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Raspodela i profil zagađujućih jedinjenja u abiotskim i biotskim matriksima multivarijacionom analizom

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U okviru disertacije analizirano je prisustvo različitih postojanih zagađujućih materija u abiotskim i biotskim uzorcima iz različitih regiona, uključujući i uzorke zemljišta iz Novog Sada i okolnih naselja, i to zagađujuće materije organskog (policiklične aromatične ugljovodonike, polihlorovane bifenile i organohlorne pesticide) i neorganskog (teški elementi) porekla. Dobijeni rezultati uvršteni su u baze zajedno sa relevantnim podacima iz međunarodnih radova i na taj način formirane su baze koje prevazilaze lokalne interese pojedinačnih istraživanja. Primenom multivarijacionih metoda analize ovakvih baza utvrđen je stepen zagađenosti ispitivanih uzoraka u odnosu na rezultate iz literature, a takođe je razmatrana struktura formiranih multidimenzionalnih baza sa ciljem analize raspodele postojanih zagađujućih jedinjenja u posmatranim matriksima i identifikacije zajedničkih izvora zagađenja. Primenom različitih (matematičkih) predtretmana podataka u bazama, a zatim njihovom analizom izabranim multivarijacionim metodama, izvršena je procena uticaja predtretmana na rezultate i mogućnosti njihove interpretacije, kao i ispitivanje zavisnosti između posmatranih veličina i grupisanje uzoraka. Specifični ciljevi istraživanja su omogućili da se:

- utvrde sličnosti i razlike pri korišćenju različitih načina izražavanja analitičkih rezultata (apsolutne vrednosti koncentracije nasuprot relativnih procentualnih udela, tzv. kompozicionih podataka) u okviru baza podataka i pri izdvajanju informacija iz multidimenzionalnih baza primenom multivarijacionih metoda,
- utvrdi uticaj različitih načina pripreme (obrade) podataka pre primene multivarijacionih metoda radi dobijanja potpunijih informacija u cilju bolje interpretacije podataka i smanjenja dimenzija baza podataka;
- ispitaju regionalne i vremenske razlike i/ili sličnosti između prisustva posmatranih jedinjenja u abiotskim i biotskim matriksima radi uočavanja dominantnih izvora zagađenja u određenim oblastima i vremenskim periodima uz istovremenu karakterizaciju eksperimentalno ispitanih uzoraka u odnosu na uzorke iz drugih regiona.

Postignuti rezultati predstavljaju jedinstvene rezultate primene multivarijacionih metoda na bazama sastavljenim od podataka dobijenim u različitim istraživanjima iz sveta o prisustvu postojanih zagađujućih materija u izabranim abiotskim i biotskim uzorcima, doprinoseći tako analizi njihove opšte raspodele.

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Abstract:
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Presence of different pollutant classes of both organic (polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides) and inorganic origin (heavy elements) were analysed in abiotic and biotic matrices from various regions, including Novi Sad and its surrounding settlements. Obtained results with available data published in the international articles were included in the sets, forming the input matrices to be analysed by chemometric techniques. Analysis of the created sets of data by multivariate approach was performed due to determining pollution level of the investigated samples, as well to elucidate the persistent pollutants distribution and profiles in the selected matrices and to identify the common pollution sources.

Using different treatments of a set of input data, influence of these procedures to results was assessed.

Specific aims of investigation were:

Determination of similarity and differences by using different ways of data expression (apsolute values of concentrations as apposed to relative percent fraction) in interpreration of multidimension data sets on the basis of multivariate statistical approach

Determination of different processing of data before multivariate statistical methods due to obtaining adequate information for interpretation of data and reducing a set of original variables

Examination of regional and temporal differences and/or similarity among presence of observed compounds in abiotic and biotic matrices due to identification of dominant pollutant sources as well as comparative characterisation of experimantally obtained data in relation to samples from another regions worldwide.

Achieved results are unique examples of multivariate methods application on large data sets with results on the occurance of pesistent organic compounds in abiotic and biotic matrices obtained in different studies all over the world.

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Mentor: Dr. Biljana Škrbić, Full prof., Faculty of Technology, Novi Sad

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SADRŽAJ

1. UVOD

Procesi industralizacije i urbanizacije, koji su intenzivirani naročito od druge polovine 20. veka, doveli su do značajnog narušavanja prirodnih ciklusa i procesa u životnoj sredini, ponekad do te mere da je kvalitet života, a ponekad i sam život ugrožen. Na sreću, može se reći da su uočeni procesi narušavanja prirode praćeni sve većim interesom za ispitivanje sredine u cilju njene zaštite, procene rizika i mogućnosti unapređenja stanja.

Jedna od glavnih tema u oblasti zaštite životne sredine za koje je potrebno globalno rešenje, predstavlja prisustvo postojanih zagađujućih materija, koje jednom emitovane zaostaju dugo u životnoj sredini, jer su zbog svojih fizičko-hemijskih karakteristika postojane u odnosu na prirodne procese razgradnje (hemijske, fotohemijske i biohemijske prirode). Preko biljaka, ova jedinjenja dospevaju u lanac ishrane te su tako prisutna u svim sferama životne sredine uključujuči abiotske i biotske uzorke, tj. mogu se naći u pedosferi, hidrosferi, atmosferi i biosferi. Različite klase jedinjenja spadaju u grupu postojanih zagađujućih materija, koje se putem atmosferskih struja prenose na velike razdaljine od prvobitnih izvora emisije. Ova jedinjenja često su bioakumulativna (koncentrišu se u tkivima) i toksična po ljude i živi svet. Ukoliko nije u pitanju akcidentna situacija i zagađenje usled direktne emisije ovih jedinjenja, postojana zagađujuća jedinjenja prisutna su u matriksima životne sredine i namirnica u veoma malim koncentracijama, ali zbog štetnog dejstva, koje mogu prouzrokovati, neophodno je stalno pratiti njihovo prisustvo radi procene rizika.

U osnovi svih naučnih ispitivanja životne sredine i problema zagađenja sredine prouzrokovanih antropogenom delatnošću, uključujući i postojane zagađujuće materije, nalaze se hemijske metode, prvenstveno instrumentalne tehnike. Naprekidni razvoj instrumentalnih tehnika ide u korak sa potrebom proučavanja i kontrolisanja sve većeg broja zagađujućih jedinjenja u životnoj sredini, često prisutnih u tragovima, čak i u tzv. ultratragovima. Pri tome, koncentracije zagađujućih materija prisutnih u životnoj sredini su veoma promenljive, bilo kao posledica razlika u “pozadinskoj” koncentraciji (koja je rezultat prirodnih procesa i stalne atmosferske difuzije i procesa kruženja materija u prirodi), različite udaljenosti od izvora i intenziteta njihove emisije i/ili vremenskih i prostornih razlika. Zbog svega ovoga ispitivanje stepena zagađenosti sredine podrazumeva određivanje sadržaja zagađujućih jedinjenja u velikom broju uzoraka kako bi dobijeni podaci što realnije odrazili stvarno stanje sredine, predvideli rizike, ukazali na izvore zagađenja, efikasnost primenjene metode prečišćavanja (remedijacije), i dr. Karakteristično za rezultate ispitivanja stanja sredine je da oni često predstavljaju međusobno zavisne promenljive, koje se ne mogu razmatrati pojedinačno, tj. izdvojeno od ostalih, već jedino zajedno. Dakle, rezultati analize životne sredine često predstavljaju obimne baze podataka dobijenih za veliki broj uzoraka te se mogu smatrati da imaju multidimenzionalnu, tj. multivarijacionu prirodu, zahtevajući primenu multivarijacionih statističkih metoda radi dobijanja sveobuhvatne slike interakcija jedinjenja i sredine od interesa. Za razliku od uobičajenih univarijacionih metoda analize, kojima se promenljive analiziraju pojedinačno te se ne može izvršiti objedinjavanje višestrukih merenja niti pravilno naučno zaključivanje, multivarijacione metode omogućavaju istovremenu analizu velikog broja podataka i izdvajanje (otkrivanje) "skrivenih" informacija iz multidimenzionalne strukture ovakvih baza podataka. Metode multivarijacione statističke analize razvijale su se postepeno i do sada su mnoge našle primenu u zaštiti životne sredine. Različite metode grupisanja, predviđanja, diskriminaciona i faktorska analize, analiza glavnih komponenata, analiza povezanosti i dr., često se koriste u istraživanjima iz oblasti praćenja prisustva različitih zagađujućih materija u životnoj sredini, identifikaciji izvora zagađenja, klasifikaciji uzoraka, itd.

1.1. Cilj rada

U literaturi postoji veliki broj podataka o prisustvu zagađujućih jedinjenja u različitim sferama životne sredine. Predmet mnogobrojnih istraživanja su i postojane zagađujuće materije u abiotskim i biotskim uzorcima uzetih sa određenih lokacija. U ovim radovima, dobijeni rezultati su poređeni sa odgovarajućim graničnim vrednostima i podacima dostupnim u literaturi za istu i/ili druge lokacije radi procene stepena zagađenja i rizika. U mnogim od ovih radova primenjene su i multivarijacione metode radi analize formiranih baza podataka za uzorke iz posmatranog regiona. Međutim, nasuprot činjenici da međunarodna naučna literatura obiluje informacijama o prisustvu zagađujućih jedinjenja iz raznih delova sveta (koje su poslednjih godina lako dostupne i u Srbiji zahvaljujući elektronskim bazama podataka Konzorcijuma biblioteka Srbije za objedinjenu nabavku (KoBSON)), pokušaji da se objedine postojeći podaci iz različitih studija i izvrši njihova analiza veoma su retki, iako se lako može pretpostaviti da bi se ovim pristupom prevazišao lokalni (regionalni) nivo postojećih istraživanja, vodeći ka opštijim zaključcima kako sa prostornog tako i sa vremenskog aspekta.

U okviru disertacije analizirano je prisustvo izabranih postojanih zagađujućih materija u abiotskim i biotskim uzorcima iz različitih regiona, uključujući i Novi Sad i okolna naselja, i to zagađujuće materije organskog (policiklične aromatične ugljovodonike, polihlorovane bifenile i organohlorne pesticide) i neorganskog (teški elementi) porekla. Dobijeni rezultati uvršteni su u baze zajedno sa relevantnim podacima iz međunarodnih radova i na taj način formirane su baze koje prevazilaze lokalne interese pojedinačnih istraživanja. Cilj rada je da se primenom multivarijacionih metoda analize ovakvih baza utvrdi stepen zagađenosti ispitivanih uzoraka u odnosu na rezultate iz literature, a takođe i da se otkriju informacije “skrivene” u formiranim multidimenzionalnim bazama radi analize raspodele postojanih zagađujućih jedinjenja u posmatranim matriksima i identifikacije zajedničkih izvora zagađenja. Primenom različitih (matematičkih) predtretmana podataka u bazama, a zatim određenih multivarijacionih metoda, izvršena je procena uticaja predtretmana na rezultate i mogućnosti njihove interpretacije, kao i ispitivanje zavisnosti između posmatranih veličina i grupisanje sličnih uzoraka. Specifični ciljevi istraživanja su bili:

- odrediti razlike pri korišćenju različitih načina izražavanja analitičkih rezultata (apsolutne vrednosti koncentracije nasuprot relativnih procentualnih udela, tzv. kompozicionih podataka) u okviru baza podataka tokom hemometrijske analize i izdvajanja informacija iz multidimenzionalnih baza primenom multivarijacionih metoda,

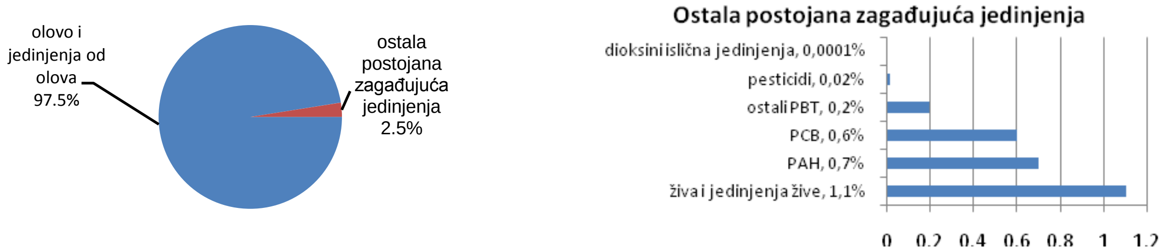
- odrediti razlike i uticaj različitih načina pripreme (obrade) podataka pre primene multivarijacionih metoda radi dobijanja potpunijih informacija u cilju bolje interpretacije podataka i smanjenja dimenzija baza podataka;
- ispitati regionalne i vremenske razlike i sličnosti između prisustva posmatranih jedinjenja u abiotskim i biotskim matriksima radi uočavanja dominantnih izvora zagađenja u određenim oblastima i vremenskim periodima uz istovremenu karakterizaciju eksperimentalno ispitanih uzoraka u odnosu na uzorke iz drugih regiona.

Dakle, postignuti rezultati predstavljaju jedinstvene rezultate primene multivarijacionih metoda na bazama sastavljenim od podataka dobijenim u različitim istraživanjima iz sveta o prisustvu postojanih zagađujućih materija u izabranim abiotskim i biotskim uzorcima, doprinoseći tako analizi njihove globalne raspodele. Rezultati prikazani u radu su međunarodno prihvaćeni i objavljeni u vidu radova u vodećim međunarodnim časopisima, koji su sastavni deo ove teze (Prilog I).

