry zvoleného expozičního scénáře pro vybrané expoziční cesty (U.S. EPA 2002; Čupr et al. 2013). Výstupním parametrem pro další hodnocení je nabídnutá dávka chemické látky, která zahrnuje informaci o množství a frekvenci příjmu, který lze dlouhodobě předpokládat. Finální kumulativní rizika pro zvolené polutanty jsou hodnocena jako suma dílčích rizik pro jednotlivé polutanty. Jak uvádí Čupr (2016), obecný model pro screeningové predikční výpočty expozice lze vyjádřit rovnicí:

$$CDI = \frac{C \ x \ IR \ x \ ET \ x \ EF \ x \ ED}{BW \ x \ AT} \qquad (-2-)$$

CDI – chronický denní příjem (obecně příjem) [např. v ng.kg^{-1}.den^{-1}]

C – koncentrace dané látky v expoziční matrici

IR – příjmová rychlost („Intake Rate“; například inhalace vzduchu v m^{3}.hod^{-1})

ET – doba expozice („Exposure Time“)

EF – frekvence expozice („Exposure Frequency“)

ED – trvání expozice („Exposure duration“) [rok]

BW – váha těla [kg]

AT – doba průměrování [den]

Jak ukazuje Čupr et al. (2010), lze tento obecný model modifikovat zahrnutím různých expozičních cest do výpočtu, zvolením cílového rizika pro karcinogenní a nekarcinogenní efekty a tvorbou místně specifických expozičních modelů. Toho bylo využito pro screeningové vyhodnocení rizik u nivních půd v záplavových oblastech a nastavení parametrů pro místní expoziční model s ohledem na charakter běžné expozice populace pohybující se na podobných typech lokalit (Sáňka et al. 2015).

Podobně jako u zdravotních rizik lze pro hodnocení ekologických rizik vyplývajících z přítomnosti chemických látek v prostředí využít poměru mezi skutečnou zátěží a na účincích založenými referenčními hodnotami. Jedním z častých způsobů pro odvození těchto hodnot je určení indikativní hranice možných ekosystémových rizik v půdách, které vyjadřují koncentraci polutantu, při níž lze očekávat v půdním prostředí potenciální ekotoxikologické účinky na některých trofických úrovních. Hodnoty se odvozují v ekotoxikologických studiích na základě hodnocení účinků pro daný vztah stresor-receptor a definováním nejzranitelnějších složek ekosystému pro danou látku (Lijzen et al. 2001; van Vlaardingen et al. 2007).

Základním cílem hodnocení zdravotních či ekologických (ekosystémových) rizik je nejen komplexní predikce a popis možných dopadů, ale také charakterizace profilu rizik na jednotlivých lokalitách. Výhodou screeningového odhadu rizik je právě možnost jednotlivé lokalitě přiřadit konkrétní expoziční parametry a vypočítat místně specifické hodnoty pro další hodnocení. Vlastní hodnocení profilu zátěže spočívá ve vyjádření podílu jednotlivých polutantů či skupin polutantů na kumulativní predikci rizika a následném hodnocení profilu rizika.

2.2.3 Geoprostorové metody vhodné pro regionalizaci znečištění půd

Důležitou vlastností všech pozorování půdních vlastností, včetně znečištění a z něho vyplývajících rizik, je vztah jednotlivých pozorování ke konkrétnímu místu a času, což formálně vyjadřuje následujíc vztah:

$$\{z_j(s_i, t): j = 1, \dots k; i = 1, \dots, n; t = 1, \dots, T\}, \qquad (-3-)$$

kde z_j vyjadřuje měření $j-t\acute{e}ho$ atributu z celkem k atributů v $i-t\acute{e}m$ bodě či areálu z celkem n sledovaných prostorových jednotek v době t z celkového počtu T sledování v čase (Haining, 2010). Využití prostorové informace tak umožňuje nejen exploraci variability cílové proměnné, ale při existenci prostorové autokorelační struktury dat (tj. funkční závislost výskytu určitého jevu v prostoru na výskytu tohoto jevu v nejbližším okolí) umožňuje také predikci v místech bez přímého pozorování. V současnosti lze sledovat posun od metod založených na modelování čistě prostorového vztahu cílové proměnné (např. interpolace inverzní vzdáleností či běžný kriging) směrem k zapojení dalších proměnných do explorace prostorové struktury a predikce pomocí kombinování informací odvozených z čistě prostorových vztahů s informacemi o statistické interferenci s dalšími proměnnými v atributovém prostoru dat. To souvisí také s extenzivním nárůstem dostupných kovariantních proměnných vlivem technologického rozvoje (McBratney et al. 2003; McKenzie & Ryan 1999). Výsledkem je adaptace klasického geostatistického přístupu v podobě regrese-krigingu (Odeh et al. 1995; Hengl et al. 2004; Lado et al. 2008) či lineárního přístupu na základě smíšených efektů (Lark 2000), ale také významné zapojení adaptivních metod odvozených z oblasti vytěžování dat. Hengl (2017) ukázal na datech o kontaminaci půd v nivě řeky Meuse výhody technik z oblasti strojového učení (metody založené na stromech a jejich varianty) při analýze nelineárních vztahů zapojením řady prediktorů včetně prostorové informace jako kovariantní proměnné a hovoří o očekávaném rozvoji těchto technik s ústupem geostatistických metod krigingu. Wälder et al. (2006) diskutují praktické aspekty využití různých geostatistických metod (běžný a vzájemný kriging, geostatistická simulace) pro sledování půdních vlastností záplavových zón kombinující analytická data a kovariantní proměnné (elevace terénu, vzdálenost od koryta, hloubka podzemní vody či biotop), přičemž výsledky porovnávají s expertními znalostmi z konvenčních mapování. Autoři upozorňují právě na vyhlazovací efekt některých geostatistických metod, který v případě mnohdy ostrých přechodů mezi biotopy a půdními vlastnostmi není žádoucí, což generuje potřebu dostatečné hustoty vzorkování či nasazení pokročilých postupů (vhodně nastavený model koregionalizace či simulační techniky), zatímco konvenční, expertní terénní průzkum půdy tyto přechody snadno odhalil.

Výhodou geostatistických modelů krigingu stále zůstává možnost kvantifikace nejistoty predikce (Goovaerts 1999), z tohoto pohledu jsou v oblasti znečištění půdy hojně využívány nelineární techniky, resp. lineární techniky krigingu na nelineárně transformovaných datech (Cressie 1993; Webster & Oliver 2009), kam patří zejména indikátorový kriging (Journel 1983) a jeho varianty (Juang & Lee 2000). Podstatou je tedy stanovení indikátorové funkce, která náhodnou funkci v daném místě transformuje na podkladě splnění podmínky (překročení prahové hodnoty), přičemž výsledky následného geostatistického odhadu krigingem jsou interpretovány jako podmíněná pravděpodobnost naplnění podmínky této funkce v místech, kde nebylo provedeno měření (Webster & Oliver 2009). Tento postup umožňuje řešit nesoulad v předpokladech modelově založených geostatistických technik (náhodná proměnná jako realizace z vícerozměrného normálního rozdělení – Marchant et al. 2011) se situací reálných environmentálních dat, která reprezentují ve většině případů více procesů a zachycují tedy více než jednu populaci (Limpert et al. 2001; Reimann & Filzmoser 2000). Zároveň tyto techniky umožňují snadné začlenění doplňkových informací do pravděpodobnostního odhadu (Brus et al. 2002; Goovaerts et al. 1997; Van Meirvenne & Goovaerts 2001) či modififikaci pomocí geostatistických simulací pro situace, kdy nás více zajímá detailní variabilita dat spíše než nejlepší odhad realizace náhodné funkce v daném místě, což mnohdy platí právě pro studium kontaminace půdy (Goovaerts 2000). Burrough a McDonell (1998) názorně demonstrují na datech kontaminace nivy řeky Meuse, jak lze podmíněné simulace využít v kombinaci s doplňkovými informacemi o pravděpodobnosti hodnot kontaminace v jednotlivých třídách četnosti záplav. Zhao et al. (2007) použili rozšířenou metodu indikátorového krigingu o geostatistické simulace za použití doplňkových proměnných k vymezení kontaminace půdy v silně industrializované deltě řeky Jang-c'-ťiang (Čína).

Další vývoj v oblasti geoprostorového hodnocení variability znečištění lze sledovat v posunu od analýzy prostorového vztahu jedné proměnné k využití vzájemných vztahů mezi proměnnými pro exploraci těchto vztahů či jejich využití pro predikci. Goovaerts a Webster (1994) či Webster et al. (1996) na příkladu rizikových prvků v půdách ukázali, že u řady prvků lze pozorovat tzv. koregionalizaci – tj. podobnosti v prostorové distribuci jednotlivých prvků. Toho využili pro pokročilé odhady jejich distribuce využitím vzájemného krigingu, a tím pro interpretaci různého původu prvků. Pro účely interpretace vztahů znečišťujících látek jsou hojně využívány vícerozměrné metody založené na redukci rozměrnosti dat a exploraci vícerozměrných vztahů (Facchinelli et al. 2001; Lucho-Constantino et al. 2005; Micó et al. 2006). Velmi efektivní z hlediska interpretačního potenciálu se ukazuje jejich spojení s geostatistickým odhadem prostorové distribuce. Jedním z přístupů je redukce dimenzionality dat a následná prostorová interpolace veličin vzniklých lineární kombinací vstupních dat (Borůvka et al. 2007; Šorša et al. 2018). Alternativou jsou potom metody, které využívají začlenění prostorové informace do vícerozměrné analýzy dat pomocí kvantifikace vztahů sousedství mezi jednotlivými pozorováními formou vážené prostorové matice ke vstupní matici pro analýzu hlavních komponent (Borcard & Legendre 2002; Dray et al. 2006), což na příkladu obsahů RP ve francouzských půdách ověřili Arrouays et al. (2011). Podobné je využití regionalizovaných vícerozměrných technik – zejména faktoriálního krigingu, který filtruje vztahy proměnných dekompozicí variability na různých prostorových měřítcích (Goovaerts 1992; Wackernagel 2003), což umožňuje sledovat podobnost či rozdíly měřítkově závislých vzorců prostorové variability jednotlivých prvků či skupin prvků, a tím např. rozlišit přirozené a antropogenní vstupy (Bourennane et al. 2003; Lin et al. 2002; Nanos & Rodríguez Martín 2012). Zhou et al. (2016) pak využitím faktoriálního krigingu sledovali měřítkově podmíněné rozdíly obsahu RP v půdách s různým využitím pod vlivem různých zdrojů znečištění v deltě řeky Jang-c'-ťiang.

Při aplikaci vícerozměrných statistických postupů založených na korelačních/kovariančních vztazích je třeba zohlednit fakt, že většina environmentálních dat má zároveň kompoziční charakter – tj. měření ve váhových či množstevních podílech (mg/kg, ppm, podíl dílčích polutantů na celkovém riziku) je vždy vyjádřením dat jako části celku, a tím jsou omezeny konstantním součtem (sumou všech částí). To znamená, že statistická interpretace naměřených koncentrací je smysluplná pouze v případě, že jsou brány v úvahu vztahy ke zbývajícím proměnným (Aitchison 1982). Statistické řešení tohoto problému označovaného pod různými termíny (problém konstantního součtu či uzavření dat) je hledáno od doby, kdy K. Pearson v roce 1897 upozornil na problematiku nahodilých korelací (*„spurious correlation“*) při použití podílových dat (Sarmanov & Vistelius 1959; Chayes 1960). Statistické řešení přinesla práce Aitchisona (1982), který navrhl a formálně definoval statistický koncept pro analýzu kompozičních dat.

Každou D-složkovou kompozici je tedy možné vyjádřit jako uzavřený vektor:

$$C[z_1, z_2, \dots, z_D] = \left[\frac{\kappa \cdot z_1.}{\sum_{i=1}^{D} z_i}, \frac{\kappa \cdot z_2.}{\sum_{i=1}^{D} z_i}, \dots, \frac{\kappa \cdot z_D.}{\sum_{i=1}^{D} z_i}\right], \qquad (-4-)$$

kde C je tzv. uzávěr ke konstantě κ (Aitchison 1986). Z toho plyne, že kompoziční data lze reprezentovat v omezeném prostoru (tzv. simplexu) – tj. ve výběrovém prostoru dat s konstantním součtem, kdy jednotlivé složky kompozice nabývají kladných hodnot mezi nulou a danou konstantou, což lze formálně vyjádřit vztahem:

$$S^D = \{(z_1, z_2, \dots, z_D) \,:\, z_1 > 0, z_2 > 0, \dots, z_D > 0;\ z_1 + z_2 + \dots + z_D = \kappa\} \qquad (-5-)$$

Hlavním motivem statistického konceptu simplexu bylo vytvoření podmínek ke statistické analýze kompozičních dat, neboť při aplikaci standardních metod (založených na vlastnostech euklidovské geometrie) na neupravená kompoziční data nelze zaručit, že výsledky nejsou artefaktem uzavření dat do konstantního součtu vlivem jejich relativního charakteru (McKinley et al. 2016). Prvotním řešením bylo využití relativní informace v kompozičních datech odvozením poměrů jednotlivých komponent, což vedlo k navržení tzv. log-poměrových transformací, zobrazujících kompozice z S^D do (D-1)-rozměrného reálného prostoru (R^{D-1}), tj. opuštění výběrového prostoru simplexu (Aitchison 1982; 1986; Egozcue et al. 2003). Detailní pochopení problematiky kompozičních dat přineslo definování vztahu mezi reálným výběrovým prostorem a omezeným výběrovým prostorem simplexu, což umožňuje přechod ze simplexu do kartézské soustavy souřadnic. Euklidovská struktura výběrového prostoru simplexu se označuje pojmem Aitchisonova geometrie (Pawlowsky-Glahn & Egozcue 2001) a vedla k definování Aitchisonovy vzdálenosti, která má řadu vhodných vlastností pro následnou statistickou analýzu kompozičních dat. Formálně se jedná o upravenou euklidovskou vzdálenost pro všechny přípustné kombinace logaritmů podílů složek kompozic *x* a *y* (Aitchison et al. 2000).

$$d_a\,(x,y) = \sqrt{\frac{1}{2D}\sum_{i=1}^{D}\sum_{j=1}^{D}\left(\ln\frac{x_i}{x_j} - \ln\frac{y_i}{y_j}\right)^2} \qquad (-6-)$$

Rozvoj metodické základny vedl k úpravám a aplikaci vícerozměrných metod pro potřeby kompoziční analýzy dat. Filzmoser et al. (2010) či Filzmoser a Hron (2009) ukázali možnosti analýzy dvourozměrných vztahů kompozičních geochemických proměnných na upravených datech ze sledování obsahu RP v mechorostech a půdních horizontech lesních půd poloostrova Kola (Rusko). Stejný datový soubor byl využit pro ověření robustních metod vícerozměrné analýzy pomocí analýzy hlavních komponent, faktorové analýzy (Filzmoser et al. 2009a; 2009b), shlukové analýzy (Templ et al. 2008) či regresního řešení pro vysvětlovanou proměnnou s kompozičním charakterem (Egozcue et al. 2011). Tolosana-Delgado a McKinley (2016) využili robustní kompoziční analýzu hlavních komponent pro interpretaci geochemických vazeb RP a makroprvků v půdách Severního Irska, kde sledovali projevy různých geologických formací na kompoziční strukturu dat. Buccianti et al. (2015) pak použili komplexní kompoziční analýzu půdních dat s obsahy RP pro stanovení geochemického pozadí a anomálií v litologicky pestrém území. Reimann et al. (2012) pak demonstrovali možnosti využití kompoziční analýzy na půdních datech z celoevropského geochemického mapování v rámci programu geochemického mapování zemědělských půd GEMAS. Problematické části geochemických databází (nulové hodnoty, hodnoty pod detekčním limitem) je možno v současnosti řešit pomocí vhodných metod imputace hodnot (Martin-Fernández et al. 2011).

Metodická základna v oblasti statistických a geostatistických metod je v současnosti velmi široká a výběr vhodné analýzy je možné přizpůsobit výzkumným otázkám (predikce vs. explorace), avšak při korektním dodržení předpokladů a zohlednění omezení těchto metod.

3 Vědecké hypotézy a cíle práce

Pro hodnocení variability rizik vyplývajících z kontaminace nivních oblastí byly stanoveny následující hypotézy:

1) Znečištění půd v záplavových oblastech vykazuje významnou prostorovou variabilitu v závislosti na existenci zdrojů znečištění. Předpokládáme, že existence jedinečných zdrojů znečištění a jejich prostorové rozmístění podél vodního toku má vliv nejen na celkovou míru znečištění, ale také na kompoziční charakter znečištění (tj. vztahy mezi jednotlivými znečišťujícími látkami v dílčích částech niv).
2) Existuje variabilita v rizicích vyplývajících z kontaminace půd mezi jednotlivými vodními toky a jejich částmi, přičemž tato variabilita je výsledkem různých procesů (atmosférické vstupy, redistribuce znečištění, bodové zdroje, difúzní zdroje, geochemicky anomální půdy).
3) Při významném využití nivních půd pro zemědělskou produkci existují relativně nízká, avšak nezanedbatelná rizika přestupu rizikových látek do zemědělské produkce. Rizika tohoto transferu mohou být v nivních oblastech zvýšená z důvodu vyšší mobility, či dostupnosti rizikových látek, dynamiky půdních vlastností a zároveň v souvislosti s pěstováním citlivé zemědělské produkce pro přímý konzum.

V souvislosti s výše uvedenými hypotézami byly stanoveny následující cíle:

1) Jedním z hlavních cílů práce je pomocí vhodných metod sledovat gradient znečištění v závislosti na existenci a typech zdrojů v povodích (zvýšené litogenní obsahy v povodí, metalogenní ložiska, průmyslové zdroje, urbanizované oblasti, zemědělství), a tím ověřit míru ovlivnění zdrojem. Kromě vlivu jednotlivých zdrojů znečištění na celkovou magnitudu bude sledován kompoziční charakter jak parametrů znečištění, tak rizik vyplývajících z tohoto znečištění toxikologicky významnými látkami.
2) Zhodnotit regionální rozdíly mezi ekosystémovými a zdravotními riziky kontaminace půd, definovat prioritní toxikologicky významné látky v jednotlivých povodích a jejich částech a na základě výsledků nabídnout referenční hodnoty pro hodnocení rizik.
3) Posoudit míru přestupu do zemědělských plodin u vybraných polutantů, které jsou toxikologicky významné a zároveň byl prokázán jejich významný příspěvek do celkového odhadu ekosystémových a zdravotních rizik v nivních oblastech ČR v experimentálních podmínkách.

4 Publikované práce

4.1 Skála et al. (2017): Prostorová diferenciace ekosystémových rizik kontaminace v nivních oblastech České republiky

Název: Spatial differentiation of ecosystem risks of soil pollution in floodplain areas of the Czech Republic.

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Spatial Differentiation of Ecosystem Risks of Soil Pollution in Floodplain Areas of the Czech Republic

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Abstract

Skála J., Vácha R., Hofman J., Horváthová V., Sáňka M., Čechmánková J. (2017): Spatial differentiation of ecosystem risks of soil pollution in floodplain areas of the Czech Republic. Soil & Water Res., 12: 1–9.

Extensive soil sampling and screening assessment of ecosystem risks combined with a multidimensional statistical analysis were used to estimate and spatially characterize the ecosystem risks stemming from the contamination of floodplain soils in the Czech Republic. We proved structural differences in regional pollution patterns where different regional/local pollution sources led to various nature and extent of the environmental load of floodplain soils. The established spatial patterns helped reveal the areas where soils do not meet soil quality standards and where the ecosystem risks were elevated. Furthermore, the results allowed to establish priority contaminants of flood affected areas in various catchments in the Czech Republic. Combining both the magnitudes of estimated ecosystem risks and structural characteristics of pollution profiles, the highest estimated risks showed the localities with high contents of organochlorine pesticides, several samples connected to geochemical anomalies of metallogenic zones (deposits), and localities with a long history of industrial load. Since extreme weather events have recently become more frequent, our results highlight the importance of a continual monitoring of pollutant turnover in floodplain soils with a high flood frequency.

Keywords: floods; persistent organic pollutants; soil contamination; spatial patterns; trace elements

In recent years, extreme weather events have become still more frequent and intense (BENISTON & STEPHENSON 2004). As for the Czech Republic, intensive floods caused significant damages in last two decades. A high and long term anthropogenic alteration of floodplains in the consequence of a high population density (TOCKNER & STANDFORD 2002) resulted in enhanced anthropogenic pressures on fluvial ecosystem. Although the quality of surface waters in Czech rivers underwent significant changes during the 1990s due to a decline in industrial and agricultural activity associated with political changes (LANGHAMMER *et al.* 2010), increased concentrations of various pollutants can still be found in alluvial soils in Central Europe (PODLEŠÁKOVÁ *et al.* 1994; STACHEL *et al.* 2003). As for the floodplains in the Czech Republic, soil contamination in the alluvial zones of the sites strongly affected by mining and metallurgy has been studied (BORŮVKA *et al.* 1996; ETTLER *et al.* 2006; ŽÁK *et al.* 2009). Regional studies attempted to describe the contamination situation in the Elbe catchment (PODLEŠÁKOVÁ *et al.* 1994; HEINISCH *et al.* 2007) or in the Morava River basin (GRYGAR *et al.* 2012; NOVÁKOVÁ *et al.* 2013) and especially the flood impacts on soil contamination in case studies (VÁCHA *et al.* 2003; ELHOTTOVÁ *et al.* 2006; HILSCHEROVÁ *et al.* 2007; PULKRABOVÁ *el al.* 2008). Since our knowledge regarding magnitudes and pollution profiles of floodplain contamination in the Czech Republic is still fragmentary, a rigorous analysis of soil contamination was conducted by an extensive soil sampling and screening assessment of ecosystem risks combined with a multidimensional statistical analysis. The study has provided

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a comprehensive spatial analysis of ecosystem risks of soil contamination in cultivated floodplains in the Czech Republic with the objectives of revealing both the spatial patterns of pollution magnitude as well as the composition of pollutants.

MATERIAL AND METHODS

Soil sampling. Since we endeavoured to characterize pollution profiles of fertile soils and potential ecological threats in cultivated floodplains, the sampling sites (n = 100) were preferably located in the areas where a high flood frequency has met a high agriculture intensity. An extensive spatial analysis of land use and soil diversity in Czech floodplains (Skála *et al.* 2013) had forgone field work so that the target sampling areas could be established using a spatial overlap of the 5-year flood inundation areas from the DIBAVOD geo-database (Digital database of water management data) and agricultural areas from the digital Land Parcel Identification System (LPIS). For each sampling site, a set of 10 individual probes was collected from an area of 1 ha using handheld auger (samples were homogenized by quartation). The sample depth was 0–10 cm for pastures and 0–30 cm for arable land. The soil samples were analyzed for a wide range of pollutants (Table 1) and basic soil properties (e.g. total organic carbon, soil texture characteristics).

Laboratory analysis. Analyses for trace elements (TEs) and soil properties were performed in the Research Institute for Soil and Water Conservation, Prague. Trace elements were determined using the aqua regia digestion (ISO 11466 1995) followed by atomic absorption spectrometry in flame (VARIAN FAAS 240; Agilent Technologies, Inc., Mulgrave, Australia – Cu, Ni, Pb, Zn), atomic absorption spectrometry with electrothermal atomization (VARIAN ETA 240Z; Varian, Mulgrave, Australia – Cd) and hydride generation mode (As). The total Hg content was assessed using the AMA method (AMA254). The analytical results underwent rigorous quality assurance procedures – analytical replicates with a relative standard deviation tolerance lower than 5%, the sample spiking and certified reference materials analyses (RM 7001, 7003). Chemical measurements for persistent organic pollutants (POPs) were performed in the Laboratory of trace analyses in the Research Centre for Toxic Compounds in the Environment, Brno. Contents of POPs were determined by gas chromatography–mass spectrometry (GC-MS) (an Agilent 7890 GC coupled to an Agilent 7000B Series Triple Quadrupole GC/MS System; Agilent Technologies Inc., Wilmington, USA) after dichloromethane extraction of samples spiked with recovery standards and clean up. Certified reference materials (Cambridge Isotope Labs soil standard RM-0002) and laboratory blanks were analyzed with each set of POPs samples.

Estimation of ecosystem risks. A screening risk assessment of soil contamination was accomplished using the Dutch method from the National Institute for Public Health and the Environment (Lijzen *et al.*

Table 1. List of pollutants determined in soil samples and their serious risk concentration (SRC) values

Pollutant	SRC (mg/kg)
Trace elements	
As	85
Cd	13
Cu	96
Hg	36
Ni	100
Pb	580
Zn	350
Organochlorines	
ΣPCBs (7)	3.4
PeCB	16
HCB	2.0
α-HCH	17
β-HCH	13
Lindane	1.2
o,p'-DDE, p,p'-DDE	1.3
o,p'-DDD, p,p'-DDD	34
o,p'-DDT, p,p'DDT	1.0
Polycyclic aromatic hydrocarbons	
Naphthalene	17
Phenanthrene	31
Anthracene	1.6
Fluoranthene	260
Benzo(a)anthracene	2.5
Chrysene	35
Benzo(k)fluoranthene	38
Benzo(a)pyrene	7.0
Indeno(123-cd)pyrene	1.9
Benzo(ghi)perylene	33

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2001; Van Vlaardingen *et al.* 2007) . The method is based on the estimation of potential ecological risks by a confrontation of environmental concentrations (PEC) with referenced values for potential ecosystem risks of soil contamination (serious risk concentration – SRC) (Eq.1). The SRC values (Table 1) are simultaneously derived using all reliable toxicity data reflecting both acute and chronic toxicity for species representing different trophic levels as well as using data for microbial processes and enzymatic reactions, where the final choice is most frequently the lowest value representing the most sensitive ecological response (RIVM 2007). The SRC values provide the effect base level where some ecotoxicological effects may be expected.

$$\mathrm{RISK}_{\mathrm{ECO}} = \frac{\mathrm{PEC}_i}{\mathrm{SRC}_i} \qquad (1)$$

A resultant ecological hazard index for *n* pollutants at each locality ($\mathrm{HI}_{\mathrm{ECO}}$ in Eq. (2)) is then calculated as a sum of quotients calculated for each *i* pollutant in Eq. (1) and poses an estimation of potential ecosystem risks (ERs).

$$\mathrm{HI}_{\mathrm{ECO}} = \Sigma_{i=1}^{n}\mathrm{RISK}_{\mathrm{ECO}} \qquad (2)$$

In the last step (Eq. (3)), we calculated relative contributions of each element/substance to the overall hazard index ($\mathrm{HI}_{\mathrm{ECO}}$).

$$p_{i_{\mathrm{RISK_{ECO}}}} = \frac{\mathrm{RISK}_{\mathrm{ECO}i}}{\mathrm{HI}_{\mathrm{ECO}}} \qquad (3)$$

Regionalization of ecosystem risks. Regional patterns of ERs were assessed by a hierarchical cluster analysis (HCA) using an average linkage clustering. A matrix transformation of relative contributions of each analyte to total $\mathrm{HI}_{\mathrm{ECO}}$ in each sample was performed prior to the HCA. The dataset was transformed by a range transformation after the matrix had been constant-row-sum normalized to generate homogeneity of variance among all variables according to Miesch (1976). The constant-row-sum transformation can reduce the influence of samples with high proportions, while the range transformation reduces the influence of determinants with a high variability. An optimal number of clusters was determined by the Mantel test as an algebraic equivalent of the Pearson's correlation between the values in the original distance matrix and binary matrices computed from the dendrogram cut at various levels (Legendre & Legendre 1998). The Kruskal-Wallis test was used to verify significant differences in pollutant concentrations by the cluster grouping. All the processes were performed using R programme (R Core Team 2012). The results were spatially visualized using ArcGIS 10.2 (ESRI, Redlands, USA).

RESULTS AND DISCUSSION

Regional patterns of soil pollution profiles. Cluster analysis was processed to verify whether soil pollution composition tends to form regional patterns in the dataset. The HCA results proved a satisfactory cophenetic correlation coefficient ($r = 0.8$) with the optimal number of 9 clusters (dendrogram in Figure 1). Basic statistics for main pollutants (Table 2) and average relative contributions of pollutants to total estimations of ERs (Figure 2) were calculated after the dataset partitioning in the HCA.

The most substantial cluster was formed of localities characterized by high contributions of TEs (Ni ~ Zn > Hg ~ Cd ~As) together with elevated contributions of industrial POPs (PCBs, HCB). Lower contributions of pesticides (especially lindane) and individual PAHs were also characteristic for this cluster. The cluster constituents reached lower or average magnitudes of estimated ERs (Figure 4). Searching for a spatial scatter of the cluster, it can be concluded that member localities can be found in all major Czech river systems (Figure 3). Cluster 1 can be considered as a characteristic profile of an overall fluvial pollution in the dataset.

Cluster 2 can be characterized by high contributions of PAHs compounds to estimated ERs. The increased PAHs contents were evident in fluvial systems of the broader North Moravian region (in the Odra and Bečva River basins). In North Moravia, manifold anthropogenic pollution sources (coal processing, metallurgy) have generated higher Cd and PAHs contamination of agricultural soils (Vácha *et al.* 2015). The elevated PAHs contents were also recorded along the Jizera River past the industrial centre of Mladá Boleslav. Impacts of local industrial enterprises in the Jizera floodplain were proved in a complex geochemical study of TEs enrichment in the floodplain sedimentary fill by Grygar *et al.* (2013). High PAHs contributions together with above-average values of $\mathrm{HI}_{\mathrm{ECO}}$ were surprisingly found in the upper courses of the Elbe and the Morava Rivers. This could only be explained by a high propensity of PAHs to atmospheric transport that may result in high concentrations of

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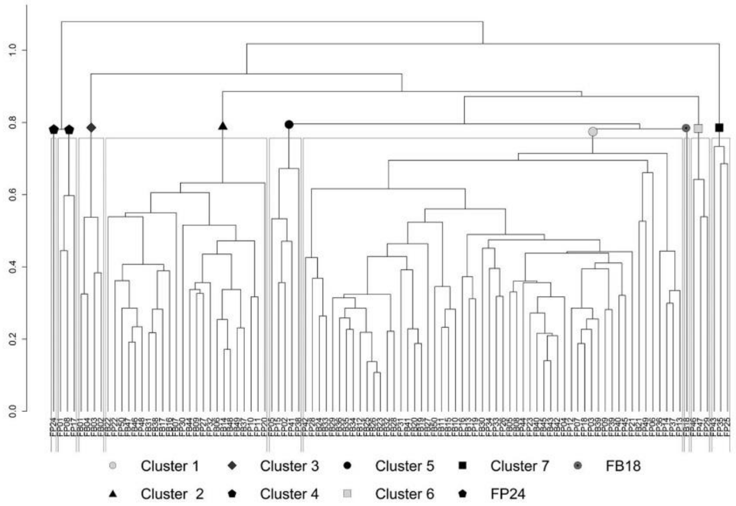

Figure 1. Dendrogram characterizing the partitioning of sampling localities according to relative contributions of pollutants to estimation of ecosystem risks (ERs)

airborne POPs in remote and unpolluted freshwater ecosystems (Grimalt *et al.* 2004).

Cluster 3 involved a toposequence of 4 soil samples near the confluence of the Morava and the Dřevnice Rivers. There was a series of higher concentrations of organochlorine pesticides (especially HCHs and PeCB) in this region (Figure 2a). Studying POPs dynamics in the dissolved phase in the water column of the Morava and the Dřevnice Rivers, Prokeš *et al.* (2012) found the highest concentrations of organochlorine hydrocarbons (especially PCBs, HCHs) at the Dřevnice sampling site.

There were higher contributions of organochlorine pesticides (DDT and its metabolites) to estimated

Table 2. Medians for main pollutants after the data partitioning in hierarchical cluster analysis (HCA) and the results of Kruskal-Wallis (K-W) test for significant differences on pollutant concentrations by the cluster grouping

Sample (n)	ΣPCB	PeCB	HCB	ΣHCH	ΣDDX	ΣPAHs	As	Cd	Cu	Hg	Ni	Pb	Zn
	(μg/kg)						(mg/kg)						
Dataset (100)	1.32	0.12	1.21	1.58	9.7	362	8.8	0.38	24.3	0.11	25.6	23.7	96.6
Cluster 1 (56)	1.21	0.12	1.21	1.58	9.2	249	8.5	0.31	23.2	0.11	25.7	22.1	94.0
Cluster 2 (24)	2.47	0.13	1.27	1.64	3.8	1 748	8.2	0.40	24.8	0.11	25.1	23.4	93.4
Cluster 3 (4)	1.59	1.52	2.26	29.50	10.1	755	8.5	0.34	18.8	0.07	28.2	17.9	67.9
Cluster 4 (3)	1.72	0.14	0.60	2.94	715	404	12.7	0.95	37.5	0.13	27.2	40.1	128
Cluster 5 (5)	1.12	0.10	1.48	1.48	72.0	262	16.3	1.50	106	0.12	25.8	47.6	188
Cluster 6 (3)	1.16	0.07	2.47	1.71	8.3	400	9.8	0.55	35.5	0.25	23.7	516	180
Cluster 7 (3)	1.13	0.04	0.96	1.58	14.5	151	35.4	0.23	19.5	0.08	20.1	16.2	76.1
FB18	0.70	0.10	1.12	0.82	157	147	9.0	0.29	20.2	0.07	69.9	16.5	79.6
FP24	3.16	0.16	0.92	1.26	3 419	434	3.0	0.74	28.8	0.15	24.9	45.9	136
K-W test	–	*	–	*	**	***	**	**	**	–	–	**	*

– not significant; *, **, ***α = 0.05, 0.01 and 0.001, respectively

ERs characteristic for Cluster 4. The cluster was spatially confined to the catchment of the Berounka River and to the lower reach of the Ohře River near the confluence with the Elbe River. Enhanced Cd and Cu contributions to ERs estimation followed the organochlorine pesticides dominance in this cluster. Pollution patterns observed in the cluster may refer to a prevalence of agricultural activity in those areas.

Cluster 5 can be characterized as a complex pollution profile where various pollutants contributed to estimated ERs and involved most of the sampling sites along the Ohře River. High TEs contributions (especially of Cd, As, Cu) may be attributed to a spatial interaction of various pollution sources in the North Bohemian region (long-term airborne pollution due to combustion of fossil fuel and chemical industry, geochemical anomalies of metallogenic zones) (Vácha *et al.* 2015). Higher TEs contents are accompanied by higher contents of various POPs of industrial as well as agricultural origin (HCB, HCHs, DDT, and metabolites). Similar ecosystem contamination caused by anthropogenic sources was reported by Kohušová *et al.* (2011) in the adjacent watershed of the Bílina River.

In Cluster 6, dominant Pb and Zn contributions to estimated ERs were reported and there prevailed localities with soils contaminated by mining- and smelting-related pollutants in historical Pb-Zn-Ag mining districts of the Příbram and Stříbro deposits. The previous studies showed a strong effect of the metal works on the sediment contamination from

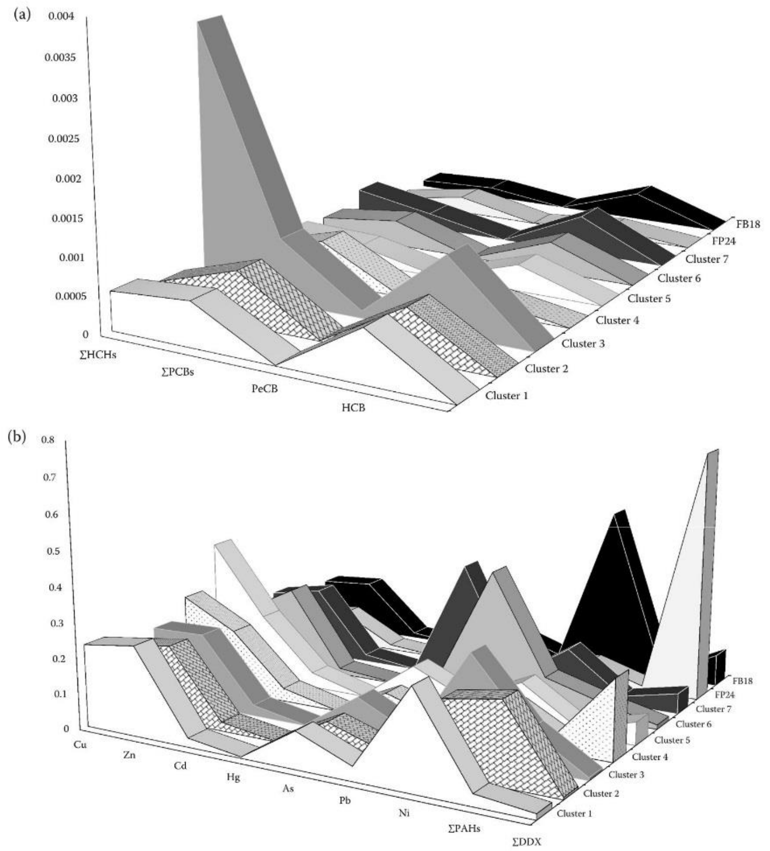

Figure 2. Average relative contribution of individual pollutants (groups) to the total estimation of ecosystem risks (ERs) for individual clusters: (a), (b) – major and minor pollutant groups, respectively

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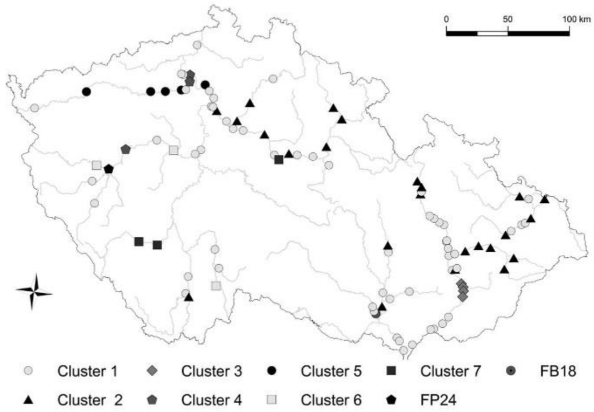

Figure 3. Spatial regionalization of the cluster analysis results

the Litavka stream (Borůvka *et al.* 1996; Ettler *et al.* 2006; Žák *et al.* 2009) as well as on the overall contamination of flood sediments of the Berounka River past the Litavka stream inflow (Navrátil *et al.* 2008). The enhanced Pb concentration was also recorded in the sample from a wet meadow in a foreland of the Rožmberk fishpond. The high Pb content trapped by the fluvic Gleysol may correspond to organic matter binding (C_{org} = 8.5) and might be connected with the regional lead glassworks (Veselý 1994). Further work incorporating broader analysis with a more detailed sampling programme would be needed to verify the lead origin.

Cluster 7 involved 3 samples that are featured by high contributions of As to estimated ERs. One sample was located in a floodplain of the Klejnárka stream draining the Kutná Hora ore region renowned for its high contamination by TEs (especially As, Zn) (Horák & Hejcman 2013). The predominant As contribution to estimated ERs was accompanied by elevated contributions of Cu and Zn in the sample. Other two samples were derived from the floodplains of the Otava River where the higher As contributions reflected the influence of the geological situation as well as an abundance of gold deposits with a high accessory As content (Fillipi *et al.* 2004; Skála *et al.* 2011).

There were reported two singular localities in the dendrogram cut at the optimum level. The first locality (No. FB18) may be considered as an outstanding branch of Cluster 1 (the dendrogram in Figure 1). A

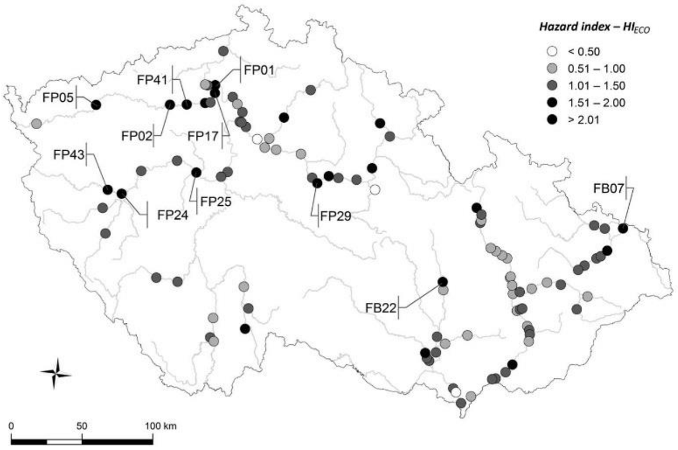

Figure 4. Spatial differentiation of ecological hazard index (HI_{ECO}) magnitude (ecosystem risks estimation) and regional hot spots (HI_{ECO} > 2.0)

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Table 3. Priority pollutants for samples with topmost estimation of ecosystem risks ($HI_{ECO} > 2.0$) – their concentrations and relative contribution to HI_{ECO}

Sample	Cluster	HI_{ECO}	Priority pollutants (relative contribution) [measured concentration; mg/kg] 1	2	3
FB22	2	3.3	ΣPAHs (0.66) [14.6]	Cu (0.12) [36.9]	Ni(0.10) [33.2]
FB07	2	2.5	ΣPAHs (0.40) [7.3]	Zn (0.23) [209]	Cu(0.13) [31.6]
FP17	4	2.6	Cu (0.42) [104]	ΣDDX (0.24) [0.72]	Zn (0.14) [128]
FP01	4	2.5	ΣDDX (0.28) [0.82]	Zn (0.20) [177]	Cu (0.15) [37.5]
FP05	5	3.0	Cu (0.55) [157]	Zn (0.18) [188]	Ni (0.08) [23.7]
FP02	5	2.7	Cu (0.40) [106]	Zn (0.22) [208]	As (0.14) [33.6]
FP41	5	3.5	Cu (0.34) [116]	Zn (0.16) [201]	ΣDDX (0.15) [0.59]
FP43	6	3.5	Zn (0.36) [438]	Pb (0.33) [680]	Cu (0.11) [35.5]
FP25	6	2.5	Pb (0.35) [516]	Zn (0.20) [180]	Cu (0.19) [44.9]
FP29	7	2.6	As (0.37) [82.9]	Zn (0.27) [246]	Cu (0.18) [45.8]
FP24	–	4.1	ΣDDX (0.72) [3.4]	Zn (0.10) [136]	Cu (0.07) [28.8]

strong influence of high Ni content and DDTs content and low contributions of industrial pollutants (PCB, HCB, PAHs) distinguished it from Cluster 1 (Figure 2a). The higher Ni content may be associated with its geochemical position in regional ultrabasic rocks (Quantin *et al.* 2008). Similarly, the singular locality FP24 is spatially as well as structurally connected to Cluster 5 because an exceptional predominance of DDT and its metabolites was proved in this sample from the Berounka River.

Regional differentiation of the estimated ecological hazard index. Since magnitudes of the ecological hazard index were calculated (Eq. (2)) and cartographically represented (Figure 4) for all sampling sites, regional hot spots of potential ecological impacts of complex soil pollution can be determined. Higher values of estimated HI_{ECO} were proved for the samples collected along the Ohře River (especially at its lower course). An increase of HI_{ECO} was recorded for the Elbe River past the Pardubice centre and floodplains adjacent to the Neratovice site confirming spatial pollution patterns in various environmental compartments of the Elbe River basin reported by Podlešáková *et al.* (1994), Heinisch *et al.* (2007), Randák *et al.* (2009), and Kolaříková *et al.* (2012). Higher magnitudes of HI_{ECO} were recorded for the whole length of the Berounka River with its increase in a consequence of some hot spots (the Litavka stream inflow or Ag-Pb-Zn deposit in Stříbro). Similarly, the elevated HI_{ECO} followed the Odra River with a regional increase near the Ostrava agglomeration. Several local contamination abnormalities were detected in a consequence of spatially confined pollution sources (Kutná Hora deposit, industrial centre of Mladá Boleslav or the Svitava River near Boskovice).