2. OPŠTI DEO

2.1. Postojana zagađajuća jedinjenja u životnoj sredini

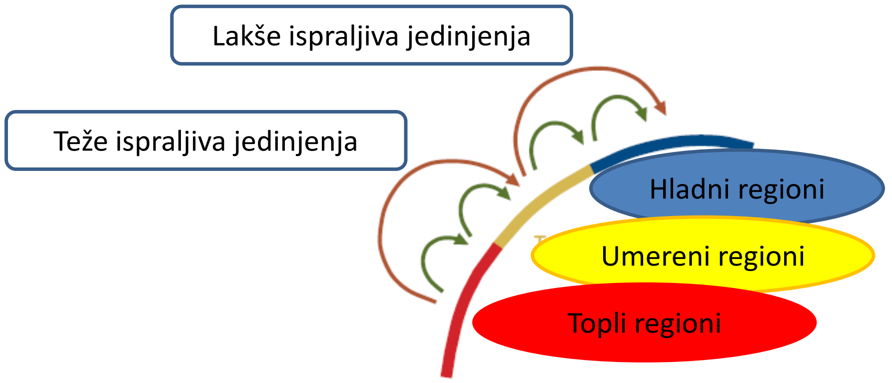
Postojana (dugotrajna, perzistentna) zagađujuća jedinjenja, poznata i pod nazivom postojana, bioakumulativna toksična jedinjenja (engleska skraćenica PBT-*Persistent Bioaccummulative Toxic*), predstavljaju materije, koje u životnoj sredini zaostaju dugo, jer su postojane u odnosu na prirodne procese degradacije, i talože se u organizmima živih bića, uključujući i ljude. Ova jedinjenja se mogu preneti na potomke putem pupčane vrpce tokom razvoja ploda u materici, ili nakon rođenja putem majčinog mleka. U ovu grupu jedinjenja spadaju hemijski različite klase jedinjenja, kao što su organska i neorganska jedinjenja, uključujući i organometalne komplekse. U SAD, olovo, živa i njihova jedinjenja čine najveću količinu postojanih zagađujućih jedinjenja emitovanih u životnu sredinu (slika 2.1), i to prvenstveno zbog velikih površina koje se koristi za iskopavanje metalnih ruda i njihovu preradu. Međutim, značaj organskih postojanih zagađujućih jedinjenja se ne sme zanemariti, jer tu spadaju veoma toksična jedinjenja sa kancerogenim i neurotoksičnim osobinama, kao i štetnim dejstvom na rad endokrinih žlezda i imunog sistema. Veliki broj ovih organskih jedinjenja su sintetička, čija je proizvodnja i korišćenje bilo dopušteno čitav niz godina (decenija); neka od njih su sporedni industrijski proizvodi, a takođe ima i onih nenamerno proizvedenih, koja najčešće nastaju razgradnjom, najčešće toplotnom (na primer, sagorevanjem), drugih jedinjenja.



Slika 2.1. Udeo emitovanih količina postojanih zagađujućih jedinjenja u SAD u 2001. god. na osnovu izveštaja "Pregled emisije toksičnih supstanci" (Vallero, 2005)

Američka Agencija za zaštitu životne sredine (EPA-*Environmental Protection Agency*) je 1999. god. definisala listu 14 postojanih jedinjenja, na kojoj su se našli: šest pesticida, polihlorovani bifenili, heksahlorbenzen, oktahlorstiren, dioksini, furani, benzo(a)piren, alkilolovo, živa i jedinjenja od žive. Većina ovih jedinjenja pripada tzv. grupi “dvanaest prljavih” (“*dirty dozen*”) postojanih organiskih zagađujućih jedinjenja (engleska skraćenica POPs prema *Persistent Organic Pollutants*) formiranoj od strane UNEP-a, čija Stokholmska konvencija uređuje ograničenja ili zabranu proizvodnje, spoljnotrgovinskog prometa i upotrebu ovih jedinjenja, ali i smanjenje, odnosno eliminaciju emisije ovih jedinjenja u životnu sredinu.

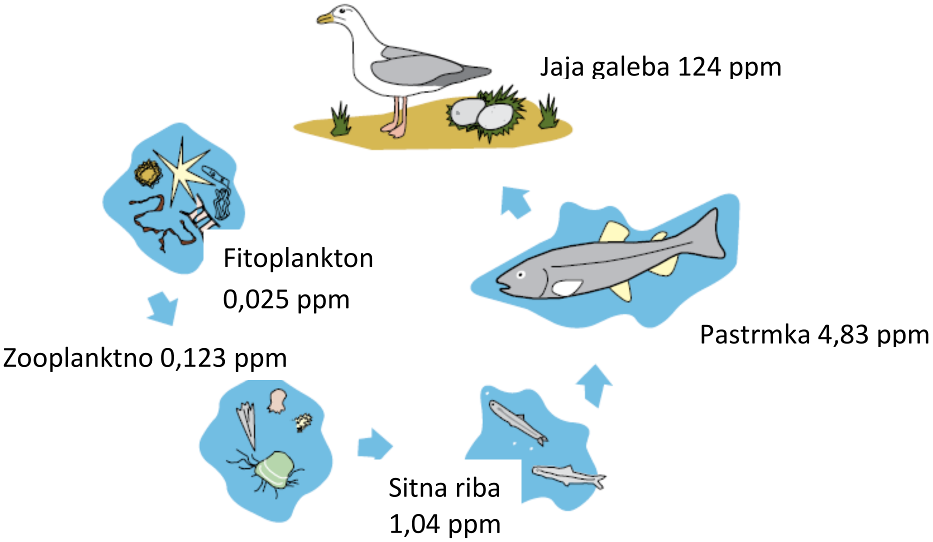
Međutim, bez obzira na ograničenja i zabrane, ova jedinjenja su široko rasprostranjena u svim sferama životne sredine u svim delovima sveta, čak i na udaljenim lokacijama, kao što je Arktik, gde proizvodnja i/ili primena nekih od ovih jedinjenja nikada nije ni postojala. Do ovoga je došla usled njihovog kretanja atmosferskim strujama na velike udaljenosti od samih izvora emisije i zbog postojanosti u odnosu na prirodne procese degradacije. Njihovo kretanje atmosferskim masama se u stvari odvija kroz kompleksni ciklus ponovljenih procesa ispravanja i kondenzovanja, koji se naziva “globalna destilacija” ili “efekat skakavca” (*“grasshopper effect”*) usled sličnosti sa načinom kretanja ovih insekata (slika 2.2).



Slika 2.2. Kretanje postojanih organskih zagađujućih materija na svetskom nivou, tzv.pojava “globalna destilacija”

Suvom ili vlažnom depozicijom (taloženjem) ova jedinjenja iz vazduha prelaze u površinski sloj zemljišta i vodene sisteme gde dolazi do njihovog nakupljanja (akumulacije), s obzirom da se prirodni procesi njihove razgradnje odvijaju veoma sporo. Na taj način i sami delovi životne sredine, naročito oni zagađeni u većoj meri u prethodnom periodu intenzivnog korišćenja postojanih organskih zagađujućih materija, mogu se smatrati izvorom emisije (reemisije) ovih jedinjenja u atmosferu u decenijama nakon uvedenih ograničenja i zabrane proizvodnje i korišćenja. Kretanje perzistentnih organskih zagađujućih jedinjenja atmosferskim strujama uvek se odvija iz pravca toplijih ka hladnijim krajevima. Čim temperatura vazduha opadne, ova jedinjenja se kondenzuju i talože na površini, a zbog nedovoljne toplotne energije za njihovo ponovno ispravanje u hladnijim regionima i na većim visinama, koncentracije ovih jedinjenja mogu biti veće u ovim nego u toplijim i nižim predelima. Ponovljenim ciklusom ispravanja, kretanja atmosferskim strujama, i taloženja, postojana organska jedinjenja mogu preći i hiljade kilometara od njihovih izvora emisije.

S obzirom da vegetacija prekriva veliki deo kopna, pri čemu se odlikuje velikom specifičnom površinom, biljke imaju značajnu ulogu u ciklusu kretanja postojanih organskih zagađujućih jedinjenja u životnoj sredini. Dakle, prilikom taloženja postojanih organskih jedinjenja iz atmosfere, ona dospevaju i na površinu biljaka, ulazeći na taj način i u lanac ishrane, gde usled bioakumulacije[1] i biomagnifikacije[2], više karike lanca sadrže veće količine ovih jedinjenja od nižih (slika 2.3).



Slika 2.3. Ilustracija pojave povećanja koncentracije postojanih organskih jedinjenja jedinjenja u vim karikama lanca na primeru prisustva organohlornih jedinjenja u lancu ishrane Velikih jezera SAD (Škrbić, 2003)

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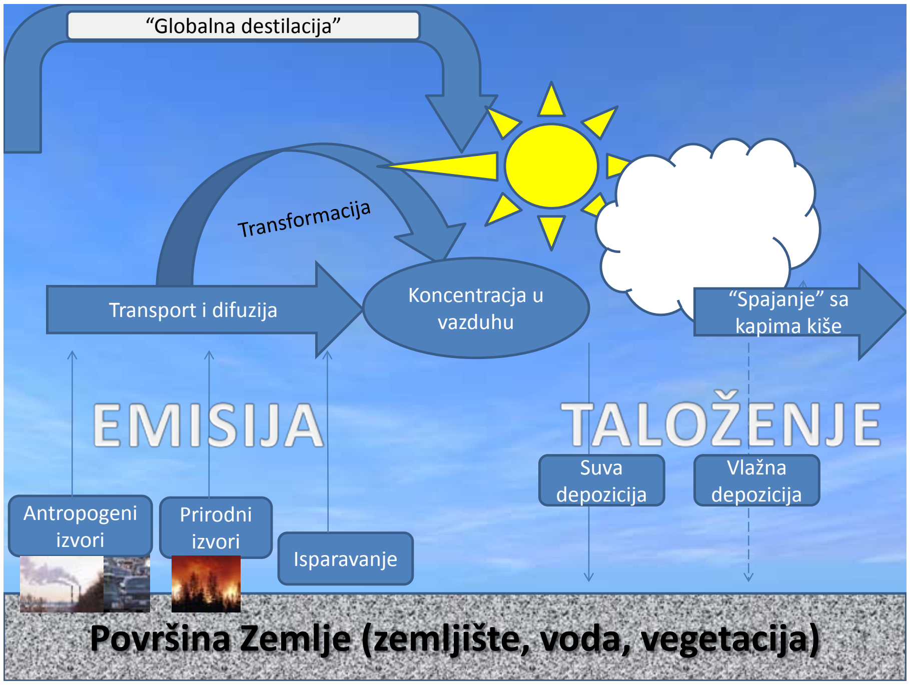
[1] Bioakumulacija – nakupljanje, koncentrisanje toksičnih jedinjenja u organizmima; javlja se kada je brzina apsorbovanja ovakvih supstanci u organizmu veća od procesa njene razgradnje i/ili izlučivanja.

[2] Biomagnifikacija – povećanje koncentracije toksičnih jedinjenja u višim karikama lanca.

Dalja sudbina postojanih organskih zagađujućih jedinjenja u životnoj sredini određena je brojnim faktorima, a najvažniji su njihove i fizičko-hemijske osobine sredine u kojoj se nalaze, klimatski uslovi, kao i blizina i intenzitet izvora emisije. Ilustracija ciklusa kruženja ovih jedinjenja u prirodi prikazana je na slici 2.4. Usled raznolikosti ovih faktora i često akcidentne prirode procesa (izvora) zagađenja, koncentracija postojanih zagađujućih jedinjenja na različitim lokacijama može biti značajno drukčija, čak kada su u pitanju i veoma bliske lokacije. Zbog toga, velika varijabilnost koncentracija ovih materija u prirodi zahteva pažljivo razmatranje i interpretaciju u cilju procene stepena zagađenja, identifikacije izvora emisije, kategorisanje uzoraka, korelacije parametara i dr., što je moguće primenom multivarijacionih statističkih procedura. Iz širokog spektra postojanih zagađujućih jedinjenja, kao predmet ovog rada izdvojeni su najčešće analizirane grupe postojanih organskih jedinjenja (polihlorovani bifenili, organohlorni pesticidi, policiklični aromatični ugljovodonici) i teški elementi.



Slika 2.4. Sudbina postojanih zagađujućih jedinjenja u prirodi

2.1.1. Postojana organska zagađujuća jedinjenja

Postojana organska zagađujuća jedinjenja su jedinjenja lipofilnog karaktera, koja ne podležu ili su slabo podložni fotolitičkoj, biološkoj ili hemijskoj razgradnji u prirodi, što dovodi do njihovog nakupljanja (koncentrisanja, akumulacije) u prirodi i u lancu ishrane. Karakteristično za sva postojana organska jedinjenja je da se prenose na velike udaljenosti od izvora emisije atmosferskim transportom što dovodi do njihove rasprostranjenosti u litosferi, hidrosferi, atmosferi i biosferi. Sve ovo dovodi i do stalne izloženosti ljudi ovim jedinjenjima. Njihove toksične karakteristike mogu prouzrokovati ozbiljno narušavanje zdravlja, kao što je pojava raka, bolesti imunog i reproduktivnog sistema, poremećaji pri rođenju, itd. Zbog donedavne široke upotrebe ovih jedinjenja i njihovog vazdušnog transporta, zagađenje postojanim organskim jedinjenjima predstavlja svetski problem (United Nations 2002).

U maju 1995. god., Upravno veće Programa o životnoj sredini Ujedinjenih Nacija (*United Nations Environment Programme Governing Council*) ukazalo je na potrebu ispitivanja postojanih organskih zagađujućih jedinjenja; tada je i definisana prva lista od 12 prioritetnih jedinjenja nazvanih „dvanaest prljavih“ (*„dirty dozen“*), koji prvenstveno pripadaju klasi organohlornih pesticida (aldrin, hlordan, DDT, dieldrin, endrin, heptahlor, heksahlorbenzen, mireks), zatim polihlorovanih bifenila, polihlorovanih dibenzo-*p*-dioksina, polihlorovanih dibenzofurana i toksafen (Tabela 2.1). Intenzivna proizvodnja, korišćenje i odlaganje većine ovih jedinjenja odvijalo se u periodu od ’30-tih do ’80-tih godina 20. veka. Za razliku od većine postojanih organskih zagađujućih jedinjenja, dioksini i furani nikada se nisu industrijski proizvodili; oni isključivo nastaju tokom procesa nepotpunog sagorevanja ili kao sporedni proizvodi pri dobijanju određenih pesticide i nekih drugih hemikalija. Zemlje i organizacije koje podržavaju Stokholmsku konvenciju su dužne da se pridržavaju mera smanjenja prisustva postojanih organskih zagađujućih jedinjenja u životnoj sredini i to na dva načina: 1) smanjenjem emisije namerno proizvedenih jedinjenja (kao što su organohlorni pesticidi i polihlorovani bifenili) prekidajući njihovu proizvodnju i korišćenje, i 2) smanjenjem emisije slučajno proizvedenih zagađujućih jedinjenja (dioksina i furana).

Tabela 2.1. Lista jedinjenja svrstanih u tzv. „dvanaest prljavih“ („dirty dozen“) grupu postojanih organskih zagađujućih jedinjenjaprema Stokholmskoj konvenciji

	Postojano organski jedinjenje	Pesticid	Industrijska hemikalija	Sporedni proizvod
1.	Aldrin	+		
2.	Hlordan	+		
3.	DDT	+		
4.	Dieldrin	+		
5.	Endrin	+		
6.	Heptahlor	+		
7.	Mireks	+		
8.	Toksafen	+		
9.	Heksahlorobenzen (HCB)	+	+	+
10.	Polihloovani bifenili (PCB)		+	+
11.	Polihlorovani dibenzo-p-dioksini (PCDD)			+
12.	Polihlorovani dibenzofurani (PCDF)			+

Lista postojanih organskih zagađujućih jedinjenja podložna je stalnim promenama, u skladu sa novim saznanjima o njihovom prisustvu i toksičnosti. Prema Stokholmskoj konvenciji, neko jedinjenje mora da ispuni sledeće kriterijume da bi se svrstalo u grupu postojanih organskih zagađujućih jedinjenja (Stockholm, 2001).

- Postojanost
    - i) vreme poluživota[3] datog jedinjenja u vodi treba da je veće od dva meseca, a u zemljištu ili sedimentu veće od šest meseci;
    - ii) ili je potrebno da postoje drugi dokazi o izraženoj postojanosti jedinjenje

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[3] Mera postojanosti jedinjenja u prirodi meri se tzv. vremenom poluživota, koje predstavlja vreme, za koje se, prvobitna količina jedinjenja smanji za polovinu.

- Bioakumulacija
  - i) biokoncentracioni faktor jedinjenja[4] ili njegov faktor bioakumulacije u vodenim organizmima da je preko 5000, ili, u nedostatku ovakvih podataka, da je logaritamska vrednost koeficijenta raspodele jedinjenja između oktanola i vode (log K_{ow})[5] veća od 5;
  - ii) ispoljava veliki stepen bioakumulacije u drugim vrstama, veliku toksičnost ili ekotoksičnost; ili
  - iii) rezultati merenja koncentracija u biotskim uzorcima ukazuju na potencijal bioakumulacije.
- Sklonost ka prenosu na velike razdaljine
  - i) izmerene koncentracije jedinjenja na lokacijama udaljenim od izvora njegove emisije ukazuju na potencijalnu opasnost;
  - ii) rezultati merenja koncentracija pokazuju da dolazi do transporta jedinjenja na velike udaljenosti putem vazduha, vode ili migracionih vrsta; ili
  - iii) osobine jedinjenja koje utiču na njegovo prisustvo i ponašanje u životnoj sredini i/ili rezultati ispitivanja modelnih sistema ukazuju da jedinjenje ima sklonost ka prenosu na velike udaljenosti putem vazduha, vode ili migracionih vrsta. Za jedinjenja koja značajno migriraju putem vazduha, vreme poluživota bi trebalo da je veće od dva dana,.
- Štetni uticaji:
  - i) jedinjenje štetno utiče na zdravlje ljudi ili na životnu sredinu;

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[4] Biokoncentracioni faktor (BCF) predstavlja odnos koncentracije jedinjenja u tkivu(ima) organizma i koncentracije tog jedinjenja u vodenoj sredini u kojoj živi taj organizam. Ovaj bezdimenzioni broj ukazuje na koncentrisanje jedinjenja u organizmima usled raspodele jedinjenja između vodene i organske faze.

[5] log K_{ow} – logaritamska vrednost koeficijenta raspodele supstance između oktanola i vode; jedinjenja koja imaju velike vrednosti K_{OW}, imaju izrazitu sposobnost vezivanja za organsku fazu u zemljištu ili vodenim sistemima, što znači da se radi o lipofilnim jedinjenjima koja će se polako kretati kroz hidrogeološke sisteme te će se uglavnom zadržavati blizu izvora zagađenja. Ovo je važna veličina, koja se koristi za predviđanje sudbine organskih polutanata u prirodi.

ii) podaci o toksičnosti ili ekotoksičnosti ukazuju na mogućnost narušavanja zdravlja ljudi ili opasnost za životnu sredinu.

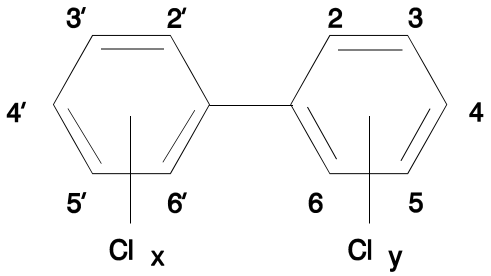
Procena jedinjenja-„kandidata“ za grupu postojanih organskih zagađujućih jedinjenja, kao i procena jedinjenja već prethodno ubrojanih u ovu grupu i ograničenje njihovog korišćenja su veoma zahtevne, jer za svaku supstancu postoje razlozi za i protiv njenog korišćenja. Jedan primer dileme oko ukidanja ili daljeg korišćenja postojanih organskih zagađujućih jedinjenja je DDT, koji spade u organohlorne pesticide, i to u “dvanaest prljavih”. Naime, neki podaci pokazuju da u svetu svakih 30 sekundi umre jedno dete od malarije (WHO, 2006). DDT je efikasno sredstvo u borbi protiv komaraca koji prenose malariju, i njegovom upotrebom u Africi, gde još uvek postoji malarija, hiljade života se spašava njegovom primenom. Sa druge strane, tragovi ovog pesticide su pronađeni u svim udaljenim delovima zemlje, čak i tamo gde nikada nije primenjivan. Takođe, poznato je njegovo neželjeno dejstvo na sistem za razmnožavanje sisara, kao i to da može izazvati rak pankreasa i neuropsihološku disfunkciju (Tiemann, 2008; Beard, 2006).

Tragovi postojanih organskih zagađujućih jedinjenja, kao i jedinjenja-„kandidata“ za ovu grupu, nađeni su u ljudskim tkivima u svim delovima sveta (krvi, različitim organima, masnim naslagama, majčinom mleku, pupčanoj vrpci (REF iz naseg rada). Glavni način unosa ovih jedinjenja u organizam ljudi je putem namirnica, a zatim udisanjem vazduha i prašine, kao i putem vode. Zbog mera ograničenja korišćenja postojanih organskih zagađujućih jedinjenja, njihova emisija je značajno smanjena, što je uticalo na smanjenje njihovih količina prisutnih u hrani, pa time i na smanjenu izloženost ljudi. Međutim, mnoga istraživanja su na primeru polihlorovanih bifenila pokazala da i nakon 30 godina od zabrane proizvodnje u Evropi, njihovo prisustvo u životnoj sredini i ljudskim tkivima se ne može zanemariti.

2.1.1.1. Organohlorna jedinjenja – OCC

Organohlorna zagađujuća jedinjenja, kao što su polihlorovani bifenili (PCB) i organohlorni pesticidi (OCP), predstavljaju najveći deo postojanih organskih zagađujućih materija definisanih Stokholmskom konvencijom (tabela 2.1). Ova jedinjenja su prisutna u svim matriksima životne sredine i predstavljaju predmet istraživanja u celom svetu kako bi se odredio njihov sadržaj u raznim matriksima, ispitalo izlaganje ljudi kao i izvršila procenena rizika po zdravlje ljudi. Postoji veliki broj radova, koji predstavljaju rezultate ispitivanja OCP i PCB u različitim uzorcima iz životne sredine, namirnicama i biološkim uzorcima. Pregled nekih od ovih radova može se naći u poglavljima 3.2.2 i 3.2.3.

POLIHLOROVANI BIFENILI su sintetska organska jedinjenja karakteristične bifenilne strukture sa vezanim atomima hlora (slika 2.5). Postoji ukupno 209 različitih PCB-jedinjenja, poznatih kao kongeneri, koji se međusobno razlikuju po broju supstituisanih atoma hlora (od 1 do 10) i njihovom položaju u molekulu bifenila.



Slika 2.5. Opšta strukturna formula polihlorovanih bifenila (x=1-5, y=1-5, $x+y \geq 1$)

Postoji više načina dodeljivanja imena polihlorovanim bifenilima, a najzastupljeniji su IUPAC nomenklatura i Ballschmiter-Zell-ovi (BZ) brojevi, koji su od 1993. godine i univerzalno prihvaćeni (Škrbić, 2003). BZ brojevi se kreću u rasponu 1-209, pri čemu su brojevima 1-3 označena 3 (mono)hlorbifenila, 4-15 dvanaest dihlorbifenila, 16-39 dvadeset četiri trihlorbifenila, 40-81 četrdeset dva tetrahlorbifenila, 82-127 četrdeset šest pentahlorbifenila, 128-169 četrdeset dva heksahlorbifenila, 170-193 dvadeset četiri heptahlorbifenila, 164-205 dvanaest oktahlorbifenila, 206-208 tri nonahlorbifenila i 209 jedan dekahlorbifenil.

Fizičke i hemijske osobine PCB kongenera zavise od položaja i broja atoma hlora u njihovom molekulu: na sobnoj temperaturi su u tečnom agregatnom stanju; slabo su rastvorljivi u vodi, a dobro u organskim rastvaračima; imaju relativno visoku temperaturu paljenja i ključanja; nisu eksplozivni; imaju malu električnu i veliku toplotnu provodljivost; poseduju toplotnu i hemijsku stabilnost, što im je omogućilo primenu u uređajima za prenos toplote (Škrbić, 2003). Njihova ispraljivost se smanjuje, a lipofilnost raste sa povećanjem broja Cl-atoma u molekulu, što takođe

utiče i na izraženiju postojanost u odnosu na prirodne procese razgradnje. U zavisnosti i položaja Cl-atoma i uslova, koji vladaju u okolini, poluživot PCB u zemljištu je nekoliko godina, a u vodi i vazduhu od nekoliko sati do 210 dana (Schwedt, 2001) Toksičnost PCB kongenera takođe zavisi od njihove strukture. Svi toksični kongeneri sadrže Cl-supstituente u 3,3',4,4' ili 3,4,4' ili 3',4,4' položajima, i nijedan, jedan ili dva Cl-atoma u orto-položajima. Ovi izrazito toksični kongeneri imaju planarnu strukturu i spadaju u jedinjenja po toksičnosti slična dioksinima (na engleskom *„dioxin-like“* PCB*)*, a njihova toksičnost se izražava u odnosu na 2,3,7,8-tetrahlordibenzo-*p*-dioksin (TCDD) – najtoksičniji halogeni aromatični ugljovodonik. Njihova toksičnost ogleda se u štetnom dejstvu na imuni sistem, sistem za razmnožavanje, razvoj centralnog nervog sistema, kao i u kancerogenosti (Baars i sar. 2004). Ostali PCB nemaju toksičnost sličnu dioksinima (*„non-dioxin-like“*), ali deluju na drukčiji način, prvenstveno utičući na rad endokrinih žlezda, bilo u slučajevima kratkoročne izloženosti velikim koncentracijama, ili u slučaju dugoročnog unosa i bioakumulacije u organizmu (ATSDR 2000) iz ove druge grupe (*„non-dioxin-like“*)*,* koji sadže od 3 do 7 atoma hlora u svojoj strukturi, češće se mogu naći u različitim delovima životne sredine u odnosu na druge kongenere i to u većim količinama nego što je zabeleženo prisustvo ostalih (Lazaro i sar. 1999; Baars i sar. 2004), zbog čega su svrstani u grupu tzv. indikatorskih PCB, jer njihovi sadržaji mogu ukazati na stepen zagađenosti. U indikatorske PCB, pored ovih 6 kongenera („non-dioxin like“) često se ubraja i 1 kongener po toksičnosti sličan dioksinu (*„dioxin-like“*), PCB 118.
Zbog svojih fizičko-hemijskih osobina PCB-ovi su našli veoma široku komercijalnu primenu u: adhezivima, transformatorima, visoko- i nisko-naponskim kondenzatorima, električnim motorima sa tečnim hlađenjem, hidrauličnim sistemima, elektromagnetima, regulatorima napona, vakuum pumpama, mikrotalasnim pećnicama, itd.

Prvi put, PCB su industrijski proizvedeni 1929. godine u Sjedinjenim Američkim Državama pod komercijalnim nazivom Askarel. Pored SAD, najveći svetski proizvođači PCB-ova su bili Francuska, Velika Britanija, Nemačka, Japan, bivši SSSR, Čehoslovačka i Poljska. Osim navedenoh, u ostalim zemljama Centralne i Istočne Ecrope, pa tako i u bivšim jugoslovenskim državama nije postojala proizvodnja PCB. PCB-ovi su se uvozili u bivšu Jugoslaviju za prateću energetsku opremu u okviru elektroprivrednih, vojnih i PTT objekata, u kojoj su služili kao izolacione tečnosti (Škrbić, 2003).

Početkom 1977. god. američka Agencija za zaštitu životne sredine (EPA) izdala je Zakon o kontroli toksičnih supstanci (TSCA-*Toxic Substances Control Act*), čime je striktno ograničena proizvodnja, uvoz, upotreba i uklanjanje PCB-ova, zbog njihove utvrđene toksičnosti i potencijalne kancerogenosti (tabela 2.2). Danas se za potrebe industrije više ne proizvode, međutim još uvek se mogu naći u mnogim poluzatvorenim i zatvorenim sistemima, na otpadima i u matriksima iz životne sredine (Škrbić, 2003). Značajno je napomenuti da je u poslednjim decenijama novi izvor ovih zagađujućih materija električni i elektronski otpad (tzv. e-otpad), i to naročito u azijskim zemljama u koje se uvozi oko 80% celokupne količine e-otpada u svetu, od kojih čak 90% ulazi u Kinu, gde prisustvo PCB u svim sferama životne sredine predstavlja veliki problem (Yang i sar., 2012).

ORGANOHLORNI PESTICIDI se danas smatraju najtoksičnijim i najzastupljenijim zagađujućim materijama prisutnim u prirodi i njihov poluživot u zemljištu se izražava godinama. U najvećoj meri oni čine grupu „dvanaest prljavih“ (*„dirty dozen“*) postojanih organskih zagađujućih jedinjenja. To su sintetička jedinjenja, koja su namerno uneta u prirodnu sredinu nanošenjem direktno na zemljište ili raspršivanjem preko useva radi povećanja poljoprivredne proizvodnje.

Primena organohlornih pesticida je u početku bila veoma intenzivna, naročito u periodu od '50-tih do '70-tih godina 20. veka, nakon čega je njihova primena zabranjena u razvijenim zemljama Evrope i Amerike zbog izrazite postojanosti i negativnog uticaja na životnu sredinu (Škrbić, i Đurišić-Mladenović, 2005). Njihova ilegalna upotreba je nastavljena, i to naročito u zemljama u razvoju, a u najkritičnije regione se ubrajaju Indija i Kina (Halliday, D.): Prema nekim istraživanjima, svega 1-3% pesticida dospe na ciljno mesto tokom primene dok se ostatak izgubi u podzemnim vodama, isparavanjem i transportom u vazduhu (Dörfler,1997). Proizvodi njihove razgradnje mogu biti mnogo toksičniji od polaznih jedinjenja čime se višestruko ugrožava zdravlje ljudi i životinja.