Relative pollution profiles for the localities with elevated values of hazard index ($HI_{ECO} > 2.0$) are reported in Table 3. When combining both the magnitudes of estimated ERs and constituent compositions of pollution profiles, 11 samples (from 6 clusters) are to be explained. Three samples (FP01, FP17, FP24) can be characterized by high contributions of organochlorine pesticides (especially DDT and its metabolites) to total ERs. A high dominance of some TEs (As, Cd, Pb, Zn) featured several samples which are spatially associated with geochemical anomalies of metallogenic zones and deposits (FP24, FP29, FP43). A pair of samples (FB07, FB22) with priority pollutants from PAHs group also exhibited elevated $HI_{ECO.}$ Last but not least, the samples from the Ohře catchment with a more complex anthropogenic load (As, Cu, Cd, Zn, HCB, DDT) reached an upper limit of HI_{ECO} variability.

CONCLUSION

The general pollution profile of flood affected areas in the Czech Republic and several regional pollution abnormalities with different pollution characteristics were defined. Regional hot spots of the potential ecosystem impacts of complex soil pollution were estimated using the screening risk assessment of soil contamination. When combining both the magnitudes of estimated ERs and structural characteristics of pollution profiles, the highest estimated ERs were associated with several localities characterized by enhanced contents of organochlorine pesticides, samples connected to geochemical anomalies of metallogenic zones (deposits), and samples with a higher anthropogenic load (airborne PAHs and TEs contamination). This suggests that the soil contamination (magnitude, pollutant associations) of Czech floodplain soils followed the character of local pollution sources (geochemical anomalies) as well as regional diffuse contamination sources (organochlorine pesticides, PAHs). The screening risk assessment of sample contamination estimated only potential ecotoxicological effects for the most vulnerable trophic levels for particular pollutants. A high probability of ecological impacts of soil pollution may be expected at several sampling sites however full consequences and details of ecotoxicological effects are beyond the scope of this paper. Obviously there is a need for the present results coupling with our consecutive results of ecotoxicity testing using various bioassays similarly to Vašíčková *et al.* (2013).

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4.2 Skála et al. (2018): Které sloučeniny nejvíce přispívají ke zvýšené kontaminaci nivních půd a s tím souvisejícím zdravotním rizikům v pramenných oblastech středoevropského povodí?

Název: Which compounds contribute most to elevated soil pollution and the corresponding health risks in floodplains in the headwater areas of the Central European Watershed?

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Article

Which Compounds Contribute Most to Elevated Soil Pollution and the Corresponding Health Risks in Floodplains in the Headwater Areas of the Central European Watershed?

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Abstract: The main topic of this study is a human health risk assessment of a defined exposure scenario in the floodplain soils of the headwater areas of the central European watershed, with the aim of exploring both multivariate and regional data structures. Flood-prone areas are recognized worldwide to be susceptible to contamination and its redistribution. Contributions of various classes of toxic compounds (organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs)) to human health risks were assessed in a screening risk assessment. However, due to the relative nature of our data and a high PAH dominancy over the data ensemble, reliance solely on the standard statistical processing of raw data might lead to incomplete insight into the structure of the multivariate data. Explanatory analysis of the data structure using the compositional approach was found to be beneficial to elucidating human health risk profiles and provided robust evidence that a contrast between agricultural and airborne industrial pollution controlled the whole human toxicological variation of persistent organic pollutants (POPs) in floodplain soils. These results were effectively quantified with the subcomposition of benzo(*a*)pyrene, DDT, and alpha-hexachlorocyclohexane (aHCH), allowing for an interpretation of structural differences in regional pollution patterns, which conferred different extents and compositions of human health risks in floodplain soils.

Keywords: soil pollution; floodplain; human health risk; compositional data

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1. Introduction

The contamination of the environment by hazardous substances such as persistent organic pollutants (POPs) is a worldwide public health concern. POPs show serious toxic effects on humans as well as wildlife in very low concentrations [1]. One of the matrixes that acts as an effective sink of these toxic chemicals is soil [1,2]. Whilst floodplain soils are renowned for their fertility, attributed to nutrient inputs, the same enrichment process renders these soils susceptible to contamination by various pollutants [3]. They are subject to further redistribution and transformation processes, which are a matter of great importance in floodplain soils [4]. Although the rivers in the Czech Republic underwent significant changes in the quality of surface waters during the 1990s due to a decline in industrial and agricultural activity associated with political changes [5], increased concentrations of various pollutants in alluvial soils in Central Europe can still be found [6–8]. The Czech Republic, as a typical Central European country, is located in the European Watershed area; hence, several European great rivers have their headwaters located there. Since ongoing climatic changes may increase the risk of extensive floods in Europe [9], both the health and environmental consequences of the old burdens as well as of emerging pollution should be monitored and controlled in the floodplains. Humans are a sensitive target of POP bioaccumulation and its associated adverse effects [10]. Also, potential transfer to the human body may occur through different pathways of direct exposure [11–13] or dietary exposure [14].

Since our knowledge of POP pollution profiles in floodplain soils in the Czech Republic is still fragmentary and there are many data gaps regarding nondietary exposure pathways, extensive soil sampling combined with a screening assessment of human health risks was conducted. To assess the health risks connected to the presence of POPs in floodplain soils, we proceeded as follows. In the first step, a countrywide inventory of floodplain soils was performed with a focus on the properties and contamination levels of cultivated soils. As a second step, an established model [15] was adapted to field data for evaluation and interpretation of exposure to toxicologically important organic chemicals. Contributions of various classes of toxic compounds (PCBs, organochlorine pesticides (OCPs), PAHs) to total human health risks were then assessed using the main principles of statistical analysis for compositional data in this study.

2. Materials and Methods

2.1. Sampling and Data Acquisition

The target areas for soil sampling were selected using a geographic information system (GIS)-based approach, bringing together nationwide digital data on soil distribution, land use, and hydrological floods in the Czech Republic. The soils were preferentially sampled in those areas vulnerable to inundation (the five-year floodplains) where the risk of extensive inundations met a high cropland extent. For each sampling site (n = 100), a mixed sample consisting of 10 individual probes with depths of 0–30 cm was collected between 2010 and 2015. The basic soil properties (e.g., total organic carbon, soil texture characteristics) were also determined.

2.2. Laboratory Analysis

Chemical measurements for POPs (PAHs, PCBs, OCPs) were performed in the accredited laboratory of in the Trace Analysis Laboratories in the Research Center for Toxic Compounds in the Environment. All soil samples (10 g) were spiked with a 50 μL solution of perdeuterated PAHs and extracted using automated Soxhlet extraction for 40 min with dichloromethane in a Büchi extraction unit (Büchi, Uster, Switzerland). The extract was divided into a ratio of 1:9 for PAHs and PCBs + OCPs. For PAH analysis, the volume was reduced under a gentle nitrogen stream at ambient temperature and further covered by silica purified using Soxhlet for 8 h with dichloromethane. The fractionation achieved on a silica gel column was then used for the analysis of the PAH content. The sample was eluted using a mixture of dichloromethane and hexane, and spiked with deuterated p-terphenyl (50 μL, 4 μg/mL) surrogate standard. PAH contents were quantified using gas chromatography–mass spectrometry (GC–MS) (Agilent GC 7890/MS-MS Triple Quadrupole 7000B-Agilent, Santa Clara, CA, USA) equipped with a 60 m × 0.25 mm × 0.25 μm DB5-MS capillary column (J&W Scientific, Folsom, CA, USA). The isotope dilution method was used for quantification of the compounds. Helium was used as an inert carrier gas. For PCBs and OCPs, the volume was reduced under a gentle nitrogen stream at ambient temperature, covered by purified silica, and transferred into a vial. Finally, PCB 121-81 (0.2 μg/mL) was added as an internal standard. The extract was cleaned on an H_2SO_4-modified (44% w/w) silica column, and analytes were eluted with a 20 mL DCM/n-hexane mixture (1:1, v/v). Samples were quantified using gas chromatography–mass spectrometry (GC–MS) (Agilent GC 7890/MS-MS Triple Quadrupole 7000B) equipped with a 60 m × 0.25 mm × 0.25 μm HT8 SGE column (SGE Analytical Science, Ringwood, Australia) and with helium as a mobile phase.

The isotope dilution method was used for quantification of the compounds. Certified reference materials (Cambridge Isotope Labs soil standard RM-0002) and laboratory blanks were analyzed with each set of POP samples.

2.3. Human Health Risk Assessment

In this study, a screening risk assessment was performed for the estimation of the human intake of soil contaminants and consequent risks as suggested by the United States Environmental Protection Agency [16]. The risks were quantified under the present environmental conditions for the selected exposure scenario for those compounds that may pose the most significant potential risk to humans. The selected human exposure pathways addressed in this study included the inhalation of particles, dermal contact, and ingestion. Risk characterization was considered separately for carcinogenic and noncarcinogenic effects.

From a numerical perspective, the potential human health risks were estimated by a confrontation of the actual environmental concentration (PEC) with the calculated soil screening level (SSL) for human health risks of soil contamination (see Equations (1) and (2)). The SSLs represented the risk-based soil concentrations determined for the involved chemicals from equations combining exposure assumptions with common toxicity criteria. The SSLs based on noncarcinogenic risks were estimated using the site-specific exposure parameters (in Table 1) substituted into Equation (1).

Human exposure risks were assessed for certain exposure scenarios. Setting the exposure parameters specified the extent to which the model accurately represented reality. The site-specific exposure parameters were set out according to typical conditions of these soils in alluvial areas (Tables 2 and 3). As such, they are a fair reflection of the exposure of farmers, although other population groups, such as residents and bystanders, may also be exposed to these compounds due to soil pollution. The detailed methodology is also described in Čupr et al. [15], whose paper includes a discussion of the factors that may result in either an overestimation or an underestimation of the risks.

$$SSL_i = \frac{THQ \cdot BW_c \cdot AT_c}{EF_r \cdot ED_c \left[\left(\frac{1}{RfD_o} \cdot \frac{IRS_c}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_o} \cdot \frac{SA_c \cdot AF_c \cdot ABS}{10^6 mg/kg} \right) + \left(\frac{1}{RfD_i} \cdot \frac{IRA_c}{VF_s \text{ or } PEF} \right) \right]} \tag{1}$$

Table 1. Exposure parameters for noncarcinogenic risk calculation.

Symbol	Parameter (Unit)	Value
THQ	Target hazard quotient	1
BW_c	Body weight, child (kg)	15
AT_n	Averaging time, noncarcinogens (days)	ED × 365
EF_r	Exposure frequency, resident (day year^{-1})	250 (8 h/day)
ED_c	Exposure duration, child (years)	25
IRS_c	Soil ingestion rate, child (mg day^{-1})	100
RfD_o	Oral reference dose (mg kg^{-1} day^{-1})	Chemical-specific
SA	Dermal surface area, child (cm^2 day^{-1})	3470
AF	Soil adherence factor, child (mg cm^{-2})	0.12
ABS	Skin absorption factor (unitless)	Chemical-specific
IRA_c	Inhalation rate, child (m^3 day^{-1})	20
RfD_i	Inhalation reference dose (mg kg^{-1} day^{-1})	Chemical-specific
VF_s	Volatilization factor for soil (m^3 kg^{-1})	Chemical-specific
PEF	Particulate emission factor (m^3 kg^{-1})	Chemical-specific

The SSLs based on carcinogenic risks were estimated using the site-specific exposure parameters (in Table 2) substituted into Equation (2). The results were compared with the carcinogenic benchmark level, i.e., exposure posing an upper-bound lifetime excess cancer risk of 1×10^{-6} (one cancer occurrence in one million people).

$$SSL_i = \frac{TR \cdot AT_c}{EF_r \left[\left(\frac{IFS_{adj} \cdot CSF_o}{10^6 mg/kg} \right) + \left(\frac{SFS_{adj} \cdot ABS \cdot CSF_o}{10^6 mg/kg} \right) + \left(\frac{InhF_{adj} \cdot CSF_i}{VF_s \ or \ PEF} \right) \right]} \tag{2}$$

Table 2. Exposure parameters for carcinogenic risk calculation.

Symbol	Parameter (Unit)	Value
SSL_i	Contaminant concentration (mg kg^{-1})	Chemical-specific
TR	Target cancer risk	1×10^{-6}
AT_c	Averaging time, carcinogens (days)	25,550
EF_r	Exposure frequency, resident (day year^{-1})	250 (8 h/day)
IFS_{adj}	Age-adjusted soil ingestion factor ((mg year^{-1})/(kg day))$^{-1}$	100
CSF_o	Oral cancer slope factor (mg kg^{-1} day^{-1})	Chemical-specific
SFS_{adj}	Age-adjusted dermal factor ((mg year^{-1})/(kg day^{-1}))	361
ABS	Skin absorption factor (unitless)	Chemical-specific
$InhF_{adj}$	Age-adjusted inhalation factor ((m^3 year^{-1})/(kg day^{-1}))	11
CSF_i	Inhalation cancer slope factor (mg kg day)$^{-1}$	Chemical-specific
VF_s	Volatilization factor for soil (m^3 kg^{-1})	Chemical-specific
PEF	Particulate emission factor (m^3 kg^{-1})	Chemical-specific

The hazard quotient assumes that there is a level of exposure below which it is unlikely for even sensitive populations to expect any adverse health effects. In our case of exposure to multiple chemicals, a final cumulative health risk (hazard index for *n* pollutants) related to each sampling site was calculated as a sum of the partial quotients for the *i* involved compounds in Equation (3). A final HI < 1 indicates that no adverse health effects are likely to occur at the present exposure dose, and the human health risks (HHRs) are currently acceptable.

$$HQ_{HUMAN} = PEC_i / SSL_i \tag{3}$$

$$HI_{HUMAN} = \sum_{i=1}^{n} HQ_{HUMAN} \tag{4}$$

In the last step we calculated the relative contribution of each substance to an overall hazard index (HI_{HUMAN}):

$$p_{i_{RISK_{HUMAN}}} = HI_{HUMAN_i} / HQ_{HUMAN}. \tag{5}$$

2.4. Data Manipulation and Statistical Analysis

Principal component analysis (PCA) and cluster analysis were performed to evaluate the compositional similarities among samples. PCA is a widely used explanatory technique in terms of variance explanation and dimension reduction. The goal of any cluster analysis is to recognize homogenous clusters with the assumption that an underlying group structure exists. Following the expository potential of both tools, these were applied to explore the compositional variability of major components in our health risk survey. Nevertheless, these techniques cannot be directly applied to compositional data (objects described by vectors comprising parts of some whole) because they do not agree with the geometrical structure of the feature space [17]. Since the benefits of using the ratios between components have been recognized in statistical theory [18], the log-ratio transformations were proposed to overcome the shortcomings of analyzing compositional data. The advantages of both the centered log-ratio (clr) transformation [18] and the isometric log-ratio (ilr) transformation [19] may be exploited in the framework of a robust PCA [20]. A matrix of relative contributions of each pollutant to total HI_{HUMAN} for each locality was prepared before the statistical analysis (Equation (5)). In order to avoid misinterpretation of the results, half of the detection limit was used in all summations and for statistical analyses. However, a sizeable proportion of all data with an identical value can influence the multivariate analysis of compositional data [21]. This may be the case of some PCBs and hexachlorocyclohexane isomers (HCHs), where congeners PCB 52 and PCB 118 as well as the bHCH isomer proved to have especially significant proportions of observations below the detection limit (see Table 3). This effect of abundant identical values may be relieved by using the relative contributions of each compound to calculate the human risks from our point of view. Hence, all of the compounds were included in the multivariate analysis. PCA was performed after the matrix had been transformed using the ilr transformation and the resulting loadings and scores were back-transformed to the clr-space—for details, see Filzmoser et al. [20]. For clustering purposes, the fuzzy *c*-means algorithm (FCM) was employed to provide a degree of membership to each one of the resulting clusters. The fuzzy clustering problem can be characterized as classifying a given set of objects to fuzzy subsets, each of which is represented by its prototype with the most typical group characteristics [22]. Palarea-Albaladejo et al. [23] and Templ et al. [21] empirically tested various clustering algorithms on compositional datasets adopting a log-ratio approach. Following their experience, the clustering results were obtained using the FCM on ilr-transformed data. In the last steps, some graphical tools were used to pool the multivariate results. Therefore, a biplot [24] was used to graphically represent the variability in the entire composition and to assist the selection of relevant subcompositions that retain as much of the total variability in the entire composition as possible. The exact procedure for constructing the biplot adapted to compositions was presented in Filzmoser et al. [20]. For its statistical interpretation, see Aitchison and Greenace [25]. Finally, PCA results led to a ternary diagram, enabling readers to obtain lower-dimensional insights into the nature of the compositional dataset. These plots were subsequently used to represent clusters using the well-suited subcomposition defined according to the PCA results. The compositional biplots constructed on the basis of PCA and ternary plots have been shown to be powerful exploratory tools for various compositions [20,25]. Following this, we used them for visualization and deeper understanding of the survey results.

Since we analyzed only some of the possible compounds in the soil sample, our chemical dataset actually represents a subcomposition. Moreover, we replaced some measured values (mass ratios, μg/kg) by some computed ones (health risk estimations combining exposure assumptions with toxicity criteria) in our analysis. When applying any statistical method to compositions, three conditions should be fulfilled: scale invariance, permutation invariance, and subcompositional coherence [18]. Thus, using a log-ratio approach was an essential step to avoid the pitfalls of compositional data.

All of the computations and visualizations were conducted with the "robCompositions" [26], "compositions" [27], "ape" [28], and "cluster" [29] packages for the R statistical software (R CORE TEAM, Vienna, Austria). The regional patterns of the multivariate analyses results were spatially visualized using ArcGIS 10.2 (ESRI, Redlands, CA, USA).

3. Results

When our findings were compared to concentrations of POPs in Czech agricultural soils reported by Holoubek et al. [1], a similar trend could be observed for all POP compounds. Median concentrations were lower in our dataset (PAHs, DDTs, HCHs, PCBs, hexachlorobenzene (HCB); see Table 3), but usually with a wider range of values (PAHs, DDTs, HCHs). The results revealed a general high variability of POP concentrations in floodplain areas. In a previous study, both the magnitude of the estimated human health risks and the magnitude of hazards quotients of involved POPs were surveyed. Moreover, the highest estimated human health risks were found only in floodplain areas with high contents of PAHs exceeding the Czech legislation limits for agricultural soils [30]. In a closed system of compositional data (summing up to a constant), there is little space for all other compositional parts to vary in the case of exceptionally high relative contributions of carcinogenic PAHs (c-PAHs) to the estimation of HHRs (i.e., benzo(*a*)pyrene > benzo(*b*)fluoranthene > benzo(*a*)anthracene in Table 3). These proportional effects may be relieved by applying a log-ratio approach to the compositional dataset [31]. This approach allows researchers to explore those variable relationships that may be forced by the overall predominance of PAHs in health risk estimations and hence allows an interpretation of both known and unexpected patterns in the opened data.

Table 3. Summary statistics for the chemical concentrations of persistent organic pollutants (POPs) in the floodplain soil dataset (minimum: MIN; median: MED; maximum: MAX; spread expressed as median absolute deviation (MAD) and percentage of observations below the detection limit (% <DL)) and a summary of the hazard quotient calculation (median (MED_HQ) and its relative proportion to the median of the hazard index (%_HI)).

POPs		**Chemical Measurement**					**Risk Estimation**	
Compound	**Abbreviation**	**MIN**	**MED**	**MAX**	**MAD**	**% <DL**	**MED_HQ**	**%_HI**
		μg/kg				%	-	%
PCB 28	PCB28	0.06	0.10	1.37	0.02	38	0.0001	0.05
PCB 52	PCB52	0.05	0.10	0.56	0.00	58	0.0001	0.05
PCB 101	PCB101	0.03	0.13	1.18	0.05	37	0.00014	0.07
PCB 118	PCB118	0.02	0.10	0.34	0.07	57	0.0001	0.05
PCB 153	PCB153	0.08	0.32	4.66	0.25	6	0.000318	0.15
PCB 138	PCB138	0.06	0.32	3.36	0.25	15	0.00032	0.15
PCB 180	PCB180	0.05	0.28	4.68	0.24	9	0.00028	0.13
Pentachlorobenzene	PeCB	0.01	0.12	1.82	0.09	16	1.79×10^{-7}	0.00
Hexachlorobenzene	HCB	0.13	1.21	8.66	0.95	0	0.000843	0.39
alpha-Hexachlorocyclohexane	aHCH	0.12	0.44	9.52	0.41	16	0.001189	0.56
beta-Hexachlorocyclohexane	bHCH	0.03	0.10	11.0	0.00	74	7.69×10^{-5}	0.04
gamma-Hexachlorocyclohexane	gHCH	0.10	0.41	3.88	0.19	15	0.000164	0.08
o,p′-DDE	opDDE	0.01	0.10	35.4	0.02	41	1.47×10^{-5}	0.01
p,p′-DDE	ppDDE	0.34	3.85	1923	4.05	0	0.000551	0.26
o,p′-DDD	opDDD	0.01	0.13	12.3	0.07	29	1.35×10^{-5}	0.01
p,p′-DDD	ppDDD	0.04	0.52	38	0.52	8	5.42×10^{-5}	0.03
o,p′-DDT	opDDT	0.05	0.49	329	0.55	9	5.58×10^{-5}	0.03
p,p′-DDT	ppDDT	0.12	4.28	1082	4.77	0	0.000493	0.23
Naphthalene	N	4.38	10.4	648	5.09	0	0.000614	0.29
Acenapthene	Ace	0.06	1.67	589	1.39	1	3.73×10^{-8}	0.00
Fluorene	Fluor	0.92	2.86	477	1.74	0	9.58×10^{-8}	0.00
Anthracene	Ant	0.67	5.27	791	5.58	0	2.2×10^{-8}	0.00
Fluoranthene	Fl	10.58	89.31	4268	95.2	0	2.95×10^{-6}	0.00
Pyrene	Pyr	8.31	71.93	2966	75.5	0	3.11×10^{-6}	0.00
Benz(a)anthracene	BaA	3.00	35.84	16,705	36.4	0	0.012255	5.73
Chrysene	Chr	4.58	45.81	1368	45.5	0	0.000158	0.07
Benzo(b)fluoranthene	BbF	5.58	53.30	1818	53.7	0	0.018431	8.62
Benzo(k)fluoranthene	BkF	2.08	23.05	624	22.3	0	0.000792	0.37
Benzo(a)pyrene	BaP	3.62	44.50	1475	43.7	1	0.152897	71.53
Indeno(1,2,3-cd)pyrene	Ipyr	2.77	33.05	966	31.3	0	0.011278	5.28
Dibenz(ah)anthracene	DBahAnt	0.10	3.29	58.43	3.37	1	0.011179	5.23

Multivariate Results

Figure 1 summarizes the compositional biplot obtained with the robust PCA using the log-ratio approach and allows the interpretation of compositional variability. The origin of the compositional biplot represents the center of the compositional dataset; links between ray vertices represent the variance of the log-ratios between two components; and rays represent the clr-transformed variables. If several rays are collinear, the relative variability within the subcomposition formed by these variables might be one-dimensional and might represent a process influencing these components in a similar way [31]. If ray vertices coincide, then the two involved compositional parts may be assumed to be redundant. Nevertheless, when interpreting rays, one has to consider their dependency on the center as they represent clr-transformed variables. Hence, the constellation of links is fundamental when interpreting the compositional covariance structure in these biplots. Short links indicate variables that are highly proportional. Orthogonal links suggest two involved subcompositions to be uncorrelated.

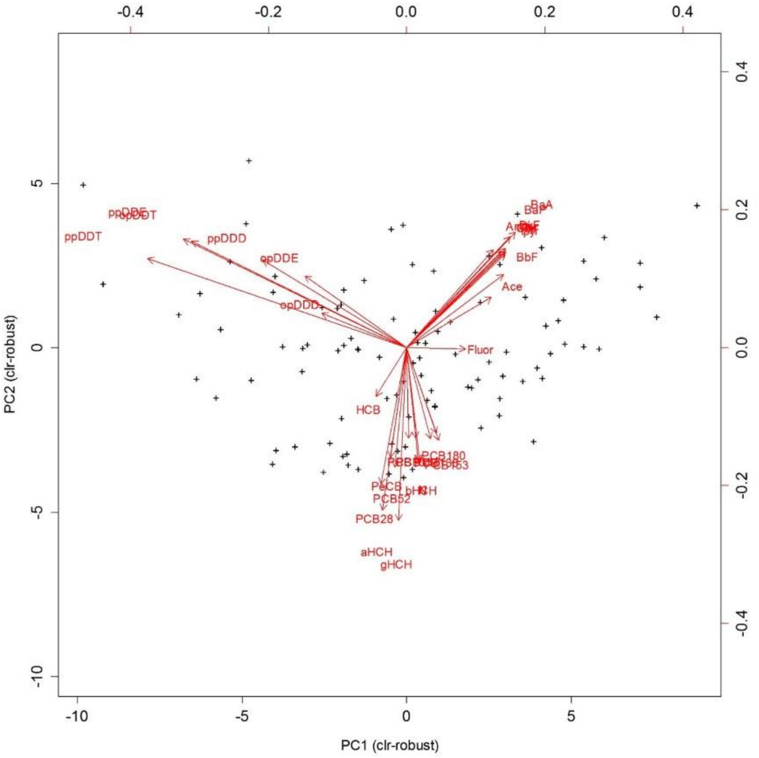

Figure 1. Biplot of the first two robust principal components (PCs) for the centered log-ratio (clr)-transformed major components (explained variation: PC1, 51%; PC2, 20%).

By applying these principles, we can clearly see several coincident rays consistently pointing towards diverging directions and connected with relative short links indicating three distinct groups of variables in Figure 1:

1 PAH compounds,
2 DDTs and metabolites, and
3 PCBs, HCHs, and PeCB.

Short links between those compounds in each group indicate variables that are highly proportional and predetermine redundant variables. On the other hand, the orthogonality of the three groups suggests some uncorrelated log-ratios (for instance, PAHs/DDTs vs DDTs/HCHs). This may be useful in the investigation of subcompositions for possible independence and the selection of variables to be visualized in ternary plots. Since such clear patterns were found in the preceding descriptive analysis, a well-suited ternary diagram of the subcomposition formed by the distinctive rays from each group could record the whole variability exceptionally well [31]. This is the case for the subcomposition (BaP, gHCH, ppDDT) in Figures 2 and 3. Since the proportion of explained variance captured by the two first principal components (PCs) reached 71%, the PCA results as well as the derived ternary diagrams may be considered a good approximation to the real structures in the data set. The robust PC1 can be seen as a contrast between the components of the PAH group and DDT group, while PC2 is dominated by elements of the third group in both Figures 1 and 2. The analysis of the compositional biplot suggests that most of the variability was controlled by two main factors—PAH contamination connected to higher atmospheric pollution inputs in the catchment, and DDT contamination connected to the agricultural intensity.

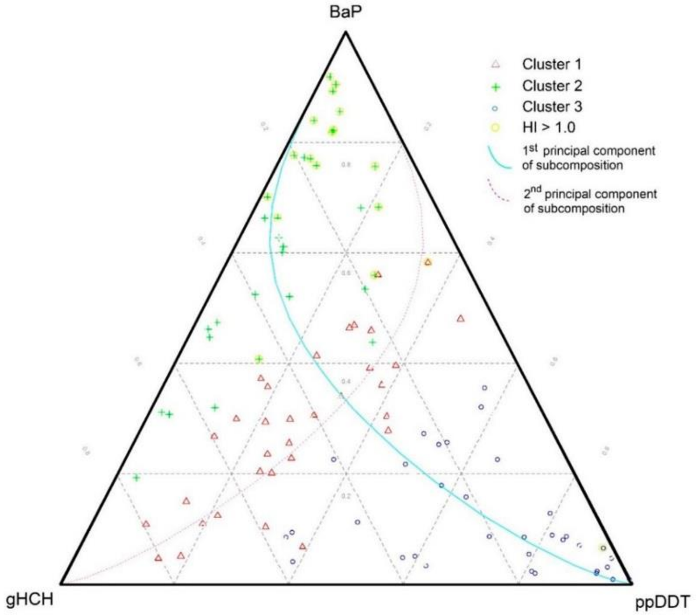

Figure 2. Ternary diagrams of the subcomposition (benzo(a)pyrene (BaP), gamma-HCH (gHCH), ppDDT) with distinguished three-group fuzzy partitions and the first two principal components (PCs) of the presented subcomposition (note that the samples with $HI_{HUMAN} > 1.0$ are highlighted with a yellow circle).

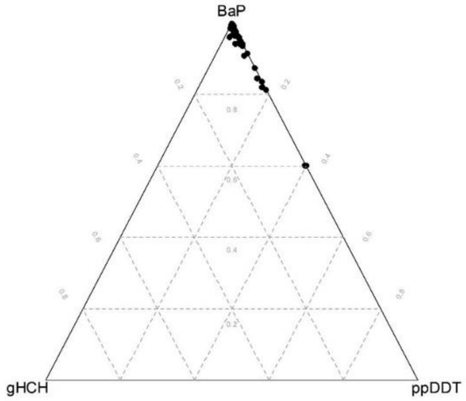

Figure 3. Ternary diagrams of the subcomposition (BaP, gHCH, ppDDT) using raw data components.

A three-group solution was considered as the optimal grouping of the dataset in the cluster analysis. The membership probabilities from the FCM approach are graphically shown for each sample in Figures 4 and 5. Comparing clustering and ordination results can be beneficial to explaining the differences between groups of sites. Compositional biplots summarize the variance relationships within the compositions; nevertheless, they are chosen to maximize the variance of the projected data cloud and are not tailored to highlight between-group differences [31]. For this purpose, a graphical representation of principal coordinate analysis (PCoA) was used on the Aitchison distance matrix, in which the eigenvectors are scaled to the square root of the corresponding eigenvalues (Figure 4). Gower [32] showed that eigenvectors scaled in this way preserve the original distance among the objects in the distance matrix. We can see that the clusters are basically defined by their projections along the first two principal components, according to their human risk patterns and the differences in relative contributions of DDTs, HCHs, and PAHs to the calculated human risks. Hence, the three-group clustering corresponded well to the variation within the composition.

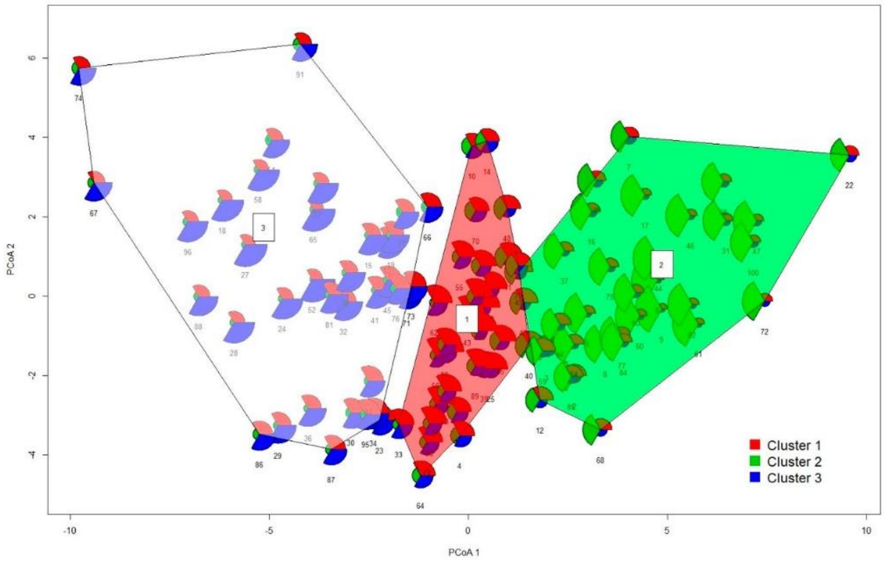

Figure 4. Membership probabilities and assigned cluster number in a graphical representation of principal coordinate analysis (PCoA) on Aitchison distances between sampling localities.

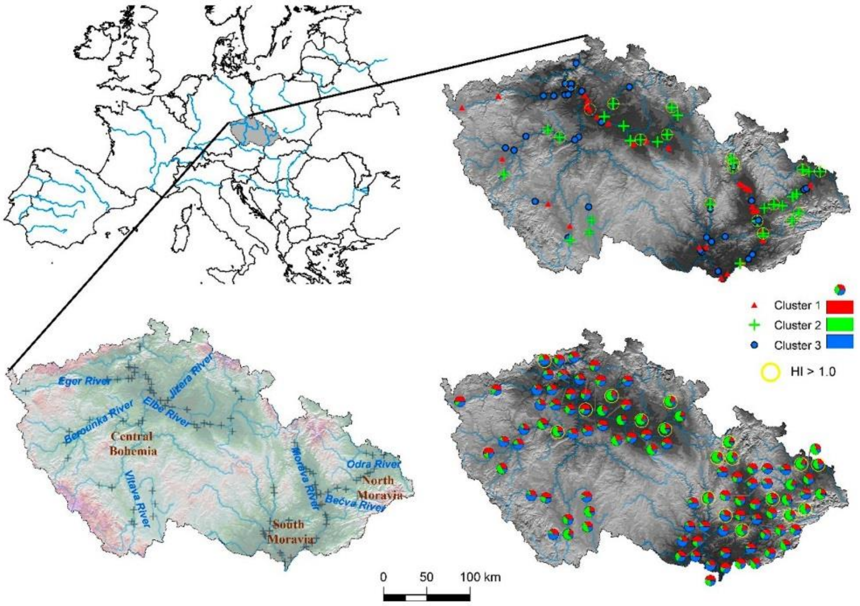

Figure 5. Membership probabilities and assigned cluster number in a geographical representation for regional interpretation (note that the samples with $HI_{HUMAN} > 1.0$ are highlighted with a yellow circle).

In fact, if we used a ternary plot (Figure 2) to represent the established subcomposition (designed by representative compositional parts formed by some of the longest rays from each group in the compositional biplot in Figure 1), the clusters are clearly distinguished. The data as much as the grid lines were centered and the first two principal components of the subcomposition were added to the ternary plot. The data were centered by calculating the closed geometric mean, which was obtained as the closure of the vector of geometric means of each component. In this way, the geometric center of the observed data could be moved to the barycenter of the simplex space, allowing us to better visualize the structure of the sample [33]. When comparing the ternary diagram obtained for raw data (Figure 3) with that obtained for the centered log-ratio-transformed data (Figure 2), we could see that the raw data tended to collapse on a vertex, obscuring the structure (BaP in our case). Hence, only limited information can be extracted from raw proportions due to the proportionality effect [31]. Comparing both diagrams, the actual benefits of the log-ratio approach can be seen. Note that the positions of the clustering groups within the subcompositional representation using ternary diagrams (Figure 2) agree with the partition results of fuzzy clustering in Figure 4. It can be again seen that Clusters 1 and 3 are the groups with the most similar characteristics, and also that Cluster 2 is the most different group. This may be explained by the fact that Cluster 1 and 3 are both dominated by relatively high contributions of various OCP compounds and thus may be both influenced to some extent by long-term intensive husbandry. Finally, the processes behind the clusters were investigated according to the relative weight of each POP component in every group using centered data, according to Palarea-Albaladejo et al. [23] (Figure S1).

4. Discussion

Cluster 1 included samples with a higher proportion of organochlorine pesticides with prevailing agricultural origin (HCHs, PeCB, HCB) together with samples with higher organochlorine compounds of industrial origin (PCBs). On the contrary, Cluster 2 was composed of samples with relatively high contributions of PAH compounds to the estimated HHRs (see Figure S1 for each cluster profile in more detail). The increased PAH content in the environment was evident in the fluvial systems of the broader Moravian Silesian region (the Odra and Bečva Rivers). In this region, the anthropogenic pollution sources (coal processing, metallurgy) have generated higher PAH air concentrations [34] and greater contamination of agricultural soils [35]. The PAH contamination in floodplains of the Bečva River may be significantly influenced by the coal tar refinery (Deza Corporation) producing aromatic hydrocarbons [36]. Elevated concentrations of PAHs were also recorded in the floodplains along the Jizera River near the industrial center of Mladá Boleslav (automobile manufacturing). Last but not least, traffic-related emissions increased exposure to PAHs at several locations with a lower distance to highways. PAHs have been determined to be elevated in soils affected by highway traffic [37,38] and have been proved to significantly contribute to AhR-mediated activity and adverse health effects of traffic-associated pollution [39,40]. Ollivon et al. [41] described how car traffic and atmospheric washout might impact river contamination in the highly urbanized area within the Seine catchment. Elevated PAH contributions, associated with above-average health risks, were surprisingly recorded in the headwaters of the Elbe and Morava Rivers. This could only be explained by an atmospheric transport of PAHs that may increase their concentrations in remote freshwater ecosystems with no other pollution sources [42]. Using a regression tree model, Kubošová et al. [43] confirmed the crucial role of industry and other primary anthropogenic sources in soil contamination by PAHs. Yet, they also identified precipitation as the main transfer route of atmospheric PAHs to soils. The resulting regional patterns of PAHs in their stochastic approach using regression trees [43] corresponded well to our results of health risk patterns in floodplain areas.

Concerning Cluster 1, two regional centers could be distinguished. One was probably associated with the former contamination of the Spolana chemical plant at the middle reach of the Elbe River. The chemical plant grounds were contaminated with dioxins, chlorinated aliphatic hydrocarbons, and OCPs [44,45]. Studying the POP bioaccumulation in the Elbe River, Randák et al. [46] also found the highest concentrations of PCBs in chub muscle in fish from the Neratovice site. Thus, multiple sources may interact, resulting in a more complex soil pollution profile and corresponding health risks. The second regional occurrence of Cluster 1 was observed at the middle reach of the Morava River, where higher concentrations of organochlorine pesticides (especially HCHs and PeCB) were found. Studying POP dynamics in the dissolved phase in the water column of the Morava River and its tributaries, Prokeš et al. [47] found high aqueous concentrations of organochlorine hydrocarbons (especially PCBs and HCHs).

Finally, the characteristic features of Cluster 3 included higher contributions of DDT and its metabolites to the estimated HHRs. DDT and its metabolites dominated most soil samples from the catchment of the Berounka River (Central Bohemia), from the lower reach of the Eger River, and from a wider region of the South Moravian catchments. The floodplains of these lowland regions belong to traditional areas of intensive agricultural production over a long period of time. The observed regional pattern of Cluster 1 showed exceptional agreement with the predicted concentrations for DDTs in a regression tree model [43] and with some field observations of sediment geochemistry [48].

Given the results of the total estimation of HHRs for all soil samples, potential regional hot spots of human health impacts may be recognized (note the yellow circles in Figures 2 and 5 highlighting the samples with $HI_{HUMAN} > 1.0$). In fact, if we display these samples in a ternary plot (Figure 2) or in the results of fuzzy clustering (Figure 5), the predominance of PAH-induced human health risks is clearly evident. Some exceptions to this included the Elbe samples collected close to the confluence with the Eger River and samples taken near the Neratovice site, which both showed more complex pollution profiles (elevated contributions of PCBs, HCHs, DDTs, and PAHs).

5. Conclusions

An elevated probability of human health impacts of soil pollution may be expected at several sampling sites under exactly defined exposure conditions. When combining both the magnitude of estimated HHRs (noncarcinogenic and carcinogenic effects) and the compositional variation of pollution profiles, several localities with high contents of PAHs proved to have the highest estimated HHRs. Concerning the intensive agricultural utilization of floodplains, the exposure of farmers can be considerable when they are exposed to polluted soils with significantly increased concentrations of POPs (mainly c-PAHs) and over long working hours. Since other population groups, such as residents and bystanders, may also be exposed to these compounds due to environmental pollution, a high degree of attention should be dedicated to human risk assessments associated with nonoccupational exposure in floodplain areas. This may especially be the case for the North Moravian region, where the population generally suffers from higher residential exposure due to air pollution. This study only focused on certain POPs and exposure scenarios and did not consider additional routes of exposure (dietary intake) or special vulnerable populations with specific exposure scenarios [49]. However, in agricultural areas it must be considered that concentrations of additional contaminants (especially formerly used or emerging pesticides [50,51], polychlorinated dibenzo-p-dioxins and dibenzofurans [52], heavy metals [3,53], or other micropollutants [54,55]) may also contribute to a higher probability of adverse effects. Likewise, health risks may be underestimated owing to the nature of the simple additive model avoiding all compound interactions and their synergic effects. According to the intensive farming in the floodplains and potential pathways for POP transfer to the human food chain, dietary exposure is expected to significantly contribute to HHRs. Various studies have provided strong evidence that the flooding of pastureland can indeed result in elevated concentrations of POPs in milk and meat produced on flood-prone land [52,56,57]. POPs are adsorbed on soil organic matter or in the plant rhizosphere so strongly that they are marginally transported to plant tissues [58]. Some problems might arise from the growing of feed crops for direct consumption, especially for plants producing consumable parts in the soil [59–61], since Trapp [58] presented a comparable adsorption of lipophilic organic substances within the rootzone with their adsorption to soil organic carbon. These risks may come into question for the localities in Cluster 3, where a high contribution of DDTs and metabolites to HHRs meets areas of intensive vegetable farming in floodplains near the Elbe and Eger confluence or in South Moravia. The regional patterns obtained in our floodplain study corresponded well with results of model-based predictions of POP concentrations in soils [43] and with some field observations of sediment, water, and biota [46–48]. This indicates the general role of floodplains as an effective sink of overall regional pollution. Since microbial degradation is a potential mechanism for the removal or transformation of POPs [62] and soil microbial characteristics have been proven to be very dynamic in human-altered riverine landscapes [63], special attention should be paid to the bioavailability mechanisms of POPs in these soils in the future. Moreover, filling the data gaps in understanding contaminant bioaccessibility is advisable to accurately assess human exposure to POPs via direct pathways [64].

Since a recent evolution of riverine landscape tends toward higher flood control in urban areas and flood-retarding inundation out of populated areas, agricultural floodplain soils will suffer the impacts of high water events. Hence, the results of this study were implemented in a national certified guideline for a complex assessment of soil pollution in flood-prone areas [65]. Additionally, these results were used to verify the relevancy of the human health limits recently adopted within the national soil protection legislation [30]. Purely from a methodical point of view, an exploratory analysis of the results of human health assessments using a compositional approach might be worth modeling and interpreting, especially when a clear dominance of c-PAH contributions outweighs the contributions of most other elements.

Supplementary Materials: The following are available online at http://www.mdpi.com/1660-4601/15/6/1146/s1, Figure S1: Visualization of cluster profiles: relative weights of POP components for every cluster in the robust cluster analysis (isometric log-ratio (ilr)-transformed and centered data).

Author Contributions: J.S. participated in the field sampling, constructed the final database, performed the statistical analysis in R software, prepared cartographical output using GIS, and drafted the manuscript. R.V. supervised acquisition of the field data and took part in performing and interpreting statistical analysis. Author R.V. conceived the study and participated in its coordination and in drafting the manuscript. P.Č. was responsible for establishing the exposure model for human health risk estimation. All authors read and approved the final manuscript.

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Conflicts of Interest: The authors declare that they have no conflicts of interest.

Abbreviations

FCM	fuzzy c-means algorithm
HCHs	hexachlorocyclohexane isomers
HCB	hexachlorobenzene
DDTs	DDT isomers and their metabolites
HHRs	human health risks; OCPs: organochlorine pesticides
PAHs	polycyclic aromatic hydrocarbons
c-PAHs	carcinogenic polycyclic aromatic hydrocarbons
PC	principal component
PCA	principal component analysis
PCBs	polychlorinated biphenyls
PeCB	pentachlorobenzene
POPs	persistent organic pollutants
SSL	soil screening level

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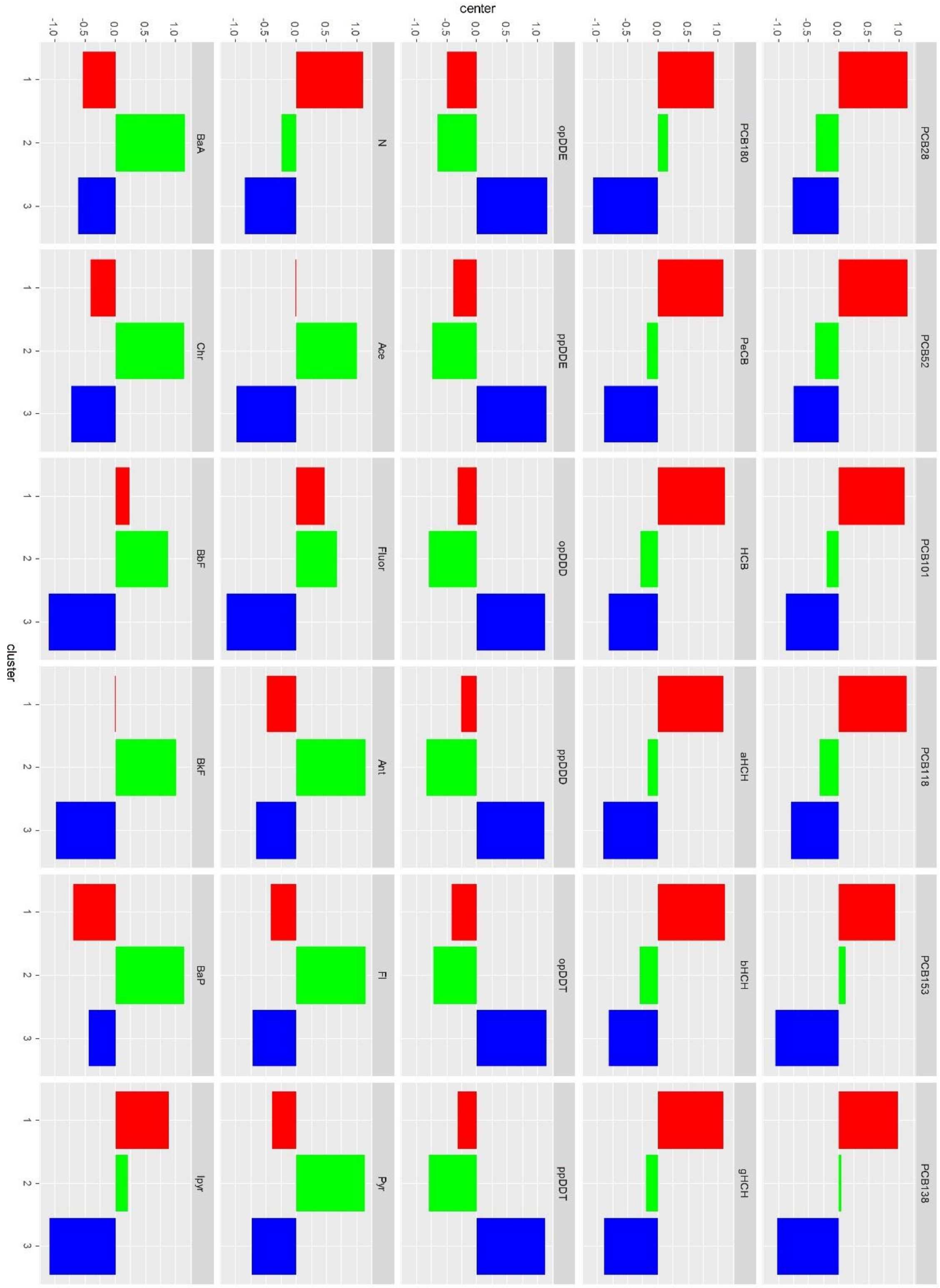
Supplementary Materials: The following are available online at www.mdpi.com/link, Figure S1: Visualisation of clusters' profiles: relative weights of POP components for every cluster in the robust cluster analysis (ilr-transformed and centered data).



4.3 Vácha et al. (2015): Rizikové prvky a perzistentní organické polutanty pocházející z průmyslových emisí v zemědělských půdách severní části České republiky

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SOILS AND SEDIMENTS IN URBAN AND MINING AREAS

Toxic elements and persistent organic pollutants derived from industrial emissions in agricultural soils of the Northern Czech Republic

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Abstract

Purpose This study reports on the surface distribution of toxic elements (TEs; As, Be, and Cd) and persistent organic pollutants [POPs; e.g., polycyclic aromatic hydrocarbons (PAHs)] in agricultural soils affected by mining and heavy industry from the industrial regions of North Bohemia and North Moravia. In this study, these regions are considered as test regions to study the impacts of heavy industry emissions on agricultural soils.

Materials and methods From 2000 to 2010, agricultural soils were sampled and their physicochemical properties and contamination levels of TEs (As, Be, and Cd) and POPs (PAHs) determined. The pseudototal content (from Aqua regia extracts) and plant available fraction (from 1 M NH_4NO_3 extracts) of TEs, as well as the total PAH content in humic horizons of arable soils and grasslands, were analyzed. The surface spatial variability of these contaminants was evaluated using the kriging method. Threshold values for the probability estimation were adapted from the limit values provided by newly proposed Czech legislation.

Results and discussion We show that the soil environments of the study area are polluted by anthropogenic material directly connected to historical mining and industrial activities, including lignite mining in North Bohemia and hard coal mining and heavy industry in North Moravia. The increased As contents in the soils contribute to the most important environmental problems in North Bohemia, where anthropogenic and geogenic sources of As interact. In North Moravia, anthropogenic pollution linked to coal combustion and metallurgy has increased Cd and PAH contents in agricultural soils. However, concentrations of these pollutants do not exceed limits for food safety in soils from these regions.

Conclusions This study shows that agriculture can coexist in regions impacted by heavy industry emissions, like the study regions documented here. Such activity requires that a suitable methodology is implemented to evaluate soil contamination and a risk assessment is carried out. In addition, suitable precautions should be undertaken in areas close to industry, such as grassing over contaminated arable lands to reduce wind erosion.

Keywords Agricultural soil contamination · Heavy industry · Mining areas · North Bohemia · North Moravia

1 Introduction

The paper describes the impact of mining activities and heavy industry on agricultural soils in two mining and industrial regions of the Czech Republic: North Bohemia and North Moravia. The history of soil contamination by toxic elements (TEs; As, Be, and Cd) and persistent organic pollutants [POPs; especially polycyclic aromatic hydrocarbons (PAHs)] close to industrial sites began in the 19th century. The most intensive industrial activity occurred during the socialist period from 1948 to 1990, which was characterized by the development of heavy industry, resulting in a huge negative impact on the environment. Data from the Czech Hydrometeorological Institute reveal that emissions reached their highest recorded values in the 1990s. At this time, the concentrations of airborne dust were typically 70–100 and up to 150 $\mu g/m^3$ close to the coal-mining areas of North Bohemia

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(Podlešáková 1992). The environmental situation in North Bohemia improved during the 1990s, in spite of continuing anthropogenic contamination (Jahn et al. 2013). This reflected technological adaptation of five coal-fired power plants in the region. Data from the ČEZ Group (2012) show huge reductions in emission outputs over the period 1996–1999, especially for SOx (−92 %), NOx (−50 %), CO_2 (−77 %), and particulate matter (−93 %). Modernization is ongoing and will be finalized in 2020. Further decreases in pollutant emission levels are expected to attain even lower levels: SOx (−57 %), NOx (−59 %), CO_2 (−31 %), and particulate matter (−39 %). In addition, all mining activities continue to be followed by landscape rehabilitation. In contrast, environmental contamination remains a serious problem in North Moravia, where emissions are connected with metallurgy and heavy industry (Šram et al. 2013). The Czech Hydrometeorological Institute (CHMI 2009) confirmed high concentrations of dust (200 mg/m^3; highest value in the Czech Republic) with particle sizes below 10 μm (PM10). The daily concentration limit for PM10 is exceeded on more than 100 days/year in many contaminated localities in this region. Likewise, levels for PAHs are exceeded in most areas (Šram et al. 2012), leading to human diseases (Rössnerová et al. 2011; Dostál et al. 2013a; Švecová et al. 2013).

The scope of this study is to provide a review of the environmental situation in these industrial regions as a test case for the study of the impacts of heavy industry on agricultural soils. A recently proposed legislation for regulating the contents of TEs and POPs in agricultural soils (Sáňka et al. 2002; Vácha et al. 2014) and geostatistics is used as a baseline for our evaluation and risk assessment.

2 Materials and methods

2.1 Regional setting

The two regions selected for our test cases are North Bohemia and North Moravia, both regions known for their strong links to heavy industry. North Bohemia comprises eight districts with a total area of 6,500 km^2 and almost 925,000 inhabitants. The landscape has four main geomorphologic formations, comprising various lithologies: one sandstone, two intrusive rock, and one effusive rock formations. The altitude ranges between 115 to 1,225 m a.s.l., with an average altitude of 272 m a.s.l. The Labe River traverses the northern part of the region, while the Ohre River crosscuts the southern part of the region. The mining areas in the North Bohemian coal basin (lignite deposits) are situated below the Ore Mountains. Mines were first opened in 1819, and active open mines still exist today. The current lignite-mining area is 870 km^2. A number of soil types, after the World Reference Base for soil resources (Food and Agriculture Organization of the United Nations 2014), are observed in this region. podzols and cambisols are developed on intrusive rocks in highland areas, while eutric cambisols are developed on effusive rocks including chernozems, gleysols, and gleyic cambisols. typically, forests cover mountainous areas, while agricultural land occurs at lower altitudes. Forests cover 37.5 % of the total area (Kozák et al. 2010). Agricultural lands cover 38 % of the total area, yielding a ratio of 0.21 ha of agricultural land per inhabitant. The use of agricultural land is as follows: 47 % arable land, 46.7 % grassland, and 6.3 % vineyards, hop fields, gardens, and orchards (Ministry of Agriculture of Czech Republic 2012). Production areas comprise beet (19.2 %), potato (42.8 %), potato oat (23 %), and highland production areas (15 %). The annual precipitation is very low in the pan area (500 mm/year), but rises sharply on the slopes of the Ore Mountains (1,100 mm/year). The average annual temperature in the pan area is 8 °C (Czech Hydrometeorological Institute).

North Moravia comprises three districts, encompassing a total area of 1,834 km^2, with 800,000 inhabitants. There are three main geomorphologic formations: two coal beds and one Carpathian shale formation. The region's highest peak is Lysa Mountain (1,323 m a.s.l.) in the Moravian–Silesian Beskydy Mountains, located in the eastern part of region. The average altitude of the mining area is 210 m a.s.l. The Odra River (west) and the Olše River (east) are the most important rivers in this area. The area is renowned for black coal mining (hard mining), but maximum production occurred in the 1980s (about 20 million tons/year). Ostrava–Karvina coal area is located in the Czech Republic, forming part of the Upper Silesian Coal Basin, which extends into Poland. The black coal is extracted using deep mining technology (OKD 2012). About 1.7 billion tons of coal have been extracted from this area. Cambisols and Podzols are developed on the Carpathian shale, occurring in mountainous area, while luvisols, gleyic cambisols, and gleysols occur at lower altitudes. Forests cover 25 % of the total area, dominating mountainous area (50 %), but sporadic in mining areas (12%) (Kozák et al. 2010). Agricultural lands cover 43.5 %, yielding a ratio of 0.11 ha of agricultural land per one inhabitant. The use of agricultural land is as follows: 61 % arable land, 26 % grassland, and 13 % vineyards, hop fields, gardens, and orchards (Ministry of Agriculture of Czech Republic 2012). The production areas comprise beet (14.7 %), potato (41.3 %), potato oats (14.4 %), and highland production area (29.6 %). The average annual precipitation is lower in pan areas (700 mm/year) compared with mountainous areas (1, 300 mm/year). The average annual temperature in the pan area is 8 °C (Czech Hydrometeorological Institute).

2.2 Soil sampling

Soil sampling was carried out in North Bohemia and North Moravia from 2000 to 2010 as part of a monitoring programme of the Czech Ministry of Agriculture. Since the focus was on food chain quality, only agriculturally relevant soils (arable soils, pastures, and meadows) were included. No forest soils were sampled. Only natural soils were sampled, since the history of urban soils and anthrosols on restored agricultural land is not well known and can involve humic horizons of different origins (Kohel 1994).

Soil samples were extracted from humic horizons of agricultural soils (to a depth of 5–15 cm) using a soil auger. This depth encompasses the main humic horizons of agricultural soils (with tillage to about 20 cm) and most grassland soils. Sampling depth was reduced in shallow soils with respect the thickness of the humic horizon. The top 0–5 cm was omitted to avoid secondary contamination by agrochemicals, agricultural traffic, etc. Each sample was compiled from ten partial samples at each locality. The sampling point net is given in Fig. 1. Sampling was carried out at least 50 m from any public highways, in accordance with the unified procedure for soil sampling to avoid traffic influence. An equidistant matrix for sampling was adhered to wherever possible, with a density of sampling of around one sample/25 km^2. In addition, individual sets of soil samples were collected for analyses of polychlorinated dibenzo-*p*-dioxins and dibenzofuranes (PCDDs/Fs). In this pilot study, 12 samples were from North Bohemia and 11 samples from North Moravia. All the samples were stored and transported in jars and stored frozen at – 18 °C. Every locality was described and the geographic coordinates recorded using a GPS.

2.3 Laboratory analyses

Soil characteristics, including soil type, soil subtype and texture, pH value (ČSN ISO 10390 1996), and C_{org} content (Zbíral et al. 2004), were documented for each sample. In addition, the contents of TEs and POPs were determined for each sample using professional laboratories. TE analysis was done at the Research Institute for Soil and Water Conservation in Prague, while POP analysis was done at accredited commercial laboratories.

The pseudototal content of TEs (As, Be, Cd, Cu, Ni, Pb, V, and Zn) in an extract of Aqua regia (ČSN EN 13346 2001) was analyzed using atomic absorption spectroscopy. The total Hg content was assessed using the Advanced Mercury Analyzer (Altec, Czech Republic) (Zbíral et al. 2004). The plant available fraction of TEs in an extract of 1 mol/l NH_4NO_3 (DIN ISO 19730 2008) was determined in selected samples and compared with the pseudototal contents and soil characteristics (pH, C_{org}). The soil reaction (pH, KCl) was analyzed following ČSN ISO 10390 (1996), and C_{org} was analyzed using the method ISO 14235 (1998).

Our study focused on the main POPs groups. The monocyclic aromatic hydrocarbons [benzene, toluene, e-benzene, and xylene (BTEX)] were measured using the US Environmental Protection Agency (EPA) Method 8260 B (1996), involving gas chromatography coupled with mass spectrometry (GC/MS). The 12 PAHs (anthracene, benzo(*a*)-anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, benzo(*ghi*)perylene, phenanthrene, fluoranthene, chrysene, indeno(1,2,3-*cd*)pyrene, naphthalene, and pyrene) were measured using the methodology TNV 75 8055 (2004), involving high-performance liquid chromatography (HPLC) coupled with a fluorescence detector. But the polychlorinated biphenyls were measured using seven indicator congeners (PCB_7)—(28, 52, 101, 118, 138, 153, and 180) in the EPA Method 8082A (2000)—involving gas chromatography with an electron capture detector (GC/ECD). A dichlorodiphenyltrichloroethane (DDT) sum was calculated as the sum of DDT, dichlorodiphenylethylene (DDE), and dichlorodiphenyldichloroethane (DDD) measurements using EPA Method 8082A (2000), involving a GC/ECD. Polychlorinated dibenzo-*p*-dioxins and dibenzofuranes (PCDDs/Fs) were observed, when 17 congeners were analyzed using a high-differentiated mass spectrometer (Ultima 2; Waters Corp., MA, USA). The International Toxic Equivalent (I-TEQ) value was calculated for each sample (Van den Berg et al. 2006).

2.4 Threshold limits, descriptive statistics, and spatial interpolation

The proposed updated limit values for TEs and POPs (Vácha et al. 2014) currently under legislative review were used to evaluate our results. The new limit values for the dominant contaminants are given in Table 1. The background values for TEs and POPs (Podlešáková et al. 1994a; Němeček et al. 1996a) are characterized as a "prevention limit." The second level limit (an indication limit) is derived, assuming an increased transfer of TEs from the soil to plants (Podlešáková et al. 2002) and taking into account the health risks of POPs in the soil (US EPA 2002; Zimová et al. 2001). The concentrations of TEs and POPs in soils were analyzed to provide descriptive statistics for each parameter in North Bohemia (Table 3) and North Moravia (Table 4). A log-normal transformation was carried out to reduce the effect of high skewness in the data. The log-transformed data were used for interpolation and were back-transformed to produce the final spatial distribution map. The descriptive statistical parameters were calculated using Microsoft EXCEL and Statistica (version 10.0; Statsoft). Subsequently, probability maps for As, Be, Cd, and PAH concentrations exceeding regulation limits in soils in these regions were generated using probability kriging, a method based on threshold values for the pollutants derived from the Czech legislation. The probabilities for exceeding for the proposed limit values for agriculture soils (Sáňka et al. 2002) are mapped for As, Be, Cd, and PAHs with GIS software ArcGIS (version 10.2), and its extension

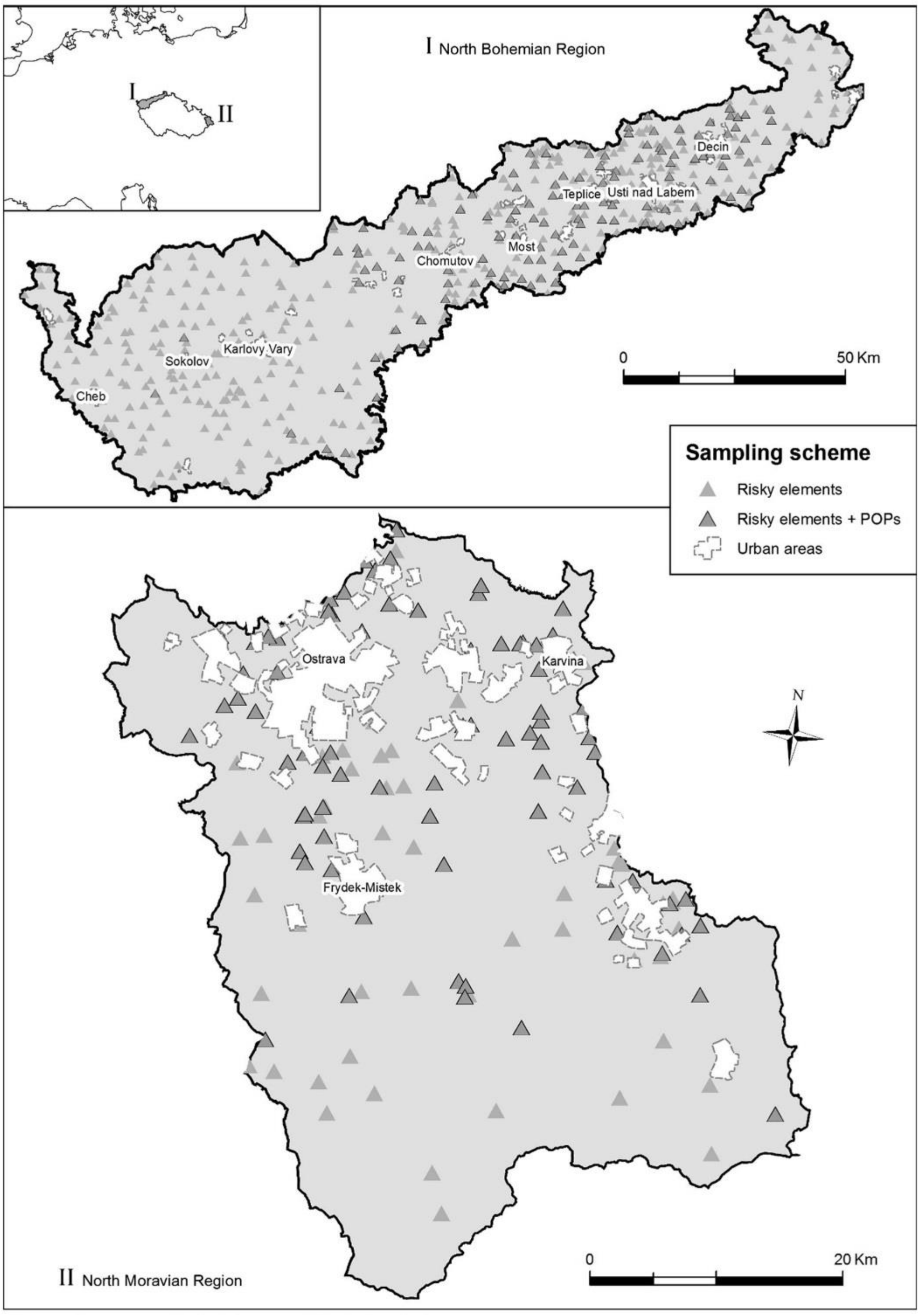

Fig. 1 The sampling points in North Bohemian and North Moravian Regions

Table 1 Proposed limit values (Vácha et al. 2014) for selected TEs (extract in Aqua regia) and POPs (mg/kg)

Limit level/contaminant	As	Be	Cd	Sum PAHs	Benzo(*a*)pyrene	PCDDs/Fs
Preventive limit (background value)	20	2	0.5	1	0.1	1[a]
Indication limit for food chain protection	[b]	No	1.5[c]	No	No	No
Indication limit for health protection	40	No	30	30	0.5	100[a]

[a] The value of I-TEQ PCDDs/Fs (ng/kg)

[b] Indication limit proposed only for As in the extract of 1 M NH_4NO_3

[c] Indication limit for soils with pH 5–6.5

component, Geostatistical Analyst. The method of probability kriging also was used for the spatial characterization of contamination in this study. Probability kriging proved to be better than indicator kriging for delineating contaminated soils (Goovaerts 1997; Juang and Lee 1998). Geostatistical modeling was customized to include the agricultural land use categories outlined in the sampling strategy and available thresholds. The estimated probabilities for other soils (urban and forest) are purely theoretical, and there is no relevance attached to exceeding the TEs and POPs limit values proposed for agricultural soils. Despite this, the location of urban and forest soils is provided in the GIS output.

3 Results

3.1 North Bohemian region

The basic characteristics of samples, separated into their main soil groups, are presented in Table 2. The TE contents of these soils were evaluated using the newly proposed limit values (Vácha et al. 2014). Only two TEs (As and Be) exceeded these values. All other TEs were below their background values in Czech agricultural soils (Podlešáková et al. 1994a; Vácha et al. 2014). Cd and Pb levels were elevated close to some industrial towns. Statistical data for TE concentrations in North Bohemia are presented in Table 3. As and Be — (pseudo)total contents for North Bohemia are presented on maps, showing the probability of exceeding their limit values. Figure 2 presents the probability distribution of TE contamination in this region. The black squares show the positions of thermal power plants in the region. It can be seen that prevention limits were often exceeded for both As and Be in this region. Levels exceeding the limit values for human health risks were previously detected in agricultural soils from the Ore Mountains and close to the Sokolov industrial district, despite the fact that human risks are usually defined for urban or restored soils (Pena-Fernandez et al. 2014; Wang et al. 2014). Be levels exceed the prevention limit (background values) in the Ore Mountains, where geogenic sources exist, i.e., in soils developed on acid-neutral magmatic rocks. A geogenic origin for Be and associated As and Pb was confirmed by profiling soils in a previous study (Vácha et al. 2002). A limit for Be was not proposed for legislation (Vácha et al. 2014).

PAH contamination presents a low risk in this region. Elevated PAH content was only sporadically detected in North Bohemia. PCB_7 and DDT levels were below their background values in agricultural soils and do not present any serious risks in North Bohemia. However, BTEX limit levels were

Table 2 Summary of soil properties in the samples of Nord Bohemian and Nord Moravian Regions

Regions and their major soil groups	Relative frequency (%)	Soil texture Range	pH Mean (standard deviation)	C_{org} Mean (standard deviation)
North Bohemian Region (n= 620)			5.45 (1.29)	2.25 (1.18)
(1) Cambisols	32	SL–CL	5.87 (0.83)	2.15 (1.07)
(2) Dystric cambisols	24	LS–SL	4.93 (1.16)	2.46 (1.07)
(3) Stagnosols	12	C	5.64 (0.88)	1.94 (0.89)
(4) Chernozems	9	L–CL	6.42 (0.62)	2.01(0.59)
North Moravian Region (n= 181)			5.67 (1.47)	1.58 (0.72)
(1) Stagnosols	27	C	5.62 (1.61)	1.53 (0.68)
(2) Luvisols	23	SL–L	5.59 (1.49)	1.24 (0.45)
(3) Cambisols	22	SL–CL	5.52 (1.57)	1.60 (0.93)
(4) Dystric cambisols	8	LS–SL	4.50 (0.80)	1.96 (0.88)

In North Bohemian Region (*n*=620), grassland is 62 %, while in North Moravian Region (*n*=181), arable land is 56 %

LS loamy/sandy, *SL* sandy/loamy, *L* loamy, *CL* clay/loamy, *C* clay

Table 3 Descriptive statistics of TEs (extract in Aqua regia) and POPs contents in soils of North Bohemian Region

Statistics	As (mg/kg)	Be	Cd	Cu	Hg	Ni	Pb	V	Zn
Samples	620	620	620	620	620	620	620	620	620
Mean	33.77	3.11	0.33	35.67	0.17	32.66	51.55	123.14	107.96
Median	20.90	2.50	0.25	27.50	0.11	25.00	40.00	105.00	98.00
Min	1.00	0.03	0.04	5.00	0.01	0.90	0.30	1.20	8.00
Max	1568.0	21.50	3.62	580.9	2.86	680.0	634.4	490.0	856.0
Standard deviation	93.89	2.31	0.33	39.18	0.24	34.41	43.15	72.29	69.90
Skewness	14.08	3.12	5.80	8.20	7.25	10.34	5.67	1.37	4.46
Statistics	∑MAHs (μg/kg)	∑PCB_7	∑DDT	∑PAHs	Benzo(*a*)pyrene				
Samples	208	208	208	208	208				
Mean	59.1	14.7	24.6	883	64.5				
Median	40.0	10.0	3.0	255.5	8.0				
Min	4.0	5.0	3.0	54.4	1.0				
Max	1,390	520.0	1,609	46,521	8,390				
Standard deviation	141.0	38.3	140.7	3,508	581.7				
Skewness	8.1	11.7	9.5	11.2	14.2				

exceeded in the Most District which is linked to the petrochemical industry. This local contamination, with a maximum value of 0.9 mg/kg, does pose a risk, but confirms an anthropogenic input into soils in this area. The POPs statistical data for North Bohemia are presented in Table 3.

The I-TEQ PCDDs/Fs values for the 12 selected soil samples show enhanced contaminant content in North Bohemia. The proposed prevention limit for Czech agricultural soils (1 ng/kg I-TEQ PCCDs/Fs) was exceeded in eight samples, with the maximum value reaching 6 ng/kg I-TEQ PCCDs/Fs. This contamination does not pose a health risk, since the proposed indication limit for human health protection is 100 ng/kg I-TEQ PCDDs/Fs (Vácha et al. 2014). Neither does it present a risk for plant production, following limit values for PCDDs/Fs for agricultural production in Netherlands (10 ng/kg I-TEQ) or Switzerland (20 ng/kg I-TEQ PCDDs/Fs) (Vegter 1993). Using the stricter German standards (LABO 2003), two localities were identified, where soil samples exceed the content of 5 ng/kg I-TEQ PCCDs/Fs. However, these values do show a trend toward increased environmental contamination in the North Bohemian Region. The values of I-TEQ PCDDs/Fs and I-TEQ PCB in soils from selected localities are presented in Fig. 5.

3.2 North Moravian region

The basic characteristics of samples, separated into their main soil groups, are presented in Table 2. Total Cd contents are presented on a map, showing the probability of exceeding its limit value. Clearly, these values show a wide-ranging contamination (Fig. 3). Highest probability of Cd exceeding its preventive limit occurs in the Moravian–Silesian Beskydy Mountains (Fig. 3). However, these values do not exceed the Cd indication limit value for food chain protection. Neither do they exceed the Cd indication limit for human health protection. Thus, this area does not pose a direct risk to human health (dermal, oral or inhalation). The TE contents of the other species only sporadically exceed the prevention limits (background values) and do not represent any serious risk to human health. TE statistical data are presented in Table 4.

PAH content and carcinogenic benzo(*a*)pyrene are shown in Fig. 4. While the PAH content indicates the magnitude of this contamination, benzo(*a*)pyrene content shows its toxicity. A map showing the probability of exceeding their preventive limit values confirms elevated surface soil contamination in North Moravia, especially for PAHs. The probability kriging maps show greater uncertainty in the southern part of this region, reflecting lower sampling density because of a higher proportion of forest soils (only agriculture land was sampled in this study). Nevertheless, benzo(*a*)pyrene levels above the preventive limit can be seen in this area. In particular, Ostrava is polluted by benzo(*a*)pyrene, with levels exceeding the indication limit for human health.

The concentrations of the other POPs (BTEX, PCB_7, and DDT) in agricultural soils do not exceed their preventive limits and therefore do not present any specific health risks in North Moravia. POP statistical data are presented in Table 4.

The quantities of PCDDs/Fs in agricultural soils from North Moravia are slightly higher than for North Bohemia. Values exceeding the preventive limit for PCDDs/Fs (1 ng/kg I-TEQ PCDDs/Fs) were detected in all 11 selected

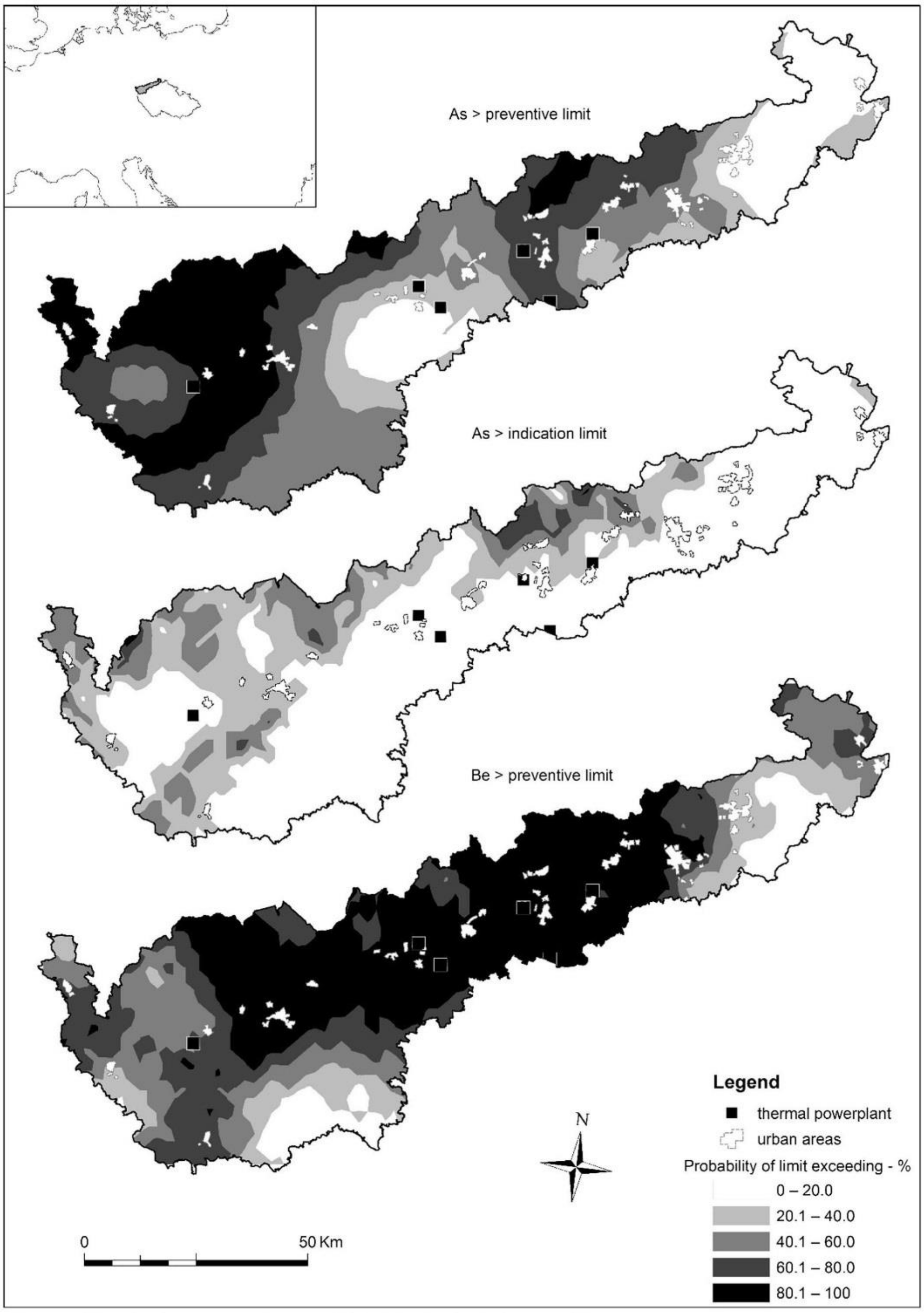

Fig. 2 The probability of limit values exceeding in the North Bohemian Region for As and Be

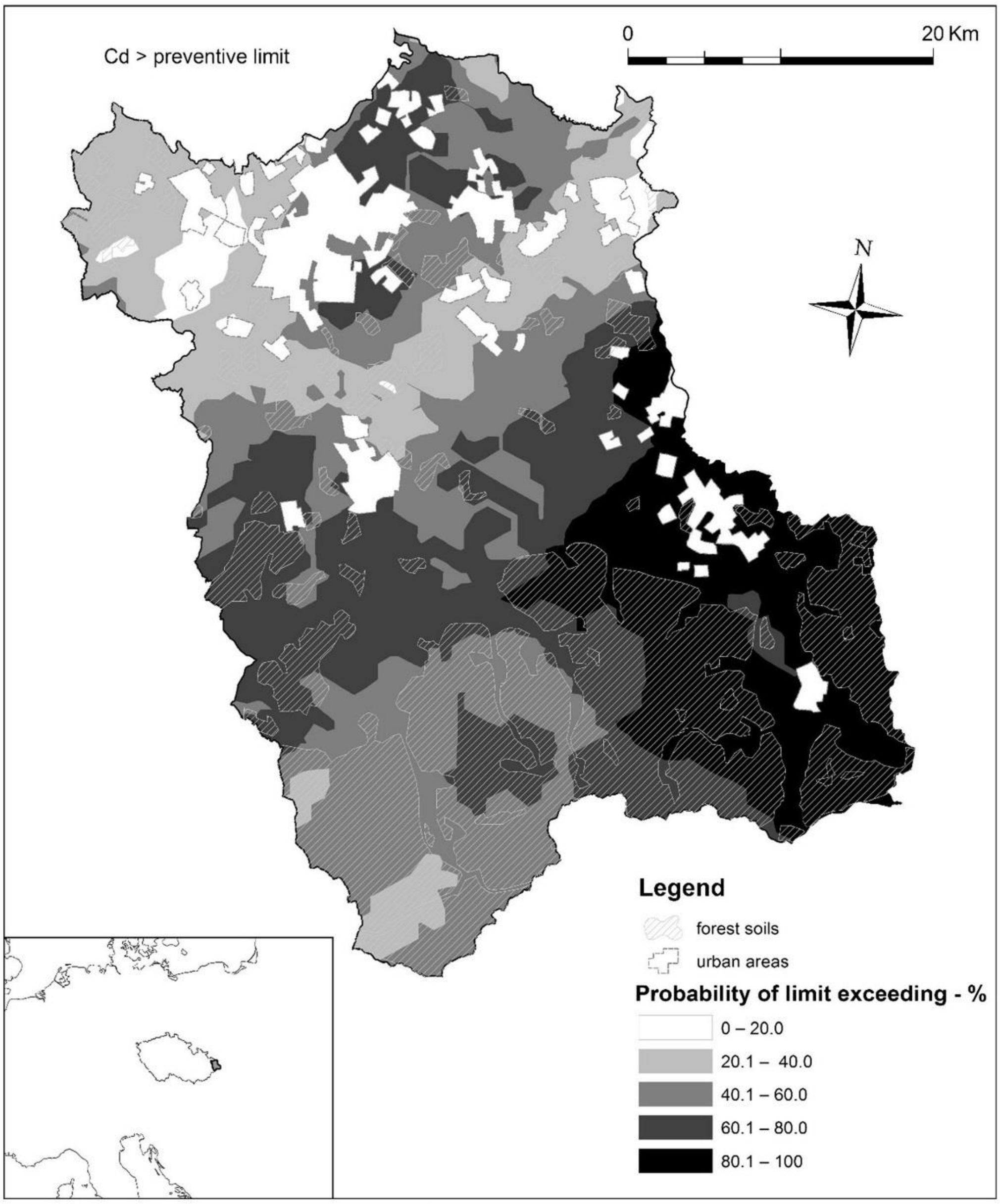

Fig. 3 The probability of prevention limit exceeding in the North Moravian Region for Cd

samples. The maximum value was 8 ng/kg I-TEQ PCDDs/Fs. As for the North Bohemian Region, this does not present any risk to human health or to the food chain. Two localities had values, where soil samples exceeded the threshold of 5 ng/kg I-TEQ PCCDs/Fs for plant production control according to German standards (LABO 2003). The values of I-TEQ

Table 4 Descriptive statistics of TEs (extract in Aqua regia) and POPs contents in soils of North Moravian Region

Statistic	As (mg/kg)	Be	Cd	Cu	Hg	Ni	Pb	V	Zn
Samples	182	182	182	182	182	182	182	182	182
Mean	13.62	1.64	0.59	24.05	0.14	21.34	44.99	96.15	127.97
Median	12.10	1.42	0.52	19.35	0.12	18.60	39.25	92.00	113.30
Min	2.15	0.40	0.06	6.60	0.02	3.70	5.00	32.80	41.70
Max	51.20	4.03	2.67	133.00	0.95	69.8	540.0	305.0	555.0
Standard deviation	7.64	0.78	0.33	16.79	0.10	9.86	40.28	41.04	73.13
Skewness	1.91	0.81	2.16	3.83	4.06	1.42	10.39	2.48	2.58
Statistic	∑MAHs (μg/kg)	∑PCB$_7$	∑DDT	∑PAHs	Benzo(*a*)pyrene				
Samples	106	106	106	106	106				
Mean	5.7	34.0	22.4	8,022	626.9				
Median	4.0	10.0	7.5	1,616	103.0				
Min	0.4	0.01	3.0	153.0	6.3				
Max	86.0	429.0	434.0	336,169	32,500				
Standard deviation	10.1	72.7	51.9	33,988	3,178				
Skewness	5.5	3.8	5.9	8.9	9.7				

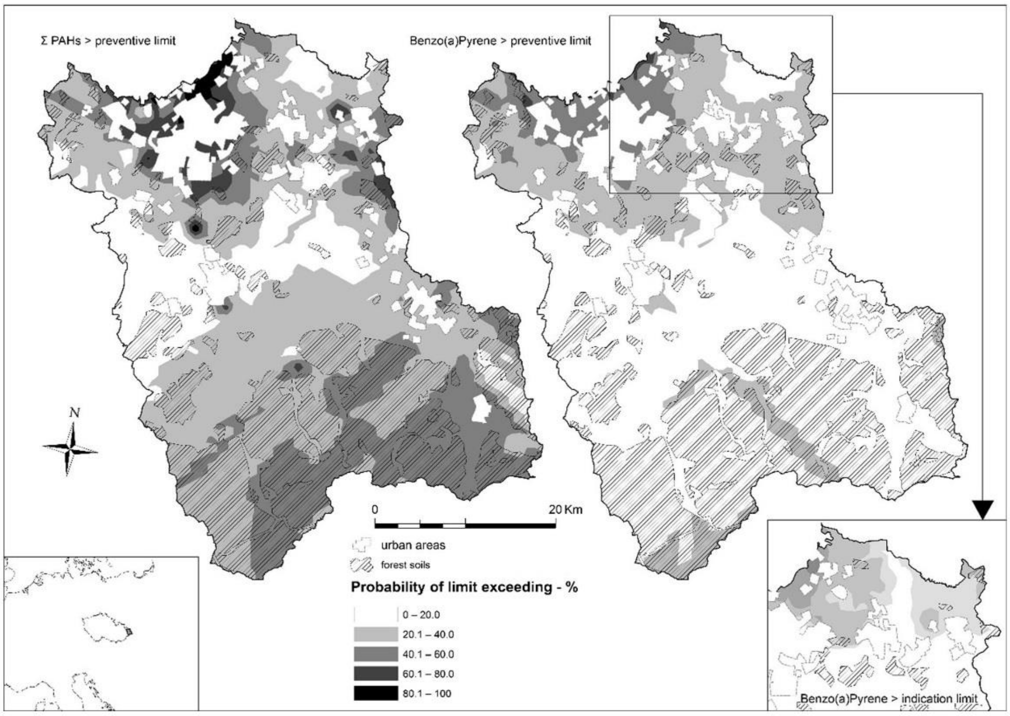

Fig. 4 The probability of limit values exceeding in the North Moravian Region for PAHs

PCDDs/Fs at specific localities in North Bohemia and North Moravia are compared with I-TEQ PCB values in Fig. 5.

4 Discussion

Arsenic poses the most severe soil contamination issue in North Bohemia. It has both anthropogenic and geogenic sources (Podlešáková et al. 1994b). Emissions from power stations, where brown coal with high As content is combusted, contribute to high levels of As in local agricultural soils as confirmed in previous works (Vácha et al. 2002, 2008; Skála et al. 2011). The As content of brown coal ranges from 0.1 to 1,290 mg/kg, with an average value of 14.6 mg/kg. In addition, historical coal combustion also contributed to contamination in this region (Šafářová and Řehoř 2006). The occurrence of soil contamination close to the Ore Mountains area is not unexpected, given the high number of anthropogenic sources (Jahn et al. 2013). However, in many other localities, there was contamination from anthropogenic and geogenic sources (Němeček et al. 1996b; Vácha et al. 2002; Drahota et al. 2012). The risk of As transfer into plants from root uptake shoot is limited because of the low mobility of As (Moreno-Jimenez et al. 2010). However, As contents that exceeded the indication limits for human health were observed in North Bohemia (Fig. 2). These localities could have an increased carcinogenic risk (Dostál et al. 2013b). This finding is supported by health assessments in the region (Zimová et al. 2001). The increased contents of Be in the soil caused by geogenic sources does not have any associated risks.