Organohlorni pesticidi koji se najčešće analiziraju su dihlordifeniltrihloretan - DDT i njegovi metaboliti (dihlordifenildihloretan - DDE, dihlordifenildihloretilen - DDD), izomeri heksahlorcikloheksana (α,β,γ,δ-HCH), heksahlorbenzen (HCB), pesticidi cikloidenske grupe (aldrin, endrin, dieldrin, hlordan, heptahlor, endosulfan), toksafen i mireks. Ova grupa pesticida se odlikuje velikom postojanošću u prirodnoj sredini uključuju zemljište, vodu i vazduh (više godina) i velikom pokretljivošću pod uticajem prirodnih procesa. Nakupljaju se u masnom tkivu čoveka i životinja, a njihova koncentracija se povećava u višim karikama lanca ishrane (tzv. biomagnifikacija). Pokazano je da su ova jedinjenja veoma toksična (Škrbić i sar., 2006)

Aldrin je insekticid koji se koristio u poljoprivrednoj proizvodnji za uništavanje skakavaca, termita, crva, itd. Pokazalo se da je takođe toksičan za ribe, ptice i sisare uključujući i čoveka. Ljudska populacija je izložena aldrinu pretežno preko mleka i mesa (Škrbić i sar., 2006)

DDT je najpoznatiji organohlorni insekticid koji se u velikoj meri koristio tokom II svetskog rata za suzbijanje malarije, tifusa i drugih zaraznih bolesti koje prenose insekti. Nakon rata intenzivno se koristio kao insekticid u poljoprivredi naročito na usevima pamuka a još uvek se koristi za suzbijanje komaraca prenosnika malarije. Tokom '70-ih godina prošlog veka, 34 zemlje zabranjuje upotrebu i proizvodnju DDT dok 34 zemlje ograničava njegovu upotrebu. DDT je veoma postojan – 50% količine koja je primenjena zaostaje u zemljištu 10 do 15 godina nakon primene. DDT je detektovan bukvalno svuda čak i na Arktiku. Dugotrajna izloženost ovom insekticidu je uzročnik brojnih hroničnih bolesti. Prisustvo DDT u majčinom mleku ozbiljno ugrožava zdravlje novorođenčadi (Škrbić i sar., 2006)

Heksahlorcikloheksan je hemikalija koja postoji u obliku osam izomera. Jedan od izomera γ -HCH ili lindan se koristio kao insekticid na voću, povrću i ratarskim usevima. Tehnički HCH sadrži 10-15% lindana u smeši sa ostalim izomerima HCH. HCH može da ostane u vazduhu dugo vremena nataložen na čestice prašine i čađi i da prevali velike udaljenosti nošen vetrom. HCH akumuliran u zemljištu, sedimentu i vodi je podložan delimičnoj biološkoj degradaciji pod uticajem nekih algi, bakterija i gljiva ali je taj proces dugotrajan. Ima osobinu da se akumulira u adipoznom tkivu riba. Čovek najčešće dolazi u dodir sa ovim pesticidom udisanjem kontaminiranog vazduha najčešće u blizini mesta njegove proizvodnje ili primene, preko kože koristeći šampone i druge preparate protiv vaši (Škrbić i sar., 2006)

Dieldrin je insekticid koji se koristio za kontrolu termita, moljaca, suzbijanje insekata koji žive u zemljištu kao i vektora zaraznih bolesti. Poluživot dieldrina je 5 godina. Veoma je otrovan za akvatičan živi svet naročito ribe i žabe. Rezidue dieldrina detektovane su u vodi, vazduhu, zemljištu, ribama, pticama, sisarima i čoveku. Čovek je dieldrinu izložen putem ishrane. Na primer, dieldrin je drugi po redu najčešći kontaminent pasterizovanog mleka u SAD (Škrbić i sar., 2006)

Endrin je insekticid koji se nanosio na listove pamuka i žita. Koristio se i za suzbijanje poljskih miševa i voluharica. Endrin metaboliše u organizmu životinja te se ne sakuplja u adipoznom tkivu tako da su procenjeni unosi ovog pesticida putem hrane ispod granice koja se smatra štetnom. Međutim, endrin je veoma postojan – vreme poluživota u zemljištu iznosi 12 godina (Škrbić i sar., 2006)

Endosulfan je insekticid koji se koristio za zaštitu useva i duvana. Transportuje se na velike udaljenosti u atmosferi. U zemljištu se nalazi u vezanom obliku. Podleže hidrolizi a pod uticajem mikroorganizama metaboliše u niz jedinjenja. Ima nižu biokoncentraciju u terestrijalnim i akvatičnim lancima ishrane u odnosu na ostale organohlorne pesticide (Škrbić i sar., 2006).

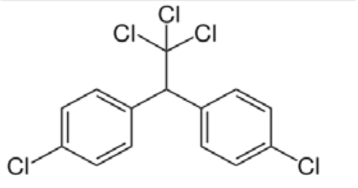
Heptahlor se takođe koristio za suzbijanje zemljišnih insekata, skakavaca, poljskih štetočina i vektora malarije. Heptahlor se svrstava u moguće uzročnike kancera kod čoveka. Hrana je glavni izvor izlaganja čoveka ovom pesticidu (Škrbić i sar., 2006).

Heksahlorbenzen je prvi put primenjen 1945. godine kao sredstvo za tretiranje semena. Koristi se i kao fungicid u ratarstvu. Detektovan je u hrani biljnog i životinjskog porekla. Veoma je toksičan. U periodu od 1954. do 1959. godine, u istočnoj Turskoj, ljudi su u ishrani koristili žitarice tretirane HCB-om i razvili niz simptoma kao što su fotosenzibilne kožne lezije, stomačni grčevi, gubitak telesne težine kao i metabolički poremećaj krvi - porfirija. Smrtnost ugrožene populacije je iznosila 14% (Škrbić i sar., 2006)

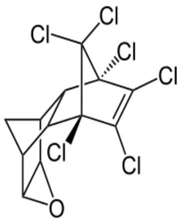
Mireks je insekticid koji se upotrebljavao kao sredstvo za uništavanja termita i mrava i kao aditiv koji sprečava gorenje u plastici, gumama i električnoj opremi. Laboratorijskim ogledima na životinjama mireks je pokazao delovanje koje ga svrstava u grupu potencijalnih kancerogenih supstanci. Veoma je postojan sa poluživotom do 10 godina. Čovek najviše dolazi u dodir sa ovim jedinjenjem konzumiranjem mesa, ribe i divljači (Škrbić i sar., 2006).

Strukture nekih pomenutih OCP-jedinjenja su prikazane na slici 2.6.

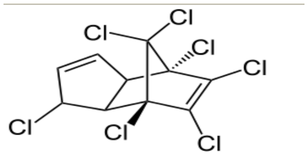
Međunarodna organizacija za istraživanje malignih bolesti (engleska skraćenica IARC – International Association on Cancer Research) pri Svetskoj zdravstvenoj organizaciji (WHO) je klasifikovala neka organohlorna jedinjenja po kancerogenosti (tabela 2.2) (Škrbić i sar., 2006).).



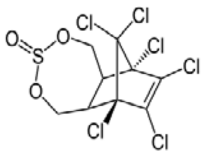
DDT



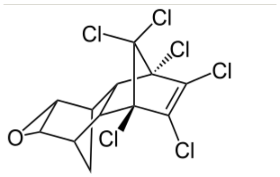
Endrin



Heptahlor



Endosulfan



Dieldrin

Slika 2.6. Struktura nekih organohlornih pesticida

Tabela 2.2. Klasifikacija organohlornih zagađujućih jedinjenja po kancerogenosti (IARC): Grupa 1 - kancerogena jedinjenja; Grupa 2A - verovatni uzročnici raka kod čoveka; Grupa 2B - mogući uzročnici raka kod čoveka; Grupa 3 - ne klasifikuju se kao kancerogena jedinjenja (Škrbić i sar., 2006)-*http://www.iarc.fr/ENG/Databases/index.php*)

Organohlorni polutanti		**Klasifikacija po IARC**
Organohlorni pesticidi	aldrin i dieldrin	grupa 3
	endrin	grupa 3
	endosulfan	nije klasifikovan
	hlordan i heptahlor	grupa 2B
	DDT	grupa 2B
	HCB	grupa 2B
	α-HCH β-HCH γ-HCH (lindan)	grupa 2B
	mirex	grupa 2B
	toxaphen	grupa 2B
PCB		grupa 2A

2.1.1.2. Policiklični aromatični ugljovodonici - PAH

Policiklični aromatični ugljovodonici predstavljaju grupu od preko 100 različitih jedinjenja karakteristične molekulske strukture sa dva ili više kondenzovana benzenova prstena. Iako prema Stokholmskoj konvenciji, PAH-ovi nisu svrstani u grupu postojanih organskih zagađujućih jedinjenja, njihove osobine i ponašanje u prirodi, kao i štetno dejstvo, koje ispoljavaju na živim organizmima, svrstava ih u tzv. „kandidate" za grupu postojanih organskih zagađujućih materija (Edlund, 2001). Za razliku od organohlornih polutanata, kao što su PCB i OCP, proizvedenih sintetičkim putem, PAH-ovi nastaju u svim procesima termičke razgradnje organske (ugljenične) materije, bilo da se ovi procesi odvijaju spontano u prirodi ili su namerno izazvani (na primer, radi dobijanja energije), bilo da se odvijaju na visokim temperaturama pri sagorevanju ili na nižim temperaturama i visokim pritiscima tokom dugog vremenskog perioda razgradnje biološkog materijala u dubini Zemlje (procesi karbonizacije). Glavni prirodni izvori PAH-ova su šumski požari i vulkani, kao i ležišta ugljovodonika i uglja. Glavni antropogeni izvori ovih zagađujućih jedinjenja su svi procesi termičke razgradnje organske materije, prvenstveno energetska postrojenja, industrijski procesi, saobraćaj, itd. Ukupna količina i sastav smese emitovanih PAH jedinjenja zavisi od uslova sagorevanja i materijala koji sagoreva (Škrbić, 2002 ; Škrbić i Đurišić-Mladenović, 2002; Škrbić i sar., 2002; Škrbić i sar., 2010). Postoji nekoliko grupa PAH jedinjenja, definisanih kao priritetna zagađujuća jedinjenja od strane različitih organizacija. U tabeli 2.3 su nabrojana jedinjenja svrstana u prioritetne liste američke Agencije za zaštitu životne sredine (tzv. 16 EPA PAH jedinjenja) i Evropske Unije (tzv. 15+1 EU PAH jedinjenja). Klasifikacija PAH jedinjenja prema stepenu kancerogenosti po IARC prikazana je takođe u tabeli 2.3. Na slici 2.7 (Škrbić, 2002). prikazani su PAH-ovi iz grupe 16 EPA PAH.

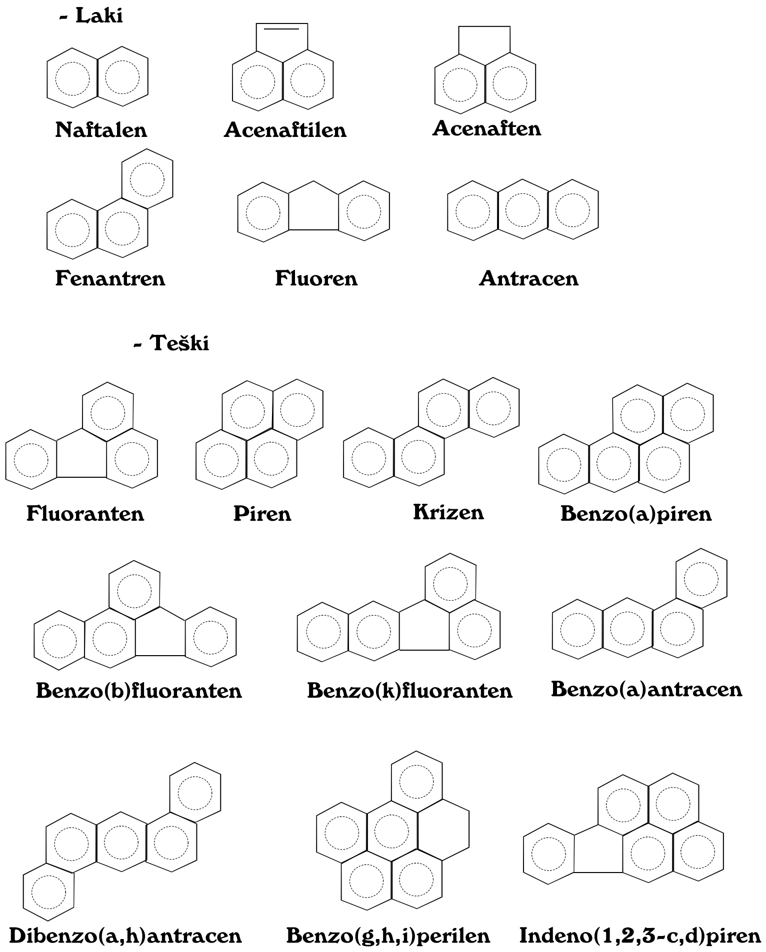
PAH-ovi su u slabo rastvorljivi u vodi, pri čemu se rastvorljivost u vodi smanjuje sa povećanjem broja kondenzovanih prstenova. PAH-ovi sa četiri i više prstenova imaju mali napon pare i zato se nalaze uglavnom adsorbovani na česticama čađi i prašine u vazduhu. Molekuli sa dva i tri kondenzovana prstena se nalaze u obliku pare u atmosferi.

Za nepušače, hrana predstavlja glavni izvor izloženosti ljudi ovim jedinjenjima. Prisustvo PAH u namirnicama može biti posledica prenosa PAH jedinjenja prisutnih u životnoj sredini u sirovine, tokom industrijskim procesa prerade i/ili neposredne pripreme hrane u domaćinstvima. Pored unosa namirnica, PAH se u organizam unose i udisanjem, što je značajan izvor izloženosti u regionima sa intenzivnim antropogenim aktivnostima.

Tabela 2.3. Klasifikacija PAH jedinjenja svrstanih u prioritetne liste američke Agencije za zaštitu prirode (EPA) i Evropske Unije (EU) po kancerogenosti (IARC): Grupa 1 - kancerogena jedinjenja; Grupa 2A - verovatni uzročnici raka kod čoveka; Grupa 2B - mogući uzročnici raka kod čoveka; Grupa 3 - ne klasifikuju se kao kancerogena jedinjenja (JRC60146 Fact Sheet PAH 3rd edition)

PAH jedinjenja	Skraćenica	Prioritetna lista	Klasifikacija po IARC
Benzo[*a*]piren	BAP	EPA, EU	1
Acenaften	ACE	EPA	3
Acenaftilen	ACN	EPA	-
Antracen	ANT	EPA	3
Benzo[*a*]antracen	BAA	EPA, EU	2B
Benzo[*b*]fluoranten	BBF	EPA, EU	2B
Benzo[*j*]fluoranten	BJF	EU	2B
Benzo[*k*]fluoranten	BKF	EPA, EU	2B
Benzo[*c*]fluoren	BCF	EU	3
Benzo[*ghi*]perilen	BGHIP	EPA, EU	3
Krizen	CHR	EPA, EU	2B
Ciklopenta[*cd*]piren	CPP	EU	2A
Dibenzo[*a,h*]antracen	DhA	EPA, EU	2A
Dibenzo[*a,e*]piren	DeP	EU	3
Dibenzo[*a,h*]piren	DhP	EU	2B
Dibenzo[*a,i*]piren	DiP	EU	2B
Dibenzo[*a,l*]piren	DlP	EU	2A
Fluoranten	FLU	EPA	3
Fluoren	FLE	EPA	3
Indeno[*1,2,3-cd*]piren	IcP	EPA, EU	2B
5-metilkrizen	5-MC	EU	2B
Naftalen	NAP	EPA	2B
Fenantren	PHE	EPA	3
Piren	PYR	EPA	3

Mnogobrojni su radovi koji se bave različitim aspektima prisustva PAH u životnoj sredini. Neki od njih su pomenuti u poglavlju 3.2.1.