In contrast, the North Moravian Region is seriously polluted by Cd and PAHs. As for PAHs, Cd is derived from anthropogenic sources in North Moravia (Galušková et al. 2011). High Cd contents in the soils are linked to emissions from black coal combustion and metallurgy in the area. However, given that the Cd indication limit for food chain protection (Table 1) was not exceeded, it could be concluded that these agricultural soils are suitable for plant production.

Elevated PAH content in the environment represents the most serious problem in North Moravia, especially with respect to health risks (Švecová et al. 2013; Šram et al. 2013), PAH emissions affect the soil quality to a serious degree, causing soil levels to frequently exceed PAH preventive limits in North Moravia. The toxicity of this contamination was confirmed at Ostrava, where benzo(*a*)pyrene exceeded safe limits. These findings are supported by Šram et al. (2012).

The trend toward increasing PCDDs/Fs contents in the soils of polluted regions, especially in mountainous areas, also was observed by Kukučka et al. (2009). Although PCDDs/Fs contents were well under safe limits, their elevated contents clearly indicate contamination of the environment by anthropogenic pollutants.

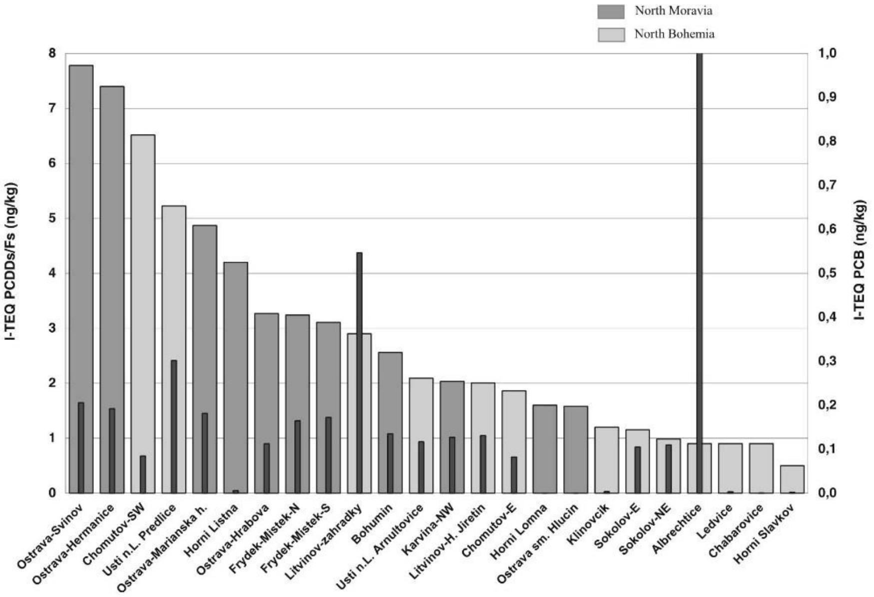

Fig. 5 The values of I-TEQ PCDDs/Fs and I-TEQ PCB in soil on individual localities

5 Conclusions

This study investigates heavy industry impacts on agricultural soils in two major industrial regions. Evaluation of their soil contamination with TEs and POPs highlighted specific regional environmental problems, namely:

- Elevated As and Be contents in the North Bohemian Region
- Elevated Cd and PAH contents in the North Moravian Region

Clearly, the soil environments of the North Bohemia and North Moravia are polluted by anthropogenic sources, directly connected with mining and heavy industry. These data confirm that agricultural activities in industrial regions need not be restricted, as long as some specific guidelines are implemented.

The North Bohemian Region is affected by lignite mining in open mines and the combustion of lignite with increased As contents in thermal power plants. Thus, agricultural soils may be used for plant production, except at the most polluted localities. Here, crop production for direct consumption (crops in the contact with soil environment—especially potatoes and other root vegetables) should be limited, and grassing over of arable soils to avoid wind erosion should be carried out.

The North Moravian Region is affected by black coal mining (hard mining), coal processing, and metallurgy. Anthropogenic Cd and PAHs influence the soil quality in this region. Control of soil acidity through liming presents a suitable solution for farmers and gardeners in areas with elevated Cd soil contents (to avoid Cd transfer into plants). The production of plants for direct consumption (e.g., potatoes, vegetable, etc.) is not recommended in areas where PAH contents exceed indication limits. Grassing over of arable soil should be carried out to avoid wind erosion of contaminated soil.

The pilot study of PCDDs/Fs contents in soils from both regions confirmed elevated PCDDs/Fs levels, consistent with anthropogenic impacts on soil environments. Our study shows that agriculture need not be restricted in areas impacted by heavy industry, as long as suitable precautions are undertaken in these regions. We present a practical methodology for soil contamination evaluation and risk assessment. Our data were provided to the Ministry of Agriculture for the Czech Republic to support monitoring of food production in these regions.

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Název: The Fluvisol and sediment trace element contamination level as related to their geogenic and anthropogenic source

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The Fluvisol and sediment trace element contamination level as related to their geogenic and anthropogenic source

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ABSTRACT

The upper values of the extractability of trace elements (As, Be, Cd, Co, Cr, Cu, Ni, Pb and Zn) in 2 mol/L HNO_3 and 0.025 mol/L ethylenediaminetetraacetic acid (EDTA) (compared with their pseudototal content in *aqua regia*) for determination of prevailing anthropogenic and geogenic soil load were proposed and compared with the results of the other 30 Fluvisol samples collected from the Labe fluvial zone. The increased geogenic load of Fluvisols was confirmed in the case of Be and As in some localities where low extractability with increased pseudototal contents were detected as opposed to the other elements when their increased pseudototal contents were followed by their increased extractability. The maps of probability of increased geogenic soil load in the area of the Czech Republic based on the comparison of geological substrates and trace element load were constructed. The combination of proposed elements extractability values for geogenic load together with developed maps is a suitable tool for the definition of prevailing Fluvisol or sediment load on some localities in the whole area of the Czech Republic. The results can be also a useful tool in the decision making processes regarding dredged sediment application on agricultural soil (support tool for legislative norms, Direction No. 257/2009 Sb.).

Keywords: soil; dredged sediments; soil contamination; geological substrates

The soil load with trace elements is caused by natural (geogenic) and anthropogenic sources of contamination. The frequent aim of chemical methods is the evaluation of critical trace element contents in soils reducing their transfer into food chains, and respectively the other matrices of the environment (Hellmann 2002). Anthropogenically induced contents of trace elements in soil support an increase of their mobility and bioavailability, generally (Němeček et al. 1996, Száková et al. 2005). Although the geogenic load is connected with low element mobility, in some cases of extreme geogenic loads an increased trace element mobility was observed (Filipinsky and Kuntze 1990, Němeček et al. 2002). These findings show the importance of contamination source determination for the prediction of trace element mobility and their subsequent transfer into plant production when different methods for prevailing contamination source; like geoaccumulation index, enrichment factor or pollution index, were described (Rafiei et al. 2010).

Generally, the load of sediments and Fluvisols is predominantly connected with anthropogenic factors in the Czech Republic (Podlešáková et al. 1994, Vaněk et al. 2005). Similar results were presented by Netzband et al. (2002) and Zerling et al. (2006) in Germany. Some authors, however, pay attention to more detailed principles of Fluvisols and sediments contamination by respecting the geogenic sources of trace elements load (Schwartz et al. 2006, Anawar et al. 2010, Deng et al. 2010). The Fluvisol contamination can markedly limit the agricultural use of these soils with high fertility potential.

Similarly, the increased trace element load of river sediments was described (Heise et al. 2005). These results restrict the use of dredged sediments in ag-

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riculture when trace element contents in dredged sediments exceed valid limits (Directive No. 257/2009 Sb.) in many cases in the Czech Republic (Vácha et al. 2011). This legislative norm allows the use of sediment with increased trace element contents of geogenic origin in agriculture (direct application on the soils) but unfortunately does not provide a suitable tool for geogenic load determination (especially mobile trace element contents criteria in sediments and soils are missing).

We utilized the results of studies focused on sensitivity of the extract of 2 mol/L HNO_3 and 0.025 mol/L EDTA for the assessment of anthropogenic and geogenic load with trace elements in the soils (Borůvka et al. 1996, Vácha et al. 2002) and we verified this data on a set of 30 Fluvisol samples. These extracts seem to be promising for Fluvisols and sediments contrary to weaker extracts of 1 mol/L NH_4NO_3 or 0.01 mol/L $CaCl_2$ for mobile trace elements contents determination because of their low contents in Fluvisols and sediments thanks to continual leaching by water in an aquatic environment (Vácha et al. 2011). The connection of proposed upper limit values of trace elements extractability for geogenic load in combination with constructed maps to determine the areas with increased geogenic load potential and the areas of Fluvial zones (polygons of the river basin of 4th order) in the area of the Czech Republic was developed as a suitable support tool for current legislation to assess the prevailing soil and sediment load (geogenic, anthropogenic) appointed to the local authorities responsible for the decision making process for example.

MATERIAL AND METHODS

The set of 30 soil samples from fluvial zones of the Labe river was collected. The Fluvisol samples (soils developed on alluvial sediments) were taken from Ap horizons of agriculturally used soils (meadows, arable soils) in widths of up to 50 m from river channels. This area is periodically flooded (in the spring usually). The length of the study area was up to 100 km (Figure 1). The coordinates of sampled localities and soil characteristics (pH_{H_2O}, C_{ox}, depth of humic horizon) were specified. The contents of trace elements (As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, V and Zn) were analysed in soil samples in the following extracts.

Aqua regia extraction (CSN EN 13346) – pseudototal content. The extract is quantified in Czech legislation giving limit values to trace elements in agricultural soils (Direction No. 13/1994 Sb.) and limit values in sediments for agricultural use (Direction No. 257/2009 Sb.).

The procedure is provided in the laboratory temperature 2 mol/L HNO_3 extraction (20°C, reciprocating shaker, 200 cycles per minute, 6 h, Zbíral et al. 2004). The extract is quantified in Czech as 0.025 mol/L EDTA extraction – potentially mobile contents of trace elements in soils and sediments (Zbíral et al. 2004).

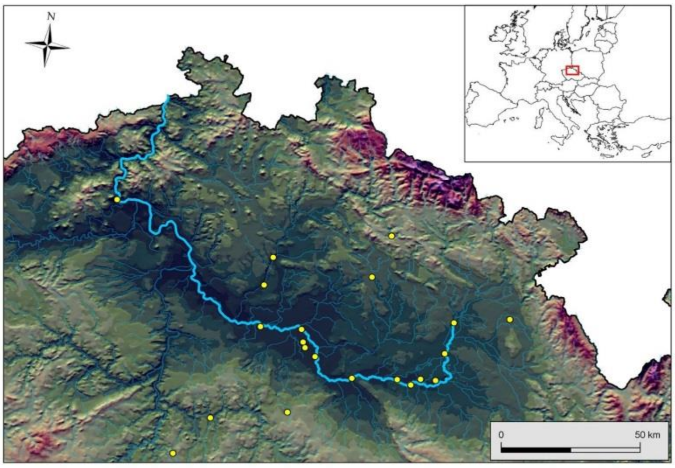

Figure 1. The Labe water basin and sample points

The soil samples for analysis were prepared from soil particles < 2 mm following the methodology CSN ISO 11464. Contents of trace elements in the extract were analysed by the Atomic Absorption Spectrometry (AAS) method using the following equipment: VARIAN AA 240Z – ETA (Palo Alto, USA; electrother-mic atomization) for Cd and Be analysis, VARIAN AA 240 – FAAS (Palo Alto, USA; flame technique) for Co, Cr, Cu, Ni, Pb and Zn analysis and VARIAN AA 240 – VGA (Palo Alto, USA; hydride technique) for As analysis.

The analyses were done in the accredited laboratory of the Research Institute for Soil and Water Conservation in Prague. The quality assurance of analytical data is guaranteed by the control process using matrix certificated materials (soils and sediments, CRM 7001–7004, Prague, Czech Republic) and certified methods of the analyses. The laboratory test protocol of every analysis is available.

The approach using geographical information system (GIS) was applied for the demarked areas (river basin) where geogenic load could be expected.

The maps of geogenic load with trace elements potentially influencing fluvial zones were generated using following sources:

Vector layer of the river basin of 4th order in the scale of 1:1 000 000 loaded in ESRI shapefile format, source Digital Base of water economic data (DIBAVOD, Prague, Czech Republic).

Geological map of the Czech Republic in the scale 1:500 000, coordinate system JTSK and S42, source atlas of maps of the Czech Republic GEOCR500, Czech Geological Institute.

The register of contaminated sites was processed by the Central Institute for Supervising and Testing in Agriculture in the Czech Republic (Kubík 2009). The database is an output of the soil agronomical testing process following the Czech legislation, Act No. 156/1998 Sb.

Based on the register of the contaminated sites database, the localities exceeding the limit values for sediment use in agriculture (Direction No. 257/2009 Sb.) were selected (at least one element exceeded the limit value on such locality). The geological map of the Czech Republic including 20 substrate units was divided into three categories based on the probability of geogenic load. On the basis of localisation of the contaminated points from the register of contaminated sites, water basins of the 4th order were delimited using an intersect function and were depicted on a layer of geological map selected on the basis of geogenic load potential.

The data was processed by the use of elementary statistical methods (Microsoft Excel, Redmont, USA) and geographic information systems (ESRI ArcGIS 9.2, Redlands, USA).

RESULTS AND DISCUSSION

The selection of extracts and trace elements extractability assessment in Fluvisol samples were calculated and evaluated with the use of previous works (Němeček et al. 1996, Vácha et al. 2002) when the extractability for individual trace elements from geogenic and anthropogenic sources

Table 1. Extractability of risk elements (%) in soils with different source of load derived from the data of Němeček et al. (1996) and Vácha et al. (2002)

Element	2 mol/L HNO_3			0.025 mol/L EDTA		
	geogenic	air deposition	fluvial	geogenic	air deposition	fluvial
As	13	40	42	3.5	9.3	25.5
Be	15*	20–50	30–90	–	–	–
Cd	70*	87	95	51	40–72	95
Cr	< 10	< 10	48–67	0.5	> 1	> 1
Cu	30	44	72	18	28	40
Mn	33	55	78	17	28	57
Ni	–	–	–	25	40	60
Pb	32	57	83	50	> 60	> 60
Zn	20	50	70	25	> 40	> 40

Be* – derived for soils developed on parent materials from acid rocks; Cd* – derived for soils developed on parent materials from weathering limestone products

Table 2. Extractability of risk elements in 2 mol/L HNO_3 (%) in set of Fluvisols (medians)

	As	Be	Cd	Cr	Cu	Ni	Pb	Zn
A	28	29	92	10	52	30	68	35
B	48	18	95	67	77	no	90	55

A – load under background values in Czech agricultural soils; B – load over background values in Czech agricultural soils. no – no relevant data analysed

was derived (Table 1). The solubility was calculated for the extracts of 2 mol/L HNO_3 and 0.025 mol/L EDTA. In our case, the *aqua regia* soluble element content was used for the calculation of the 2 mol/L HNO_3 and 0.025 mol/L EDTA soluble element portion instead of the pseudototal content (*aqua regia* extract). The borderline extractability for the load from geogenic sources was derived. The relevance of calculated extractability values was verified on the set of 30 Fluvisol samples.

The values of trace elements extractability in 2 mol/L HNO_3 (extract in 2 mol/L HNO_3/extract in *aqua regia* × 100) derived from the set of 30 Fluvisol samples and calculated as median values are presented in Table 2. The extractability for fluvial load under and over background values were calculated separately. It is documented that an increased load of Fluvisols by trace elements is followed by its increased extractability. Sharp differences were found in cases of elements with generally low mobility. Cr, As and Pb caused the enrichment of anthropogenic load increases the extractability of elements markedly. For the most mobile Cd gives rise to a low difference between the extractability of background and increased load prospective regardless of the differences in the case of Zn are surprisingly much more evident.

Be shows an opposite trend where increased Fluvisol load is followed by lower extractability in an observed set of Fluvisol samples. General Be extractability values in 2 mol/L HNO_3 did not reach the extractability values for fluvial load in Table 1 but overcome the value of geogenic load and are still typical for anthropogenic load. The extractability value for Ni was calculated only for low Fluvisol load because no increased Fluvisol Ni load was observed. On the basis of this fact and previous works (Němeček et al. 1996, Vácha et al. 2002) it could be concluded that 2 mol/L HNO_3 is not a suitable agent for Ni geogenic load evaluation.

The number of samples exceeding background values of 1 of trace elements in Czech soils is shown in Table 3 together with the samples with low trace elements extractability that is typical for geogenic load (exceeding 2). The samples with trace elements contents over their background values and low trace elements extractability (geogenic load) are presented as exceeding 3. The data shows that the most problematic are Be, Zn and Cd. The low extractability typical for geogenic load was observed in Fluvisols in the case of Cr >> Cd > Be > As and Zn. Cu and Pb show increased extractability in all samples and their prevailing anthropogenic inputs into Fluvisols could result. Opposed to this, low extractability typical for Cr could be connected with geogenic load especially in the Fluvisols with low Cr load. Increased Cr contents (3 samples)

Table 3. Number of samples exceeding background values of risk elements and number of samples with risk elements extractability value under value typical for geogenic load

	As	Be	Cd	Cr	Cu	Ni	Pb	Zn
Background	20	2	0.5	90	60	50	60	120
Exceeding 1	5 *n*	10 *n*	8 *n*	3 *n*	4 *n*	0 *n*	4 *n*	7 *n*
Exceeding 2	1 *n*	4 *n*	5 *n*	14 *n*	0 *n*	–	0 *n*	1 *n*
Exceeding 3	1 *n*	3 *n*	0 *n*	0 *n*	0 *n*	–	0 *n*	0 *n*

Background – risk elements background values in Czech agricultural soils; exceeding 1 – exceeding number of risk elements background values in a set of Fluvisol samples; exceeding 2 – samples number of extractability values under value of geogenic load in a set of Fluvisol samples; exceeding 3 – samples number of extractability values under value of geogenic load in a set of Fluvisol samples and with increased load over background values simultaneously are connected with increased Cr extractability. Similarly, increased Cd contents in the Fluvisols reflect anthropogenic load. Nevertheless, Be (3 samples) and As (1 sample) show that increased trace element contents in the Fluvisols could be related to geogenic load in some cases.

The extractability of 0.025 mol/L EDTA shows comparable values with 2 mol/L HNO_3 when sharper differences were observed in the case of Cr (20 times lower) and were problematic in the case of Be. The values of Be extractability in EDTA differed in the set of samples with different loads and no statistically relevant data could be derived. The same situation occurs at evaluation of Ni extractability results in 2 mol/L HNO_3 and the combination of both extracts can be recommended to avoid the described problems. On the basis of selected data the values of trace elements extractability for both extracts (2 mol/L HNO_3 and 0.025 mol/L EDTA) defined as upper limits for geogenic load in Fluvisols and sediments were proposed (Table 4). The samples with trace elements extractability equal to and lower than the defined limit values could be designated as the samples with prevailing geogenic load.

The observed load of Fluvisol of the Labe River is in good agreement with the results of Netzband et al. (2002). These authors document an increased load with As, Cd and Zn. The extractability of trace elements indicates their increased anthropogenic inputs into Fluvisols in most cases. The load with Cd and Zn could be connected especially with anthropogenic inputs as it was also confirmed e.g. by Zerling et al. (2006) in the European context. The load of Fluvisols with trace element contents under background values is proven by geogenic sources and is more evident (lower extractability) than in Fluvisols with trace elements contents exceeding background values (higher extractability). The data confirms that geogenic sources of trace elements play an important role in uncontaminated Fluvisols (Deng et al. 2010), but increased contents are usually related to anthropogenic load (Podlešáková et al. 1994). This trend could be presented using the example of Cr especially. Nevertheless, in the case of As and Be it was documented that a strong influence of geogenic load resulting in an increased load of alluvial sediments could not be excluded. In these cases quantitative load with As and Be from geogenic sources leads to exceeding their background values in the soils. The low extractability in 2 mol/L HNO_3 confirms prevailing geogenic sources. The observed data confirmed a predominance of anthropogenic load in loaded Fluvisols but the existence of prevailing geogenic load over anthropogenic load was confirmed also (As, Be) in the Fluvisols with their increased contents. The construction of maps presenting the probability of increased geogenic load in the area of the Czech Republic was realized. The probability of geogenic contamination of agricultural soils was derived as the correlation of geological substrate categories with GIS layer showing the samples which exceed limit values on the area of the Czech Republic (Kubík 2009) and with GIS layer showing the polygons of river basin of the 4th order. The combination of these three individual GIS layers into one complex GIS layer gives the information on which localities or just river basin of the Czech Republic area with increased trace element contents it can be detected and highlights if these cases could be related to geogenic load.

This approach was done in two main steps. In the first step only two GIS layers were combined and the resultant map (Figure 2) shows the areas of river basins of the 4th order and shows sampling sites with increased contents of trace elements in the area of the Czech Republic. In the final map (Figure 3), the third GIS layer showing areas of probability of geogenic contamination was added.

The described approach based on the comparison of trace elements extractability in 2 mol/L HNO_3 and 0.025 mol/L EDTA (with the existence of the proposed upper values for geogenic load) and the comparison of observed data with the map overview showing the presence of the areas with increased geogenic sources is a suitable tool for the differentiation of anthropogenic and geogenic load of Fluvisols and sediments and can serve as

Table 4. Upper limits of risk elements extractability (%) in 2 mol/L HNO_3 and 0.025 mol/L EDTA for geogenic load in Fluvisols and sediments

Extract	As	Cd	Be	Co	Cr	Cu	Ni	Pb	Zn
HNO_3	15	70	15	30	10	30	–	30	20
EDTA	5	50	–	25	0.5	25	25	50	25

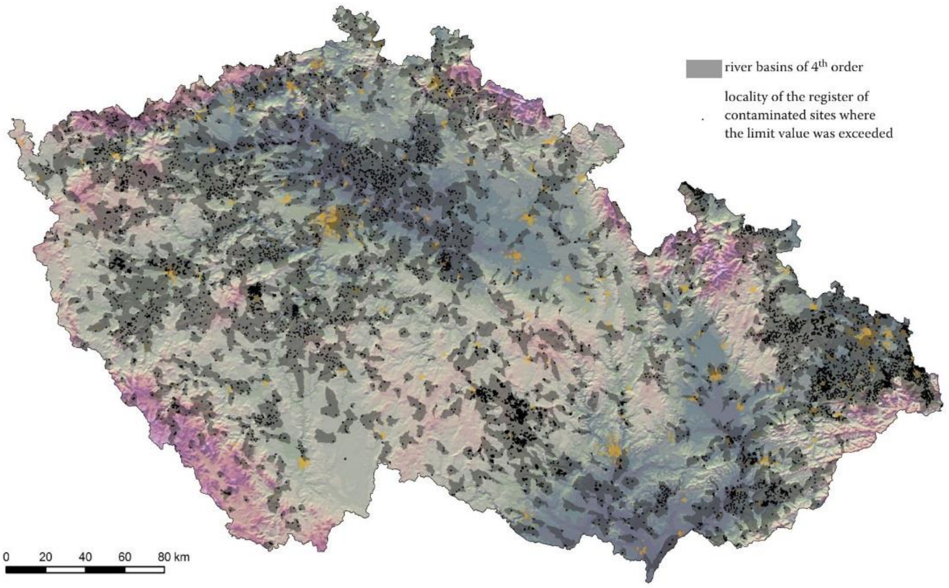

Figure 2. Localisation of the river basins of 4th order with sampling sites (Kubík 2009), where the limit value for risk element content was exceeded

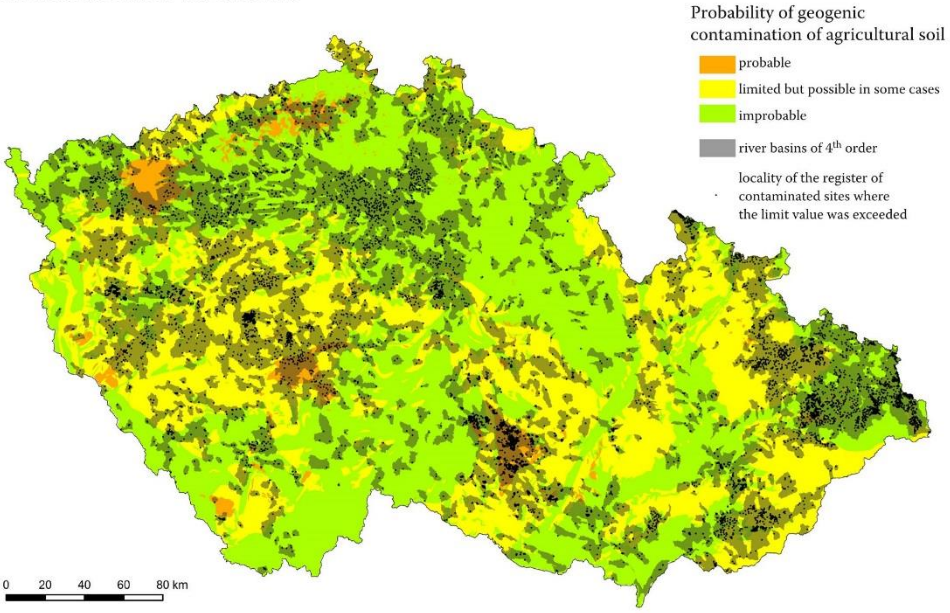

Figure 3. Probability of geogenic contamination of agricultural soils – correlation of geological substrate categories with sampling sites (Kubík 2009), where the limit value for risk element content was exceeded and polygons of river basin of 4th order

an informative source in any decision-making process concerning the application of sediments on agricultural land (Direction No. 257/2009 Sb.).

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4.5 Skála et al. (2019): Regionální geochemická zonace zemědělských půd údolních niv – hodnocení kvality půdy analýzou a mapováním víceprvkových vztahů v nivě podél řeky Ohře v České republice

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Regional geochemical zonation of cultivated floodplains–analysing and mapping multi-element associations for evaluating patterns in soil quality along the Ohře (Eger) River, Czech Republic

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Abstract

Floodplains are dynamic ecosystems wherein intensive farming can meet increased environmental concentrations and bioavailability of a number of trace elements. Therefore, the primary objective of this study was to investigate the partial digestion of selected trace elements in surficial soil samples (depth up to 40 cm) across a gradient of environmental conditions along the Ohře River and determining the elements of high priority, while also exploring their geographic variation. The established agrochemical testing of Czech soils provides a valuable resource to determine the geochemical differences of multi-element associations in cultivated areas (arable crops and hop fields) in periodically inundated areas in the catchment with a number of potential pollution sources. The topsoil samples were digested using the nitric acid (2 mol/L HNO_3), analysed for trace elements (Be, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) using inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS), and for their total Hg content. Data (n = 130) were modelled against the sample location and cultivation using the log-ratio approach. The structural spatial analysis (based on the Mantel's correlation test and the generalised distance covariance test and involving the use of the compositional Aitchison's distance and two types of spatial distances quantified the geospatial continuity of the geochemical composition with the correlation statistics $r_M = 0.46$ resp. $r_d = 0.43$. The explanatory and inferential statistical tools (PCA, MANOVA) adapted for compositions, combined with a simple spatial ranking and land-use information defined effective discriminating subcomposition (Cu–Hg–Ni) that were able to describe the changes of geochemical domains in floodplains and retained a decent representation (46 %) of the entire compositional variability in our dataset. Mapping the Cu–Hg–Ni subcomposition using the RGB composite enabled to display the high-dimensional multivariate dataset with reduced information and enabled to discriminate spatial domains representing geochemical signatures related to changes in element inputs along the watercourse. The analysis of our results within the compositional framework showed a changing pattern of relative enrichment/depletion of the partially digested trace elements in which a regional contrast between groups of the chalcophile elements (Cu, Pb, Zn, and partly Cd), siderophile transition metals (Cr, Co, Ni, and V) and single elements (Hg, Be) was source-apportioned to the effect of point pollution sources (Hg, Ni, Cr, Co) as well as diffuse sources (Cu, Zn, Pb, Cd).

Keywords

Floodplains; trace elements; soil geochemistry; compositional data; geochemical mapping

Highlights

- Geospatial continuity of the compositional structure was evident for partially digested trace elements as far as the stream distance of 40 km in the Mantel's correlation test.
- Topsoil pattern revealed a regional contrast between groups of the chalcophile elements (Cu, Pb, Zn), transition metals (Cr, Co, Ni) and single elements (Hg, Be).
- The changing impacts of local dominant sources featured effectively the Cu–Hg–Ni subcomposition and its mapping.

1. Introduction

Soil is an important sink for metals that are released into the environment as a result of human activity. The high and long-term anthropogenic alteration of floodplains as a consequence of high population density has resulted in enhanced anthropogenic pressures on riverine systems. Few studies have focused on semi-terrestrial soils, particularly floodplain soils, as compared to terrestrial soils, although they reveal some specific features; these include elevated levels of pollutants (Rinklebe et al., 2007; Luster et al., 2014; Schwartz et al., 2006), high spatio-temporal heterogeneity due a dynamic interactions among various environmental media (Wälder et al., 2006), and long-term and intensive cultivation practices (Tockner and Stanford, 2002). As our research goals were targeted at the geochemical patterns within cultivated soils in floodplains, tillage practices may effect spatial variations in soil properties. On comparing the spatial patterns of chemical elements in the topsoil and subsoil horizons over a geologically contrasted and weakly contaminated area, Bourennane et al. (2003) proved that the local geology may be partially disguised by the tillage-based redistribution of elements and homogenisation of soils. In addition, the statistical processing of multi-element geochemical data is further hampered by the closure problem and possible spurious correlations (Aitchison, 1986; Pawlowsky-Glahn et al., 2015; McKinley et al., 2016). In statistics and mathematical geosciences, the log-ratio approach is currently being developed to overcome these disadvantages in compositional analyses (Aitchison and Egozcue, 2005).

Agricultural soils of floodplains and the determination of their geochemical characteristics are areas of increasing interest, as these soils are subject to intensive farming; food chain contamination via transfer of pollutants is also a matter of concern. Bioavailability is the key factor responsible for the toxic potential of trace elements (TEs) with respect to the environment and living organisms (Adriano, 2001). Therefore, the present research was conducted to determine whether the analysis of a horizontal spatial variability in selected TEs in partially digested surficial-soil samples has the potential to trace the regional changes of the geochemical signatures, and to apportion these changes to potential sources. For these purposes, the log-ratio approach was used to explore whether some particulate subcompositions may be used to discriminate spatial domains representing geochemical signatures related to changes in element inputs along the watercourse. After the analysis, we focused on obtaining a quantitative measurements of the spatial structure and tested the efficiency of the Mantel's correlation test and its generalisation (Borcard and Legendre, 2012; Omelka and Hudecová, 2013). As reliable geochemical maps are required in environmental research and for communicating relevant geochemical findings to environmental regulators and policy makers (Reimann et al., 2012), we combined the results of the compositional and spatial analysis into integrative maps that facilitated the interpretation of the spatial patterns of geochemical features, along with an effective selection of the priority TEs regionally influencing the soil quality of cultivated floodplains within the case study watercourse (the Ohře River in the Czech Republic).

2. *Materials and methods*

2.1 Sampling design and study area

The Czech Republic is a country with a long-term industrial history. This is especially the case along the Czech–Saxony border, where industrial growth was encouraged by mining activities in the opencast coal fields and historical polymetallic mining districts. The evidence of various pollution sources was recorded in the broad region of the Ore Mountains (Vácha et al., 2015) with proven symptoms in the fluvial sedimentary archives of the Ohře River and its tributaries (Grygar et al., 2016).

To research on the soil quality of cultivated floodplains, we took advantage of the long-established agrochemical testing of soils that was aimed at helping Czech farmers to meet lawful terms according to the Act on Fertilizers (Act No. 156/1998 Coll., as amended). The countrywide agrochemical testing included information regarding the contents of the major and TEs in soils, and their comprehensive characterisation was presented in detail in another study (Bednářová et al., 2016). The country-wide database containing approximately 50,000 soil samples was used for data filtering on the basis of digital water management data (water course model, inundation areas of the 100 -year flood).

Agricultural soils	Sampling density	Mixed sample	Depth	Number of samples*
Arable crops	1 sample/ 7–10 ha	30 individual probes	up to 30 cm	90
Hop fields	1 sample/3 ha	30 individual probes	10 – 40 cm	40

* *Number of samples involved in this study*

***Table 1** Summary of soil prospecting for the agrochemical testing of the Czech soils*

The spatial filtering of the agrochemical data, excluding some samples owing to analytical reasons (an abundance of unavailable and below-detection values), provided values for 130 samples with a complete geochemical record for surficial concentrations of ten TEs in cultivated soils within the inundation areas of the 100-year flood along the Ohře River (Table 1). The sampling within the Czech agrochemical testing of soils has been carried out according to the unified soil prospecting practice - Klement (2014). One composite sample consists of 30 individual probes to depths of 30 cm or 40 cm on arable land and hop fields, respectively. The spatial distribution of the composite samples is arranged so as to achieve approximately 1 soil composite sample per 7 - 10 ha of arable crops and 3 ha of hop fields and represented agricultural plots with monotonous cultivation (same crop plant under same cultivation conditions) (Table 1). The depths of the soil sampling are designed to represent chemical composition in the plough layer - cultivated soil volume that is relatively rich in organic matter, contains many live roots and is subjected to land preparation (e.g. ploughing, harrowing etc.) with the possible tillage-based homogenisation of soils. The impact of such purposive soil prospecting resulted in a sampling gap at the middle reach of the Ohře River owing to the absence of cultivated floodplains along the channelized river near the Sokolov coal field and in the narrow valley with wooded slopes comprising mafic volcanic rocks and basaltic lavas/tuff below the Karlovy Vary municipality.

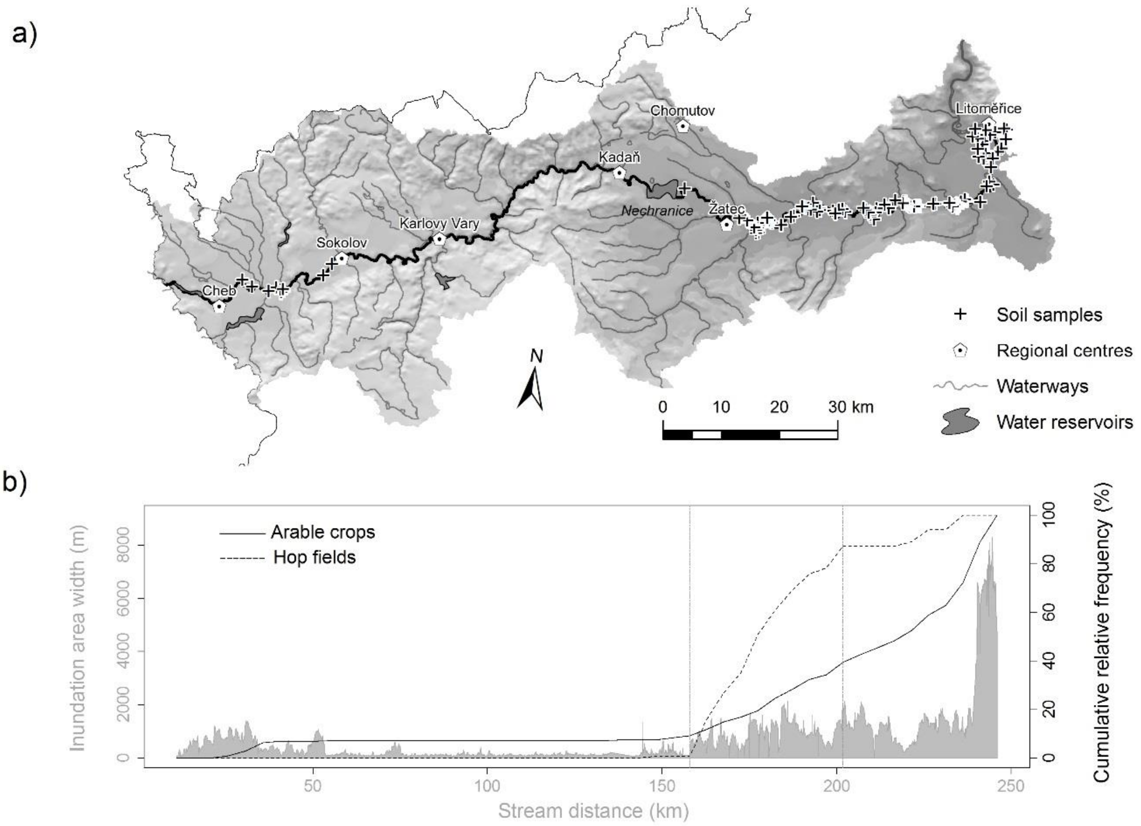


***Figure 1** Geography of the research basin: a) the basic topography of the catchment, b) the width of the floodplain inundated by floods with 100- year periodicity and cumulative proportions of hop fields and arable crops*

Because of the rationale and nature of soil prospecting within Czech agrochemical testing, there is an inherent uncertainty in our samples being representative of the cultivated soils and geochemical situation of the entire floodplain. In particular, neglecting the effects of natural sorting in river systems (owing to the mixed sampling strategy of cultivated soils and sieving the samples; Bábek et al., 2015 or Grygar and Popelka, 2016) together with the absence of sampling for natural traps for sediment-associated heavy metals in wetlands and swale soils caused our assessment to be conservative to some extent. Although the present limitations concerning the diverse alluvial depositional patterns are indisputable, we emphasise that the uncertainty in our analysis was outweighed by the insights that our results provided for the quality status of the cultivated soils.

2.2 Chemical analysis

The soil samples were homogenized by being stirred in a modified mixing device, after stirring each sample was divided by quartering and tested for homogeneity. All soil samples were air-dried (at the temperature below 40°C) and after major parts of the skeleton and possible roots had been removed the sample was sifted on a special soil-sifting machine according to ISO 11464. The prepared samples contained particles of the size less than 2 mm, and then extracted using the nitric acid (HNO_3). Dry soil (10 g) was shaken in 100 ml of cold 2 mol/L HNO_3, and 20 ml of the extract was filtered for analysis. The extraction procedure was performed at 20 °C, in a reciprocating shaker (200 cycles/min, 6 h) (Zbíral et al., 2004). Using chemical extraction media of different strengths, it is possible to differentiate between the inactive, mobile, and mobilisable (extractable or leachable) metal fractions (Gupta et al., 1996). The mobile and mobilisable metal fractions provide a risk-based assessment. The use of HNO_3 or EDTA extractions is advisable for assessing mobilisable metal fractions in a fluvial environment, as the weaker extracts (i.e., 1 mol/L NH_4NO_3 or 0.01 mol/L $CaCl_2$) have very low metal concentrations owing to their continual leaching by water in an (semi-) aquatic environment (Vácha et al. 2013). The HNO_3–extractable fraction of the TEs was measured and compared with the pseudo-total contents of the TEs in the aqua regia extract (according to ISO 11466) for a number of samples (Supplementary Table A.1). The solubility results were also compared between the samples within the inundation areas (n=32) and those within the 5-km buffer zone outside the inundated areas during the largest known meteorological flood in the study area (n=28). The results showed that HNO_3 extraction may completely recover Cd and may partially (or fully) recover Be, Cu, and Pb, while it may provide partial recovery for Cr, Ni, V, and Zn. On comparing the solubility of the floodplain and near-floodplain samples, a small shift in equilibrium between the pseudo-total contents and HNO_3–extractable fraction was observed, confirming differences in the available chemical forms of TEs in Czech fluvial soils compared to standard agricultural soils (Podlešáková et al., 1999).

The contents of Be, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn were determined using inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectroscopy (AAS). Mercury was analysed using a total mercury analyser (TMA). All the analyses were conducted in the National Reference Laboratories of the Central Institute for Supervising and Testing in Agriculture, which are certified authority for the chemical testing of soils, according to CSN EN ISO/IEC 17043:2010. The comprehensive characterisation of quality control was presented in detail in previous studies (Bednářová et al., 2016; Meloun et al., 2005). Precision and accuracy of the analysis was assessed using replicates at a rate of 1 in 10 samples and by comparison to known in house analytical standards linked to certified reference materials with the assessed uncertainty through the validation and using laboratory blanks. The detection and quantification limits are presented in Table 2. Samples with an abundance of unavailable and below-detection values were omitted at the early stage of filtering the dataset in order to prevent the occurrence of the rounded-zero problem in the compositional data analysis.

2.3 Data analysis

Geochemical data are generally (sub)compositions and do not belong to the classical Euclidean space but are required to be considered in their own geometry on the simplex (Aitchison, 1986; Pawlowsky-Glahn and Egozcue, 2001). In mathematical geosciences, the orthonormal coordinate representation which is coherent with the geometrical structure of the simplex sample space is currently an area of active research (Egozcue et al., 2003; Egozcue and Pawlowsky, 2005; Fišerová and Hron, 2011) with an inherent proliferation into applied environmental geosciences (Reiman et al. 2012; McKinley et al. 2016; Tolosana-Delgado and van den Boogaart, 2013). While exploring the geochemical zoning of the cultivated soils within the study catchment, we focused our attention on the quantitative measurement of the spatial relations of the TEs and an effective spatial mapping of the results. The first was achieved by relating the Aitchison’s distance matrix to two tailored spatial matrices using the global Mantel’s correlation (Mantel, 1967) and by enumerating mutual spatial relations of distances in the Mantel’s correlogram (Oden and Sokal, 1986). In the attribute space of our dataset, a distance metric in the simplex space (called the Aitchison’s distance) may be defined as the Euclidean distance between the clr-vectors (i.e. the transformed compositions by the centered logratio function according to Eq.2) (Aitchison, 1992; Aitchison et al., 2000).

In the spatial domain of the dataset, two matrices were set based on the geographical position of the samples:

a) The Euclidean distance matrix is based on the straight-line distance between the geographical positions of the samples within the floodplain.

b) The stream distance matrix is calculated as the shortest stream-line distance between the geographical positions of the samples, after the samples had been manipulated to cling onto the watercourse line using the nearest distance to the stream line (see Supplementary Fig. A.1.)

These spatial matrices were related to the Aitchison’s distance matrix using a normalised Mantel’s correlation coefficient to quantify the surficial-soil TEs in cultivated floodplains along the Ohře River, thereby determining the spatial continuity in geochemical composition of the soils. As several objective criticisms raised methodical concerns regarding the statistical power of the Mantel’s test (Dutilleul et al., 2000; Legendre and Fortin, 2010), we verified the results using a generalisation of the test based on the distance covariance described by Omelka and Hudecová (2013). In the next step, the spatial distances were resolved into k distance classes using Sturge’s rule, and the normalised Mantel’s statistics r_M as a simple Pearson’s linear correlation coefficient between the matrices of distances were recomputed for the combinations of the Aitchison’s distance matrices against the binary matrices, representing the membership of sites to the distance class being tested, by the following relationship:

$$r_M = \frac{1}{d-1}\sum_{i=2}^{n}\sum_{j=1}^{i-1}\left(\frac{x_{ij}-\bar{x}}{s_x}\right)\left(\frac{y_{ij}-\bar{y}}{s_y}\right) \quad 1)$$

where $\bar{x}$ and $\bar{y}$ are the means of the values in each of the lower-triangular distance matrices X and Y, and s_x and s_y are their standard deviations, and $d= n(n-1)/2)$ is the number of dissimilarity measures in one of the upper triangular matrices (Borcard et al., 2018). Each rM value for the distance class is then tested using a permutation test (n = 999). The resulting correlation statistics rM were plotted against the distance classes k in the multivariate Mantel’s spatial correlogram (Oden and Sokal, 1986). According to Boccard et al. (2018), the Mantel’s correlogram was proved useful for the spatial correlation analyses in those cases wherein the response data are modelled by a distance function that is not Euclidean.