Slika 2.7. Policiklični aromatični ugljovodonici iz tzv. grupe 16 EPA PAH

2.1.2. Teški elementi

Metali u prirodi potiču iz različitih izvora. Poreklo metala u prirodnim zemljištima potiče prvenstveno iz litosfere, i to od stena i minerala, koji sačinjavaju Zemljinu koru. Na osam elemenata (O, Si, Al, Fe, Ca, Na, Ka, Mg) otpada 98,6% u izgradnji Zemljine kore, a na sve ostale svega 1,4%.

Sa stanovišta zaštite životne sredine, najznačajniji metali su oni iz grupe teških elemenata, koji se u prirodi nalaze u tragovima, i to prvenstveno oni, koji se smatraju indikatorima antropogenih aktivnosti, kao što su Pb, Cd, Cu, Fe, itd. Iako se pojam teških metala koristi dugi niz godina, tačna, naučna definicija, od strane autorizovanih tela, kao što je na primer IUPAC, ne postoji. Preko 60 godina ovaj pojam se koristi da bi označio različite grupe elemenata, često slične, ali ne u potpunosti identične, bilo na osnovu njihove gustine (pri čemu su predložene različite granične vrednosti gustine za podelu elemenata metala na teške i lake), atomske mase, atomskog broja, drugih hemijskih osobina (na primer, reaktivnost u odnosu na ditizone) ili toksičnosti. Zbog toga, IUPAC preporučuje iznalaženje nove klasifikacije, koja bi se bazirala na periodnom sistemu elemenata i koja bi odražavala hemijske osnove toksičnosti, omogućavajući predviđanje toksičnih uticaja (Duffus, 2002). U ovakvim uslovima, bez usvojene jedinstvene definicije, u radu će se koristiti pojmovi „teški metali“ i „teški elementi“, nasuprot kontraverzi koju stvaraju, a uzimajući u obzir široku rasprostranjenost ovih termina u (citiranoj) naučnoj literaturi.

Teški metali mogu biti emitovani iz raznih izvora: industrijskih postrojenja, termoelektrana, motornih vozila i sl. Izduvni gasovi vozila u najvećoj meri doprinose opterećenju gradske sredine različitim zagađujućim materijama, među kojima su i teški metali. Ukoliko se zemljište koristi u poljoprivrednoj proizvodnji, primena veštačkih i stajskog đubriva i pesticida, koji mogu sadržati različite teške metale kao nečistoće, takođe se smatra izvorom teških metala (Gimeno-Garcia i sar. 1996). Teški metali mogu da dospeju u zemljište ne samo sa mineralnim đubrivima (posebno upotrebom fosfornih, koja se odlikuju većim sadržajem nekih teških metala) već i tečnim stajnjakom. Utvrđeno je da sistematsko korišćenje otpadnih voda sa stočnih farmi dovodi do nakupljanja nekih teških metala, prvenstveno Cu, Cd, Pb i Fe, u zemljištu. Korišćenje prerađenog kanalizacionog mulja i otpadnih voda u poljoprivredi mogu takođe dovesti do zagađenja zemljišta. Gradske i industrijske otpadne vode posle odgovarajućeg tretmana često se rasprskavaju po obradivim površinama. Industrijski otpaci i nusproizvodi često se nude kao đubrivo ili sredstvo za melioraciju zemljišta. S pesticidima se u zemljište unose i teški metali. Do '70-tih godina 20. veka korišćeni su insekticidi kao što su olovoarsenat i barijumsilikofluorid. Danas se primenjuju soli bakra, kao i neorgansko-organski fungicidi na bazi kalaja, žive, mangana i cinka.

Emitovani metali dospevaju do zemljišta atmosferskom depozicijom. Metali u zemljištu zaostaju veoma dugo, a povećana emisija metala tokom vremena može dovesti do značajnog nakupljanja i zagađenja životne sredine, prvenstveno zemljišta. U zemljištu metali se nalaze u imobilozovanom (nepokretnom) (u obliku sulfida, fosfata, silikata i dr.) i mobilnom obliku, pri čemu je mobilna frakcija važna za procenu migracije metala u životnoj sredini i unos u biljke. Povećanje pokretljivost metala u zemljištu može ugroziti podzemne vode i biljni svet. Na pokretljivost metala u zemljištu (pa tako i njihovu biodostupnost, tj. ulazak u lanac ishrane) utiču različiti parametri: pH, organska materija i tekstura zemljišta, kao i kiselost atmosferskih padavina.

Poznato je da hemijski sastav biljaka odražava elementarni sastav podloge na kojoj rastu. Više biljke apsorbuju metale iz vazduha ili vode preko svojih izdanaka, pri čemu se apsorpcija preko korena smatra glavnim putem unosa elemenata u biljku (Kabata-Pendias i sar., 2000). Razna istraživanja su pokazala da zagađenje zemljišta dovodi i do zagađenja useva koji na njemu rastu, a i namirnica proizvedenih od tih useva (Fergusson, 1990; Younas i sar. 1998; Nan i sar. 2002) Isto tako, prerada sirovina i proizvodni uslovi (aditivi, pH itd.) mogu uticati na kvalitet prehrambenih proizvoda i sadržaj metala u njima (de Brujin i sar., 1999; Mohamed, 1999; Škrbić i sar., 2007;Škrbić i Đurišić-Mladenović, 2005).

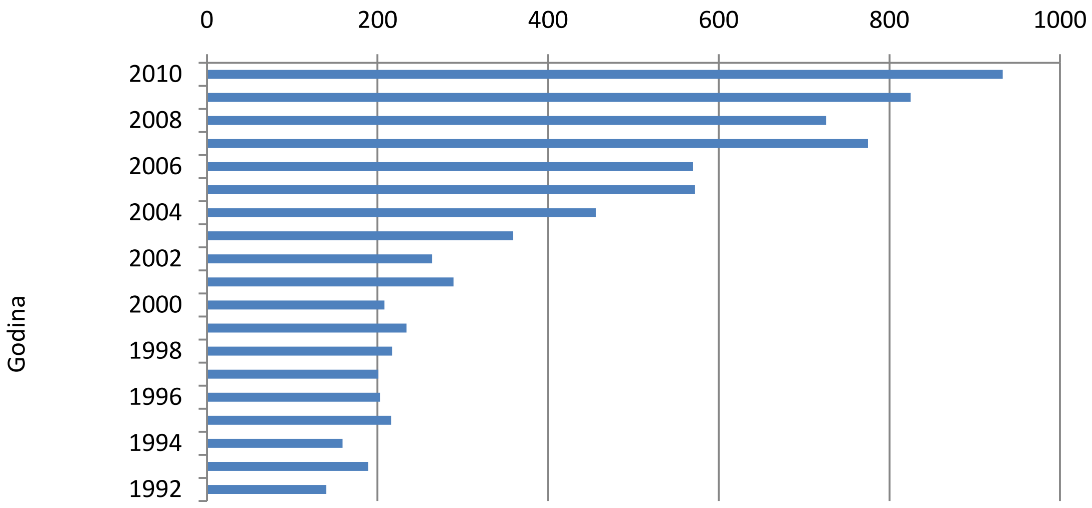
Dakle, ekološka važnost metala u zemljištu je tesno povezana za ljudsko zdravlje usled značajnog potencijala transfera (Morton-Bermea i sar., 2009), naročito kada je u pitanju zemljište urbanih sredina, gde je izloženost ljudi teškim metalima povećana, bilo putem udisanja, unosa preko digestivnog trakta ili kontakta preko kože (Wong i sar. 2006). Druge indirektne posledice zagađenja životne sredine teškim metalima ogledaju se u njihovoj migraciji u vodene sisteme i uticaju na vodene organizme kroz bioakumulaciju i biomagnifikaciju, utičući na lanac ishrane (Zyadah i sar., 2000; Ip i sar., 2005; Vinodhini i sar., 2008).

Iako stepen zagađenja životne sredine, prvenstveno zemljišta, zavisi ne samo od ukupnog sadržaja metala, već i od udela mobilnih i biodostupnih oblika, ukupni sadržaj teških metala se često koristi za procenu uticaja antropogenih aktivnosti na životnu sredinu (Morton-Bermea i sar., 2008). Takođe, zemljišta na koje antropogene aktivnosti direktno imaju uticaja, mogu poslužiti kao sveobuhvatni zapis brojnih procesa tokom vremena, kao i neto efekata ljudskih aktivnosti tokom dužeg vremenskog perioda. Mnoga ispitivanja su bila posvećena određivanju izvora i stepena zagađenja životne sredine na osnovu prisustva teških metala u zemljištu (Manta i sar. 2002; Škrbić i sar., 2004; Coskun i sar. 2006; Lee i sar. 2006; Christoforidis i sar., 2009; Franco-Uria i sar. 2009)

2.2. Hemometrija

Sve složeniji zahtevi za istraživanjima u oblasti hemije, dovela su i do porasta značaja instrumentalnih analiza naročito od ‘50-tih godina 20. veka, što je propraćeno i naglim razvojem instrumentalnih tehnika i, posledično, do porasta obima analitičkih rezultata. Sve ovo je stvorilo potrebu za iznalaženjem načina jasne prezentacije, uključujući i vizuelizaciju, i tumačenje velikih baza podataka. S obzirom da je razvoj instrumentalnih analitičkih tehnika bio praćen razvojem kompjuterske nauke i tehnologije, primena kompjutera i naprednih statističkih i matematičkih metoda od strane istraživača postala je omogućena i gotova obavezna, stvarajući novu poddisciplinu u okviru hemije – hemometriju.

Pojam hemometrije se povezuje prvi put sa švedskim naučnikom Svante Woldom sa Umeå Univerziteta početkom 70-tih godina prošlog veka. Razvoj hemometrije se može propratiti i brojem naučnih radova u međunarodnim časopisima sa SCI liste (slika 2.8).



Slika 2.8. Ilustracija porasta značaja hemometrijskih metoda: godišnji broj radova u međunarodnim časopisima iz elektronske baze SCIENCE DIRECT *u kojima se pojavljuje reč* “chemometric” *(podaci iz marta 2011. god.)*

Od kraja 80-tih godina pojavili su se i međunarodni časopisi specijalizovani u oblasti hemometrije i to su *Chemometrics and Intelligent Laboratory Systems* (sa petogodišnjim impakt faktorom 2007-2009 od 2,436 u 2009. god.) i *Journal of Chemometrics* (sa petogodišnjim impakt faktorom 2007-2009 od 1,859 u 2009. god.). Takođe, organizuju se i međunarodne konferencije posvećene različitim oblastima primene ovih metoda, a jedna od najznačajnijih je i *Chemometrics in Analytical Chemistry (CAC)*, koja se organizuje svake druge godine (u toku 2012. god. organizovana je 13. po redu CAC konferencija). Na internet stranici http://rcs.chph.ras.ru/rcscon.htm nalazi se spisak konferencija, koje su održane od 2003. god., a posvećenesu hemometriji.

Hemometrija predstavlja poddisciplinu u oblasti hemije, koja se bavi primenom matematičkih, statističkih i drugih logičkih metoda sa ciljem procene i interpretacije podataka (analitičkih, hemijskih), radi optimizacije i modelovanja procesa i eksperimenata (analitičkih, hemijskih) i radi izdvajanja maksimalne količine informacija iz eksperimentalnih podataka. Očigledno je da je hemometrija interdisciplina, koja povezuje hemiju, matematiku i kompjutersku tehnologiju. Slično hemometriji, u drugoj polovini 20. veka nastale su i druge poddiscipline bazirane na statističkim metodama uz primenu kompjuterskih programa, kao što su biometrika, ekonometrika, i dr. Pojam envirometrika (engleski *envirometrics)* uveden je da bi se označila oblast primene hemometrijskih metoda na polju nauke o životnoj sredini i njene zaštite; međutim i ova oblast se često uvrštava u hemometriju.

2.2.1. Multivarijacione statističke metode u analizi stanja životne sredine

U osnovi svih naučnih ispitivanja životne sredine i problema zagađenja sredine prouzrokovanih antropogenom delatnošću, uključujući i one kao posledica postojanih zagađujućih jedinjenja, nalaze se prvenstveno instrumentalne tehnike. Njihov neprekidni razvoj stvara potrebu praćenja i kontrole sve većeg broja zagađujućih jedinjenja u životnoj sredini, često prisutnih u tragovima, čak i u tzv. ultratragovima. Pri tome, koncentracije zagađujućih jedinjenja prisutnih u sredini su veoma promenljive, bilo kao posledica razlika u “pozadinskoj” koncentraciji, različite udaljenosti i intenziteta emisije antropogenih izvora i/ili vremenskih i prostornih razlika. Zbog svega ovoga ispitivanje stepena zagađenosti sredine podrazumeva analizu zagađujućih jedinjenja u velikom broju uzoraka kako bi dobijeni rezultati što realnije odrazili stvarno stanje sredine, predvideli rizike, ukazali na izvore zagađenja, efikasnost primenjene metode remedijacije, i dr. Karakteristično za rezultate ispitivanja stanja životne sredine je da oni često predstavljaju međusobno zavisne promenljive, koje se ne mogu razmatrati pojedinačno, tj. izdvojeno od ostalih, već jedino zajedno. Dakle, rezultati analize životne sredine često predstavljaju obimne baze podataka sastavljene od rezultata dobijenih za veliki broj uzoraka te se može smatrati da su multivarijacione, tj. multidimenzione prirode, zahtevajući primenu multivarijacionih statističkih metoda radi dobijanja sveobuhvatne slike o međusobnim vezama između svih izmerenih veličina (kao na primer, sadržaja velikog broja jedinjenja i osobina analiziranog matriksa).

Multivarijaciona analiza predstavlja skup statističkih metoda koje istovremeno analiziraju veći broj promenljivih dobijenih za veći broj uzoraka.

Za razliku od uobičajenih univarijacionih metoda analize, kojima se promenljive analiziraju pojedinačno te se ne može izvršiti objedinjavanje višestrukih merenja niti pravilno naučno zaključivanje, multivarijacione metode omogućavaju istovremenu analizu velikog broja podataka i izdvajanje "skrivenih" informacija i strukture ovakvih baza podataka. Metode multivarijacione statističke analize razvijale su se postepeno i do sada su mnoge našle primenu u zaštiti životne sredine. Različite analize grupisanja, predviđanja, diskriminaciona i faktorska analiza, analiza glavnih komponenata, analiza varijabilnosti, povezanosti i raspodele često su primenjivane u okviru istraživanja iz oblasti merenja različitih zagađujućih materija u životnoj sredini, identifikaciji izvora zagađenja, klasifikaciji uzoraka, itd.

Klasifikacija metoda multivarijacione analize se zasniva na različitim kriterijumima. Prva klasifikacija metoda je bazirana na ispitivanju međuzavisnosti promenljivih, odnosno na ispitivanju međuzavisnosti uzoraka. Kada se ispituje međuzavisnost promenljivih, tada se posmatraju kolone matrice podataka. Jedan od načina određivanja međuzavisnosti promenljivih je baziran na izračunatom koeficijentu korelacije među njima. Osnovu ovih metoda multivarijacione analize predstavlja kovarijaciona ili korelaciona matrica. Kod drugog pristupa, u cilju poređenja dva uzorka, posmatraju se odgovarajući redovi u matrici podataka, odnosno definišu se različite mere bliskosti između parova uzoraka. Osnovu ovih metoda multivarijacione analize predstavlja matrica odstojanja između uzoraka.

Prema drugoj klasifikaciji, metode se dele u dve grupe: metode zavisnosti i metode međuzavisnosti. Ukoliko se u istraživanju ispituje zavisnost između dva skupa promenljivih, gde jedan skup predstavlja zavisne promenljive, a drugi nezavisne promenljive, tada se odgovarajuća klasa metoda naziva metode zavisnosti. S druge strane, ako nema apriornog, teorijskog osnova za podelu promenljivih na dva podskupa promenljivih (zavisnih i nezavisnih), tada se koriste metode međuzavisnosti.

Statistička obeležja mogu biti kvantitativna (merljiva) ili kvalitativna (nemerljiva). Kvantitativne promenljive su one kod kojih se vrednosti razlikuju po veličini, a kvalitativne su one kod kojih se vrednosti razlikuju ne po veličini nego po vrsti. Klasifikaciju metoda multivarijacione analize moguće je izvršiti i prema vrsti podataka koji se koriste. Primer takve klasifickacije uz ranije uveden kriterijum podele metoda na metode zavisnosti i međuzavisnosti prikazan je u tabeli 2.4 (Kovačić, 1994).

Tabela 2.4. Klasifikacija metoda multivarijacione analize (Kovačić, 1994)

		Kvantitativne promenljive	Kvalitativne promenljive
Metode međuzavisnosti		Analiza glavne komponente Faktorska analiza Analiza grupisanja Kvantitativno višedimenziono proporcionalno prikazivanje	Kvalitativno višedimenziono proporcionalno prikazivanje Loglinearni modeli
Metode zavisnosti	Jedna zavisna promenljiva	Višestruka korelacija VIšestruka regresija	Diskriminaciona analiza (samo zavisna mora biti kvalitativna) Logit analiza
	Više zavisnih promenljivih	Višedimenziona regresija Višedimenziona analiza varijanse Kanonička korelaciona analiza	Kanonička korelaciona analiza sa veštačkim promenljivima

Od spomenutih metoda, najčešće korišćene u analizi rezultata merenja sadržaja zagađujućih jedinjenja u prirodi i namirnicama su analiza glavnih komponenata, faktorska analiza i analiza grupisanja, sve tri metode međuzavisnosti, kojima se ispituju stepen povezanosti (korelacije) između većeg broja promenljivih, kao i sličnosti i razlika između uzoraka. U manjoj meri, u radovima koji se bave prisustvom zagađujućih materija u životnoj sredini i namirnicama, mogu se naći i primeri korišćenja metoda zavisnosti, kao što su diskriminaciona analiza, višedimenziona (multipla) regresija i dr. Primeri korišćenja ovih hemometrijskih tehnika prikazani su u tabeli 2.5. S obzirom na veliki broj radova, u kojima su korišćene različite multivarijacione metode analize za obradu dobijenih podataka, pregled primene ovih metoda višestruko bi prevazilazio obim disertacije, te je u tabeli 2.5 prikazan samo mali broj relevantnih radova sa ciljem ilustracije širina primene hemometrijskih tehnika u nauci o zaštiti životne sredine, prvenstveno analize glavnih komponenata i analize grupisanja.

Teorijske osnove multivarijacionih metoda analize mogu se naći u knjigama različitih autora, kao što su Massart i sar., 1997; Vandeginste i sar., 1998; Einax i sar. 1997; Kovačić, 1994, i dr.

Tabela 2.5. Pregled primene multivarijacionih metoda (analize glavnih komponenata-PCA; analize grupisanja-CA; diskriminacione analize-DA; višestruke regresije-MR) u analizi podataka o prisustvu zagađujućih jedinjenja u abiotskim i biotskim uzorcima (broj uzoraka i jedinjenja uključenih u analizu navedeni su ukoliko je taj podatak postoji u citiranom radu)

Vrsta uzorka (broj uzoraka, n)/broj i vrsta zagađujućih jedinjenja	Primenjena multivarijaciona tehnike	Cilj primene izabrane hemometrijske tehnike	Izvor
Rečna voda (n=31)/53 PCB	PCA	identifikacija izvora zagađenja	Bremle G., Larsson P., *Long-term variations of PCB in the water of a river in relation to precipitation and internal sources,* Environ. Sci. Technol. **31** (1997) 3232-3237
Vazduh (n=259)/>100 isparljivih organskih jedinjenja	FA CA	identifikacija izvora zagađenja i ispitivanje sličnosti uzoraka u odnosu na mesto i sezonske promene	Perez-Pastor R.M., Garcia Alonso S., Quejido Cabezas A.J., *Volatile organic compounds in the area of Madrid: A chemometrical approach*, Environ. Monit. Assess. **75** (2002) 33-50
Lanac ishrane na otvorenom moru (pelagijska zona): zoo- i fitoplanktoni, tkiva morskog sisara (*Phocoena phocoena*) i ptice (*Phalacrocorax carbo sinensis*)/brojni PCB kongeneri	PCA	analiza međuzavisnosti i razlika u prisustvu PCB u različitim karikama lanca ishrane	Falandysz J., Wyrzykowska B., Strandberg L., Puzyn T., Strandberg B., Rappe C., *Multivariate analysis of the bioaccumulation of polychlorinated biphenyls (PCBs) in the marine pelagic food web from the southern part of the Baltic Sea, Poland,* J. Environ. Monit. **4** (2002) 929-941
Uzroci šećerne repe, ekstrahovanih rezanaca šećerne repe, suvih rezanaca šećerne repe, melase, šećera, zemljišta (n=27)/7 teških elemenata	PCA CA	analiza međuzavisnosti sadržaja teškihelemenata u različitim uzorcima, sličnosti profila teških elemenata u različitim uzorcima, identifikacija izvora elemenata	Škrbić B., Đurišić-Mladenović N., Mačvanin N. Determination of Metal Contents in Sugar Beet (Beta vulgaris) and Its Products: *Empirical and Chemometrical Approach***,** Food Sci. Technol. Res., **16** (2010) (2) 123-134
Zrno pšenice (n=14)/8 teških elemenata	PCA CA	analiza međuzavisnosti sadržaja teških elemenata, sličnosti i razlika između pšenice uzgajane u različitim regionima i identifikacija izvora	Škrbić B., Đurišić-Mladenović N., Cvejanov J. *Principal Component Analysis of Trace Elements in Serbian,* Wheat, J. Agric. Food

		elemenata	Chem., **53** (2005) 2171-2175.
Sediment (n=45), ulična prašina (n=13), čestice iz vazduha (brojni uzorci)/30 nesupstituisanih PAH, 18 alkilovanih homologa PAH, 7 S- i O-PAH jedinjenja	PCA	identifikacija izvora zagađenja	Mai B., Qi S., Zeng E. Y., Qingshu Y., Zhang G., Fu J., Sheng G., Peng P., Wang Z., *Distribution of polycyclic aromatic hydrocarbons in the coastal region of Macao, China: Assessment of input sources and transport pathways using compositional analysis,* Environ. Sci. Technol. **37** (2003) 4855-4863
Sediment (n=407)/17 PCDD i PCDF	CA DA	identifikacija izvora zagađenja pomoću CA; DA je poslužila za potvrdu rezultata dobijenih CA i uočenih grupa uzoraka	Gotz R., Lauer R., *Analysis of sources of dioxin contamination in sediments and soil using multivariate statistical methods and neural networks,* Environ. Sci. Technol. **37**(2003) 5559-5565
Gasovita i čestična faza iz vazduha/39 PAH	FA/PCA [a]	identifikacija izvora zagađenja i razlike u prisustvu PAH u atmosferi dva grada	Ohura T., Amagai T., Fusaya M., Matsushita H., *Spatial distribution and profiles of atmospheric polycyclic aromatic hydrocarbons in two industrial cities in Japan,* Environ. Sci. Technol. **38** (2004) 49-55
Zemljište (n=37)/14 PAH	CA	analiza sličnosti i razlika između lokacija na kojima su uzeti uzorci	Motelay-Massei A., Ollivon D., Garban B., Teil M.J., Blanchard M., Chevreuil M., *Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France,* Chemosphere **55** (2004) 555-565
Gasovita i čestična faza iz vazduha/11 PCB, 5 PCDD, 6 PCDF	PCA MR	analiza korelacija između koncentracija ispitivanih jedinjenja i predviđanje značajnih izvora koji utiču na uočene razlike u koncentracijama	Ogura I., Masunaga S., Nakanishi J., *Quantitative source identification of dioxin-like PCBs in Yokohama, Japan, by temperature dependence of their atmospheric concentrations,* Environ. Sci. Technol. **38** (2004) 3279-3285
Zemljište (n=88)/16 EPA PAH	PCA	analiza korelacija između sadržaja	Golobočanin D.D., Škrbić B., Miljević

	CA	jedinjenja u uzorcima sa zagađenih i nezagađenih lokacija	N., *Principal component analysis for soil contamination with PAHs,* Chemom. Intell. Lab. Syst. **72** (2004) 219– 223
Zemljište (n= 53)/14 PAH	PCA/CA [b]	analiza korelacija između sadržaja jedinjenja i identifikacija izvora emisije	Yhang H.B., Luo Y.M., Wong M.H., Yhao Q.G., Yhang G.L., *Distributions and Concentrations of PAHs in Hong Kong Soils,* Environ. Poll. **141** (2006) 107-114
Gasovita i čestična faza iz vazduha/16 EPA PAH	PCA	identifikacija izvora zagađenja	Ravindra K., Bencs L., Wauters E., Hoog de J., Deutsch F., Roekens E., Bleux N., Berghmans P., Van Grieken R., *Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities,* Atmosph. Environ. **40** (2006) 771-785
Gasovita i čestična faza iz vazduha (n=51)/16 EPA PAH	FA/PCA [a] MR	identifikacija izvora zagađenja i sezonske razlike	Li J., Zhang G., Li X.D., Qi S.H., Liu G.Q., Peng X.Z., *Source seasonality of polycyclic atomatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China,* Sci. Total Environ. **355** (2006) 145-155
Humano mleko (n=61)/17 PCDD i PCDF	PCA	analiza prisustva i raspodele jedinjenja u uzorcima iz različitih zemalja (Japan i Kina)	Sun S.-J., Zhao J.-H., Liu H.-J., Liu D.-W., Ma Y.-X., Li L., Horiguchi H., Uno H., Iida T., Koga M., Kiyonari Y., Nakamura M., Sasaki S., Fukatu H., Clark G.C., Kayama F., *Dioxin concentration in human milk in Hebei province in China and Tokyo, Japan: Potential dietary risk factors and determination of possible sources,* Chemosphere **62** (2006) 1879-1888

Gasna faza vazduha iz prostorija različitih namena (n=92)/37 PCB i 9 PBDE[6]	PCA	identifikacija izvora zagađenja	Hazrati S., Harrad S., *Causes of variability in concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in indoor air,* Environ. Sci. Technol. **40** (2006) 7584-7589
Humani serum (n= 87)/80 PCB	PCA	identifikacija izvora izloženosti	Park H., Lee, S.-J., Kang J.-H., Chang Y.-S., *Congener-specific approach to human PCB concentrations by serum analysis,*, Chemosphere **68** (2007) 1699-1706
Kućna prašina (n=31)/41 PCB	PCA	identifikacija izvora zagađenja poređenjem raspodele jedinjenja u uzorcima sa komercijalnim PCB smesama (Aroclor)	Tan J., Cheng S.M., Loganath A., Chong Y.S., Obbard J.P., *Selected organochlorine pesticide and polychlorinated biphenyl residues in house dust in Singapore,* Chemosphere **68** (2007) 1675-1682
Čestice iz vazduha (n=63)/16 EPA PAH	PCA	Identifikacija izvora emisije	Ravindra K., Wauters E., Van Grieken R., *Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses,* Sci. Total Environ., **396** (2008) 100-110
Čestice iz vazduha/14 PAH	FA/PCA [a]	identifikacija izvora zagađenja	Akyuz M., Cabuk H., *Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey,* Sci. Total Environ. **405** (2008) 62-70
Zemljište (n=35)/11 PAH (nesupstituisanih i alkil-supstituisanih)	PCA	analiza razgradnje PAH (tzv. „weathering“ procesa)	Lamberts R., Johansen A.R., Andersen O., Christensen J.H., *Univariate and multivariate characterization of heavy fuel oil weathering and biodegradation in soil,* Environ. Poll. **156** (2008) 1-9
Adipozno tkivo porodilja	PCA	analiza korelacija između sadržaja	Tan J., Li Q.Q., Loganath A., Chong

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[6] PBDE-polibromovani difenileter