In the next step, the explanatory analysis was employed to select and use sub-compositions to spatially delineate the zones with distinct geochemical characteristics of surficial soils in cultivated floodplains using the colour composite map (Albanese et al., 2011; Zuzolo et al., 2018; Kirkwood et al. 2016). To highlight the geochemical contrasts within the composite map, an orthonormal basis for the ilr-transformation was tailored to allow ilr-coordinates to contain all the relative information of one compositional part with respect to the other parts (Filzmoser et al., 2009a). These univariate ilr-coordinates were then spatially interpolated using the inverse distance weighting (IDW) interpolation technique. The interpolated grids were normalised and reclassified using a 256-interval scale to produce three monochromatic maps for each RGB colour. These maps were combined into the RGB composite grid in which the value of each pixel, as a result of the colour triplet, represented the influence/domination of the associated element in relation to the others. The interpolated grids were proceeded for the coordinates of those TEs’ triplets that retained a decent representation of the entire compositional variability pattern within the three-part subcompositions, as determined through the explanatory analysis targeting a decomposition of compositional variability. The use of three-part subcomposition conveniently allowed for full representation in the RGB colour space. Care should be taken when interpreting these results as the univariate ilr-coordinates do not accurately represent the multivariate data information (Filzmoser et al., 2009a); their interlinking in a multivariate fashion is in violation of the fundamental requirement of subcompositional coherence. Since compositional data are multivariate by definition, the component-wise approach (i.e., clr-values and univariate ilr-coordinates) does not explicitly show all the mutual impacts of other variables and fails to provide deep insights into the multivariate structure of the data (Reimann et al., 2012). McKinley et al. (2016) declared that a high-dimensional multivariate information may be hard to display and read, hence the keystone is the univariate or oligovariate mapping using sub-compositions for gaining insight into geochemical processes. The challenge in finding those sub-compositions to be mapped was based on the data explanatory analysis using statistically determined projections that best capture certain patterns and elemental associations in the geochemical dataset and we proceeded as follows.

1) The basic statistical parameters were calculated after the data matrix had been centred-log ratio (clr) transformed in which each variable x_D is divided by the geometric mean $g(x)$ of all the measured elements, followed by a log-transformation (Aitchison, 1986):

$$clr\ (x) = \left[\ln \frac{x_1}{g_{(x)}} \quad \ln \frac{x_2}{g_{(x)}} \quad \ldots \quad \ln \frac{x_D}{g_{(x)}} \right] \qquad 2)$$

2) The compositional structure of our data was first described using the variation array, i.e. a symmetrical matrix where the upper diagonal contains the log-ratio variances and the lower diagonal contains the log-ratio means (Aitchison, 1986). The log-ratio variance allows us also to identify the stability of the parts as a measure for a statistical association between compositional parts (Aitchison, 1986; Buccianti Pawlowsky-Glahn, 2005; Filzmoser et al., 2010). The pair-wise variance of the simple log-ratios (or its normalisation) may determine the components, which are highly proportional, but does not allow to distinguish between positive and negative associations (Reimann et al., 2017). We advanced the geochemical relationships using the isometric log-ratio transformation (ilr-transformation) based on the expression of compositions in terms of their real coordinates with respect to an orthonormal basis of the simplex (Egozcue et al., 2003). For the purpose of advance pairwise variable associations, the orthonormal basis was tailored to highlight a correlation structure of the compositional data using the symmetrical coordinates that were mathematically defined by Kynčlová et al. (2017) and effectively applied in geosciences by Reiman et al. (2017) or Hron et al. (2017). The advantage of using the symmetrical coordinates enabled the visualisation of associations using the heatmap technique combined with the rearrangement of the correlation matrix via a distance-based clustering of correlations (Reimann et al. 2017).
3) Multivariate analysis techniques can help to identify interesting log-contrasts to map. Principal component analysis (PCA) adapted to compositions, along with a compositional biplot (Aitchison and Greenacre, 2002), were then employed to visualise and understand the variability in the variation array. Here the use of the PCA together with subcompositional analysis (Aitchison, 1984) seems to be reasonable to define the 3-part subcomposition to be employed for the mapping and that may retain as much as possible of the variability in the entire composition and that can best capture certain effects, patterns and elemental associations. To visualise the geochemical contrasts in geographic space, the data were spatially ranked according to the stream distance of the sampling sites from the river mouth within the compositional biplot and also for the selected three-part subcompositions within the corresponding ternary diagrams. Finally, we compared the relative differences of geochemical compositions between groups according to the cultivation (arable crops vs. hop fields) using the geometric mean barplots and MANOVA adapted in terms of log-ratio approach (Martín-Fernández et al., 2015).

All the steps of compositional data analysis were performed in the R programme for windows (R Core Team, 2012) using the robCompositions package (Templ et al., 2011). The stream distances were processed in the riverdist package (Tyers, 2017), the Mantel's correlation analysis was conducted using the vegan package (Oksanen et al., 2017), the nonparametric multivariate inference was processed using the npmv package (Woodrow et al., 2017), and the generalised distance covariance test was performed using the energy package (Rizzo and Székely, 2013). All the spatial mapping was processed in the ArcGIS 10.2 software (ESRI, Redlands, CA).

3. *Results and discussion*

3.1 Geospatial continuity of geochemical compositions

We expected that there is a substantial spatial variation of the soil TEs along the river gradient. To verify this hypothesis statistically, spatial continuity of the compositional structure was quantified using the global Mantel’s correlation, verified in the generalised distance covariance test, and finally regionalised using the Mantel’s correlogram. First, a calculated correlation was found between the Aitchison’s distance matrix and Euclidean distance matrix based on the coordinates with the resulting $r_M = 0.46$ in the Mantel’s test (resp. $r_d = 0.51$ in the covariance distance test) and with the statistical significance in the permutation test. The correlation between the Aitchison’s distance matrix and stream distance matrix was then calculated. The resulting Mantel’s correlation coefficient $r_M = 0.46$ (resp. the test statistic $r_d = 0.430$) was proved to be statistically significant via permutation for both tests.

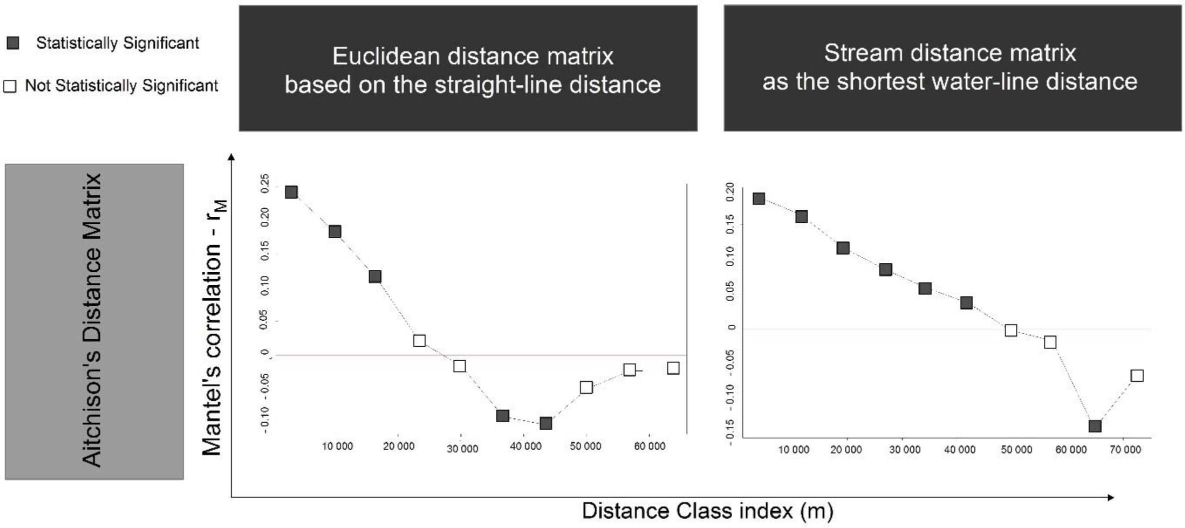


Figure 2 *Mantel’s correlogram of normalised Mantel’s statistics r_M between the Aitchison’s distance matrix and two spatial matrices*

In the next step, the Mantel’s correlograms visualised the normalised Mantel’s statistics rM between the Aitchison’s distance matrix and two spatial binary matrices wherein pairs of sites belonging to the same distance class received a value of 0, and the other pairs, a value of 1 (Legendre and Legendre, 2012). The Mantel’s correlograms reported similar trends for the changes in compositional similarities among the samples in relation to a spatial distance binding for both the spatial matrices (based on the Euclidean straight-line distance and stream-line distance)–see Fig. 2. The results demonstrated the significant positive spatial correlation in the first three resp. six distance classes of the straight-line resp. stream-line distance matrix. Close sample sites tended to show a very similar compositional structure as far as the straight-line distance of 20 km resp. stream-line distance of 40 km. The decrease in the compositional distance was more gradual in the case of the stream distance matrix as compared to the Euclidean distance matrix in reporting the complexity of the channel geometry. Nevertheless, both correlograms are informative owing to the different spatial definitions of both distances used for the plotting. Interpreting the processes occurring at several spatial scales would be more informative if the geostatistical modelling of the variation-variograms and their eigenvalue decomposition using the sill matrices were applied (Tolosana-Delgado and van den Boogaart, 2013). However, it may be complicated to develop valid spatial covariance models for variables spatially structured along a river network (Cressie et al., 2005; Peterson and Ver Hoef, 2010). Hence, we employed the multivariate statistical tools to explore and explain the compositional variability within the dataset, and then used an univariate interpolation for the ilr-coordinates containing all the relative information of one compositional part with respect to the other parts similarly to Zuzolo et al. (2018).

4. *Explanatory data analysis*

Once the geospatial continuity of the compositional structure was proved, we explored the compositional variability to interpret the patterns using the expository and inferential tools (PCA, MANOVA). Table 2 shows the tabulated results of the statistical parameters for the raw concentrations and clr-transformed variables that can be used to interpret the relative abundance of an element in the (sub)composition of ten TEs in our dataset.

	Clr-transformed concentrations of TEs				**Raw concentrations of TEs**			
	Q50	Range	IQR	MAD	X_D/X_Q	Q50	MAD	CVR
Be	-1.55	1.67	0.39	0.30	0.06/0.197	1.1	0.7	65
Cr	-0.24	3.11	0.51	0.26	0.598/2.179	4.7	1.8	39
Cd	-2.03	2.25	0.48	0.31	0.061/0.196	0.7	0.7	99
Co	0.10	1.42	0.35	0.25	0.658/2.203	6.4	2.3	36
Cu	1.80	2.41	1.04	0.80	0.515/1.821	28	28	99
Hg	-3.59	5.86	0.64	0.51	0.02/0.06	0.1	0.1	59
Ni	0.33	1.50	0.56	0.40	0.574/1.992	7.9	1.8	23
Pb	1.77	1.14	0.33	0.21	0.957/2.916	30	21	72
V	0.75	1.97	0.43	0.28	1.611/5.764	13	4.8	36
Zn	2.24	1.92	0.63	0.45	1.37/3.979	48	47	98

Table 2 *Summary statistics: clr-transformed and raw concentrations of TEs; agricultural soil. All clr-values are log-ratios, and hence, dimensionless. Min: minimum; Q: quantiles (Q50 = median); Max: maximum; MAD: median absolute deviation, IQR: interquartile range. Raw concentrations:* X_D/X_Q*: analytic detection limit/quantification limit for each TE [mg/kg]; Q50: median [mg/kg]; MAD: median absolute deviation [mg/kg]; CVR: robust coefficient of variation [%].*

High median values for clr(Zn), clr(Pb), and clr(Cu) indicated average dominance of the elements as compared to the geometric mean of the entire composition. In contrast, low median values indicated the TEs that have relative abundances lower than the geometric mean (e.g., Be, Cd, and Hg). An interquartile range (IQR) and median absolute deviation (MAD) provide estimates of the variance of the clr-transformed variables, in that a higher variance for a component indicates its greater influence on the multivariate data ensemble (Reimann et al., 2012). Our high variance values for clr(Cu), clr(Zn), and clr(Hg) induced a high influence of these TEs on the variability of the soil quality in the region, and they were expected to be a distinctive feature determining the surficial-soil patterns. The first insight into these spatial patterns can be made by mapping the clr-values via dot maps. Using the example of clr(Cu) (see Supplementary Fig. A.2), it is apparent that, relative to the geometric mean, Cu was abundant in the floodplain soils in the middle reach of the Ohře River. A very similar pattern was recognised for the Zn clr-values. The clr-values for Hg, Cr, and Ni showed a changing pattern of relative enrichment/depletion/enrichment in the sequence of upper/middle/lower reaches (see Supplementary Fig. A.3).

	Be	**Cr**	**Cd**	**Co**	**Cu**	**Hg**	**Ni**	**Pb**	**V**	**Zn**
Be		0.45	0.37	0.29	0.60	0.55	0.25	0.18	0.22	0.26
Cr	-1.48		0.75	0.35	**1.02**	0.60	0.31	0.46	0.25	0.72
Cd	0.63	2.11		0.42	0.17	**1.24**	0.42	0.12	0.54	0.14
Co	-1.68	-0.21	-2.31		0.70	0.62	0.10	0.22	0.14	0.41
Cu	-3.36	-1.89	-3.99	-1.68		**1.55**	0.74	0.28	0.81	0.24
Hg	1.95	3.43	1.32	3.63	5.31		0.62	0.78	0.53	**1.06**
Ni	-1.89	-0.41	-2.52	-0.21	1.47	-3.84		0.23	0.11	0.46
Pb	-3.24	-1.77	-3.87	-1.56	0.12	-5.19	-1.35		0.24	0.14
V	-2.40	-0.93	-3.03	-0.72	0.96	-4.35	-0.51	0.84		0.47
Zn	-3.69	-2.21	-4.32	-2.01	-0.33	-5.64	-1.80	-0.45	-1.29	

***Table 3** Variation array for the soil TEs: Upper triangle - simple log-ratio variances; Lower triangle – simple log-ratio means*

The described trends were further summarised by the variation array. The sample mean value of the simple log-ratio of the corresponding parts are in the lower triangle in Table 3. For instance all mean log-ratios for Zn-pairs were negative and indicated that, in mean, Zn had higher values over than rest of TEs (consistent with the high median value for the Zn clr-values in Table 2). Concerning a decomposition of total variance in simple log-ratios in the upper triangle, there are important the high variances of simple log-ratios for Cu, or Hg along the river (bold numbers in Table 3). On the contrary the simple log-ratio variances for Pb, Cu, Zn and Cd were lower. Also the variances of log-ratios for Cr over Ni or Co, V were small, hence indicating proportionality of these TEs across the river gradient. Aitchison and Greenacre (2002) proposed to display the compositional variability in the form of biplot, representing a projection of the first orthonormal principal components. On interpreting the compositional biplot according to the fundamental principles in Aitchison and Greenacre (2002), it was possible to distinguish three distinctive groups of TEs with a high in-group proportionality of log-ratios (Fig. 3). The collinear rays and short links within the groups of the chalcophile elements (Cu, Pb, Zn, and partly Cd) and siderophile transition metals (Cr, Co, Ni, and V) were definitely not new. The siderophile association was proved to be usually controlled by a similar lithology in previous studies of various geological formations (Borůvka et al., 2005; Facchinelli et al., 2001; Petrik et al., 2018; Steckemann et al., 2006; Tolosana-Delgado and McKinley, 2016). The association for Cr or Ni was also proved to have been preserved in the Czech floodplain environment by Bednářová et al. (2015). To summarise the results of the compositional PCA, the first two PCs explained approximately 73 % of the total variance and provided satisfactory hints regarding the subcompositional variability in the dataset. The first principal component was rather related to the links between the chalcophile elements (Cu, Pb, Zn, and partly Cd) and the rest of TEs – this corresponded to the variances of simple log-ratios in Table 3. Negative values corresponded to a larger proportion of chalcophile elements and seemed to be spatially determined by the cultivation changes and TEs inputs at the middle reach of the Ohře River. The second principal component can also be interpreted as a kind of spatial contrast between the upper and lower part of the river in which the log-ratios for transition metals, Hg and Be were part of this pattern.

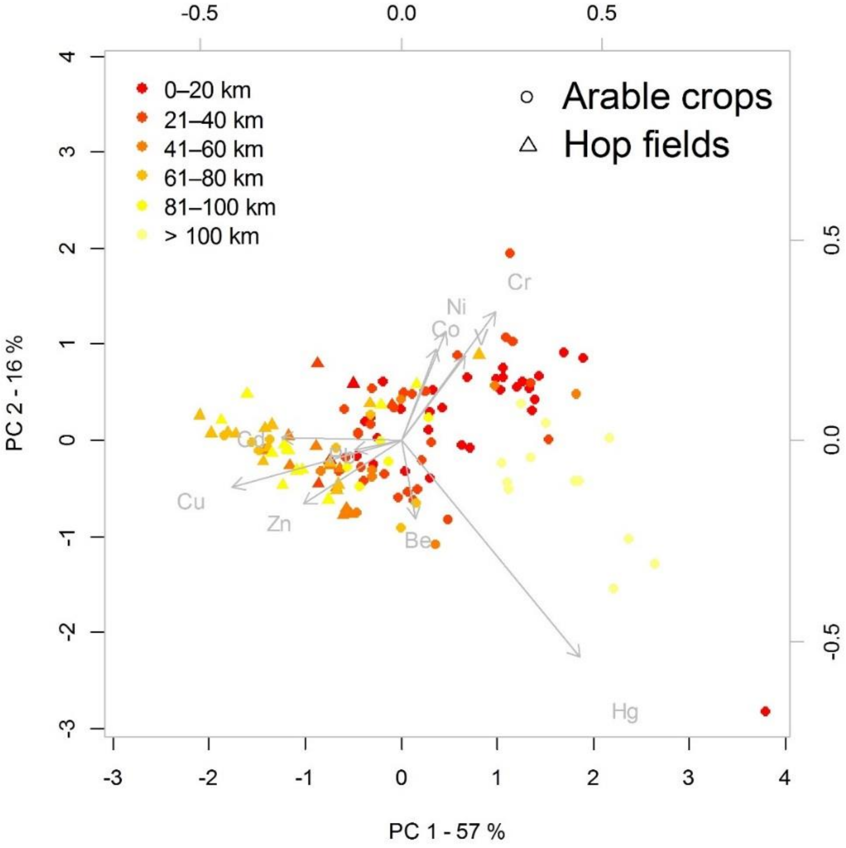


Figure 3 *Biplot of the first two principal components for the clr-transformed components (explained variation–PC1: 57 %, PC2: 16 %) with the samples ranked according to the stream distance of the sampling sites from the river mouth*

A more detailed understanding of the compositional covariance structure resulted in the ranking of the samples according to the stream distance from the river mouth within the compositional biplot (Fig. 3) and within the ternary diagrams for the well-defined subcompositions (Fig. 4). Even a cursory examination of these visual tasks allows substantial zoning of the multi-element associations within the flood-prone soils in the catchment. A relative Hg-enrichment was featured in the cultivated soils in the headwater areas of the Ohře River. Hg-enrichment has been widely recognised as a response to human activities in floodplains (Rinklebe et al., 2010; Schwartz et al., 2006; Stachel et al., 2006). Regional Hg-pattern determined in our study might be interpreted with reference to the Marktredwitz chemical plant (no longer in existence) near the cross-border tributaries of the Ohře River in Bavaria (Grygar et al., 2016). The environmental consequences of the Hg-contamination were proved to be serious in terms of its bioaccumulation in fish, as reported from the Skalka Dam (Maršálek et al., 2005) or the potential risk of Hg-volatilisation from floodplain soils (Grygar et al., 2016; Rinklebe et al. 2010; Wallschläger et al. 2000). Furthermore, using forest soil profiles, Navrátil et al. (2014) indicated that power plants potentially contribute to the diffuse Hg-contamination in the headwater areas of the Czech–Saxony borderland. A local turnover of the relative Hg-enrichment was also evident at the confluence of the Ohře with the Elbe

River (see Fig. 4, and the spatial point pattern for clr-Hg in Supplementary Fig. A.4). A similar increase was recorded in the Hg-dataset by Majerová et al. (2018). We expected to observe the effect of pollution inputs by flooding waters from the Elbe River into the inundated soils of the confluence area. The changes in the surficial soil Hg-pattern might reflect a persistent effect of the former electrolytic preparation of sodium amalgam on the surrounding environment of the Spolana Neratovice plant (Heinisch et al., 2007; Navrátil et al., 2017). In contrast to Hg, Be can enter the soil mainly via release from the bedrock; nevertheless, Be-mobilisation may be enhanced by acidification, especially in soils with a reduced ability of the base cations to neutralize acidity (Hruška and Krám, 2003). Krám et al. (1993) reported that Be-mobilisation from the soil exchange complex may be increased due to human-induced inflow of acidic water (with mobile anions) to the mineral soil developed on coarse-grained granite. These risk factors were known to be present at the upstream areas where the bedrock consists of numerous granite types and where the environmental impacts of coal ash deposition have been reported (Hruška et al., 2002; Navrátil, 2000; Navrátil et al., 2008).

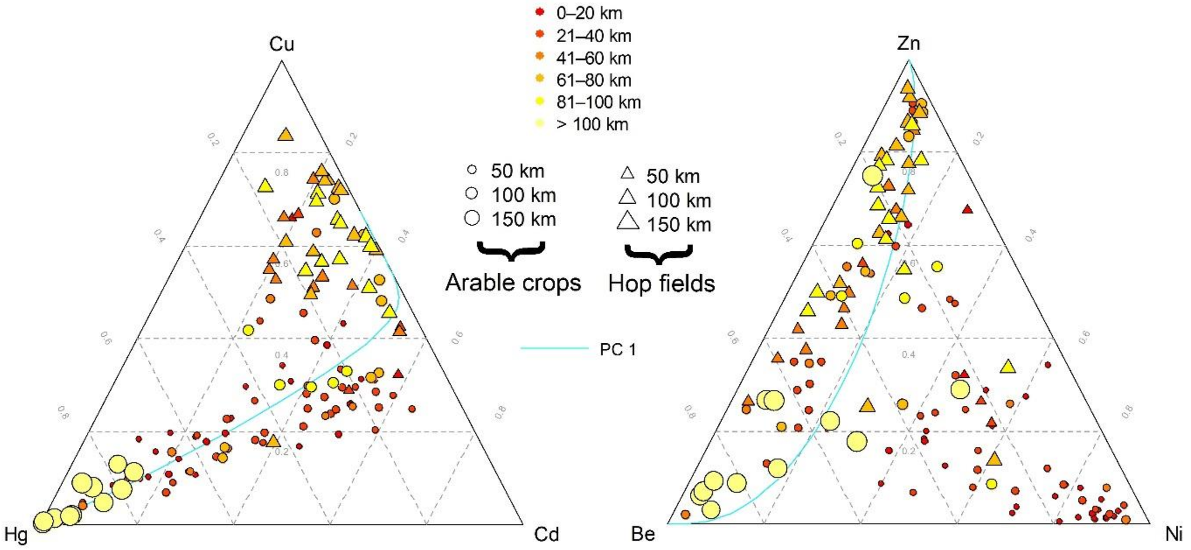


__Figure 4__ Ternary diagrams of three-part subcomposition of Cd–Cu–Hg and Be–Zn–Ni triplets (retaining 46 % resp. 16 % of the entire compositional variability in our dataset); the area and colour of the points refer to the absolute resp. categorised stream distance; the 1st principal component (PC 1) of the subcomposition is depicted and accounted for the 92 % resp. 71 % explained variance

The relative enrichment of transition metals was found at the lower reach of the Ohře River, as can be seen in the ranking of the samples according to the stream distance from the river mouth within the compositional biplot (Fig. 3) and within the ternary diagrams (Fig. 4). The spatial point pattern for clr-Cr in Supplementary Fig. A.3 illustrated the relative enrichment as well. On comparing these results with the established countrywide database of old ecological burdens (Contaminated Sites Database System administered by the Ministry of the Environment of the Czech Republic–Suchánek, 2013), a geochemical signature match was found which conformed to contaminated site of the former tannery. Sameš (1994) mentioned the existence of several old waste lagoons of the tannery sludge in the confluence area. The site-specific risk analysis indicated metal accumulation—especially Cr, Ni, and Co—and the potential spread of these metals from the tannery grounds into nearby soils and ground waters owing to repeated inundations (Kodrová and Paulin, 2012). The topsoil enrichment for Cr, Co, and Ni has also been recognised as a response to human activities in tanneries in the Sarno Basin in Italy (Petrik et al., 2018; Thiombane et al., 2018).The results of the subcompositional analysis within the spatially ranked ternary diagrams (Fig. 3) indicate that the Cu- and Zn-subcompositions had similar spatial patterns with a relative enrichment at the middle reach of the river near the Žatec municipality. One possible explanation for this pattern is the treatment of the hop fields with Cu and Zn, supplied either as fungicides and bactericides or as manurial treatments. The effect of Cu-based plant protection has been widely documented in a number of vineyard regions (Bednářová, et al. 2016; Brun et al., 1998; Cicchella et al., 2015; Komárek et al. 2008; Saby et al., 2011). The high proportionality of log-ratios was also evident for Cu, Zn over Cd (a low simple log-ratio variation in Table 3). It can probably indicate the well-known effect of mineral P-fertilisers with relatively high Cd concentrations (Birke et al., 2017; Nziguheba and Smolders, 2008).

On observing the detailed chemostratigraphical profiles of floodplain sediments by Grygar et al. (2016), the base of the Cu–Pb–Zn-polluted layer was locally proved to be older than the middle of the 20th century. These findings supported the hypothesis of the contribution of ancient ore mining and processing to geochemical signatures in a broader region of the middle reach of the Ohře River catchment. Grygar et al. (2016) presented a detailed overview of the pollution sources and their historical chronology with some crucial hints:

1) As, Pb, Cu, and Zn enrichment from the mountainous tributaries also impacted the Ohře floodplain downstream of their inflows.
2) The contiguous middle reach of the Ohře River below Karlovy Vary acts as a transfer zone owing to the existence of a solid bedrock and sloped river valley with sparse floodplains.
3) A very late impact of the Nechranice Dam (built in 1961–1968), that altered only the recent contamination patterns of the floodplain soils, was effectively recorded by a depth distribution of ^{137}Cs.

The hypothesis of the increased contribution of ancient ore mining and processing in a broader region of the Ohře River catchment was also supported by the increased association of Cu-Zn with Pb, evident from their proportionality in variation array (low simple log-ratio variances in Table 3). The correlation analysis using the symmetrical coordinates was also used to verify these geochemical signatures in the region. On correlating the entire compositional dataset, the groups of two strong clusters along the main diagonal of the plot represented the established dichotomy between the chalcophile elements (Cu, Pb, Zn, and partly Cd) and siderophile transition metals (Cr, Co, Ni, and V) (Figure 4a). Apart from this dichotomy, the Hg–Be symmetric coordinates posed the pair with similar correlation structure (especially in their correlation against the group of transition metals). The dendrograms showed a strong positive correlation for element pairs such as Cu/Zn, Cu/Pb, Cu/Cd, Ni/Cr, and Ni/Co. The general pattern of the correlation structure remained relatively unchanged when taking into consideration the plantation (hop field versus arable crops) for the floodplain samples from the river section between its 158th and 214th km, where a patchy assemblage of hop fields and arable crops dominates the region (see Fig. 1). Generally, the correlation between those elements from the chalcophile group and transition metals group presents more contrasting results for arable soils (Figure 5b and 5c). The strong positive correlations of individual transition metals were considerably weaker in the hop fields as compared to the arable crops. The local impact of the hop fields with the relative Cu–Zn-enrichment did not change the geochemical association of the chalcophile elements but affected the degree of relative enrichment/depletion of some elements.

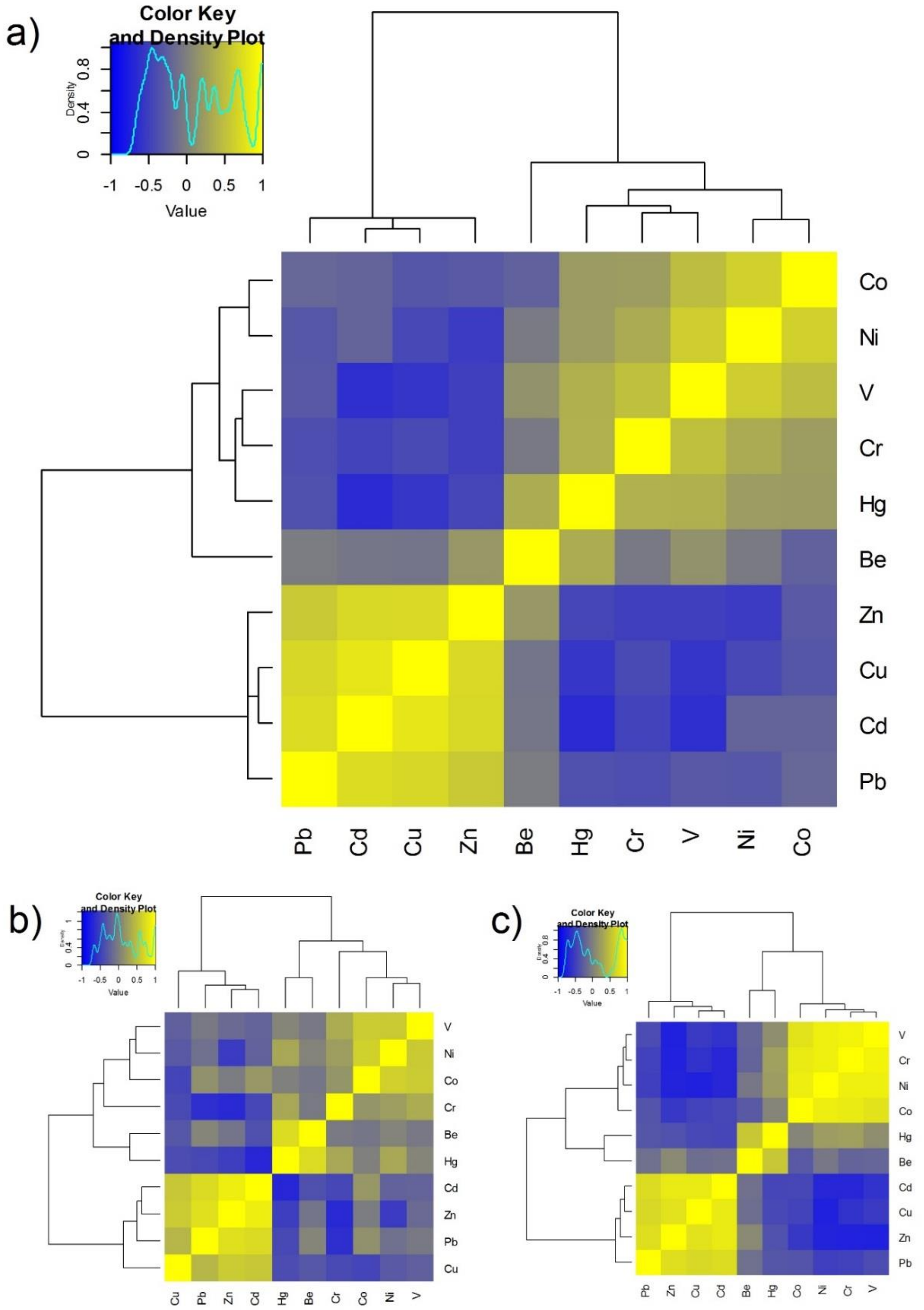
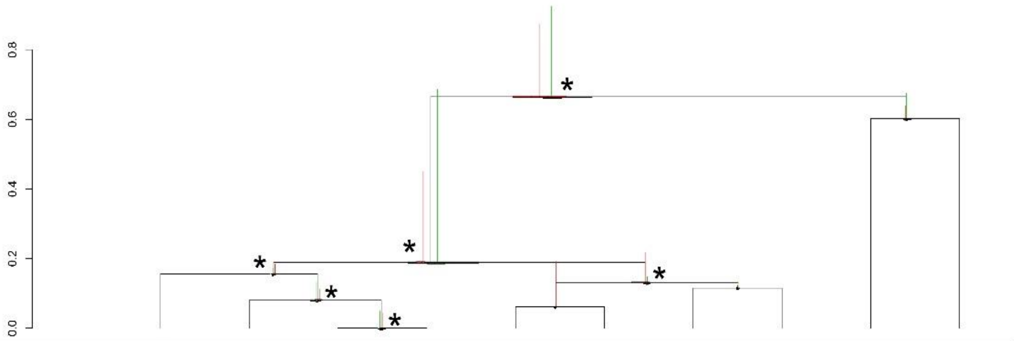


***Figure 5** Heat map of correlation based on the symmetric coordinates for the entire topsoil dataset a) and for the samples from the river section between its 158th and 214th km grouped into the hop fields – b) and arable crops – c)*

The variation decomposition and the correlation analysis suggested that among the important factors characterising the differences in geochemical composition was to count for the cultivation. The concentrations of TEs for the floodplain samples from the river section between its 158th and 214th km, where a patchy assemblage of hop fields and arable crops dominates the region, were divided by crop cultivation, giving rise to a classification into two populations to explore their differences using the following visual and inferential statistical tools:

1) The ratio between the whole geometric mean and the geometric mean of two groups according to the cultivation is compared in a logarithmic scale using the geometric mean barplot similarly to Mateu-Figueras et al. (2015) (Supplementary Fig. A.5). When compared with the whole geometric centre, the largest differences appeared in the group of chalcophile elements.

2) To confirm these visual differences statistically, inferential techniques using the nonparametric MANOVA contrasts may be used for ilr-coordinates following the principle of working on coordinates (Mateu-Figueras et al., 2015). The sequential binary partition of balances and the CoDA dendrogram were used to get and explore ilr-coordinates (Egozcue and Pawlowsky-Glahn, 2005; 2011). The results of the multivariate analysis of compositional variance within the PCA assisted to choose the appropriate basis and perform sequential binary partition to obtain balances (Figure 6). Balances are particular ilr-coordinates (isometric-logratio) and full set of ilr-balances forms an orthonormal basis of the compositional data vectors bases which can be interpreted in the D-1 (D=dimension) real space as ratios of elemental associations (Egozcue et al., 2003). The results of the McKeon's F approximation for the Lawley–Hotelling's test and McKeon's F approximation for the Bartlett-Nanda-Pillai's test on nine ilr-coordinates suggested rejecting the null hypothesis that the multivariate distributions did not differ across the both cultivation groups because the p-value provided by the modified contrast statistic was lower than 0.05. For this case, we investigated which log-ratio coordinates contributed to these significant differences between two groups. After applying nonparametric approximations for MANOVA tests to the ilr-balances across the both cultivation groups (arable crops, hop fields), we obtained significant differences for several coordinates derived within the sequential binary partition (Figure 6). The significant differences were proved between the log-ratio contrasts between the groups of chalcophile elements, transition elements and single elements (Hg, Be), and especially among all the log-ratio contrasts within the group of chalcophile elements (Figure 6). The nonparametric relative effects (REs in Figure 6) quantified the tendencies observed in the data in terms of probabilities. REs are defined as the probability that a randomly chosen subject from the group displayed a higher ilr-contrast than a subject that was randomly chosen from both of the groups (Acion et al., 2006; Woodrow et al., 2017). For example, each of the ilr-variables from the 3rd, 7th, 8th and 9th step of the SBP decently discriminated the cultivation effects. Those ilr-balances exhibited high relative effects either of the cultivation mode, hence rather strong differences between arable crops and hop fields.



HF–RE^1	AC–RE^2	ILR	Cd	Pb	Zn	Cu	V	Cr	Co	Ni	Be	Hg
0.74	0.26	**ilr1**	-	-	-	-	-	-	-	-	+	+
0.71	0.29	**ilr2**									-	+
0.82	0.18	**ilr3**	-	-	-	-	+	+	+	+		
0.80	0.20	**ilr4**					-	-	+	+		
0.70	0.30	**ilr5**							-	+		
0.39	0.61	**ilr6**					-	+				
0.18	0.82	**ilr7**	-	+	+	+						
0.10	0.90	**ilr8**		-	+	+						
0.12	0.88	**ilr9**			-	+						

***Figure 6** Sequential binary partition of balances tailored to get interpretable ilr-coordinates for the inferential tools (MANOVA) to compare geochemical composition under cultivation partition; the length of coloured vertical bars and their intersection with the horizontal segment represent the variability of each balance and the location of the balance's mean for arable crops (green) and hop fields (red); * the p-value provided by the nonparametric approximations for MANOVA tests lower than α=0.05; the relative treatment effects (REs) for the hop-fields (HF–RE) resp. arable crops (AC–RE) – see the text for explanation.*

The insights of this explanatory data analysis demonstrated that various compositional tools, combined with a simple spatial ranking and land-use information, may enhance the effective selection and interpretation of the subcomposition for the geochemical zoning of surficial-soil TEs in cultivated floodplains. Based on these results, we defined effective discriminating subcomposition (Cu–Hg–Ni) that was able to describe the geochemical domains in floodplains as effectively as the entire composition and that was able to enhance the interpretation of the multi-element association with the presence of trace constituent inputs (both diffuse and point sources along the river). As the Mantel's test proved the spatial structuration, and the effective subcomposition was defined by explanatory analysis, we finally mapped the geochemical patterns using the Cu–Hg–Ni subcomposition and its tailored expression using univariate ilr-coordinates. The normalised univariate ilr-coordinates were gridded using the IDW interpolation method with a cell size of 50 × 50 m (Figure 7). Although there exist many interpolation methods, the IDW interpolation was selected because the sampling strategy in the study area was systematic with a relatively high density, and because the structural analysis proved the compositional data to be spatially correlated in the Mantel's test. The results of the subcompositional analysis and the geospatial mapping of the tailored ilr-coordinates enabled us to highlight the geochemical contrasts between the river sections and to extract priority elements to be managed in the cultivated soils in the particulate river section (see Figure 7). With respect to the upper part of the Ohře River, the relative enrichment of Hg and potentially mobile contents of Be hold an attention and has been before-mentioned and analysed. At the middle reaches of the Ohře River, the higher degree of Cu-enrichment was source-apportioned to recent intensive cultivation and ancient ore mining and processing using the compositional approach. The confluence area with the Elbe River was found to have a peculiar trace constituent composition with a relative Hg-enrichment along with that of transition metals (Cr, Ni, and Co), and relative depletion of chalcophile elements (Cu–Zn–Pb–Cd) with the established influence of the old tannery burden.

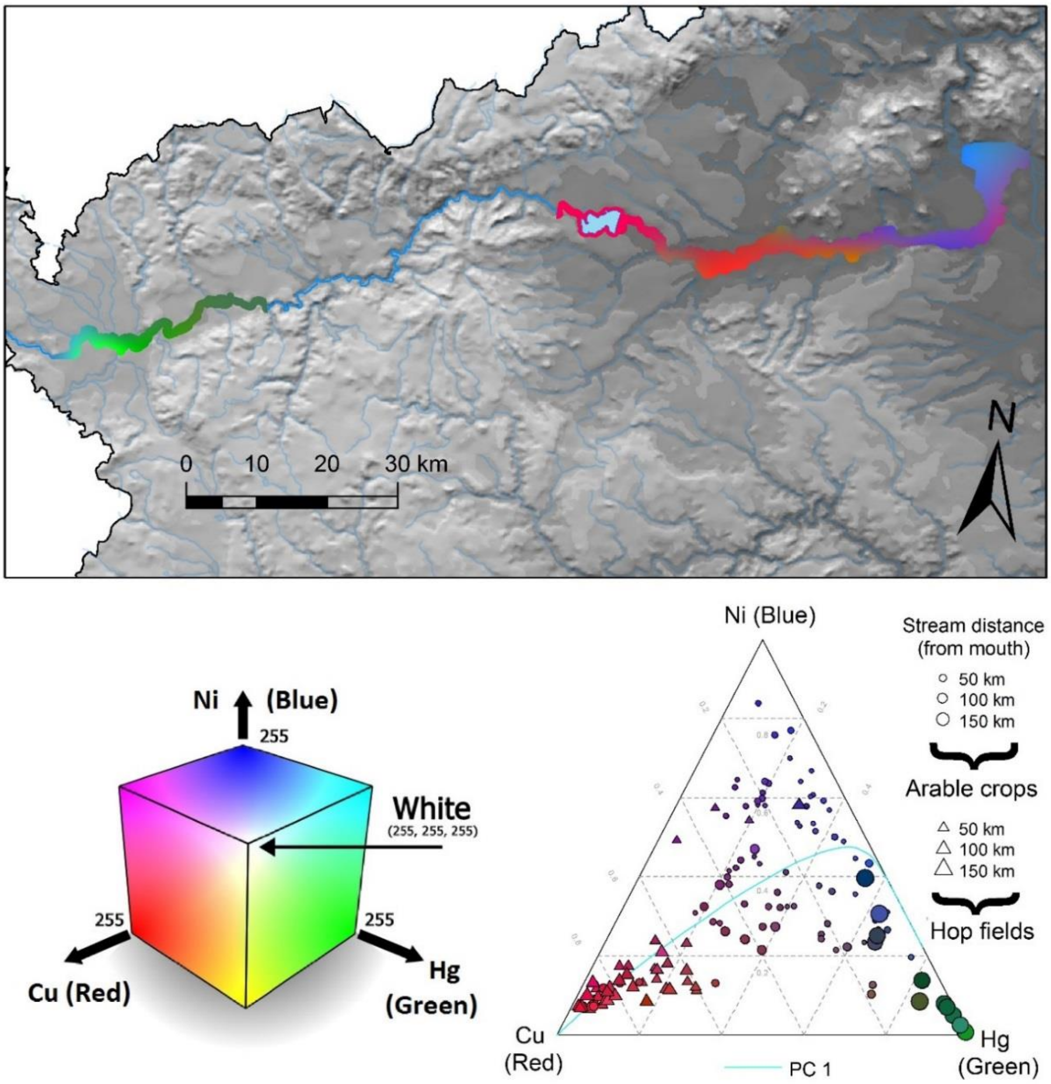


Figure 7 *Visualisation of three-part subcomposition in a gridded map and ternary diagram of Cu–Hg–Ni triplet (retaining 45 % of the entire compositional variability in our dataset) using RGB composite (the colour scheme is the same for the grid map and ternary diagram; the 1st PC accounted for 80 % of the explained variance; the colour cube image has been modified from https://www.medialooks.com)*

5. *Conclusions*

Based on the results of our study, following conclusions can be drawn:

1) The application of the explanatory analysis of compositional data, particularly PCA and subcompositional analyses, aided in identifying broad regional geochemical trends of TEs in a plough layer of cultivated soils, and aided in discriminating between geochemically distinct domains within the particular river reaches. The first two principal components of the trace constituent composition and the final composite maps showed a significant regional contrast between groups of the chalcophile elements (Cu, Pb, Zn, and partly Cd) and siderophile transition metals (Cr, Co, Ni, and V). Based on these results, we defined several effective discriminating subcompositions that were able to describe the geochemical domains in floodplains as effectively as the entire compositions.