(n=83)/10 OCP, 41 PCB, 7 PBDE, 27 karakteristika donora iz upitnika (telesne osobine majke i novorođenčeta, način ishrane, bolesti, itd.)	regresija parcijalnih najmanjih kvadrata (PLSR) parcijalni najmanji kvadrati-diskriminaciona analiza (PLS-DA)	ispitivanih jedinjenja u tkivu i karakteristika donora	Y.S., Xiao M., Obbard J.P., *Multivariate data analyses of persistent organic pollutants in maternal adipose tissue in Singapore,* Environ. Sci. Technol. **42** (2008) 2681-2687.
Zemljište (n=7)/16 EPA PAH	FA/PCA [a]	Identifikacija izvora zagađenja	Agarwal T., Khillare P.S., Shridhar V., Ray S., *Pattern, sources and toxic potential of PAHs in the agricultural soil of Delhi, India,* J. Hazard. Mat. **163** (2009) 1033-1039
Zemljište (n=168)/9 teških elemenata, 7 PCDD, 10 PCDF	PCA	identifikacija izvora zagađenja	Vives I., Muller A.,Umlauf G., Christoph E.H., Mariani G., Skejo H., Cenci R.M., Sena F., Beone G.M., *Levels of PCDD/Fs and trace elements in superficial soils of Pavia Province (Italy),* Environ. Int. **34** (2008) 994-1000
Mleko (n=347)/proteini, masnoća, 5 makroelemenata, 9 elemenata u tragovima	PCA	analiza sezonskih i prostornih promena, korelacija između jedinjenja, uočavanje glavnih izvora promenljivosti sastava	Sola-Larranga C., Navarro-Blasco I., *Chemometric analysis of minerals and trace elements in raw cow milk from the community of Navarra, Spain,* Food Chem. **112** (2009) 189-196
Sediment (n=300)/8 teških elemenata, suma 12 PAH, suma 7 indikatorskih PCB, ukupni sadržaj organskog ugljenika, procenat „najfinijih“ čestica (tj. onih	CA PCA	analiza sličnosti i razlika između lokacija na kojima su uzeti uzorci, identifikacija izvora zagađenja	Casado-Martinez M.C., Forja J.M., DelValls T.A., *A multivariate assessment of sediment contamination in dredged materials from Spanish ports,* J. Hazard. Mater. **163** (2009) 1353-1359
Čestice iz vazduha/9 elemenata	PCA	identifikacija izvora zagađenja	Đorđević D., Mihajlidi-Zelić A., Relić D., Ignjatović Lj., Huremović J., Stortini A.M., Gambaro A., *Size-segregated mass concentration and water soluble inorganic ions in an urban aerosol of the Central Balkans (Belgrade),* Atmosp. Environ. **46** (2012) 309-317

Sediment (n=35)/12 elemenata	PCA CA	identifikacija izvora zagađenja	Sakan S., Đorđević D., Dević G., Relić D., Anđelković I., Đuričić J., *A study of trace element contamination in river sediments in Serbia using microwave-assisted aqua regia digestion and multivariate statistical analysis,* Microchem. J. **99** (2011) 492–502
Med (n=15)/20 elemenata	PCA CA	klasifikacija uzoraka prema određenim sadržajima elemenata i analiza sličnosti i razlika između lokacija na kojima su uzeti uzorci	Yucel Y ., Sultanoglu P., *Determination of industrial pollution effects on citrus honeys with chemometric approach,* Food Chem. **135** (2012) 170–178
Rečna voda (n=4032)/16 elemenata	PCA FA CA	analiza prostornih razlika u sadržajima elemenata u rečnim vodama sa različitih lokacija, identifikacija izvora zagađenja	Li S., Zhang Q., *Spatial characterization of dissolved trace elements and heavy metals in the upper Han River (China) using multivariate statistical techniques,* J. Hazard. Mat. **176** (2010) 579–588
Sediment (n=50)/20 PCB	PCA	analiza prostornih razlika u sadržajima jedinjenja u sedimentima sa različitih lokacija, identifikacija izvora zagađenja	Yang H., Zhuo S., Xue B., Zhang C., Liu W., *Distribution, historical trends and inventories of polychlorinated biphenyls in sediments from Yangtze River Estuary and adjacent East China Sea*, Environ. Poll. **169** (2012) 20-26
Zemljište, kora drveta, ulična prašina, bele plesni (n=8) /10 teških elemenata	PCA	identifikacija izvora zagađenja	Škrbić B., Milovac S., Matavulj M., *Multielement profiles of soil, road dust, tree bark and wood-rotten fungi collected at various distances from high-frequency road in urban area,* Ecolog. Ind. **13** (2012) 168–177

[a] U radu se pojmovi faktorska analiza i analiza glavnih komponenata, kao i pojmovi faktor i komponenta koriste kao sinonimi, što upućuje da je do pogrešnog korišćenja ovih pojmova koji se odnose na slične, ali ipak različite tehnike, kao što je opisano u poglavlju 2.2.1, došlo zbog toga što se u programu za primenu statističkih metoda, opcija za PCA nalazi pod FA.

[b] Najpre je izvršena analiza glavnih komponenata ulaznih podataka, nakon čega su dobijeni rezultati (tzv. „*score*“ vrednosti) podvrgnuti analizi grupisanja.

2.2.1.1. Analiza glavnih komponenata

Analiza glavnih komponenata (engleska skraćenica PCA prema *Principal Component Analysis*) je tehnika formiranja novih (izvedenih) promenljivih, koje su linearne kombinacije izvornih (polaznih) promenljivih. Tako, PCA predstavlja metodu smanjenja većeg broja promenljivih na manji broj novih promenljivih, koje se nazivaju glavne komponente. Najčešće manjim brojem ovih novih promenljivih – glavnih komponenti – objašnjen je veći deo varijanse[7] polaznih promenljivih, što omogućava lakše sagledavanje multidimenzione prirode originalnih podataka, uključujući i vizuelno predstavljanje izvornih podataka (multidimenzione prirode). Mogućnosti analize glavnih komponenata opisana je još s početka 20. veka (Pearson, 1901) ali šira primena ove tehnike, zbog kompleksnog računa, pričekala je razvoj personalnih računara u poslednjim decenijama prethodnog veka (Manly, 1986)**.** Često se uz analizu glavnih komponenata veže **faktorska analiza (FA)**, bliska, ali koncepcijski različita tehnika. Naime, faktorska analiza je slična metodi glavnih komponenata, i takođe se koristi za opis varijanse između promenljivih na osnovu manjeg broja novih promenljivih (tzv. faktora). Kod faktorske analize, za razliku od analize glavnih komponenata gde se objašnjava varijansa, cilj je objašnjenje kovarijanse[8], tj. onog dela ukupne varijanse, koji jedna promenljiva deli sa ostalim iz posmatranog skupa promenljivih (Pecina, 2006). Razlog više za čestu zamenu pojmova analize

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[7] Varijansa ili disperzija je pojam iz teorije verovatnoće i statistike. Oznaka varijanse u odnosu na celu populaciju je σ^2, dok je za izdvojeni skup uzoraka iz populacije S^2 ili s^2 (zavisno od načina izračunavanja objašnjenih u narednom tekstu). Ona predstavlja srednju vrednost odstupanja vrednosti slučajne promenljive od njene srednje vrednosti; najčešće korišćena formula za izračunavanje varijanse skupa izdvojenih uzoraka je $S^2 = \frac{\sum(X-M)^2}{N}$ ili $s^2 = \frac{\sum(X-M)^2}{N-1}$ gde je M srednja vrednost uzoraka, X izmerena vrednost, N broj uzoraka. Određivanje varijanse je prvi korak pri određivanju standardne devijacije, σ (ili s), koja predstavlja meru odstupanja u populaciji (ili skupu uzoraka izdvojenih iz populacije), a računa se kao kvadratni koren vrednosti varijanse. Obe vrednosti predstavljaju apsolutne vrednosti odstupanja (rasipanja) vrednosti oko srednje vrednosti, dok se kao relativni pokazatelj odstupanja često koristi relativna standardna devijacija izražena u procentima, izračunata kao $RSD = \frac{s}{M} \cdot 100$.

[8] Kovarijansa je mera međusobne (linearne) zavisnosti (ili mera jačine veze) dve slučajne veličine (na primer, X i Y). Kada se radi o dve iste promenljive njihova kovarijansa jednaka je varijansi. Kovarijansa se označava kao σ_{XY} ili cov(X,Y) za populaciju, tj s_{XY} za izdvojeni skup uzoraka iz populacije; matematički to je srednja vrednost proizvoda razlika slučajnih veličina i njihovih (odgovarajućih) srednjih vrednosti: $s_{XY} = \frac{\sum(X-M_X)\cdot(Y-M_Y)}{N-1}$

glavnih komponenata i faktorske analize je i činjenica da se PCA u nekim statističkim paketima (kao što je STATISTICA i SPSS) pronalazi kao opcija FA.

Ulazni set sa podacima za analizu glavnih komponenata čine *p* promenljivih smeštenih u kolonama i *n* uzoraka (slučajeva) u redovima; dobijeni set ima oblik matrice *p* x *n* (tabela 2.6).

Tabela 2.6. Prikaz ulaznih podataka za analizu glavnih komponenata

	Promenljive				
	X_1	X_2	X_3	...	X_p
Uzorak 1	x_{11}	x_{12}	x_{13}		x_{1p}
Uzorak 2	x_{21}	x_{22}	x_{23}	...	x_{2p}
:	:	:	:	...	:
Uzorak n	x_{n1}	x_{n2}	x_{n3}	...	x_{np}

Cilj analize je kreiranje *p* linearnih kombinacija izvornih promenljivih, koje se nazivaju glavne komponente (Pecina, 2006).

$$\xi_1 = w_{11} X_1 + w_{12} X_2 + \ldots + w_{1p} X_p$$
$$\xi_2 = w_{21} X_1 + w_{22} X_2 + \ldots + w_{2p} X_p$$
$$: : : : : :$$
$$\xi_p = w_{p1} X_1 + w_{p2} X_2 + \ldots + w_p p X_p \qquad 2.1$$

gdje su ξ_1, ξ_2 ... ξ_p , *p* glavnih komponenata i w_{ij} su koeficijenti (*weights* i) tj. konstante koje čine koeficijente *j*-te promenljive za *i*-tu glavnu komponentu.

Konstante w_{ij} se procenjuju tako da:

1. prva glavna komponenta, ξ_1, objašnjava maksimum varijanse podataka, druga glavna komponenta, ξ_2, objašnjava maksimum varijanse, koja je ostala neobjašnjena prvom, i tako dalje.

2. $w^2_{i1} + w^2_{i2} + \ldots + w^2_{ip} = 1 \quad i = 1 \ldots p \qquad 2.2$

3. $w_{i1}\, w_{j1} + w_{i2}\, w_{j2} + \ldots + w_{ip}\, w_{jp} = 0$ za sve $i \neq j \qquad 2.3$

Konstante w_{ip} nazivaju se svojstveni vektori ili „skriveni“ vektori (tzv. *eigenvectors*) i geometrijski su, u dvodimenzionalnoj strukturi, u stvari, *sinusi* i *cosinusi* uglova između novih osa tj. glavnih komponenata. Transformisane vrednosti izvornih promenljivih putem jednačine 2.1 predstavljaju rezultate glavnih komponenata (*principal component scores*) (Pecina, 2006) tj. koordinate pozicija uzoraka u novom koordinatnom sistemu zadržanih glavnih komponenata.

Suma varijansi svih izvornih promenljivih je ukupna varijansa. Deo te ukupne varijanse objašnjen jednom glavnom komponentom naziva se svojstvena vrednost ili „skriveni“ koren (tzv. *eigenvalue*). Svojstvena vrednost je, kako je već objašnjeno u načinu procene svojstvenih vektora, w_{ij}, najveća za prvu glavnu komponentu i za svaku sledeću njena je vrednost sve manja. Suma svih svojstvenih vrednosti jednaka je ukupnoj varijansi. Cilj je, iteracijskim postupkom, izdvojiti što veći deo ukupne varijanse sa samo nekoliko prvih glavnih komponenata, što se uobičajeno izražava u kumulativnim procentima ukupne varijanse, i na taj način izvršiti smanjenje izvornih promenljivih (tj. dimenzionalnost ulaznog seta podataka). Proces dobijanja svojstvenih vektora i vrednosti ključni su matematički problem u analizi glavnih komponenata, koji se rešava pomoću rastavljanja svojstvenih vrednosti (S*ingular Value Decomposition*, SVD) (Pecina, 2006)

U radu sa PCA očekuje se da će većina novih promenljivih (glavnih komponenata) objašnjavati tako malu varijansu ulaznih podataka da se ona može zanemariti, tj. da će većinu informacija poneti prvih nekoliko glavnih komponenti (ξ), čije su varijanse značajne veličine. Dakle, cilj je da se iz velikog broja izvornih promenljivih izdvoji tek nekoliko glavnih komponenti, koje nose većinu informacija.

PCA nije osetljiva na probleme normalnosti, linearnosti i homogenosti varijansi. Čak šta više, određena doza multikolinearnosti čak je i poželjna, jer se bolji rezultati mogu postići kad su izvorne varijable značajno pozitivno ili negativno korelisane (Pecina, 2006).

2.2.1.2. Analiza grupisanja

Analiza grupisanja (engleska skraćenica **CA** prema *Cluster Analysis*) je takođe metoda smanjenja dimenzije podataka. Ovom metodom vrši se grupisanje uzoraka u relativno homogene grupe (klastere), tako da su uzorci koji pripadaju nekoj grupi sličniji jedan drugom (u odnosu na promenljive od interesa), nego što su to uzorci koji pripadaju drugim grupama (Pecina, 2006). Geometrijski koncept analize grupisanja je vrlo jednostavan: svaki uzorak se prikazuje kao tačka u *p*-todimenzionalnom prostoru, gdje je *p* broj promenljivih, koje opisuju uzoraka.

Moguće je izvršiti grupisanje i promenljivih, pri čemu su promenljive u jednoj grupi slične s obzirom na određene posmatrane uzorke. Geometrijski, slično grupisanju uzoraka, sada se u *n*-todimenzionalnom prostoru uzoraka prikazuju promenljive. Cilj analize grupisanja ove vrste je identifikacija grupa, koji sadrže promenljive međusobno slične u posmatranom setu uzoraka.

Prvi korak u analizi grupisanja je izbor merila sličnosti, koje u dvodimenzionalnom prostoru predstavlja udaljenost između dve tačke. Sledeći korak je izbor između dve osnovne vrste analize grupisanja: hijerarhijske i nehijerarhijske.

Hijerarhijska analiza grupisanja, kako i samo ime kaže, radi na principu algoritma, koji formira grupe (klastere) po hijerarhiji tako da je u svakom sledećem nivou broj klastera manji za jedan. Ova metoda analize se najčešće prikazuje grafički, dendrogramom. Dva su osnovna tipa ove metode:

a) aglomerativna ili rastuća, u kojoj svaki uzorak (objekat) započinje kao zasebni klaster, čiji se broj u sledećim koracima smanjuje dok se svi na kraju ne grupišu u jedan veliki klaster. Specifičnost analize grupisanja je da su rezultati iz prethodnog nivoa uvek uključeni u naredni;

b) diviziona, ukoliko proces grupisanja ima drugi smer, tj. opadajući, koji započinje jednim velikim klasterom sa svim uzorcima, a zatim se u sledećim koracima deli.

Obe metode dovode do istog rezultata, ali obrnutim redosledom.