2) As illustrated in both the interpolated grids and the spatially ranked ternary diagrams, there were regional-scale differences in the geochemical associations. The structural spatial analysis, based on the Mantel's correlation test and generalised distance covariance test using the compositional Aitchison's distance and two spatial distances, is an essential part of this study. Its results demonstrated that the topsoil data represented a spatial pattern and quantified the spatial continuity of the compositions. Moreover, the methodology used appears to be a very simple and effective tool for defining the spatial structure in the compositional modelling, wherein the spatial (dis)continuity of the compositional structure may reflect various aspects of soil pollution. We assume that a similar methodology can also be successfully used in analysing other floodplain regions affected by various pollution sources.

3) The use of compositional coordinates resulted in an enhancement in the interpretation of the multi-element association with the presence of trace constituent inputs owing to which the possible geochemical signatures could be observed. For extracting or zoning these geochemical signatures, it was desirable to combine single element ratio maps into colour composite maps and explore the multivariate patterns using explanatory and inferential tools. The results showed a changing pattern of relative enrichment/depletion of the partially digested trace elements in which a regional contrast between groups of the chalcophile elements (Cu, Pb, Zn, and partly Cd), siderophile transition metals (Cr, Co, Ni, and V) and single elements (Hg, Be) was source-apportioned to the effect of point pollution sources (Hg, Ni, Cr, Co) as well as diffuse sources (Cu, Zn, Pb, Cd). One practical implication of this is that significant turnovers in the compositional structure of TEs may be used to recognise distinctive priority elements that are required to be managed in inundated agro-ecosystems within a particular river section. TEs determined through partial digestion of the samples upon HNO_3 extraction reflected the associated pollution risk to the agro-ecosystem more accurately than the total contents, as the elements present in the residual fraction were not potentially bioavailable and mobile.

While it is possible to draw these conclusions, it should be noted that floodplains are variable in their depositional trajectories, and the mixed sampling of the arable crops and hop fields represented a certain degree of homogenisation and, as such, do not represent all the conditions at a local level. Grygar et al. (2016) found the majority of the historical pollution to be deposited in former (abandoned or laterally shifting) channels rather than in overbank fine-grained materials in the Ohře River catchment. The local tracing of the historical ore pollution and their signals would be more precise if the vertical core samples were combined with an advanced knowledge of site geomorphology and sedimentology (Grygar and Popelka, 2016).

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Appendices - Supplementary materials:

	Near-floodplain samples (N= 28)[1]		Floodplain samples(N=32)[2]	
***TEs[3]**	Q50[4]	RE[5]	Q50	RE[5]
Be*	0.54	0.18	0.74	0.82
Cd	0.81	0.31	0.92	0.69
Co	0.51	0.27	0.52	0.73
Cr	0.14	0.48	0.20	0.52
Cu*	0.54	0.20	0.76	0.80
Ni	0.39	0.40	0.42	0.60
Pb	0.74	0.30	0.78	0.70
V	0.23	0.36	0.26	0.64
Zn*	0.33	0.08	0.58	0.92

[1] *The samples within the 5-km buffer zone outside the area inundated during the largest known meteorological flood in the study area (in January 2011 according to the Digital Base of Water Management Data, T. G. Masaryk Water Research Institute)*

[2] *The samples within the inundation areas of the 100-year flood.*

[3] *The differences between flood and non-flood samples was highly significant, and there was good agreement between the McKeon's F approximation for the Lawley–Hotelling's test and McKeon's F approximation for the Bartlett-Nanda-Pillai's test. The differences in solubility of each TE were assessed in the nonparametric MANOVA using the above-mentioned tests (made by the R package "npmv") and asterisked for the statistical significance.*

[4] *The median value of solubility S for each trace element where* $S = S_{HNO_3}/S_{aqua\ regia}$

[5] *The nonparametric relative effect (RE) defined as the probability that a randomly chosen subject from the group displays a higher solubility than a subject that is randomly chosen from both of the groups (Acion et al., 2006; Woodrow et al., 2017).*

Table A.1 *Comparison of median values for the solubility of TEs under one-way classification of floodplain samples against near-floodplain samples*

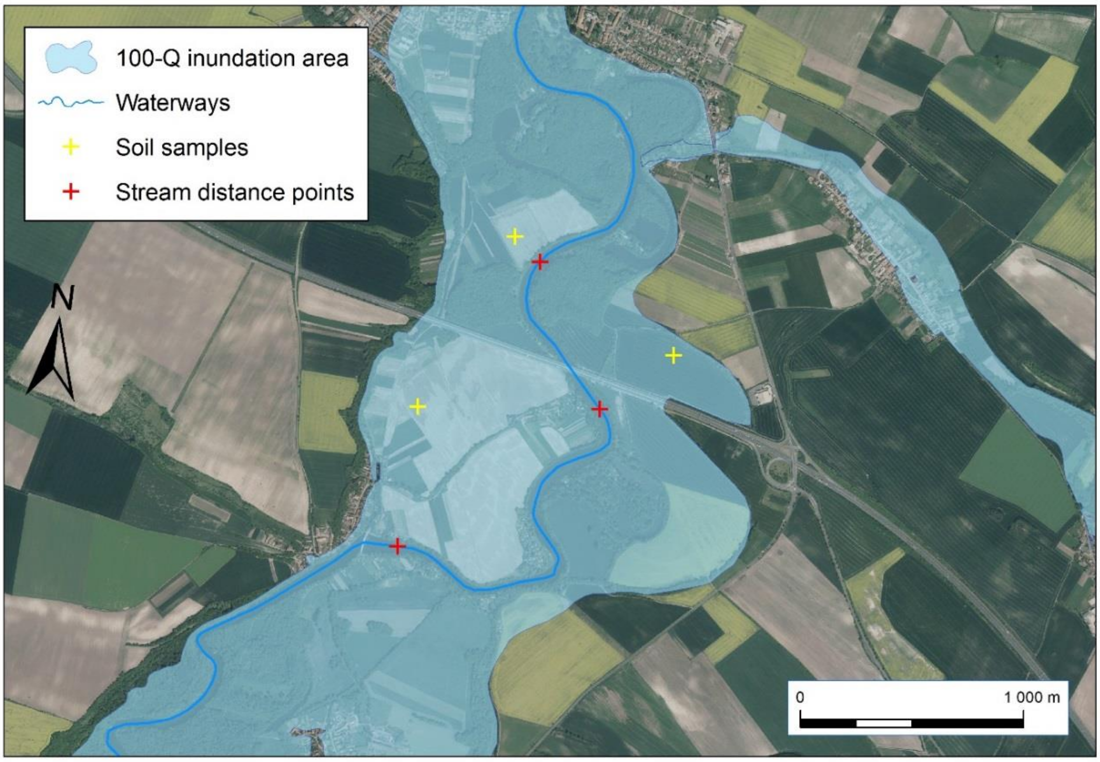

Figure A.1 *Assigning the stream distance points as the nearest waterline vertices for particular soil samples for the purpose of stream distance matrix*

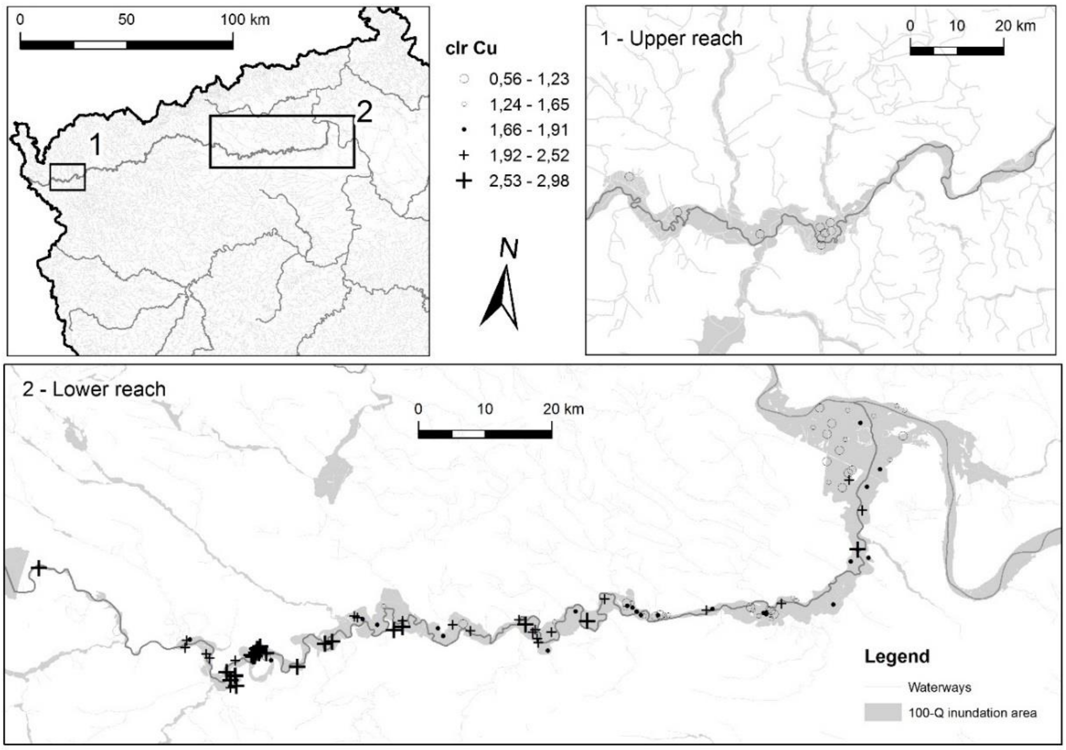

Figure A.2 *Maps of the regional distribution of the clr-transformed Cu contents classified based on percentiles (0, 5, 25, 75, 95, and 100) along the Ohře River*

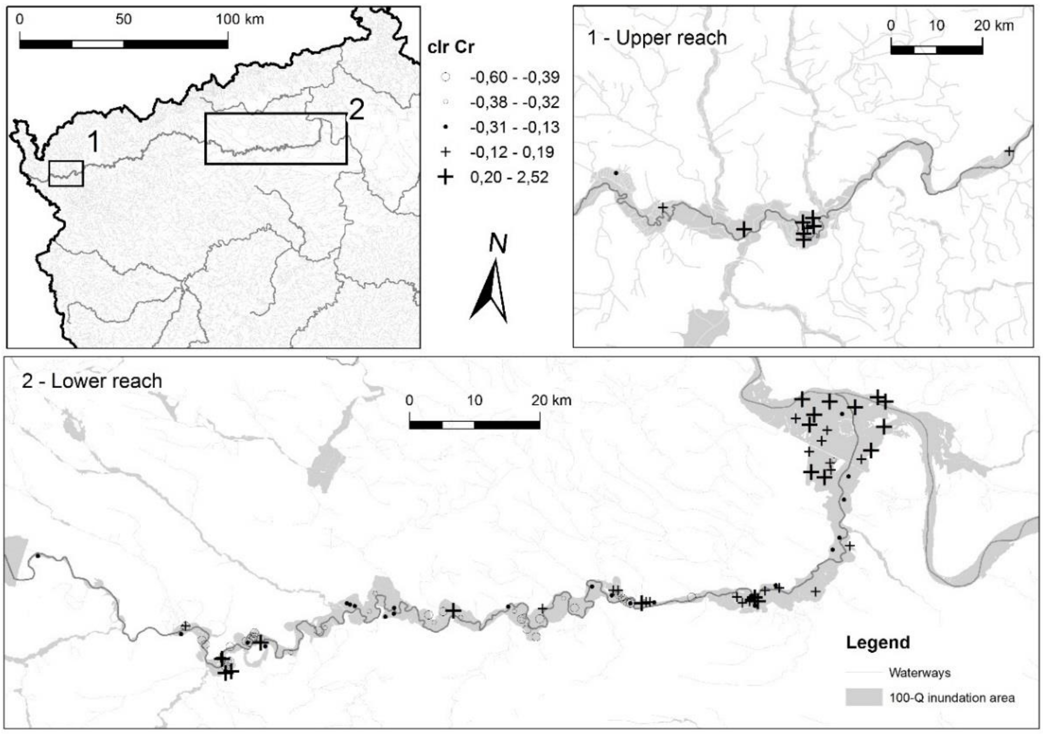

Figure A.3 *Maps of the regional distribution of the clr-transformed Cr contents classified based on percentiles (0, 5, 25, 75, 95, and 100) along the Ohře River*

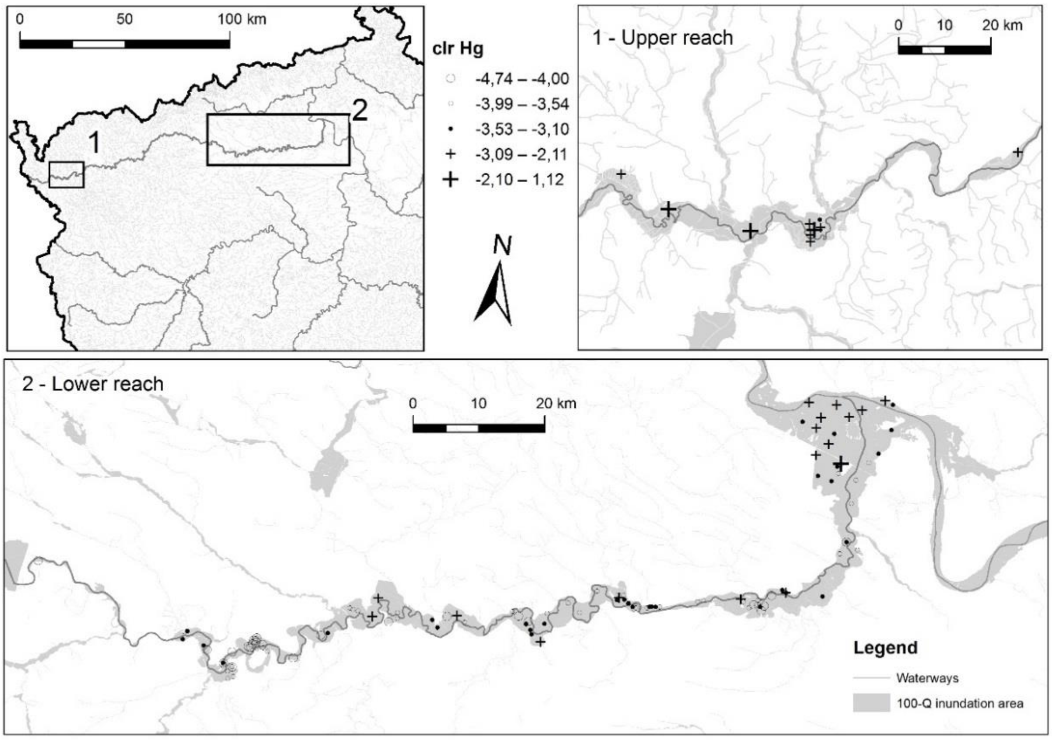

Figure A.4 *Maps of the regional distribution of the clr-transformed Hg contents classified based on percentiles (0, 5, 25, 75, 95, and 100) along the Ohře River*

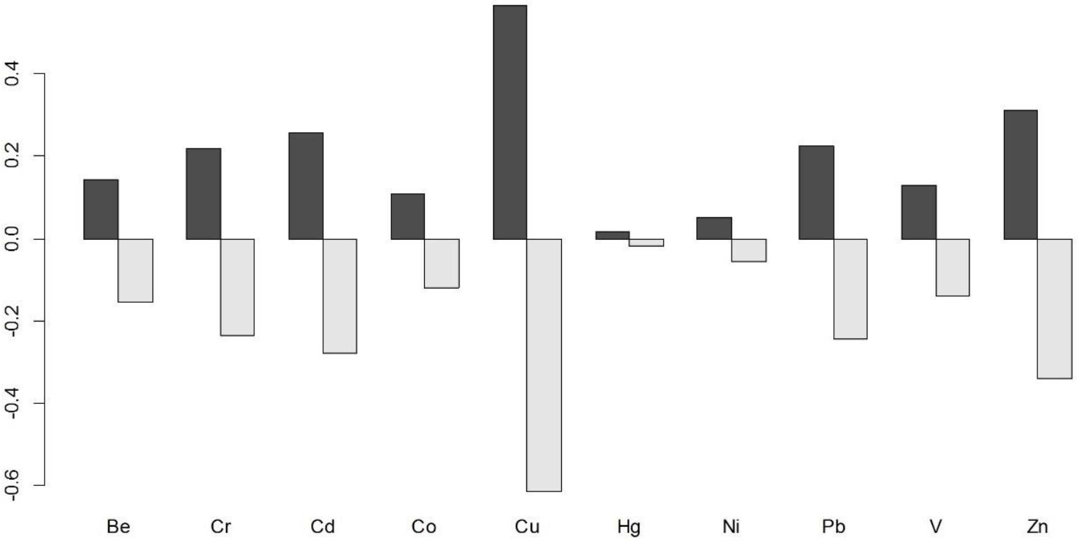

Figure A.5 *Geometric mean barplot for the soil TEs within two crop cultivations along the Ohře River: hop fields (black), arable crops (grey)*

4.6 Čechmánková et al. (2011): Fytoextrakce těžkých kovů ze silně a středně kontaminovaných půd pomocí zemědělských plodin pěstovaných v monokultuře a osevním postupu

Název: Heavy metals phytoextraction from heavily and moderately contaminated soil by field crops grown in monoculture and crop rotation

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Heavy Metals Phytoextraction from Heavily and Moderately Contaminated Soil by Field Crops Grown in Monoculture and Crop Rotation

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Abstract: The uptake of Pb, Cd, Zn and biomass production of the plants *Brassica juncea* v. Opaleska, *Triticale hexaploides* var. Gabo and *Helianthus annuus* v. Maritza were observed in a field (trial) and a pot experiments during four years. The plants were grown in monoculture variants and also in crop rotation. The field experiment (plots about 1 × 1 m) was set up in heavily contaminated Haplic Fluvisol in the Litavka River alluvium. Pb, Cd, and Zn phytoextraction from the identical Haplic Fluvisol and Haplic Cambisol less contaminated mainly by atmospheric deposition was observed in the pot experiment. The application of 0.2 g EDTA (ethylenediaminetetraacetic acid)/kg and 1 g citric acid/kg into the soils of field (250 kg of soil/m^2 plot) and pot (6 kg of soil/pot) experiments was realized. The comparison was accomplished between natural phytoextraction efficiency of *B. juncea*, *H. annuus*, and *T. hexaploides*. Crop rotation with and without chemical induction was tested. EDTA application had an immediate strong mobilization effect on the elements tested in both experiments and both soils. In the pot experiment, Pb, Cd, and Zn were more mobilized in Cambisol with initial lower mobile contents of elements in comparison with Fluvisol. The highest mobilization by EDTA was achieved for Pb. Strong Pb mobilization in Cambisol after EDTA addition resulted in a high Pb uptake and translocation from the roots of *B. juncea* into the shoots. EDTA application increased Pb phytoextraction by harvested *B. juncea*. Naturally grown *H. annuus* proved the high phytoextraction efficiency for Cd and Zn in the experiment. The assumed effect of the cultivation method, i.e. crop rotation vs. Monoculture, was not statistically proved in our experiments.

Keywords: *Brassica juncea*; Cd; heavy metals contamination; *Helianthus annuus*; mobilization; Pb; phytoextraction; *Triticale hexaploides*; Zn

The use of higher plants to remediate contaminated land is known as phytoremediation, the term known since 15 years ago (Vamerali *et al.* 2010). Phytoextraction has been suggested as a viable alternative to the traditional restoration practices for heavy metal-contaminated soils (e.g. soil removal and disposal in landfill areas), in view of the lower costs and lower environmental impact (De Andrade *et al.* 2009). Phytoextraction is considered as the removal of heavy metals (HMs) from the soil by the harvest of overground biomass where the contaminants are taken up and transferred by the plant (Wenzel *et al.* 1999). The uptake and accumulation of HMs were mostly studied on endemic plant species of metallic soils, hyperaccumulators (Prasad & Hagemeyer 1999). Hyperaccumulator plants are able to concentrate high levels of specific metals in the over-ground harvestable biomass. The small shoot and root growth of these plants and the absence of their commercially available seeds have stimulated studies on biomass species, including field crops (Vamerali *et al.* 2010). Kumar *et al.* (1995) found out that *B. juncea* and *Brassica nigra* have the highest

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ability out of twelve monitored farmed species *Brassica* spp. to receive heavy metals from the substrate and concentrate them in the overground biomass. Sunflower (*H. annuus*) is highly tolerant to heavy metals, showing a large intake of heavy metals into the roots, but poor translocation into the overground biomass (Madejón *et al.* 2002). *Poaceous* species also prove resistance to high contents of heavy metals in soil (Ernst 1996).

The main limiting factors of phytoextraction are contaminant bioavailability in the soil and the biomass yield. Based on the study of element mobility and their transfer into plants (Podlešáková *et al.* 1999), the elements with high and pH dependent mobility and high transfer into plants can be exempt (Cd and Zn). Lead is an element with a potential mobility (Podlešáková & Němeček 2000) and occurs as a constituent of insoluble compounds (phosphates, carbonates and hydroxides) in soil (Lasat 2002) or bound on soil organic matter (Száková *et al.* 2003). Different chemical agents (EDTA – ethylenediaminetetraacetic acid, HEDTA – hydroxyethylethylenediaminetriacetic acid, citric acid etc.) mobilize the tightly bound metals from the soil matrix into the soil solution, enhance the plant uptake of metals, and thus increase their phytoextraction from the soil (Kos *et al.* 2003). Of the five chemical agents tested, EDTA showed the most effective Pb mobilization (Huang *et al.* 1997), however EDTA is little biodegradable and can enhance leaching of metals to groundwater (Grčman *et al.* 2001). Due to the potential risks, chemical agents with high biodegradability, low phytotoxicity and chelating strength (NTA, citric acid and succinamic acid) were proposed for the chemically assisted phytoextraction of HMs (Quartacci *et al.* 2005).

The calculations of the time required for soils remediation based on laboratory, hydroponics, pot, and trial experiments are based on short-term observation and repetition of the plant grown in monoculture. Monocultures have generally the disadvantage of a significant decline in the biomass yield due to the depletion of nutrients, occurrence of diseases, pests, and weeds, and have a negative impact on the soil fertility (Lasat 2000). The yield reduction then results in a significant reduction in the plant phytoextraction efficiency. Two to three years' monoculture may be acceptable for soil phytoremediation. However, for a longer duration, as considered for most phytoremediation processes, it cannot be expected to clean up the soil only by one plant species used exclusively in monoculture, especially if more harvests per growing season are expected. Banuelos (1998) recommend changing the plant species with risk elements accumulation capacity for technical crops in crop rotation, by which the improvement of economic balance and of the growth and yield of phytoaccumulator can be achieved.

The aim of this paper is to compare the efficiency of two chemical agents, low strength EDTA and citric acid, on the metals uptake by *B. juncea* in the pot and field experiments, and to test the phytoextraction efficiency of *T. hexaploides* and *H. annuus* naturally grown (without chemical treatment) on the tested soil as well. Two differently contaminated soils – Fluvisol (fluvial contamination) and Cambisol (atmospheric contamination) – were used for the detection of Pb, Cd, and Zn mobilization after chemical agent addition, and for the Pb, Cd, and Zn accumulation and the growth ability of the trial plants assessment. The plants were grown in monoculture and in crop rotation.

MATERIAL AND METHODS

The district of Příbram is located in the Central Bohemian Region and belongs to the areas in the Czech Republic most contaminated with heavy metals. The reasons for the contamination are, besides geological conditions, historical HMs mining and metallurgical activities. The vast contamination of the area (approximately 1500 ha including arable land) was caused by atmospheric deposition coming from the lead ores processing. Except this large surface contamination, there is a smaller contamination focus in the alluvium of the Litavka River. The flood water loaded by the wastes from metallurgical sediment storage basins resulted in an extremely high contamination of the alluvium by HMs (Borůvka *et al.* 1996; Vácha *et al.* 2002).

Field experiment

The experimental field was localized for four years near the village of Trhové Dušníky in the Litavka River alluvium on heavily contaminated Haplic Fluvisol. The soil is classified according to the World Reference Base (IUSS 2006). Single experimental plots (1 × 1m) were dug up and dolomitic limestone was added to increase the very low pH in the soil depth of 0–20 cm (5 g/kg of soil) in August 2005. The soil samples were taken up before liming, and 3 weeks and 8 months after liming. All soil samples were air dried to constant weight, sieved through a stainless sieve (diameter 2 mm), and homogenized. Mean total, mobile (extracted with 1 mol/l NH_4NO_3) and potentially mobile (0.025 mol/l Na_2EDTA) contents of the risky elements in the experimental soil at the beginning of the experiment are summarised in Table 1.

The plant sowing was done each year in May; the fields were sown with 36 plants per field. Chemical agents were applied into the chosen variants seeded with *B. juncea* 10 days before the plants harvest for achieving maximal biomass production. 0.2 g Na_2EDTA/kg and 1 g citric acid/kg of soil in different variants were added into the soil in the form of solution. Low strength agents should prevent strong HMs mobilization and subsequent leaching into the groundwater. The harvest was done during the flowering phase, 10 days after the chemical agent addition. The plants were thoroughly washed with drinking water, separated into the shoots and roots, checked for fresh and dry (at 45°C) biomass, and analysed after the harvest. Additional soil samples were taken up by pooled sample method before the chemical agent addition and 4 h and 10 days afterwards. After that, dolomitic limestone in the dose of 2.5 g/kg was applied for the soil stabilization. Single trial variants (Table 2) had two replicates.

Pot experiment

Parallel pot experiment was set up in autumn 2005 and two experimental soils were used: Haplic Fluvisol identical with that in the field experiment, and moderately polluted Haplic Cambisol, contaminated by atmospheric deposition stemming from the lead ores processing; this soil was taken up from the arable land near the local smelter. Both soils were taken up from humic horizon (0–20 cm), sieved through 5 mm mesh, and magnesium limestone in the dose of 5 g/kg was added into each pot with Fluvisol and thoroughly homogenized (6 kg of experimental soil per pot). Cambisol was not limed because of the initial sufficient soil pH. The soil samples of Fluvisol and Cambisol were collected before liming. Further Fluvisol samples were taken up from the pots 3 weeks and 8 months

Table 1. Characteristics of field experiment soil and the limit values for total metals content

	Pb	Cd	Zn	pH (KCl)	C_{ox} (%)
Haplic Fluvisol					
Total content (mg/kg)	1099	14.2	1732	5.35	3.32
1M NH_4NO_3 (%)	0.08	5.8	3.6		
0.025M Na_2EDTA (%)	75.1	90.3	19.3		
Limit values (Directive of the Ministry of the Environment of the Czech Republic No. 13/1994)					
Light-textured soils	140	1	200		
Other soils	100	0.4	130		

Table 2. Field experiment variants

Variant	Remediation process (plot experiment)
Halpic Fluvisol	
1	*Brassica juncea* var. Opaleska grown in monoculture with citric acid application before harvest
2	*Brassica juncea* var. Opaleska grown in monoculture with EDTA application before harvest
3	*Brassica juncea* var. Opaleska grown in monoculture without application
4	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) with citric acid application before harvest of *Brassica*
5	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) with EDTA application before harvest of *Brassica*
6	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) without application
7	*Helianthus annuus* var. Maritza grown in monoculture without application
8	*Triticale hexaploides* var. Gabo grown in monoculture without application

after liming. Mean total, mobile (extracted with 1 mol/l NH_4NO_3), and potentially mobile (0.025 mol/l Na_2EDTA) contents of the risky elements in the experimental soils at the beginning of the experiment are summarised in Table 3.

The plant seeds sowing was performed in the four years in May, the pots were sown with 5 plants per pot. The pots sown with *B. juncea* seeds were treated with 0.2 g Na_2EDTA/kg 10 days before the harvest. The plant and soil samples were taken up and treated in the same way as in the field experiment. Single pot variants (Table 4) obtained three repetitions.

Analyses

The measurements were performed in the central laboratory of the Research Institute for Soil and Water Conservation in Prague. The exchangeable soil pH (0.2M KCl) and the content of organic carbon were measured in the soil samples by the modified Tjurin method. Total soil element concentration was determined after decomposition using a mixture of $HNO_3 + HClO_4 + HF$. The soil samples were extracted with 1 mol/l NH_4NO_3 (mobile) at a ratio of 1:2.5 (w/v) and 0.025 mol/l Na_2EDTA (potentially mobilized risky elements) at a ratio 1:25 (w/v) and the extracts were analysed for the risky element concentrations. The plant samples were washed with distilled water and decomposed using the dry ashing procedure. The elements concentrations in the extracts were determined by flame atomic absorption spectrometry (VARIAN FAAS 240 – Cd, Pb and Zn), and flameless one (VARIAN ETA 240Z – Cd and Pb). Certified reference materials RM 7001 Light Sandy Soil and RM 7003 clay-loamy soil were applied for quality verification of the analytical data. For statistical evaluation Statistica 9 programme was used.

RESULTS AND DISCUSSION

Pb, Cd, and Zn mobilization and their contents in the soil

Total content of metals confirmed particularly serious contamination of both soils tested (Tables 1 and 3). The Directive of the Czech Ministry of Environment of the Czech Republic No. 13/1994 of the Coll. was used for the contamination extent assessment. Limit values are listed in Tables 1 and 3. Total content of Pb in Cambisol was comparable with that in Fluvisol whereas the contents of Cd and Zn were significantly lower in Cambisol. Pb was not found in the mobile fraction, but Pb was considerably extracted with Na_2EDTA. On the other hand, Cd was found to be highly represented in the mobile soils fractions and especially in the potentially mobilizable soil fractions. The very low portion of mobile Pb was not further decreased by the liming of Fluvisol. Cd and Zn, as more mobile elements in the soil, decreased their mobile contents in the soil after dolomitic limestone addition; whereas stronger immobilization was found for Zn. EDTA application had an immediate strong mobilization effect on all tested

Table 3. Characteristics of pot experiment soils and the limit values for metals total content

	Pb	Cd	Zn	pH (KCl)	C_{ox} (%)
Haplic Fluvisol					
Total content (mg/kg)	1536	16.1	3136	5.90	4.16
1M NH_4NO_3 (%)	0.03	2.5	0.8		
0.025M Na_2EDTA (%)	73.8	95.6	33.9		
Haplic Cambisol					
Total content (mg/kg)	1288	5.57	280	6.14	2.04
1M NH_4NO_3 (%)	0.10	3.2	0.4		
0.025M Na_2EDTA (%)	89.8	92.6	16.5		
Limit values (Directive of the Ministry of the Environment of the Czech Republic No. 13/1994)					
Light-textured soils	140	1	200		
Other soils	100	0.4	130		

Table 4. Pot experiment variants

Variant	Remediation process (pot experiment)
Halpic Fluvisol	
1	*Brassica juncea* var. Opaleska grown in monoculture with EDTA application before harvest
2	*Brassica juncea* var. Opaleska grown in monoculture without chelating agent application
3	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) with EDTA application before harvest of *Brassica*
4	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) without application
5	*Helianthus annuus* var. Maritza grown in monoculture without application
6	*Triticale hexaploides* var. Gabo grown in monoculture without application
Halpic Cambisol	
7	*Brassica juncea* var. Opaleska grown in monoculture with EDTA application before harvest
8	*Brassica juncea* var. Opaleska grown in monoculture without chelating agent application
9	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) with EDTA application before harvest of *Brassica*
10	Crops rotation (*Brassica, Helianthus, Triticale, Brassica*) without application
11	*Helianthus annuus* var. Maritza grown in monoculture without application
12	*Triticale hexaploides* var. Gabo grown in monoculture without application

elements in both experiments and soils. The highest mobilization by EDTA was achieved with Pb. Pb was more mobilized in the pot Cambisol with the initial lower mobile contents of elements in comparison with pot Fluvisol. Citric acid showed lower ability of metals mobilization, however, its influence had been already statistically proved. The increased Pb, Cd, and Zn mobility caused by chemical agent addition returned after 10 days to the level existing before the application. This could be explained by the long term incidence of liming and thus an increased buffering capacity of the soil regarding the increased $CaCO_3$ supply. Mobilization effect of EDTA on the observed metals is listed in Table 5. Liming increased pH of the field and pot Fluvisols from 5.35 and 5.9 up to 7.0 and 6.8, respectively, and the chemical agent application did not influence the soil pH.

The trends in the risky elements behaviour after the chemical agent application were confirmed by the results of the experiments in all the years of observation. EDTA and citric acid effects on heavy metals mobilization were proved by Wilcoxon signed rank test. The test confirmed the positive influence of chemical agent EDTA on the metals mobile content in soils as statistically significant on the significance level $\alpha = 0.01$ for Pb and Zn ($\alpha = 0.05$ for Cd). The influence of citric acid on metals mobile contents in the soils was statistically significant on thr significance level $\alpha = 0.01$ for Pb and $\alpha = 0.05$ for Cd and Zn. The mobilization stages are graphically illustrated by the example of lead (Figure 1).

Pb, Cd, and Zn contents and phytoextraction efficiency of plants

The natural ability of *B. juncea* plants to take up heavy metals (especially Pb) was observed (Kumar *et al.* 1995; Schulman *et al.* 1999). However, in our experiment The Czech and European regulations (Directive No. 169/2002 Coll. and the Directive 2002/32 EC; chosen for the possibility of comparison of the results) were exceeded in the field experiment with EDTA treatment (Table 6 and 7). The Czech and European limits for Pb were not exceeded even in the plants grown on heavily contaminated soils in the case of naturally grown *B. juncea* (without EDTA addition). Naturally grown *B. juncea* blocked Pb mainly in the roots. EDTA addition resulted in an enhanced Pb transfer from the roots into the shoots. The enhanced amount of Pb taken up by *B. juncea* was proved after EDTA addition into the pot Cambisol and to a smaller extent in the field and pot Fluvisol. The high Pb content in the shoots of *B. juncea* observed in all experimental years responds to the pronounced mobilization of Pb in the pot Cambisol. Citric acid influenced Pb mobilization in soil and did not influence Pb uptake by the experimental plants. Most of the plants exceeded the

Table 5. Mobile fraction proportions (%) from total risk elements content before application of EDTA and 4 h after application during trial and pot experiment

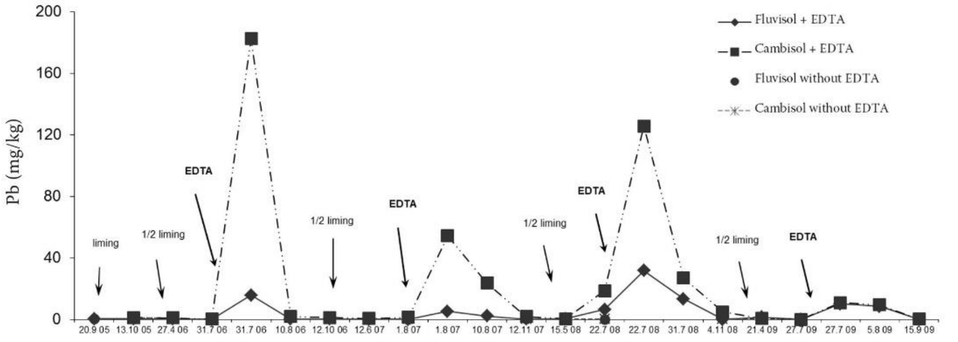
	Trial Fluvisol			Pot Fluvisol			Pot Cambisol		
	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn
Before EDTA application									
	0.001	0.76	0.07	0.004	1.24	0.17	0.01	0.98	0.06
4 h after EDTA application									
2006	11.0	38.1	5.76	1.02	13.1	1.68	14.2	37.1	4.11
2007	9.00	15.5	5.22	0.35	2.94	0.44	4.21	12.7	1.24
2008	7.69	29.0	4.78	2.07	22.9	3.08	9.76	23.7	3.96
2009	3.41	1.06	0.17	0.66	0.53	0.30	0.85	0.24	0.69

shoots Pb contents reported by Kabata-Pendias (2001) to be in normal plant 10 mg/kg. Our values of Pb contents in *B. juncea* are comparable with the average 55 mg Pb/kg in the shoots of *B. juncea* planted in soils contaminated by acid sludge (Clemente *et al.* 2005).

The Czech and European regulations (Tables 6 and 7) for Cd, Zn contents in animal feed were more exceeded in the overground biomass than in the roots of *B. juncea* plants grown without EDTA addition. The uptake of Cd, Zn, and Pb into roots significantly prevailed in the case of *T. hexaploides* plants. In spite of that, Cd content in the overground biomass reached the relevant limit values for animal feed in all grown variants. High amounts of Cd and Zn were taken up into the overground biomass by *H. annuus* grown without chemical treatment. The risky elements contents in all naturally grown plants exceeded the relevant limit rates whereas Pb limit was exceeded just in the roots. The pot experiment results revealed a higher uptake of elements from Cambisol than from Fluvisol.

The biomass yield is also an important factor of phytoextraction efficiency. All plants used in the field experiments proved tolerance and growth ability in soils with a high total content of risky elements. The chemical agents application before the harvest did not reduce the yield of *B. juncea* biomass. A significantly higher yield of the overground biomass and roots was achieved with *H. annuus*, a lower yield was reached with *T. hexaploides*. The plants grown in crop rotation did not show higher biomass yields compared to the same plants grown in monoculture.

The plant potential for phytoextraction use can be also defined according to the risky elements uptake from the soil, determined by the element content taken up by the biomass of plants from the



Wilcoxon signed rank test for EDTA, P-value = 0.000021

Figure 1. Mobile content of Pb extracted with 1M NH_4NO_3 (mg/kg) from tested soils after liming and chelating agents additions through four years of pot experiment

Table 6. Metals average content in shoots and roots of variants grown in all years and limit values exceeding in pot experiment (in mg/kg)

Variant	Pb		Cd		Zn	
	shoots	roots	shoots	roots	shoots	roots
Haplic Fluvisol						
1	45.0	30.5	4.95	5.78	361	238
2	6.85	27.1	6.91	5.54	387	210
3	32.0	70.9	4.33	7.33	364	315
4	29.3	58.3	6.84	7.26	411	380
5	6.67	51.8	5.64	7.70	403	499
6	3.80	105	0.99	5.30	231	413
Haplic Cambisol						
7	162	156	4.20	5.58	84.6	49.1
8	6.76	29.1	3.61	2.09	43.9	34.9
9	54.9	108	3.27	8.76	105	48.2
10	5.28	70.0	2.67	3.30	38.0	37.8
11	14.6	79.3	3.62	5.60	42.4	45.1
12	6.66	77.7	0.64	4.66	40.0	72.4
Limit values	Directive of the Ministry of Agriculture of the Czech Republic, No. 169/2002					
	40	40	1	1		
	Directive 2002/32/EC of the European Parliament					
	40	40	1	1		

area. The results indicate a significant potential of Cd and Zn phytoextraction in the case of naturally grown *H. annus* plants. Only *B. juncea* proved the ability of Pb uptake after EDTA application. The influence of EDTA treatment on Pb transfer from various soil types into the overground biomass of *B. juncea* plants was statistically tested using two-factor analysis of variance. Both a significant influence of two factors (the EDTA application, soil type) on Pb content in the overground biomass and the factor interaction were proved on the significance level $\alpha = 0.01$ by the ANOVA.

Remediation factor (Rf) expresses the proportion (%) of metal removed by biomass harvest from the total, eventually mobile amounts in the soil. Rf was determined in 20 cm of soil depth (250 kg soil per plot) where predominant roots distribution is presumed in the field experiment and for the whole volume of the pot (6 kg of soil). Rfs for the environmentally risky mobile metals fraction were determined in relation to 1M NH_4NO_3 extractable metals in the soils. This mobile fraction must be decreased simultaneously to prevent the possible metals movements and leaching into the groundwater sinks. However, even if preferential metals uptake by plants comes from the available (mobile) fraction, metals are continuously mobilized from the less available fractions in the soil by many factors (Wenzel *et al.* 1999) and it is necessary to observe the mobile fraction in the soil permanently.

Total four-year removal from the pot soils (the sum of shoots and roots) and Rfs based on total metals content in soils are demonstrated in Figure 2. The chemical agents added into the field Fluvisol EDTA increased Pb removal and Rf of *B. juncea*. Significantly higher Rfs were achieved in the pot experiment, which was caused by the smaller amount of soil and thus a lower Pb supplement in the pot. EDTA addition into the Cambisol had a greater effect on the improvement of Pb removal. Chemical addition did not significantly influence Cd and Zn uptake by *B. juncea* plants. On comparing the results of Cd and Zn Rfs (numerically expressed as the Rf sum of all experimental years), it may be claimed that *H. annuus* grown in monoculture without chemical agents application revealed the highest phytoextraction efficiency. The

Table 7. Metals average content in shoots and roots of variants grown in all years and limit values exceeding in field experiment (in mg/kg)

Variant	Pb		Cd		Zn	
	shoots	roots	shoots	roots	shoots	roots
1	8.96	17.7	8.52	5.60	381	252
2	29.7	26.4	8.27	4.31	440	195
3	9.16	17.2	8.02	6.83	351	205
4	13.2	40.2	7.57	6.65	293	255
5	15.2	34.6	8.51	5.88	318	233
6	14.1	52.4	9.06	6.88	315	280
7	15.7	58.2	10.2	8.51	425	354
8	13.2	252	1.83	14.3	161	551
Limit values	Directive of the Ministry of Agriculture of the Czech Republic, No. 169/2002					
	40	40	1	1		
	Directive 2002/32/EC of the European Parliament					
	40	40	1	1		

higher phytoextraction efficiency of *H. annuus* in comarison with *B. juncea* was not fully assumed regarding the results published by Madejón *et al.* (2002) who mention that *H. annuus* is tolerant of HMs contamination and proved a high HMs intake into the roots, but a low transfer into the overground biomass was observed. On the other hand, De Andrade *et al.* (2009) found out that, the chemical agent addition did not induce the heavy metal uptake by *H. annuus*, and that *H. annuus* should be preferred for phytoremediation in the soils of mining and metallurgy areas. Sinegani & Khalilikhan (2010) mention sunflower (*Helianthus annuus)* as a potential phytoextraction plant accumulating high concentrations of Cd from metal-contaminated soils and give the removal efficiency of Cd from the soil as 0.15% whereas Rf rated by us was 0.42% from pot Cambisol. The effect of the cultivation method (monoculture vs. crop rotation) was not statistically proved in our experiments. However, we cannot exclude the growing importance of this factor due to the plants fragility in monocultures and declining yields of the plant species in monoculture during longer-time experiments.

For the practical use of phytoextraction, the question of the target values should be discussed. These are the values that should be achieved during remediation to minimise the risk ofr the site in terms of the receptor. The proposal of an amendment to the regulation of the Czech Ministry of Environment No. 13/1994 Coll. (Sáňka *et al.* 2002) was used for the assessment. The proposal works with three levels of limits – first degree, preventive limits, coming from the upper measure of the background values of the risky elements content in the Czech soils, the values are set for the surface soil horizon.

The indication limit is based on the studies of the risky elements transfer through the soil-plant pathway and indicates the possible level of the element transferring risk from the soil at a level that does not meet the chemical requirements for food or animal feed safety. The values are set for ploughing or humus horizon of the agricultural soils. Rendering limit – the value characterizing the level of the contents of hazardous elements and substances in the soil, in which an imminent risk exists of adverse effects on plants, animals and humans, and possibly other components of the ecosystem.

The values are set for all types of the land use. We counted how much time it would take to clean the contaminated soil used in our experiment to the level of indication limit. The results of the pot experiment are given in Table 8.

The proposal of an amendment to the regulation of the Czech Ministry of Environment No. 13/1994 Coll. (Sáňka *et al.* 2002) also involves the indication limits for the environmentally risky mobile metals fraction extractable with 1M NH_4NO_3. The limit value was only exceeded in the case of Zn, Cd in our experiments. Rfs were determined based on

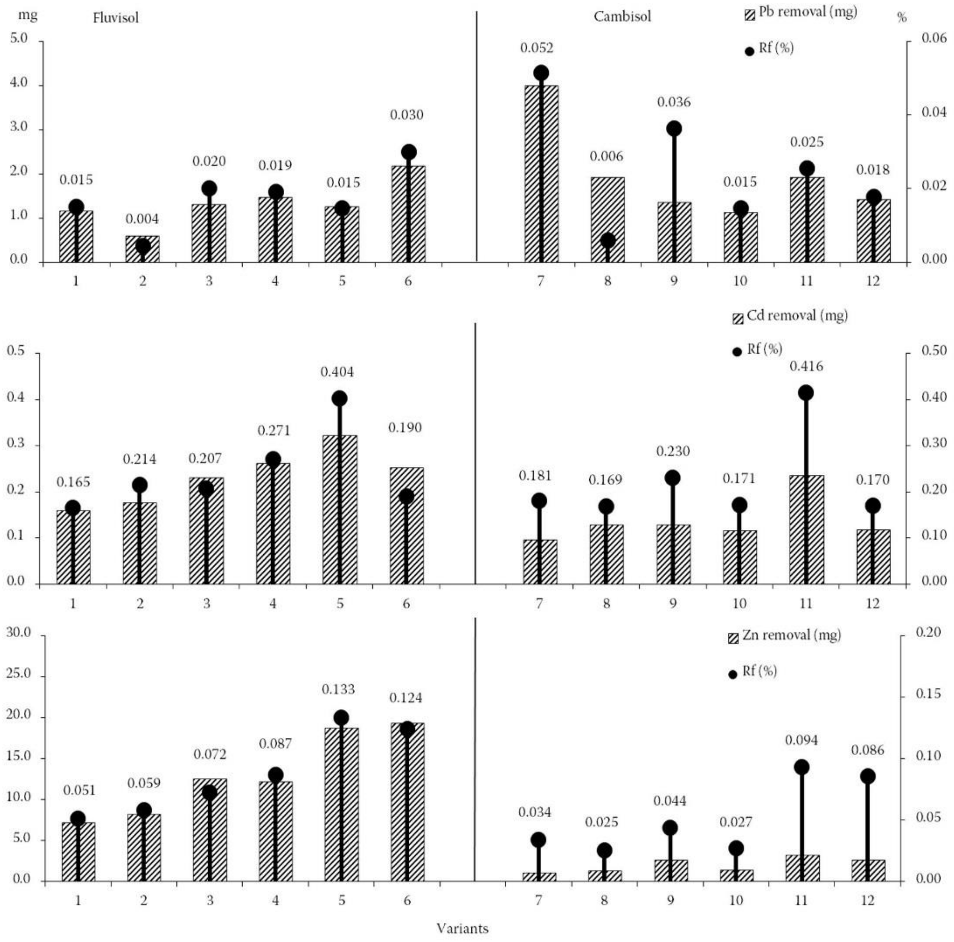


Figure 2. Total four-year removal (the sum of removal by shoots and roots) and Rf based on total metals contents in soils of pot experiment

the mobile metals fraction content and the time needed for the remediation was calculated. The results of the pot experiment are given in Table 9. The results, however, can be misleading, because metals are continuously mobilized from the less available fractions in the soil, the results manifest the favourable phytoextraction efficiency of the trial plantation for the riskiest mobile fraction of heavy metals. The best result was obtained especially with *H. annuus* plants.

The phytoremediation efficiency of the field crops in our experiment was not high and the results confirm that the soil phytoremediation using crop rotation or monoculture is a very long term process. But a great growth potential in the contaminated soils should be positively assessed, as well as the improving of the landscape and reducing of the mobility of the risky elements through water and wind erosion. The phytoremediation potential lies in conjunction with the conventional methods of decontamination in terms of the subsequent cleaning treatment of the site. The methods of phytoremediation are financially accessible and, in general, well accepted by the public.

Table 8. Years needed for remediation to indication limit value (total content) in pot experiment

	Pb	Cd	Zn		Pb	Cd	Zn
Content in soil (mg/kg)	1536	16.1	3136		1288	5.57	280
Indicating limit (mg/kg)	70	h2	160		70	2	160
Years per remediation to indication limit value							
Variant	Haplic Fluvisol			variant	Haplic Cambisol		
1	25322	2126	7399	7	7335	1411	4999
2	85291	1634	6484	8	63681	1512	6795
3	18958	1692	5241	9	10407	1107	3887
4	20028	1292	4364	10	25911	1490	6351
5	26208	868	2847	11	14861	613	1832
6	12733	1843	3058	12	21245	1505	2002

Table 9. Years needed for remediation to indication limit value (mobile content extractable with NH_4NO_3) in pot experiment

	Cd	Zn		Cd
Content in soil (mg/kg)	0.45	35.5		0.18
Indicating limit (mg/kg)	0.1	20		0.1
Years per remediation to indication limit value				
Variant	Haplic Fluvisol		variant	Haplic Cambisol
1	53	33	7	3
2	41	29	8	3
3	42	23	9	2
4	32	19	10	3
5	22	13	11	1
6	46	13	12	3

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4.7 Vácha et al. (2010): Polycyklické aromatické uhlovodíky v půdě a vybraných plodinách

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Polycyclic aromatic hydrocarbons in soil and selected plants

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ABSTRACT

The influence of soil load with polycyclic aromatic hydrocarbons (PAHs) on their contents in selected plants was investigated. A set of experiments was realized in three years. The influence of extreme soil load with PAHs (soil contaminated by floods and sludge application) on their content in plants was observed in a pot trial. A laboratory column extract trial investigated PAHs transfer from the soil into soil solution in different conditions. The results showed that the transfer of PAHs into plants is influenced mainly by chemical characteristics of the substances (the number and position of aromatic nuclei); by soil characteristics (content and quality of soil organic matter) and by plant characteristics (plant species and plant bodies). The roots of tested plants were loaded with PAHs thanks to the transfer of less-nuclei compounds (2–3 nuclei) in soil solution into the roots and thanks to the binding of more nuclei compounds (4–6 nuclei) on organic substances in epidermis and primary bark of roots. These results were confirmed by a laboratory column trial.

Keywords: polycyclic aromatic hydrocarbons (PAHs); soil load; mobility; plant production

Polycyclic aromatic hydrocarbons (PAHs) are substances with of 2 and more aromatic nuclei and belong to the group of persistent organic pollutants (POPs). Attention is paid to this group of contaminants in many compartments of the environment, including soil. The persistence of different compounds of POPs and PAHs can differ according to the environment. Many substances decompose in soil in the span of a few years (naphtalene, anthracene) and some substances, such as benzo(ghi)perylene, are persistent (Starke et al. 1991) in spite of degradation processes in the soil environment (microbial activity, photodegradation, hydrolysis etc.).

Increased PAHs content in agricultural soil does not usually lead to acute intoxication of humans. On the other hand, health problems can be sometimes connected with symptoms of chronic intoxication. Carcinogenic, mutagenic, terratogenic effects, genotoxicity, an increased level of cholesterol in the blood or reproduction defects were observed after long-term POPs exposure and confirmed by toxicological experiments (Janošek et al. 2007).

In the Czech Republic, research on the most important POPs compounds in agricultural soils was begun in the early 1990s. The compounds in the 'Dutch List', including 13 PAHs compounds, were accepted and the proposal of the limit values of POPs in agricultural soils (background values) for the legislation purposes was prepared (Němeček et al. 1996).

The identification of the main inputs of PAHs into soils is the result of long-term observation of POPs in Czech agricultural soils (Podlešáková et al. 1998, Vácha et al. 2003). The main sources of increased soil load with PAHs are imission out-puts of industrial areas, emission out-puts from local furnaces in settlements, contaminated water in fluvial areas of some rivers, sludge and sediment application on agricultural soils.

The use of toxicity equivalents that maintain the toxicity of each compound seems to be a more progressive approach for the evaluation of the load in comparison with sum contents. The toxicity equivalents were derived from human toxicological studies focused on carcinogenic risk. The value of toxicity equivalent 1 is given to the most toxic compounds (benzo(a)pyrene from PAHs group). The total value is calculated as the sum of the products of equivalents and the contents of each compound. The resulting value is used as a sum of toxic equivalents in the case of PAHs (TEQ PAHs sum).

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Limit values of POPs (including PAHs) in agricultural soils are included in the directive of the Ministry of Environment of the Czech Republic (Directive No. 13/1994 Coll). These limit values were not derived from the values relevant for the soil in the Czech Republic and were based on the correction of external samples. As the suitability of these limit values for the evaluation of the load of Czech agricultural soils is problematic, an update of the directive was proposed. New limit values maintain the background values of POPs in Czech agricultural soils (Němeček et al. 1996) and are proposed as 'preventive limits' for legislative use. At present, the higher level of limit values, based on POPs transfer into plant production, is not available; their development is complicated by different level of persistence of individual compounds in soil and their decomposition and transformation into other forms. The microbial decomposition of PAHs in the soil seems to be one of the most important factors regarding degradation processes. Thiele and Brümmer (1999) defined the part of PAHs in the soil that could be decomposed by microbial activity, by using different chemical extract agents (a solution of acetone and toluene, tenzides). They compared the natural decline of PAHs in soil over a five-year field trial and the contents of PAHs in individual extract agents.

The observation of the transfer of PAHs into plants is complicated by other factors. Krauss et al. (2005) compared atmospheric and biological sources of plant loads by PAHs in a tropical area. Thiele and Brümmer (2002) confirmed the formation of PAHs in soil by plant material decomposition. They observed formation of 4–6 nuclei PAHs predominantly.

The behaviour and distribution of individual PAHs compounds of different molecular weights in the environment can differ markedly. Brandt et al. (2002) presented the information on low availability of compounds with a high value of K_{ow} partition coefficient (octanol/water) for plants. These compounds have high affinity to fat and the value of bioaccumulation in the animal tissues increases rapidly. The affinity to soil organic matter (K_{oc} partition coefficient) of 4–6 nuclei PAHs is two or three times higher than that of 2–3 nuclei PAHs (Holoubek 2005). It was investigated that the transfer of the chemicals with high hydrophobicity trough plant tissues occurs predominantly through pore water (Trapp et al. 2007) and the effect of 'growth dilution' influencing bioconcentration of PAHs in potatoes was described. Trapp (2002) presents a model for prediction of the transfer of PAHs from soil into plant tissues. He concluded that for the substances with low or medium lipophilicity (log $K_{ow} < 2$) there was no difference between developed dynamic model and equilibrium approach. For lipophilic substances equilibrium approach can be used only for prediction of their contents in the peel (tested on carrot), while for prediction of their contents in the core a dynamic (steady-state) flux model is more realistic. Mikeš et al. (2009) analysed the load of roots, bulbs and shoots of radish planted on contaminated soil by polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). They observed a decrease of bioaccumulation factors (BCF) of substances with increasing log K_{ow} value in the bulbs. Opposite root BCF values were constant and did not correlate with log K_{ow}. The authors confirmed the influence of chemicals concentrations in the air on the load of shoots of plants and the used prediction model of Trapp (2007) correlated with the measured values. Based on analytical data they concluded that soil resuspension and subsequent deposition of soil particles on leaf surfaces is dominant transport pathway and they also described entering of the compounds from the air into plant tissues of the shoot and even bulbs of radish. In spite of high affinity of lipophilic substances to soil organic matter some authors observed an increased load of plants by 4–6 nuclei PAHs after sludge application into soil in spite of a high content of soil organic matter (Oleszuk and Baran 2005). Trapp (2002) presents that the absorption of lipophilic organic substances to root is comparable with their absorption to soil organic carbon. At the same time the roots of plants can influenced the fate of PAHs in the soil. Rezek et al. (2009) used some plants (*Betula pendula*, *Morus rubra*, *Lolium perenne*) for bioremediation of contaminated soil by PAHs. The contents of fluoranthene and pyrene markedly decreased (to 50%) after 1 year of plant cultivation. They even observed successful degradation of benz(a)pyrene. On the contrary, benzo(ghi)perylene and indeno(cd)pyrene were very persistent in soil and practically undegradable. The potential of phytoremediation in soils loaded with PAHs was confirmed by Cheema et al. (2010) in the study focused on phenantrene and pyrene degradation by combined plant cultivation. The other ways to decrease PAHs in soil can be soil washing with some organic substances, like fatty acid methyl esters (Gong et al. 2010), vegetable oils (Yap et al. 2010) or products of mushroom metabolites (Li et al. 2010), for example.

Holoubek (2005) specifies the intake of PAHs by plants via the intake by roots from the soil solution (depending on the plant water regime and the content of lipid compounds in the root), the absorption of PAHs on root surface, the absorption of volatilised PAHs (from the soil) on the shoot and the absorption of PAHs on leaves of plants (from imission fall-outs). Some PAHs could be synthesised in plant metabolisms.

The limit value for the content of benzo(a)pyrene in some foods was brought forward to the European Union legislation (Directive 208/2005/EC). The limit of benzo(a)pyrene in fats and oils for direct consumption is 2 μg/kg and the limit for children's food is 1 μg/kg. The regulation of the Czech Ministry of the Health, No. 305/2004 Coll., limits the values for nine PAHs compounds in edible oils with the maximum of 2 μg/kg for each individual compound.

MATERIAL AND METHODS

The study was performed on the basis of three experiments: pot trial, field plot trial and laboratory column experiments.

Pot trial. The trial was based in 2004 (October) and sieved for the first time in 2005 (April). The trial was finished in autumn 2007. The experimental soil contaminated by floods with increased PAHs contents was taken out on the basis of terrain monitoring as loaded variant L1 (Modal Fluvisol – FLm). Sludge from a wastewater factory was used as another source of increased PAHs contents. The mix of the sludge and the soil used in the control variant (Arenic Cambisol – CAa) in a mass rate 1:1 simulated the increased load of soil by PAHs after the sludge application (loaded variant L2). The soil used as the control variant (Arenic Cambisol – CAa) with PAHs contents under background values has comparable chemical and physical characteristics (pH, Cox, particle-size composition) as loaded variant 1. The sum of PAHs is comparable in the soil of L1 and L2 variants but TEF value is evidently higher in the soil of L2 variant with sludge application because of increased content of the substances with carcinogenic effect in used sludge. The characteristics of soils and PAHs contents are presented in Table 1. The contents of potentially risk elements in used sludge were under the limits of regulation of the Czech Ministry for Environment No. 504/2004 Coll. The same sludge was used in field trial in extremely increased dose and we had to fulfil the criteria for sludge contamination with limited contaminants at least. From this viewpoint the phytotoxicity due increased contents of risky elements in used sludge was eliminated. The pot trial was placed in a fenced area and was performed in four replications.

Mitscherlich pots filled with 6 kg of sieved soil were used. Soil acidity was treated on the value of 6.5 pH (dolomitic limestone, Ca and Mg in the form of $CaCO_3$ and $MgCO_3$) and basic fertilisation with N, P and K was realised. Soil samples for PAHs analyses were taken out after 20 days from the trial establishing. The pots were seeded with radish (*Raphanus sativus* var. *radicula*), Duo variety in 2005, with carrot (*Daucus carota*), Nantes 3 variety in 2006 and with parsley (*Petroselinum crispum*), Dobra variety in 2007. Only five plants were left in every pot after germination.

Seeded pots were periodically irrigated with a constant volume of drinking water (500 ml). The samples of soil and plants for PAHs analyses were taken out after the termination of the vegetation period (second week in October). Plant samples were analysed in the form of washed hypocotyles (radish 'bulbs') and washed and unwashed shoots. Plant washing was done with demineralised water in laboratory conditions. The samples of carrot and parsley were analysed in the form of washed roots separated into two parts – primary bark (external part) and central cylinder (inner part). Only roots of comparable size (carrot roots of cca 15 cm length and 2.5 cm thickness and parsley roots of cca 8 cm length and 1.5 cm thickness) were used for the analyses. The differences between the size of carrot and parsley roots were caused by lower yield of parsley plants.

Field plot trial. The field trial was located in the clean area of the Czech-Moravian Highlands (Jihlava district) and was based on a typical

Table 1. The characteristics of soils and PAHs contents

Soil	Variant	Particle-size class	Substrate	Σ PAHs	Σ TEF PAHs
				(mg/kg)	
Typic Fluvisol	L1	3	alluvial river sediments	21.05 ± 1.39	2.462 ± 0.20
Arenic Cambisol + sludge	L2	3	gneiss	24.59 ± 1.21	6.218 ± 0.51
Control – Arenic Cambisol	Co	2	terrace sands	0.454 ± 0.08	0.058 ± 0.02

Cambisol (CAm, acid variety, on gneiss). Sludge application (sludge identical with pot trial) in the dose of 25 kg/m of dry matter was used for increased PAHs load simulation in April 2005. The extent of individual plots was 2 × 2 m. The soil was seeded with mustard (*Sinapis alba*) in 2005 and 2006 and with carrot (*Daucus carota*) in 2007 in four replications. The samples of soil and plants were taken after the harvest (October). Plant samples were used in the form of washed and unwashed shoots in the first year and unwashed shoots in the second year of the trial. Only roots of carrot were used for PAHs analysis in the third year. The roots were separated into three parts, epidermis, primary bark and central cylinder.

Laboratory column experiment. The column experiment focused on the observation of the transfer of PAHs from the soil into the solution was realised in 2006. Plastic columns with an outlet in the bottom part were used. The bottom part was fitted with a 0.2 mm sieve. The columns were filled with 100 g of soil identical with the pot trial. The soil in the columns was saturated with demineralised water (the value of field capacity) and then was leached with 200 ml of solutions (in three repetitions) during 24 h in the following order:

demineralized H_2O
demineralized H_2O acidified by H_2SO_4 on the value pH 3
a 0.2% solution of the tenzide – $C_{12}H_{25}NaO_4S$ in demineralized H_2O

The use of a tenzide solution was derived from the work of Thiele and Brümmer (1999), which defined the mass fraction of PAHs extracted from the soil by a 0.2% tenzide solution as microbial degradable. The extractability by water and 0.2% and 4% tenzide solutions were compared in laboratory conditions. The extraction proceeded gradually and the weakest extract agent, the demineralized water, was firstly used. The extraction of the same sample by acidified water (pH 3) followed and the 0.2% tenzide solution extraction was the last step in this approach.

The obtained extract was centrifuged (2500 rpm) to separate the colloidal phase from the solution. Only 33% of PAHs contents flowed in an aqueous phase and the prevailing mass of PAHs was bound to the colloids (Holoubek 2005). The treated extract was analysed in a commercial accredited laboratory by standard methods of a PAHs analysis. Laboratory column trial was replicated three times and median values are used in the presentation.

Experimental data were processed by elementary statistics using the Excel programme (average, geomean, standard deviation, median, maximum, minimum, Pearson correlation coefficient).

PAHs analysis. The laboratory determination of the PAHs contents in the soils, plants and solution was realised in the accredited laboratory Aquatest JSC. The solid sample analysis comprises the exsiccation using waterless sulphate and the extraction procedure in the acetone solution. The raw extract is analysed without purifying. PAHs are determined by the high-performance liquid chromatography (HPLC) with fluorescence detection (mobile phase – acetonitrile/water). One instrument measured some PAHs portions during isocratic elution under invariable wavelength and the second plant detected the other PAHs portion on equal terms. Two detectors in series assemble the instrument configuration, and thus two different wavelengths are involved in the detection. Such procedure minimises the difficulties with the gradient elution and with the alteration of the wavelength setting during analysis by the division of unpurified samples.

The concentration levels of individual compounds, the sum values of the compounds (the PAHs sum), the sum value of 2–3 nuclei PAHs and of 4–6 nuclei PAHs were used for the assessment of the load of soils and plants. The sum of toxic equivalency factors for PAHs (the TEF PAHs sum) was involved as well to take into account various toxicological characteristics of individual PAHs compounds. The TEF PAHs sum is defined as the sum of the products of the concentration of each compound multiplied by the toxic equivalent value for carcinogenic compounds. The following compounds were used:

Benzo(a)pyrene and Dibenzo(a,h)anthracene – toxic equivalent value = 1
Benzo(a)anthracene, Benzo(b)fluoranthene and Indeno(1,2,3-cd)pyrene – toxic equivalent value = 0.1
Benzo(k)fluoranthene – toxic equivalent value = 0.01

The soil organic matter analysis. The selected characteristics of the content and quality of soil organic matter (SOM) were assessed in the central laboratory of the RISWC. The characteristics are defined below.

C_{org} – organic carbon indicative of the carbon content in primary SOM. It may be used for the humus content calculation (1.72 × C_{org}). The determination procedure is based on the chromic acid oxidation of organic carbon under the sulphuric acid abundance and elevated temperature. Unexpended chromic acid is determined by the iodometric method. The accredited method SOP 4/02 is the modification of the ISO 14235 norm. The assay of weakly and tightly bounded humus materials includes the determination of the humic acid carbon (C-HA), fulvic acid carbon (C-FA), humus matter carbon (C-FA + C-HA) and the assessment of the colour coefficient (Q4/6) indicating the humus quality. The determination procedure is based on the sample extraction using mixed solution of sodium diphosphate and sodium hydroxide, the carbon contents (C-FA, C-HA) are determined by titration and the coefficient Q4/6 results from the photometry.

C_{ws} – water-soluble carbon, indicating the quality of primary SOM (bioavailable carbon for soil microorganism). Laboratory determination consists in an hour sample extraction using 0.01M $CaCl_2$ solution (1:5 w/V) and in the determination of oxidizable carbon in the filtrate evaporation residue through the heating of filtrate with chromium sulphuric acid and the subsequent titration with Mohr's salt.

C_{hws} – hot water-soluble carbon, being similar in the assessment purpose to water-soluble carbon. After an hour soil sample boil in 0.01M $CaCl_2$ solution (1:5 w/V), the oxidizable carbon in filtrate evaporation residue is determined through the heating of filtrate with chromium sulphuric acid and the subsequent titration with Mohr's salt.

RESULTS AND DISCUSSION

The characteristics of content and quality of soil organic matter in the soil of the pot trial are presented in Table 2.

The highest values of C_{org} content were detected in the soil of L2 variant, the soil of L1 variant reached almost the same C_{org} value as the Co variant.

The content of hot water-soluble carbon (C_{hws}) indicated the content of an active micro degradable carbon fraction within the total organic matter. The highest value of C_{hws} was observed in the soil with sludge-L2 variant; control variant had a value ten times lower, while the lowest value was detected in the soil of L1 variant.

Similar ratios of values could be found in the case of water-soluble carbon (C_{ws}) that also indicated the quality of primary organic matter (Kolář et al. 2009). The highest total carbon content of humic substances (C-HS) was observed in the soil with sludge-L2 variant and the lowest in the soil of L1 variant. The quality of humic substances, according to the HA/FA ratio is comparable to that of the soil of L2 variant and control variant, where the predominance of humic acids was detected. A balanced humic and fulvic acid ratio was observed in the soil of L1 variant. The values of the Q4/6 coefficient confirm the lowest quality of humus substances in the soil of L1 variant, and the similar humus quality of the soils of the control variant and the variant with sludge – L2.

The PAHs total contents in soil were comparable between L1 variant and L2 variant, with concentrations moving from 20 000 µg/kg up to 30 000 µg/kg. Differences between the contents before and after the vegetation period were observed simultaneously. An increased PAHs content was detected in poor and sandy soil of L1 variant after the vegetation period, in comparison with that previously considered. This could be connected with PAHs syntheses by plant material decomposition in the soil (Thiele and Brümmer 2002, Holoubek 2005). On the contrary, the content of PAHs in the soil of L2 variant was lower after the vegetation period in the first year. The existence of soil heterogeneity could not be excluded in this case, because a perfect interfusion of the sludge with the soil is not realistic. A corresponding trend shows the values of TEF PAHs, indicating carcinogenic risk in the soils of the considered variants. The soil samples were taken only after the vegetation period in the following years and an increase of the sum of PAHs in L1 variant (more than 40 000 µg/kg) and a slight decrease in L2 variant (18 000 µg/

Table 2. The content and quality of soil organic matter, pot trial

Variant	C-HA	C-FA	HA:FA	C-HS (pyro) %	Q4/6 (pyro)	C_{org} (%)	C_{ws}	C_{hws}
	(pyro) %						(mg/kg)	
Typic Fluvisol	0.06	0.07	1:1	0.13	4.3	1.6	34	175
Arenic Cambisol + sludge	0.83	0.5	1:0.6	1.33	2.7	5.23	204	1944
Control – Arenic Cambisol	0.33	0.2	1:0.6	0.53	2.3	1.66	89	489

C-HA – humic acid carbon; C-FA – fulvic acid carbon; C-HS – humus substances carbon; Q4/6 – colour coefficient; C_{org} – organic carbon; C_{ws} – water soluble carbon; C_{hws} – hot water soluble carbon

Table 3. The median values of PAHs content in washed and unwashed radish shoot planted in pot trial

	PAHs (µg/kg of dry matter)													
	Fl	P	Ph	B(b)F	B(a)A	A	I(cd)P	B(a)P	B(k)F	B(ghi)P	Ch	N	D(ah)A	Sum PAHs
L1 unwashed	1000 ± 117.4	741 ± 29.32	644 ± 26.92	446 ± 16.44	402 ± 13.73	129 ± 17.18	232 ± 17.01	493 ± 34.62	231 ± 13.06	455 ± 23.28	403 ± 18.45	100 ± 10.7	68 ± 8.28	5344 ± 331.84
L2 unwashed	120 ± 45.95	60 ± 7.46	40 ± 7.87	130 ± 15.82	50 ± 10.46	< 10	90 ± 19.42	130 ± 15.05	80 ± 11.98	140 ± 20.36	90 ± 16.42	100 ± 17.84	< 10	< 1050
Control unwashed	90 ± 11.15	60 ± 9.33	70 ± 9.75	20 ± 8.67	20 ± 8.72	< 10	< 10	20 ± 8.66	< 10	20 ± 4.69	30 ± 12.11	100 ± 12.08	< 10	< 470
L1 washed	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 130
L2 washed	15 ± 2.45	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 135
Control washed	< 10	< 10	15 ± 2.87	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 135

L1 – Typic Fluvisol; L2 – Arenic Cambisol + sludge; Control – Arenic Cambisol

kg) were observed in the second year. The PAHs contents were comparable in the soil L1 variant between the second and third year and decreased slightly in the soil of L2 variant in the third year. Comparable values of TEF PAHs in these variants suggest the hypothesis of a more rapid decrease of less-nuclei and less carcinogenic PAHs substances and confirm the increased persistence of more-nuclei PAHs in the soil. The contents of PAHs in the soil of the control variant moved under their background values in Czech soils (1 000 µg/kg) in the intervals from 400 µg/kg up to 600 µg/kg even if a slight increase of their contents after the vegetation period was observed. This increase could relate with described effect of the influence of air load with PAHs on soil content in time (Mikeš et al. 2009).

Differences between PAHs contents in the plants were also observed. The increase of PAHs contents in unwashed radish shoots in L1 variant in comparison with L2 variant and especially with control variant was statistically significant at the 0.05 significance level. The contents of PAHs in the radish shoots decreased rapidly after washing the shoots and they are comparable in all variants of the trial. The increased PAHs contents in radish shoot in L1 variant – Typic Fluvisol in comparison with L2 variant – Arenic Cambisol + sludge relates with higher soil particles mobility in sandy soil very probably. The data are presented in Table 3. The results confirm the predominance of contamination on the surface of the plant shoots (dust articles in the air, surface contamination by soil particles during the irrigation) in comparison with the root intake. In spite of this finding the trend of a PAHs content increase in radish bulbs (hypocotyles) in the loaded variants (L2 variant < L1 variant) was observed. The values of TEF PAHs in radish roots showed similar trends, but on the other hand, PAHs were not analysed in the peel and inner part of radish bulbs and in the hair roots of radish separately where the differences in the accumulation of the substances depending on $\log K_{ow}$ value were described by some authors (Trapp 2002, Mikeš et al. 2009).

The load of unwashed radish shoots in L1 variant (493 µg/kg of dry matter) and L2 variant (130 µg/kg of dry matter) must be evaluated as extremely increased in comparison with the limit value of benzo(a)pyrene (2 µg/kg) in food for direct consumption (Directive 208/2005/EC). The contents of benzo(a)pyrene decreased under the detection limit (10 µg/kg of dry matter) after washing the shoots of all the variants. Increased contents of benzo(a)pyrene were also detected in radish bulbs in L1 variant (42 µg/kg of dry matter). The load of radish bulbs in L2 variant reached the value of 10 µg/kg of dry matter of benzo(a)pyrene and the content of the control variant moved under the detection limit. The decrease of PAHs contents in radish bulbs after washing supports the hypotheses of the influence of soil load with PAHs on their contents in radish bulbs, although Mikeš et al. (2009) confirmed a significant influence of air load on radish bulbs.

Differences between PAHs and TEF PAHs sum contents in primary bark and central cylinder of carrot (second year of the trial) are presented in

Figure 2. The increased contents of PAHs in the central cylinder in comparison with the primary bark were observed in the control variant and especially in L1 variant. On the contrary, the ratios of PAHs contents between the upper and inner parts of the carrot root were opposite in L2 variant. We lean to the hypothesis about the root intake of some PAHs substances and their transfer to the central cylinder of the carrot root in the case of poor and sandy organic matter of Karvina fluvisol (L1 variant) loaded with PAHs. Trapp (2002) describes in his model of POPs transfer into plant the input from soil and output to plant stems of the substances with log $K_{ow} < 2$ with transpiration stream where no relevant difference between dynamic model and equilibrium approach was observed, also less lipophilic substances have higher tendency to enter plant tissues via vascular system. In spite of the fact that minimal log K_{ow} value for PAHs is almost 4 (3.92 for acenaphtene) the observed trend follow these principles. The PAHs and TEF PAHs sums in the central cylinder of the carrot in L1 variant reached increased values in comparison with the control variant, whereas these values in the primary bark are comparable. Only slightly increased contents of PAHs were detected in the central cylinder of the carrot root in L2 variant, but rapidly increased PAHs contents were found in the primary bark of the carrot root in this variant in comparison with the control variant. It could be concluded that stronger bindings of PAHs on soil organic matter in the variant with sludge are impaired in the rhizosphere zone, while mobilised PAHs are consecutively bound onto organic substances in the external layer of the carrot root (lipids, plant pigments, growth regulators etc.). The intensive binding of PCBs on carotene in carrot roots is presented by Bobovnikova et al. (2000) for example.

On the basis of the comparison of 2–3 nuclei PAHs and 4–6 nuclei PAHs contents in carrot roots (Figure 1), an increased transfer by root intake seems to be evident in the case of less-nuclei PAHs.

Marginal transfer of 4–6 nuclei PAHs into the central cylinder of the carrot root via the primary bark could be hypothesised, considering their increased contents in the primary bark of the carrot roots in all the variants. Trapp (2002) analysed that the contents of benzo(a)pyrene in peel of carrot was up to 100 times higher in comparison with the core. These trends were confirmed by the use of parsley samples in the third year of pot trial. Nevertheless, PAHs contents were higher in parsley roots in comparison with carrot roots very probably thanks to lower parsley yield – smaller size of roots. The effect of 'growth dilution' is presented by Trapp et al. (2007) and is described also by Mikeš et al. (2008). It means an increase of root surface in contrary to root volume that could lead to the increase of PAHs intake. The problem with the limit values of benzo(a) pyrene in plant products for direct consume seems to be evident in this case (Figure 2). These results also show that not only carotene (Bobovnikova et al. 2000) plays the important role in the bindings of organic pollutants in the root of plants. Especially more nuclei PAHs with higher log K_{ow} value are close to the phase equilibrium with soil in the peel of roots and the adsorption of lipophilic compounds to root surfaces is similar to the adsorption to soil organic matter (Trapp 2002).

The results of the laboratory column experiment confirm findings coming from the pot trials. The sum contents of 2–3 nuclei PAHs and 4–6 nuclei PAHs in extracts (µg/l) are presented in Figure 3.

Intensive wash of 2–3 nuclei PAHs from the soil of L1 variant was predominantly observed after the first extraction step, while marginal wash of PAHs from the organic bindings in the soil of L2 variant

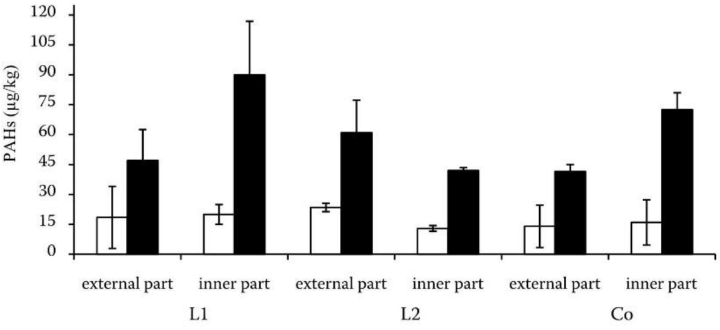

Figure 1. Comparison of 4–6 nuclei (white) and 2–3 nuclei (black) PAHs contents in carrot roots (µg/kg of DM)

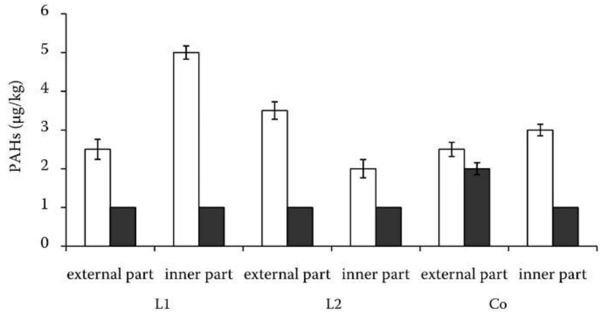

Figure 2. The contents od benzo(a)pyrene (white) and dibenzo(ah)anthracene (black) in parsley roots of pot trial (µg/kg of DM)

was detected. A decrease of PAHs content in the extract was observed after the second extraction step by the acidified water in L1 variant. A relatively low decrease was detected in the case of 4–6 nuclei PAHs thanks to their relatively low wash after the first extraction step related to their stronger binding with soil organic matter. The change of pH value of the solvent did not have a stronger influence on the extractability of PAHs from the soil with sludge (L2 variant). The use of the tenzide during the third extraction step led to the erosion of PAHs bindings on soil organic matter in the soil of L2 variant and massive wash of 2–3 nuclei > 4–6 nuclei PAHs from the soil to the extract was detected. The increased PAHs wash during the third extraction step was observed in L1 variant in comparison with the second extraction step, but this wash was significantly lower in comparison with the first extraction step. Simultaneously, the content of 4–6 nuclei PAHs was higher than the content of 2–3 nuclei PAHs in the third extraction and it could be concluded that lower weight PAHs with lower affinity to organic matter were washed predominantly during the first extraction step from the soil of L1 variant.

Other key factors could be derived from the comparison of the contents of individual compounds in the extracts (Figure 4).

The highest transfer of 2-nuclei naphthalene with a simple molecular structure from the soil into the liquid phase is visible. Its effect on the total PAHs content is the highest in the water extract from the soil of L2 variant and is the highest in soil organic matter and with the use of the weakest extraction agent. During the second extraction by acidified water, the proportion of naphthalene decreased at the expense of 2-nuclei fluorene with a more complexly structured molecule. The decrease of 3-nuclei phenanthrene at the expense of more-nuclei PAHs was also registered. It could be concluded that the second extraction by the acidified water slightly influenced the proportion of individual PAHs on the total PAHs content in the extract. The third extraction by the tenzide solutions strongly influenced this proportion, where the amount of more-nuclei PAHs increased.

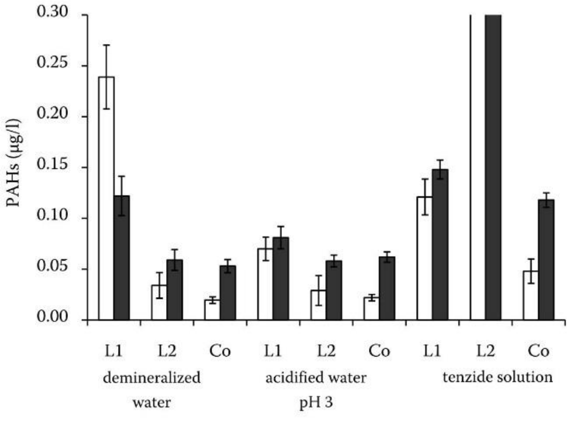

Figure 3. The sum contents of 4–6 nuclei (white) and 2–3 nuclei (black) PAHs in the extracts (µg/l)

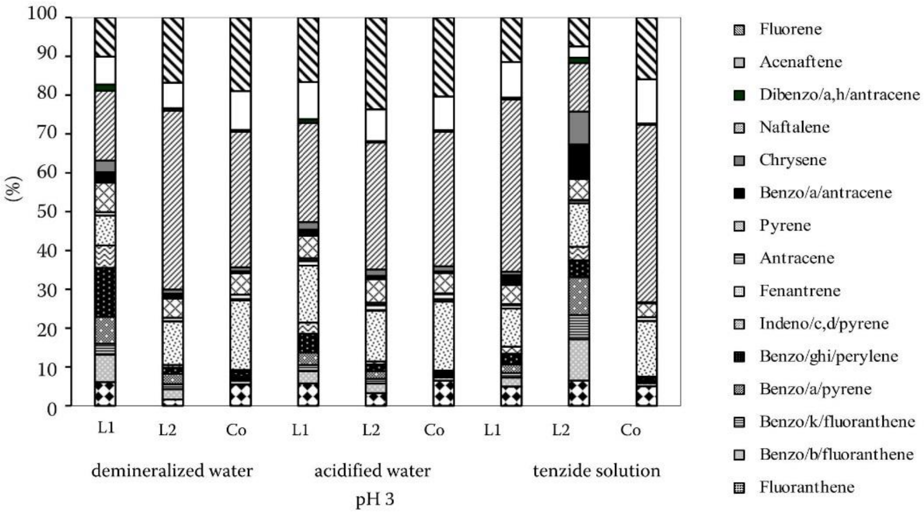

Figure 4. Comparison of the contents of individual PAHs compounds in the extract (%)

The mobilisation effect on PAHs by the tenzide solution from the soil with sludge (L2 variant) is comparable with the first extraction by L1 variant water, where the wash of non-bound PAHs from poor sandy soil was realised. The increased content of more-nuclei PAHs in the extract of L2 variant relates to the increased content in the sludge.

No verifiable changes of the proportion of individual PAHs during three extraction steps were observed in the case of the control variant (Figure 4) and low-nuclei PAHs were predominantly extracted. Cave et al. (2010) measured bioaccessible PAHs fraction in the soil (varied from 10–60%) and the multiple regression showed that the PAHs bioaccessible fraction could be explained using the PAHs compound, the soil type and the total PAHs to soil organic carbon content.

The results of field trial confirmed the trends of pot trial. The differences between loaded variant (sludge application) and control variant did not reached the level of pot trial because of lower dose of sludge in the soil of field trial. In spite of this fact, the dose of sludge was 50 times higher compared to the Czech regulation for sludge application on agricultural soils (Regulation of Ministry of Environment No. 504/2004 Sb). PAHs contents in shoots of mustard were comparable in loaded variant and control variant (550 μg/kg vs. 520 μg/kg of dry matter, respectively). The median values of sum of PAHs in carrot epidermis were 148 μg/kg on loaded variant with sludge compared to 75 μg/kg of dry matter in the control. PAHs contents in carrot primary bark were 105 g/kg vs. 60 μg/kg of dry matter and the PAHs contents in carrot central cylinder were 50 μg/kg vs. 55 μg/kg of dry matter, respectively.

On the basis of the above reported findings, it could be concluded that the increased load of the soil by PAHs influenced the root load of the tested plants. This load was caused by PAHs transfer (low-nuclei PAHs especially) into the plant vascular system by the soil solution or by PAHs binding (especially more-nuclei PAHs) to organic substances in the external root layer dependent on the soil properties. Different types of soil loads with PAHs, including sludge or sediment application, could cause the plant contamination with PAHs. It was confirmed by other authors (Oleszuk and Baran 2005, Zohair et al. 2005). Results of the pot trial led to conclusion that the plant shoots were predominantly loaded with over ground contamination. The similar trend was showed also in the field trial. The fulfilment of limit values of PAHs – especially of benzo(a)pyrene, in commodities for direct consumption could be problematic in the localities with increased PAHs load, with respect to the limit values in the Directive 208/2005/EC.

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5 Souhrnná diskuze

Hlavním cílem práce bylo poskytnout dostatek relevantních podkladů pro hodnocení potenciálních rizik znečištění v záplavových půdách a ověření vybraných metod pro regionalizaci těchto rizik. Výzkum probíhal na zájmových územích na několika prostorových měřítcích – od národního, přes regionální po lokální.

V první části této kapitoly jsou proto shrnuty a diskutovány závěry z dvou prací, které prezentují metodické postupy použité pro hodnocení jednak humanotoxikologických, a jednak ekosystémových rizik na národní úrovni. V obou článcích je kladen důraz na prostorovou složku (regionalizaci) zjištěných výsledků. Základním vstupním požadavkem pro predikci zdravotních a ekosystémových rizik vyplývajících ze znečištění půdy je získání spolehlivých a reprezentativních koncentrací toxikologicky významných chemických látek v půdách. V publikovaných pracích je využit datový soubor z uceleného vzorkování půd, který vznikl v rámci projektu Ministerstva vnitra ČR č. VG20102014026 – Dopady povodní na kontaminaci půd a potravních řetězců rizikovými látkami. Pro potřeby vědeckého výzkumu byl získaný datový soubor zajímavý především šíří stanovených látek (viz Tab. 1 v podkapitole 4.1). Systematický byl také výběr lokalit, který byl založen na prostorovém výběru ploch z oblastí s významnou výměrou obhospodařovaných půd s vysokou frekvencí záplav. Vlastní hodnocení rizik je pak v návaznosti na kapitolu 2.2.2 prováděno na základě sumárního indexu rizika (tzv. hazard indexu) a úpravy dat tak, aby bylo možné hodnotit příspěvek jednotlivých polutantů do celkového rizika i variabilitu či podobnost jednotlivých lokalit z hlediska profilu znečištění. Z důvodu kompozičního charakteru vstupních dat byla data před vstupem do analýzy transformována pomocí různých přístupů – transformace rozsahem a normalizace řádkovým součtem v případě analýzy ekologických rizik (podkapitola 4.1), log-poměrová transformace ve studii humanotoxikologických rizik (podkapitola 4.2).

Hodnocení zdravotních rizik či rizik přechodu kontaminace do potravního řetězce se stalo také podkladem pro nastavení legislativního rámce ochrany půdy v ČR, neboť takto odvozené hodnoty podložené vědeckým výzkumem byly implementovány do nové vyhlášky č. 153/2016 Sb. Nově navržený hierarchický systém limitních hodnot se svým pojetím přibližuje systému hodnocení rizik. V druhé části diskuzní kapitoly 5.1 jsou proto prezentovány poznatky z publikace (podkapitola 4.3), ve které byl popsán jednak způsob odvození nových legislativních kritérií pro rizika odhrožení zdraví člověka, jednak ověření jejich relevance a využitelnosti v regionální studii, kde pomocí kombinace nově navržených legislativních limitů a geostatických nelineárních technik byl proveden odhad prostorové distribuce překročení úrovně kontaminace v regionech pod vlivem dlouhodobého znečištění prostředí RP a PAU.

Jak vyplývá z rešerše literatury, má z hlediska hodnocení rizik znečištění významnou roli pochopení vztahu mezi kontaminací nivních půd a existencí bodových či difúzních zdrojů znečištění. Proto jsou v navazující kapitole praktické části (5.2) shrnuty poznatky z vědeckých článků, ve kterých je věnována pozornost hodnocení vlivu jak přirozených (geogenních) zdrojů na geochemické vlastnosti (semi)terestrického prostředí údolních niv (podkapitola 4.4), tak vymezení potenciálního vlivu lidskou činností podmíněných bodových či difúzních zdrojů znečištění (podkapitola 4.5). V obou vědeckých publikacích byly využity datové podklady Registru kontaminovaných ploch Ústředního kontrolního a zkušebního ústavu zemědělského (ÚKZÚZ), které jsou zajímavé především územním detailem sledování RP.

Ve třetí části sumární diskuze jsou prezentovány dvě vědecké studie zaměřené na potenciální přestup RP a PAU v lokálních experimentálních podmínkách (polních a nádobových pokusech), kde byly použity regionálně zatížené nivní půdy ze dvou významně rizikových oblastí (imisně postižené oblasti s významnou zátěží PAU a nivní půdy pod vlivem těžby polymetalických zrudnění v povodí) jako experimentální půdy pro srovnávací studii přestupu RP a PAU z půdy do zemědělských plodin.

5.1 Regionalizace zdravotních a ekosystémových rizik vyplývajících ze znečištění nivních oblastí v ČR

Ve dvou prvních vědeckých publikacích bylo použito screeningové hodnocení ekosystémových (podkapitola 4.1), resp. zdravotních rizik (podkapitola 4.2), přičemž byly srovnávány environmentální koncentrace a referenční koncentrace představující na účincích založenou indikativní hranici možných rizik v půdách. Hodnoty tohoto poměru by neměly být vyšší než 1, především pak hodnoty vyšší než 2 již identifikují případy, kdy je nutné posuzovat riziko zvýšené až významné (Sáňka et al. 2015). Výsledky pro oba typy sledovaných rizik vykazují regionální rozdíly z hlediska celkové magnitudy odhadnutého rizika (Obr. 4 v podkapitole 4.1). Pro zhodnocení regionálních rozdílů v příspěvcích jednotlivých RP a POP do celkového screeningového odhadu ekosystémových rizik byla použita shluková analýza, kdy vstupní příspěvky byly před analýzou transformovány rozsahem a normalizovány řádkovým součtem (Miesch 1976). Tento postup byl úspěšný jednak z hlediska klasifikace jednotlivých profilových zátěží (Obr. 2 v podkapitole 4.1), jednak pro sledování prostorových vazeb vytvořených shluků (profilů) zátěže (Obr. 3 v podkapitole 4.2). Následné vyhodnocení profilu zátěže na lokalitách s vysokými hodnotami indexu rizika pro ekosystémové funkce (HI > 2) umožnilo definovat prioritní polutanty, které se nejvíce podílely na zvýšení ekotoxikologických rizik. Obecně lze tyto poznatky shrnout, že zvýšená rizika pro ekologické funkce půdy představují lokality, kde docházelo k interferenci zátěží organickými polutanty (PAU > organochlorové pesticidy - OCP > PCB) s rizikovými prvky (především pak As, Cu, Pb, Zn) – viz Tab. 3 v podkapitole 4.1. Změny indexu rizika a profilu zátěže ve fluviálních půdách v různých úsecích Labe (např. za Pardubicemi, od Neratovic k soutoku s Ohří u Litoměřic) dobře korespondovaly s výsledky environmentálního monitoringu nejen půd (Podlešáková et al. 1994; Heinisch et al. 2007), ale také dalších složek biosféry (Randák et al. 2009; Kolaříková et al. 2012). Velmi významně se odlišovala také část Labe na přítoku Klejnárky, kde byl, jak závažností rizika (HI = 2,6), tak jeho profilovým složením (As, Cu, Zn), potvrzen vliv kutnohorského polymetalického revíru, což koresponduje například se zjištěními Horáka a Hejcmana (2013). Významný příspěvek As do rizika byl zachycen také v zemědělských půdách střední Otavy, což si vysvětlujeme zvýšeným výskytem zlatonosných ložisek s akcesorickým doprovodem minerálů arzenu v širším povodí Otavy (Fillipi et al. 2004; Skála et al. 2011). Zvýšené hodnoty indexu rizika také provázely skupinu lokalit dobře vymezených jednak profilem znečištění s dominancí příspěvku PAU, spolu s prvky Zn, Cu a Cd, a jednak jednoznačným regionálním vymezením v oblasti širšího Severomoravského imisního regionu (povodí Odry či Bečvy), což potvrzuje sledování zdravotních dopadů v regionu (Šrám et al. 2012; 2013; Švecová et al. 2013). Zajímavým poznatkem bylo, že podobnou profilovou zátěž, avšak s celkově relativně nižšími hodnotami indexu rizika, prokázaly některé lokality na horních tocích s vyšší nadmořskou výškou v severní části republiky (horní tok Labe či Moravy). Tuto skutečnost lze vysvětlit vyšší náchylností PAU k dálkovému přenosu znečištění, což indikuje pravděpodobný vliv vertikálního (výškového) gradientu u některých PAU, což obecně potvrzují sledování zvýšených obsahů PAU v půdách či vodních zdrojích v relativně neznečištěných odlehlých lokalitách (Grimalt et al. 2004). V regionalizaci rizik byly dobře zachyceny také vlivy bodových zdrojů v návaznosti na metalogenní zóny a historické těžební aktivity v povodích. Jedná se především o oblast Berounky, kde se na středním toku projevila dotace kontaminovaných sedimentů z povodí Litavky, která patří k dobře zdokumentovaným (Borůvka et al. 1996; Ettler et al. 2006; Navrátil et al. 2008; Žák et al. 2009), a dále v povodí Mže byl velikostí výsledného indexu rizika i profilovým složením potvrzen také vliv důlního revíru Stříbro. Analogicky byly pomocí shlukové analýzy zpracovány výsledky screeningového hodnocení zdravotních rizik nivních půd, publikované jako kapitola v odborné knize (Vácha et al. 2016). Poznatky získané při tvorbě této publikace vedly k dalším výzkumným otázkám následně vědeckým publikacím:

1) Výsledky shlukové analýzy ukázaly, že v kompoziční struktuře příspěvku jednotlivých polutantů silně dominují látky ze skupiny PAU (Obr. 3 v podkapitole 4.2). Vstupní transformace dat pro stabilizaci rozsahu a normalizace řádkovým součtem sice umožnily zmírnit efekt uzavření kompozičních dat, nicméně statisticky korektním řešením je využití kompoziční analýzy dat založené na log-poměrovém přístupu dle Aitchisona (1984), který je v posledních letech aktivní oblastí výzkumu v přírodních vědách (Aitchison & Egozcue 2005; Reimann et al. 2017). Aplikace metod vícerozměrné analýzy dat upravené pro kompoziční data umožnila lepší náhled na kompoziční strukturu relativních příspěvků organických polutantů do celkových zdravotních rizik a klasifikaci lokalit s podobnou kompoziční strukturou v situaci, kdy některé komponenty výrazně dominovaly v kompoziční struktuře (Tabulka 3 v podkapitole 4.2). Průzkumová vícerozměrná analýza kompozičních dat pak umožnila lepší pochopení kompoziční variability dat. Pomocí upravené kompoziční shlukové analýzy byly vymezeny tři významné shluky, které umožňovaly odlišit kromě lokalit s významnou dominancí látek ze skupiny PAU i další dva shluky lokalit, kde byla kompoziční variabilita pod vlivem skupiny organochlorových pesticidů ze skupiny DDT a jeho metabolitů v prvním případě a organochlorových látek ze skupiny polychlorovaných bifenylů (PCB) a izomerů hexachlorcyklohexanu (HCH) ve druhém případě (Obr. 1 a 4 v podkapitole 4.2). Tyto shluky pak indikovaly převládající difúzní zdroje v povodích jako širší imisní zátěž povodí a vliv krátkého i dálkového transportu atmosférických polutantů, difúzní vliv intenzivní zemědělské produkce a pohybu reziduí pesticidů vlivem jejich zvýšeného historického použití a také vliv dílčích bodových zdrojů v širších průmyslových aglomeracích podél vodních toků. Fuzzy přístup ke klasifikaci ve shlukové analýze pak umožňoval sledovat míru diferenciace mezi jednotlivými typy dle kompoziční struktury (Obr. 4 v podkapitole 4.2). Následná regionalizace

výsledků ukázala prostorové souvislosti této klasifikace (Obr. 5 v podkapitole 4.5). Kompoziční profil zátěže indikující vliv intenzivní zemědělské činnosti dobře determinovaly příspěvky izomerů DDT a jeho metabolitů, což bylo prostorově identifikováno v profilu zdravotních rizik v povodí Berounky, Ohře a v širší oblasti jižní Moravy. Vliv atmosférického transportu byl dobře vymezen příspěvky PAU do celkového rizika, přičemž tento shluk byl podmíněn jednak regionálně situací v oblasti severní Moravy, jednak zonálně vyššími nadmořskými výškami či odlehlejšími oblastmi bez výraznějších ostatních zdrojů (horní toky Moravy, Labe, jižní Čechy). Poslední klasifikovaný shluk byl z hlediska kompoziční i regionální variability méně jednoznačně vymezen, nicméně profil zátěže určovaly jednak polychlorované bifenyly (především v povodí Labe pod Neratovicemi, méně pod Pardubicemi), a jednak izomery HCH či pentachlorbenzen (střední tok Moravy přibližně od Olomouce k soutoku s Dřevnicí). Vzorky z dolního Labe pod Neratovicemi byly také dobře vymezeny specifickým složením zátěže PCDD/F (Skála et al. 2014). Zjištěné výsledky dobře korespondovaly s výsledky stochastického modelu distribuce vybraných organických látek založeného na regresních stromech (Kubošová et al. 2009), i s regionálními výsledky monitorování v (semi)akvatickém prostředí (Heinisch et al. 2007; Randák et al. 2009; Franců et al. 2010; Prokeš et al. 2012).

2) Druhým směrem výzkumu bylo ověření nově navržených legislativních limitů, které se svým pojetím přibližují jednoduchému hodnocení rizik. V této části bylo sledováno jejich překročení v reálných podmínkách českých půd s využitím geostatických nelineárních technik pro odhad prostorové distribuce překročení úrovně kontaminace, což umožňuje predikci zvýšených rizik kontaminace a souačasně i možnost odhadu nejistot prostorového modelu. Široce využívanou je metoda indikátorového krigingu, která modeluje pravděpodobnosti splnění podmínky překročení prahové hodnoty v místech, kde nebylo provedeno měření (Journel 1983; Webster & Oliver 2009). Kritickým místem indikátorového krigingu je pevné stanovení překročení hodnoty Booleovou logikou, a tím dochází k určité ztrátě informace pro pozorování významně odlišná od prahových hodnot (tzv. „order relation problem“) (Juang & Lee 2000). Z tohoto důvodu byl indikátorový kriging rozvinut pomocí začlenění relativní informace o vztahu daného pozorování a prahové hodnoty. Při řešení byla využita normalizovaná pořadí jednotlivých pozorování jako doplňkové proměnné pro vzájemný kriging v tzv. pravděpodobnostním krigingu (Sullivan 1984; Juang & Lee 2000). Tato metoda byla použita ve vědecké práci uvedené v podkapitole 4.3. Vlastní vymezení území s vyšší

pravděpodobností překročení limitních hodnot pro ohrožení zdraví člověka pro sumární hodnoty PAU a benzo(a)pyren v Severomoravském regionu velmi dobře korespondovalo s výsledky hodnocení rizik údolních niv (Obrázek 4 v podkapitole 4.3). Ukazuje se, že nelineární metody pro odhad překročení prahových hodnot mohou být efektivními nástroji pro prostorovou analýzu rizik kontaminace. Jak dále ukazují Gay a Korre (2009), lze geostatistickým odhadem rozšířit i přímo metody pravděpodobnostního modelování rizika humanotoxikologické expozice kontaminovanou půdou zpřesněním biokoncentračních faktorů přestupů prvků do rostlin a potravního řetězce. Podobně van Meirvenne a Goovaerts (2001) navrhli pomocí nelineárních metod krigingu lokální kritické hodnoty obsahu Cd v půdě na základě doplňkových informací o půdních vlastnostech (zejména pH). McKinley et al. (2013) pak kombinují geoprostorové odhady znečištění s epidemiologickými daty o výskytu nádorových onemocnění, což umožňuje porovnání potenciálních rizik a reálných sledování.

Analýza rizik pomocí nelineárních geostatistických metod má však také slabá místa. Výzvou pro nelineární metody odvozené z indikátorové funkce pro překročení stanovené hodnoty je fakt, že samotné měření daného parametru je zatíženo chybou. Aldworth a Cressie (2003) proto vyvinuli metodický postup, který umožňuje zohlednit nejistoty měření v nelineárních geostatistických odhadech překročení prahových hodnot a Hofer et al. (2013) metodu úspěšně použili pro odhad kontaminace na mikroregionální úrovni. Další otázkou je riziko rozpadu kompoziční struktury dat při geostatistickém odhadu (Pawlovsky et al. 1995; Tolosana-Delgado et al. 2016). Tolosana-Delgado et al. (2008) vycházejí z předpokladu, že pravděpodobnostní funkce hustoty překročení prahové hodnoty je kompozice kladných prvků s jednotkovým součtem, což generuje potřebu nového přístupu k indikátorovému krigingu na podkladě algebraicko–geometrické struktury výběrového prostoru kompozice pravděpodobnostní hustoty. Standardní geostatistické metody jsou využity pro kartézské souřadnice indikátorových dat transformovaných na ortonormální základně kompozice a výsledné odhady jsou zpětně transformovány na pravděpodobnosti. Výsledkem je nejlepší nestranný lineární odhad, kdy výsledné pravděpodobnosti respektují konstantní součet, nabývají kladných hodnot, a zároveň je metoda robustní z hlediska geometricko-algebraického řešení přechodu z omezeného výběrového prostoru simplexu do reálného (euklidovského) prostoru. Využití těchto nových metod představuje potenciál pro rozšíření a zpřesnění výsledků získaných v rámci uvedené publikace.

5.2 Vztahy znečištění nivních půd a potenciálních zdrojů

Odhalení a popis prostorových vzorců prvků a identifikace potenciálních zdrojů rizikových látek jsou dlouhodobě v centru zájmů environmentální geochemie. Pro tyto účely se dlouhodobě využívají různé metody hodnocení, kdy jsou sledovány prostorové a statistické distribuce nejen jednotlivých prvků a jejich forem, ale také simultánní vztahy mezi prvky. Z hlediska kontaminace RP se doplňují zdroje přirozené (tj. geologicky podmíněné) se zdroji antropogenními. Vědecká publikace v podkapitole 4.4 nabízí metodické nástroje pro jednoduché a efektivní rozlišení dominance geogenních a antropogenních vstupů pro specifické prostředí (semi)terestrických půd v nivních oblastech.[2] Toto téma má svůj význam nejen z hlediska vědeckého, ale také z hlediska praktických aspektů pro rozhodování na základě legislativních norem, neboť právě pro geochemicky anomální půdy lze uplatňovat specifický přístup z hlediska platných zákonných limitních hodnot pro půdy. Zároveň riziko přestupu rizikových prvků do zemědělské produkce z geochemicky anomálních půd je podstatně nižší, ve srovnání s antropogenní kontaminací půdy (Němeček et al. 1996). Jednoduchý metodický nástroj pro odlišení převládajících vstupů do půdy je žádoucí, zároveň u půd v nivních oblastech je z hlediska jejich geneze situace komplikovanější.

Dle Němečka et al. (2010) lze v České republice vymezit skupiny půd, vyvinutých na substrátech se zvýšenými obsahy některých RP. Ze závěrů práce Němečka et al. (1996) a Váchy et al. (2002) vyplynulo, že celkové obsahy RP na půdách z geochemicky anomálních substrátů mohou několikanásobně překročit legislativně stanovené limitní obsahy RP v zemědělských půdách, avšak při vyjádření mobility RP v půdách poměrem jejich mobilních a potenciálně mobilních obsahů se mobilita snižuje právě u půd geochemicky anomálních,

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[2] *Ve vědecké literatuře jsou dnes při studiu říčních sedimentů a nivních půd hojně používány faktory obohacení a indexy akumulace, které jsou založeny na odvození litogenního pozadí (Covelli & Fonotolan 1997). Odvození regionálního pozadí vyžaduje robustní metodické nástroje, které jsou dostatečně citlivé k faktorům variability půdy či sedimentu (Reimann & Garett 2005; Dung et al. 2013; Grygar et al. 2013). Mezi tyto faktory patří vlivy pedogeneze (reduktomorfní procesy, biogeochemické změny, bioturbace), post-depoziční migrace. Vhodný výběr místa odběrů vzorků, analýza stratigrafie (identifikace zastoupených sedimentárních facií) spolu s výběrem vhodných prvků pro normalizaci obsahů je zásadní pro robustní hodnocení prostorové a hloubkové závislosti koncentrací rizikových prvků na zastoupených sedimentárních faciích (Grygar et al. 2013). To vede nejen k možnosti vyhodnocení míry kontaminace sedimentárních záznamů, ale také k odlišení antropogenně kontaminovaných vrstev sedimentů, a tím k nepřímému datování sedimentárních profilů (Grygar et al. 2010; 2014). Toto robustní stanovení místního litogenního pozadí respektuje přirozenou variabilitu a vývoj sedimentace na daném místě, a nabízí tak jeden z podkladů pro hodnocení míry kontaminace a historického vývoje znečištění a ovlivnění říčních systémů člověkem (Nováková 2014).*

a tento poměr lze tedy využít při identifikaci převládajícího typu zátěže půd. V práci v podkapitole 4.4 jsou uvedeny výsledky ověření této možnosti u specifických půd v nivních oblastech. Orientačního rozlišení antropogenního a geogenního původu obsahu RP v nivních půdách bylo dosaženo porovnáním rozpustností RP, vyjádřených jako poměr jejich obsahů v extrakčních činidlech (2 mol/l HNO_3 a 0.025 mol/l EDTA) vůči jejich obsahu v extraktu lučavky královské. Pro identifikaci převládajících zdrojů zátěže byla s dostatečnou spolehlivostí odvozena kritéria pro porovnání rozpustností vypočítaných z extraktu 2 mol/l HNO_3 ve fluviálních půdách především pro řadu prvků As, Cd, Cr, Cu, Pb a Zn (Tabulka 4 v podkapitole 4.4). Možnost transparentního rozlišení převládajícího typu zátěže nebyla prokázána v případě Ni. Při použití extraktu 0.025 mol/l EDTA bylo dosaženo dobrých výsledků u As, Cu, zejména Pb, menší průkaznost byla zjištěna u Cr a zejména Be. Celkově lze konstatovat, že ve fluviálních půdách je vhodné použití těchto relativně silnějších extrakčních činidel oproti např. 1 mol/l NH_4NO_3 či 0.01 mol/l $CaCl_2$, kdy tyto extrakty nemusí být vhodné pro (semi)akvatické pevné matrice, neboť jsou vystaveny kontinuálnímu či epizodickému působení vody a lehce rozpustné podíly rizikových látek jsou z nich intenzivněji vyluhovány. Právě použití extraktu 2 mol/l HNO_3 má v českých podmínkách specifické postavení, neboť v minulosti byly takto definované hodnoty maximálně přípustných obsahů v zemědělských půdách legislativně závazné (původní vyhláška č. 13/1994 Sb.) a zároveň jsou k dispozici výsledky dlouhodobého stabilního programu vzorkování ve velkém územním detailu v podobě Registru kontaminovaných ploch v gesci ÚKZÚZu. Tento datový set byl použit pro doplnění metodického postupu rozlišení převládajícího typu zátěže mapovými výstupy, které umožňují identifikaci předpokladů pro zvýšené obsahy RP v návaznosti na výskyt geochemicky anomálních substrátů a půd (Obr. 3 v podkapitole 4.4).

Stejný datový soubor ÚKZÚZ byl využit také následně pro účely identifikace potenciálních zdrojů a hodnocení jejich vlivu na nivní půdy v modelové studii v povodí Ohře (podkapitola 4.5), kde bylo cílem ověřit možnosti popisu a interpretace změn korelační struktury kompozičních dat v závislosti na změnách podél vodního toku (tj. existenci potenciálních zdrojů). Jak je uvedeno v kapitole 2.2.3, analýza kompozičních dat vyžaduje specifický přístup z důvodu algebraicko–geometrické struktury výběrového prostoru kompozičních dat (Aitchison 1984), neboť právě korelační vztahy podílových dat jsou z hlediska uzavření dat a rizika nahodilých korelací velmi citlivé (Aitchison 1982). Z tohoto důvodu byly použity metody pro průzkumovou analýzu adaptované pro kompoziční data – analýza hlavních komponent (Filzmoser et al. 2009b) a kvantifikace podkompoziční variability (Aitchison 1984). Průzkumová analýza dat sloužila k definování vhodných 3-složkových podkompozic, které uchovávaly dostatečnou míru celkové kompoziční variability. Velmi dobře celkovou kompoziční variabilitu dat v modelovém povodí Ohře zachovávala 3-složková podkompozice Cu-Hg-Ni, která zachovávala 45 % celkové kompoziční variability celého datového setu. Definováním vhodných podkompozic bylo pak možné při odpovídajícím použití ortonormálních souřadnic usuzovat na relativní obohacení či ochuzení půd vybranými RP, definovat prioritní polutanty, a tím odhadnout vliv jednotlivých zdrojů. Ortonormální souřadnice byly spočítány pomocí izometrické log-poměrové transformace (ilr-transformace) (Egozcue et al. 2003) upravené pro jednorozměrné log-kontrasty (Filzmoser et al. 2009c). Takto relativně vyjádřené podkompozice pomocí ilr-souřadnic byly následně po normalizaci interpolovány inverzní vzdáleností (IDW) a převedeny do RGB kompozitního vyjádření (Albanese et al. 2007; Zuzolo et al. 2018). Tato metodika umožnila efektivní intepretaci změn víceprvkové kompoziční struktury při vyhodnocení potenciálních vstupů v povodí (Obr. 7 v podkapitole 4.5). Výsledky z modelového povodí Ohře ukazují, že lze zachytit jak bodové zdroje, tak difúzní zdroje různého původu – kontaminace Hg pod vlivem staré zátěže Marktredwitz (Bavorsko), vliv použití Cu-fungicidů ve chmelnicích na středním toku, vstupy Ni, Cr na dolním toku v souvislostech vlivu staré zátěže bývalé Litoměřické koželužny. Přeshraniční vliv dřívějšího hot spotu Hg-kontaminace z bavorských zdrojnic Ohře (Kőssein a Rösslau) byl popsán v sedimentárních říčních záznamech (Grygar et al. 2016; 2017; Majerová et al. 2018). K popsaným rizikům této kontaminace patří zvýšená bioakumulace (Maršálek et al. 2005) či zvýšené obsahy v zemědělsky využívaných půdách (Miler 2011). Kodrová a Paulin (2012) na základě rizikové analýzy staré zátěže bývalé Litoměřické koželužny konstatují pravděpodobné šíření zvýšených obsahů Cr, Ni, Co do okolních půd, přičemž starší zpráva Sameše (1993) popisuje existenci historických odkalovacích nádrží s odpadními kaly z bývalé koželužny v širší nivě na dolním toku. Vliv kožedělného průmysl na zvýšené obsahy Cr, Ni sledovali také Petrik et al. (2018) či Thiombane et al. (2018) v povodí řeky Sarno v Itálii. Významné změny korelační struktury na středním toku mezi ornou půdou a chmelnicemi (Obr. 5 v podkapitole 4.5) byl prokázán korelační analýzou upravených ilr-souřadnic, které byly matematicky navrženy Kynčlovou et al. (2017). Na změnách korelační struktury se podílely především prvky Cd, Zn a Cu. Tyto výsledky potvrzují, že na středním toku se projevuje v oblasti chmelnic vliv aplikace prostředků na ochranu rostlin na bázi Cu, což je obecně známo především z oblasti vinic (Brun et al. 1998; Komárek et al. 2008; Cicchella et al. 2015; Bednářová et al. 2016), v případě Cd lze usuzovat na vliv v minulosti zvýšených obsahů tohoto prvku v minerálních hnojivech aplikovaných do zemědělských půd (Nziguheba & Smolders 2008; Birke et al. 2017). Rozdíly mezi kulturami orné půdy a chmelnicemi byly poté potvrzeny také neparamaterickými metodami statistické interference (MANOVA) po odvození vhodných ortonormálních souřadnic pomocí izometrické log-poměrové transformace (ilr-souřadnice) a sekvenčního binárního členění (Egozcue et al. 2003; Egozcue & Pawlowsky-Glahn 2005) – viz Obr. 6 v podkapitole 4.4. Inovativním přístupem navrženým v článku je potom využití modifikované Mantelovy korelace (Mantel 1967; Omelka & Hudecová 2016) a Mantelova korelogramu (Oden & Sokal 1986) pro korelace matice strukturálních podobností profilu znečištění na základě Aitchisonovy vzdálenosti (dle rovnice 6 v kapitole 2.2.3) s maticemi prostorové (geografické) vzdálenosti na základě říční vzdálenosti. Výsledky ukazují na střední míru Mantelovy korelace ($r_M = 0.46$) a statistickou významnost korelačního vztahu v permutačním testu. Výsledky prostorové dekompozice této korelace pomocí Mantelova korelogramu (Obr. 2 v podkapitole 4.5) ukazují trend klesající kompoziční podobnosti v závislosti na rostoucí říční vzdálenosti mezi lokalitami. Geochemická víceprvková kompozice tak vykazuje prostorové podobnosti a regionální zonaci, kterou lze interpretovat na základě existence potenciálních zdrojů v povodí. Zároveň signifikantní změny profilu zátěže na malém prostoru (mezi blízkými lokalitami) pomáhají i odhadovat existenci neznámých zdrojů znečištění, změny podmínek depozice vodního toku či změny půdních podmínek.

5.3 Rizika přestupu znečištění do plodin v agroekosystému nivních půd

Ochrana potravního řetězce patří k zásadním otázkám ochrany lidského zdraví, neboť pro řadu polutantů je právě dietární přestup z potravních řetězců důležitým prvkem celkového exposomu člověka (Choi et al. 2015). Proto součástí hodnocení rizik nivních půd je také otázka přestupu rizikových látek do rostlinné produkce, neboť zvýšená zátěž a často i zvýšená biologická dostupnost se potkává v nivních oblastech se zvýšenou produktivitou půd a příhodnými podmínkami pro intenzivní zemědělskou činnost jako např. rovinný reliéf, či dostupnost vody pro závlahy (Zavadil 1999). Proto v této kapitole jsou shrnuty poznatky ze dvou vědeckých publikací, které cílí právě na rizika přestupu dvou toxikologicky nejvýznamnějších skupin rizikových látek v experimentálních půdách – RP a PAU.

V případě rizikových prvků je v publikaci 4.6 věnována pozornost zejména Cd, Cu, Pb a Zn. Ačkoliv primárním cílem studie, situované v silně kontaminovaném aluviu řeky Litavky, bylo ověřit přestupy rizikových prvků do zemědělských plodin s fytoextrakčním potenciálem (rody slunečnice *Helianthus,* tritikále *Triticale,* brukev *Brassica*) pěstovaných v monokulturách a v osevních postupech v polním a nádobovém pokusu, získané výsledky přinesly obecnější poznatky přestupu rizikových prvků ze silně kontaminovaných niv do zemědělské produkce. V průběhu pokusu byl zároveň pro část variant ověřován potenciál zvýšení mobilních specií pomocí chelatačních činidel pro zvýšení přestupu RP do plodin. Cílem bylo zvýšit fytoextrakční potenciál, avšak poznatky jsou zajímavé i z hlediska přestupu RP v dynamických podmínkách změn mobility prvků v půdě. Vliv mobilizace rizikových prvků aplikací chelatačních činidel byl v souladu s literaturou (Huang et al. 1997; Komárek et al. 2007; Neugschwandtnera et al. 2012), neboť výsledky Wilcoxonova párového testu potvrdily statisticky významný vliv aplikace (Obr. 1 v kapitole 4.6). Při přestupu do plodin neměla však mobilizace statisticky průkazný efekt, což sledovali také Neugschwandtner et al. (2012). Důležitou informací je především fakt, že zvýšení mobility prvků bylo dočasné (sledováno rozpustností RP dle extraktu NH_4NO_3) – tj. po 10 dnech od dynamického zásahu se vrátily obsahy mobilních frakcí na úroveň kontrolních variant (Obr. 1 v podkapitole 4.6), což řádově odpovídá výsledkům Neugschwandtnera et al. (2012) pro vodorozpustné obsahy Pb a Cd. Obecně vyšší obsahy pro většinu RP byly sledovány v plodinách pěstovaných na půdním typu fluvizemě bez většího efektu aplikace chelatačních činidel či způsobu pěstování (střídání plodin vs. monokultura), přičemž zvýšené obsahy byly sledovány jak v kořenovém systému, tak nadzemních částech (Tab. 6 a 7 v v podkapitole 4.6). Z pěstovaných plodin reagovaly na změnu dynamiky prvků v půdě nejvíce rostliny *Brassica* pěstované na kambizemi, přičemž efekt mobilizace byl nejvýraznější v případě Pb, což ukazuje na pravděpodobný vliv změn vazeb v systému prvek-organická hmota. V souladu s Borůvkou a Drábkem (2004), právě Pb vykazovalo odlišné zákonitosti distribuce mezi frakcemi organické hmoty ve srovnání se Zn a Cd. V případě Zn a Cd byly také sledovány zvýšené přestupy do nadzemní biomasy zejména u rostlin brukve či slunečnice, což je v souladu s výsledky pro tyto prvky také v případě rostlin kukuřice (Kacálková et al. 2009) či ječmene (Tlustoš e al. 1997). Nejvyšší přestup RP z půdy do nadzemních částí byl sledován pro rostliny *Helianthus* pěstované na kontaminované fluvizemi. V případě rostlin *Triticale* byl celkový odběr RP také zvýšený, nicméně nedocházelo k translokaci do nadzemních částí rostlin. Důležitým zjištěním je, že krátkodobé, chemicky podpořené změny dynamiky a zásoby mobilních prvků průkazně nezměnily příjem RP plodinami (efekt chelatace byl patrný pouze v případě přestupu Pb). Přesto je třeba konstatovat, že i přes nízký potenciál zemědělských plodin pro fytoextrakci ve srovnání s Blaylock et al. (1997), jsou výsledné hodnoty v nadzemní biomase plodin pěstovaných na extrémně kontaminovaných fluvizemích z hlediska potenciálních rizik zvýšené (Tab. 6 a Tab. 7 v podkapitole 4.7) a srovnatelné s hodnotami v rostlinách slunečnice či brukve pokusně pěstovaných na lokalitě podobně zatížené fluviálně uloženými důlními odpady (Madejón et al. 2002; Clemente et al. 2005).

V případě POP jsou v publikaci v podkapitole 4.7 prezentovány poznatky o rizicích přestupu PAU do rostlin, přičemž experimentální část zahrnovala srovnání fluviální zátěže z oblasti severní Moravy se simulovanou zátěží po aplikaci kalů z čistíren odpadních vod (ČOV) a kontrolní variantou. Celkové obsahy, spolu s hodnocením toxicity směsi PAU pomocí konceptu faktorů ekvivalentní toxicity, jsou zobrazeny v Tabulce 1 v podkapitole 4.8. Modelovými plodinami byly citlivé plodiny kořenové zeleniny (ředkev *Raphanus*, mrkev *Daucus*, petržel *Petroselinum*), které jsou vzhledem k charakteru nivních pásem často pěstovanou zemědělskou plodinou. Experimentální sledování probíhalo formou nádobového a polního pokusu a bylo doplněno kolonovým extrakčním pokusem pro odhad vazeb PAU v půdě pomocí extrakce půdního prostředí různě silnými vyluhovadly po dobu 24 hodin v pořadí demineralizovaná voda, demineralizovaná voda okysličená H_2SO_4 na hodnotu pH=3 a 0,2 % roztok tenzidu laurylsíranu sodného $C_{12}H_{25}NaO_4S$. Byly prokázány rozdíly mezi vymytím různých skupin PAU mezi půdou s fluviálním obsahem PAU a simulovanou zátěží aplikací kalů ČOV (Obr. 3 v podkapitole 4.7). V případě fluviální zátěže půd došlo k extrakci jednodušších PAU (2-3 aromatická jádra) již v prvním extrakčním kroku. Při opakované extrakci po úpravě pH došlo k poklesu obsahu PAU v extraktu, přičemž na tomto poklesu se podílely především jednodušší PAU, jejichž zásoba byla omezena prvním extrakčním krokem. Extrakce tenzidem vedla k opětovnému nárůstu obsahu PAU, avšak s nižším celkovým obsahem PAU v extraktu ve srovnání s prvním krokem a výrazně vyšší dominancí PAU s více aromatickými jádry (Obr. 3 v podkapitole 4.7). V případě experimentální simulované zátěže půd kaly ČOV došlo v kolonovém extrakčním pokusu ke srovnatelnému vymytí PAU do roztoku až ve třetím extrakčním kroku, což lze vysvětlit pravděpodobným rozvolněním vazeb PAU na organickou hmotu. Uvedené poznatky nabývají na důležitosti v nivních pásmech jednak z důvodu častých fluktuací hydrologických a hydraulických vlastností půd, jednak z důvodu variability půdních vlastností ovlivňující sorpci rizikových látek (např. rozdíl v obsahu organické hmoty, zrnitosti v různých částech nivy). V době povodňových událostí existuje také riziko dotace právě povrchově aktivních látek vlivem vyplavování bodových zdrojů.

Při sledování přestupu PAU do rostlin byl prokázán relativně nízký přestup PAU transferovou cestou půda-kořen. Při sledování obsahu v kořenové části zeleniny byly sledovány odlišnosti z hlediska obsahu PAU mezi centrálním válcem rostlin a primární kůrou mezi fluviální zátěží a simulovanou zátěží aplikací kalů ČOV (Obr. 2 v podkapitole 4.7). Zatímco v případě simulované zátěže aplikací kalů byly zjištěny vyšší obsahy PAU v povrchové části kořene pod vlivem těsnější vazby PAU na organickou hmotu, v případě fluviální zátěže determinovaly půdní vlastnosti sorpčně chudé a zrnitostně lehké fluvizemě vyšší přestup PAU do centrálního válce (Obr. 1 v podkapitole 4.7), což odpovídá poznatků z přestupu PCB v práci Javorské et al. (2009). Odlišnosti byly sledovány také v návaznosti na fyzikálně-chemické vlastnosti molekul PAU, kdy u molekul s nižší molekulovou hmotností (tj. s nižším počtem aromatických jader) roste rozpustnost ve vodě a klesá rozdělovací koeficient oktanol-voda K_{ow}, a tím roste možnost vstupu těchto látek do cévního systému rostlin (Trapp 2002; Holoubek 2003; Mikeš et al. 2009). Naopak molekuly s vyšší molekulovou hmotností mají tendenci interakce s organickou hmotou s následnou vazbou na povrch kořene v rhizosféře pod vlivem jejich zvýšené afinity na lipidické a jiné organické složky (Kipopoulou et al. 1999; Bobovniková et al. 2000; Javorská et al. 2007). Souhrnně lze říct, že kořenové části v kontaktu s kontaminovanou půdou mají zvýšené obsahy PAU v biomase, přičemž v závislosti na půdních vlastnostech a vlastnostech chemických sloučenin se mění převládající způsob přestupu skrze půdní roztok a cévní systém rostlin či jejich zadržení ve rhizosféře na povrchových vrstvách kořene. Důležitým zjištěním pak byly potvrzené rozdíly v obsahu PAU v kořenových částech mezi očištěnými a neočištěnými kořeny, což má praktické důsledky.

6 Závěry a doporučení

Ačkoliv byla zvýšená akumulace rizikových látek v nivních územích potvrzena tuzemským i světovým výzkumem, menší odborná pozornost je věnována hodnocení potenciální rizikovosti této akumulace. Z tohoto důvodu jsem se v této práci zabýval systémovým přístupem k hodnocení potenciálních rizik znečištění v záplavových půdách, jehož cílem bylo poskytnout dostatek relevantních podkladů pro hodnocení těchto rizik na různých měřítkových úrovních a zároveň ověřit některé progresivní metody statistické analýzy dat vhodné pro regionalizaci těchto rizik. Kombinace hodnocení celkové úrovně rizik a jejich kompoziční struktury ukázala, že v nivních půdách ČR jsou zvýšená rizika regionálně podmíněna zvýšenou zátěží PAU a lokálně zvýšenými obsahy RP. Z hlediska metodologického byla možnost regionalizace rizik pomocí vícerozměrných statistických metod komplikována dominantním příspěvkem některých rizikových látek do celkových rizik, což vzhledem ke kompozičnímu charakteru dat znesnadňuje interpretaci kompoziční variability. Řešením bylo využití metod kompoziční analýzy dat založených na log-poměrovém přístupu, což umožnilo lepší náhled na kompoziční variabilitu a odhalení vztahů mezi prvky kompozice, které byly maskovány vlivem dominance některých látek v celkovém riziku. Výsledkem byla úspěšná klasifikace rizikových profilů pomocí shlukové analýzy, sledování prostorových vazeb vytvořených shluků a definování prioritních kontaminantů v dílčích částech povodí na základě relativních vztahů uvnitř kompozice. Celková míra rizika vyjádřená jako sumární index rizika umožnila vymezit lokality se zvýšenými riziky, kdy výsledky z celé ČR ukazují především na lokální význam akumulace toxikologicky významných látek v nivních půdách v návaznosti na konkrétní zdroje v povodí. Přístup navržený v této práci poskytuje hlubší náhled na relativní strukturu rizik kontaminace, a tím efektivnější a statisticky korektní možnosti jejich regionalizace.

Pochopení vztahu mezi kontaminací a umístěním zdrojů bylo jedním z cílů práce, neboť má z hlediska hodnocení rizik významnou roli. Orientačního rozlišení převládajícího původu zátěže půd RP v nivních půdách bylo dosaženo porovnáním rozpustností RP, vyjádřených jako poměr jejich obsahů v slabších extrakčních činidlech (2 mol/l HNO_3 a 0.025 mol/l EDTA) vůči jejich obsahu v extraktu lučavky královské. Na základě výsledků byly odvozeny referenční hodnoty rozpustnosti pro vybrané RP, a zároveň byly odvozeny mapové podklady pro sledování oblastí se zvýšenou pravděpodobností geogenních vstupů RP pro celou ČR na mikroregionální úrovni. V regionální studii v povodí Ohře bylo pak prokázáno, že změny korelační struktury kompozičních dat umožnily sledovat a efektivně vizualizovat relativní obohacení či ochuzení půd vybranými RP, definovat prioritní RP pro dílčí části povodí, a tím odhadnout vliv jednotlivých zdrojů. Metodicky novým přístupem pak byla kvantifikace geoprostorové kontinuity kompoziční struktury dat využitím Mantelovy korelace a Mantelova korelogramu pro korelace matice strukturální podobností profilu znečištění na základě Aitchisonovy vzdálenosti s maticemi říčních vzdáleností. Výsledky ukazují na střední míru Mantelovy korelace (r_M= 0,5), což potvrzuje, že geochemická víceprvková kompozice vykazuje regionální zonaci, kterou lze interpretovat na základě existence potenciálních zdrojů v povodí.

Odhalení míst rizikové akumulace kontaminace generuje potřebu odhadu lokální variability rizikových látek na postižených lokalitách. Toho lze úspěšně dosáhnout, jak ukazuje případová studie v oblasti průmyslově zatížených regionů, pomocí kombinace diferencovaných legislativních limitů vyhlášky č. 156/2013 Sb. vztažených ke konkrétním rizikům (ohrožení zdraví člověka, ohrožení jakosti či výnosu zemědělské produkce) a geostatických nelineárních technik pro odhad prostorové distribuce překročení relevantní úrovně kontaminace se současnou možností odhadu nejistoty prostorového odhadu. Výsledky dvou lokálních experimentů v nivách silně kontaminovaných RP resp. PAU pak ukázaly odlišnosti přestupu rizikových látek do zemědělských plodin z hlediska půdních vlastností, pěstovaných plodin a fyzikálně-chemických vlastností kontaminantu, což ukazuje klíčové faktory pro místní hodnocení rizika přestupu kontaminace do plodin – tj. vymezení nepříznivých kombinací těchto faktorů, které mohou rizika přestupu v nivních půdách zvyšovat.

Závěrem mohu říct, že jsem naplnil cíle dizertační práce, neboť systémový přístup poskytl kvalitní a hodnověrné poznatky o potenciálních rizicích zvýšené akumulace toxikologicky významných látek na různých měřítkových úrovních. Na základě závěrů práce lze doporučit podrobné sledování lokálních akumulací rizikových látek. Na těchto lokalitách pak odhadnout lokální variabilitu kontaminantů, kde lze budoucí výzkum zaměřit na perspektivní spojení nelineárních geostatistických metod a kompoziční analýzy dat, na nelineární metody z oblasti strojového učení či využití spektrálních dat. Lze také doporučit sledování změn na těchto lokalitách po povodňových událostech. I to bylo důvodem, proč vybrané poznatky ze souboru vědeckých publikací sloužily jako podklad pro vydání metodiky pro zemědělskou praxi (Sáňka et al. 2015), která poskytuje podklady pro komplexní hodnocení rizik znečištění v záplavových územích, a to včetně relevantních referenčních hodnot.

7 Seznam použitých zkratek

ČOV	čistírna odpadních vod
DDT	1,1,1-trichlor-2,2-bis(4-chlorfenyl)ethan
EDTA	kyselina ethylendiamintetraoctová
GEMAS	Geochemické Mapovaní Zemědělských Půd Evropy
HCH	hexachlorcyklohexan
HI	index rizika (hazard index)
IDW	vážení inverzní vzdáleností
ILR	isometric log-ratio - izo-metrický log-poměr
K_{aw}	bezrozměrná Henryho konstanta - rozdělovací koeficient vzduch-voda
K_d	rozdělovací koeficient půda-voda
K_{oc}	rozdělovací koeficient organický uhlík-voda
K_{ow}	rozdělovací koeficient oktanol-voda
OCP	organochlorové pesticidy
PAU	polyaromatické uhlovodíky
PCB	polychlorované bifenyly
PCDD/F	polychlorované dibenzo-p-dioxiny a dibenzofurany
POP	perzistentních organických polutantů
RP	rizikové prvky
SSL	Soil Screening Levels - na účincích založené referenční hodnoty pro půdu
U.S. EPA	Agentura pro ochranu životního prostředí Spojených států amerických
ÚKZÚZ	Ústřední kontrolní a zkušební ústav zemědělský

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