Nekoliko je metoda poznato za formiranje grupa (klastera):

1. metoda centroida - svaku grupu predstavlja prosečni uzorak, tj. centroid, a udaljenost između klastera je Euklidsko rastojanje[9] ili kvadrat Euklidskog rastojanja između njihovih centroida;

2. pojedinačna povezanost ili metoda najbližeg suseda (engleski *Single Linkage or the Nearest Neighbor Method*) - minimalna udaljenost između svih mogućih parova uzoraka u dve grupe;

3. potpuna povezanost ili metoda najdaljeg suseda (engleski *Complete Linkage or Farthest Neighbor Method*) - najveća udaljenost između svih mogućih parova uzoraka u dve grupe;

4. prosečna povezanost (engleski *Average Linkage*) - prosečna udaljenost između svih mogućih parova uzoraka u dve grupe;

5. Ward-ova metoda (metoda najmanje sume kvadrata) – najčešće korišćena metoda kod koje se ne izračunava udaljenost između grupa, nego maksimizira homogenost unutar grupe. Merilo homogenosti je suma kvadrata unutar grupe (*error sum of squares - ESS*). U početku je svaki uzorak predstavljen jednim klasterom, te u svim klasterima ESS iznosi nula. U sledećem koraku se dva uzorka, iz svih mogućih kombinacija, stapaju u jedan klaster, sa najmanjom ESS, pa je broj klastera za jedan manji od broja uzoraka.

Za razliku od hijerarhijske, u nehijerarhijskoj klaster analizi (takođe poznata kao metoda *k*-sredina, engleski *k*-means clustering method) broj klastera (*k*) i njihovi centroidi moraju biti poznati pre analize. Početni klasteri formiraju se uklapanjem svih preostalih $n - k$ uzoraka najbližem centroidu. Rešenje ovoga tipa analize daleko je više zavisno od sposobnosti analitičara pri izboru centroida u početnoj fazi. U primeni nehijerarhijskih metoda grupisanja mora se voditi računa da su ove metode osetljive na prisustvo nestandardnih opservacija („*outliers*“)[10].

Interpretirati uočenih grupa znači objasniti njihov sadržaj, tj. opisati uočene grupe (klastere) rečima ili im dati ime.

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[9] Osnovna mera udaljenosti između pojedinačnih uzoraka je Euklidsko rastojanje. Jednostavno Euklidsko rastojanje (*simple euclidean distance*), D_E, geometrijski, je dužina hipotenuze pravouglog trougla (koja spaja uzorke 1 i 2) u kojem su katete vrednosti dve promenljive (*X* i *Y*). U mnogim analizama koristi se kvadrat Euklidskog rastojanja *(squared euclidean distance)* D_E^2: $D_{E\,12}^2 = (x_2-x_1)^2 + (y_2-y_1)^2$. Što su dva uzorka (1 i *2*) sličnija u odnosu na dve posmatrane promenljive *X* i *Y*, to je vrednost D_E^2 manja. Iako više od tri promenljive fizički nije moguće predstaviti u koordinatnom sistemu, matematički je moguće predstaviti kvadrat Euklidskog rastojanja za *p* promenljivih (Pecina, 2006): $D_{E\,ij}^2 = \sum(x_{ik} - x_{jk})^2$, gdje je $D_{E\,ij}^2$ kvadrat Euklidskog rastojanja između uzoraka *i* i *j* , x_{ik} je vrednost *k*-te promenljive za *i*-ti uzorak, x_{jk} je vrednost *k*-te promenljive za *j*-ti uzorak, a *p* je broj promenljivih.

[10] Nestandardne opservacije ili uzorci („*outliers*“) nemaju preciznu definiciju u statistici. Pod njima se podrazumevaju oni uzorci koji su nekonzistentni sa preostalim delom podataka (Kovačić, 1994).

2.2.1.3. *Diskriminaciona analiza*

Diskriminaciona analiza (**DA**) ima široku primenu u situacijama gde je osnovni cilj uočavanje grupe kojoj neki uzorak pripada, tj. predviđanje uspešnosti grupisanja uzoraka u prethodno definisane podgrupe u okviru polaznog skupa uzoraka, kao i pronalaženje one promenljive (ili više njih) koja je najzaslužnija za postignuto grupisanje (Pecina, 2006).

Diskriminaciona analiza je određena diskriminacionom funkcijom, pod pretpostavkom da postoji normalna raspodela unutar grupa, a da je promenljivost i struktura kovarijansi grupa jednaka (Pecina, 2006).

Linearni model diskriminacione funkcije je:

$$Z = W_1 X_1 + W_2 X_2 + W_3 X_3 + ... + W_n X_n \qquad 2.4$$

gdje je Z diskriminacioni rezultat (*score*), W_i je diskriminacioni koeficijent (ili opterećenje) promenljive *i*, a X_i je nezavisna promenljive *i.* Diskriminaciona funkcija 2.4 linearna je kombinacija diskriminacionih promenljivih, koja maksimizuje udaljenost sredina grupa, tj. razdvaja grupe. Grupe se bolje razdvajaju ukoliko se manje njihovi elementi (pojedinačni uzorci) preklapaju. Sredina grupe je centroid, i predstavlja srednju vrednost diskriminacionih rezultata („skorova“), *Z*, za sve elemente unutar određene grupe. Metoda određivanja udaljenosti zavisi od tipa problema, promenljivih, reda veličina, itd. Većina situacija može biti rešena određivanjem Mahalanobis-ove udaljenosti[11].

Maksimalni broj diskriminacionih funkcija koje se mogu izvesti je: ili jedna manje od broja grupa ili jedna manje od broja diskriminirajućih promenljivih - koji god je od ovih brojeva manji. Pouzdanost diskriminacione analize može se ispitati multivarijacionim testovima, pri čemu je često korišćem Wilks’ λ test.

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[11] Mahalanobis-ova udaljenost, *DM*, predstavlja statističku udaljenost između dve tačke koja uključuje kovarijanse ili korelacije između promenljivih. To je, ujedno, i jedna od najpouzdanijih mera udaljenosti između dve multivarijacione skupa uzoraka. Formula za izračunavanje kvadrata Mahalanobis-ove udaljenosti, $D_M^{\,2}$, između uzoraka *i* i *j* sa dve promenljive, 1 i 2, je:

$$D_M{}^2{}_{ij}=\frac{1}{1-r^2}\left(\frac{(x_{i1}-x_{j1})^2}{s_1^2}+\frac{(x_{12}-x_{j2})^2}{s_2^2}-\frac{2r\left(x_{i1}-x_{j1}\right)+(x_{i2}-x_{j2})}{s_1 s_2}\right)$$

gde su s_1^2 i s_2^2 varijanse za promenljive 1 i 2, a r je njihov korelacioni koreficijent.

Primena i tumačenje diskriminacione analize vrlo je slična višestrukoj regresiji (ukratko predstavljena u narednom poglavlju). Ključna razlika je u vrsti zavisne promenljive: ona je u višestrukoj regresiji merna (kvantitativna), dok je u diskriminacionoj analizi kategorijska (kvalitativna).

Diskriminaciona analiza je osetljiva na multikolinearnost nezavisnih promenljivih i na odnos veličine uzorka i broja nezavisnih promenljivih. Mnoge studije ukazuju da je potrebno zadovoljiti odnos da na 20 uzoraka ide po jedna nezavisna promenljiva, ali je važno spomenuti da smanjivanjem veličine uzorka i njenim približavanjem broju nezavisnih promenljivih rezultati analize postaju nepouzdani. Analiza zavisi i od veličine samih grupa: veličina najmanje grupe mora biti veća od broja nezavisnih promenljivih. Čak i onda kada su svi ovi uslovi ispunjeni, velika odstupanja u veličinama grupa mogu uticati na klasifikaciju uzoraka: veće grupe tada imaju disproporcionalno veću šansu u klasifikaciji, te je takvu situaciju potrebno korigovati pre same analize.

2.2.1.4. Višestruka regresija

Višestruka (multipla regresija) je statistička je metoda za analizu povezanosti kvantitativnih promenljivih i i to: između jedne zavisne (Y) i više nezavisnih promenljivih (X_1, X_2, X_3, ...X_n). Može se opisati modelom:

$$Y_1 = X_1 + X_2 + X_3 + ... + X_n \quad 2.5$$

Cilj analize višestruke regresije je predviđanje promene zavisne promenljive kao reakcije na promene u nekoliko nezavisnih promenljivih. Ovaj cilj se najčešće postiže principom najmanjih kvadrata (*least squares*). U stvari, višestruka regresija je tehnika pronalaženja adekvatnog modela tj. linearne kombinacije, koja se sastoji od skupa ili podskupa q nezavisnih promenljivih X_i, i = 1, ... , q, koje procenjuju nepoznatu regresijsku funkciju zavisne promenljive Y (Pecina, 2006).

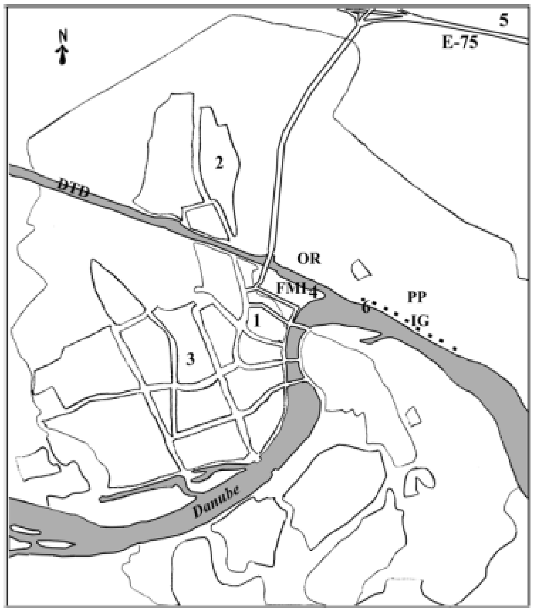
3. EKSPERIMENTALNI DEO

U okviru ovog dela najpre su predstavljene metode analize izabranih zagađujućih jedinjenja u različitim uzorcima, čiji rezultati su uključeni u baze podataka analizirane primenom izabranih hemometrijskih tehnika. Nakon opisa analitičkih metoda, sledi opis formiranih baza podataka i postupaka pri njihovoj hemometrijkoj obradi.

3.1. Analiza zagađujućih jedinjenja u izabranim uzorcima

3.1.1. Analiza PAH u zemljištu

Uzimanje uzoraka površinskog zemljišta u Novom Sadu je izvršeno na pet lokacija u gradu i okolini (Škrbić i sar., 2005). Uzorci su uzimani u toku jednog dana, bez vetra i padavina na početku januara meseca 2001. godine. Uzorci zemljišta su uzeti sa dubine 0-5 cm pomoću čelične lopatice. Na svakoj lokaciji uzeta su četiri pojedinačna uzorka (~250 g) sa površine 20 x 50 m. Uzorci sa jedne lokacije su pomešani radi dobijanja kompozitnog, reprezentativnog uzorka, i to iz školskog dvorišta (uzorak br. 1 u centru grada, u blizini međumesne autobuske stanice i br. 2 u predgrađu, u blizini Rafinerije nafte), iz privatne bašte u širem centru Novog Sada, u stambenoj zoni sa individualnim grejanjem domaćinstava (br. 3), industrijske zone, u blizini silosa za smeštaj pšenice, na obali kanala Dunav-Tisa-Dunav, nasuprot Rafinerije nafte (br. 4) i sa obradivog zemljišta pored autoputa Beograd-Novi Sad, u blizini benzinske pumpe (br. 5) (prikazano na slici 3.1).



Slika 3.1. Mapa Novog Sada sa lokacijama na kojima su uzeti uzorci zemljišta (brojevi 1-5 označavaju lokacjie na kojima su uzeti uzorci zemljišta, OR-rafinerija nafte, PP-termoelektrana, FMI-silosi za pšenicu, IG-reni bunari; na lokaciji br. 6 uzet je uzorak sedimenta koji nije predmet istraživanja u ovom radu)

Uzorci su stavljeni u staklene flaše prethodno pripremljene po procedure pranja posuđa koje se koristi za analizu zagađujućih organskih jedinjenja[12] i odneti u laboratoriju. Pre analize izvršeno je njihovo mešanje i prosejavanje kroz sito, prečnika otvora 2 mm, radi uklanjanja krupnijih grumena i biljnih ostataka. Na ovaj način je dobijeno pet kompozitnih uzoraka zemljišta (oko 1 kg), koji su smešteni u tamne staklene flaše i ostavljeni na temperaturi od 4°C do analize.

Korišćeni organski rastvarači su bili visokog stepena čistoće (za analizu rezidua). Natrijum sulfat, silika gel i aluminijum oksid su pre upotrebe aktivirani zagrevanjem na 180°C u toku 24 sata; destilovana voda je pre korišćena prečišćena heksanom. U toku rada, posuđe je umotavano u aluminijumsku foliju radi sprečavanja degradacije PAH-ova u dodiru sa svetlošću.

Primenjena metoda za izdvajanje PAH-ova se bazira na metodi Lee-a i sar. 1987. Ukratko, izvršena je Soxhlet ekstrakcija 10 g uzorka sa smesom aceton/heksan (59:41 v/v) u toku 12 h. Dobijeni ekstrakt je ispran 2%-tnim rastvorom $KHCO_3$, a zatim je heksanska faza odvojena i

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[12] Posuđe se pere prvo deterdžentom, ispira česmenskom i destilovanom vodom, redom, a zatim acetonom, nakon čega se vrši sušenje na 110°C u toku 24 sata.

propuštena kroz sloj bezvodnog Na_2SO_4. Tako dobijeni ekstrakt je koncentrisan uparavanjem na rotacionom vakuum uparivaču, nakon čega je prebačen u kolonu sa aktiviranim i kondicioniranim silika gelom na čijem vrhu se nalazi sloj bezvodnog Na_2SO_4. Kroz kolonu je najpre propuštan heksan (odbačen), a zatim smesa dihlormetana i heksana (40:60 v/v). Ovaj drugi eluat je sakupljen, uparen i rastvoren u i-oktanu, nakon čega je vršeno njegovo dalje prečišćavanje na sloju aluminijum oksida (zaštićen od vlage sa slojem bezvodnog Na_2SO_4). Heksanski eluat je odbačen, a frakcija sa PAH-jedinjenjima je potisnuta sa sloja pomoću toluena. Dobijeni eluat je koncentrisan do tačno poznate zapremine (gravimetrijski proverene) i analiziran na gasnom hromatografu sa plameno jonizacionim detektorom (HP 6890). Korišćena je kapilarna kolona HP-5 (dužine 30 m, unutrašnjeg prečnika 0,32 mm, debljine filma 0,25 µm). Razdvajanje PAH-jedinjenja izvršena je korišćenjem sledećeg temperaturnog programa: početna temperatura 50°C, 3 min, 10°C/min do 300°C, 4 min. Gas nosač je helijum, protoka 2,2 ml/min. Temperatura injektora je podešena na 290°C, a detektora na 310°C. Zapremina uzorka koji se unosi u gasni hromatograf je 1 µl. Kvantitativna analiza je izvršena metodom spoljašnjeg standarda, korišćenjem pet kalibracionih rastvora smese 16 EPA PAH jedinjenja, a identifikacija PAH-ova je izvršena poređenjem retencionih vremena. Granice detekcije za primenjenu metodu za pojedinačna jedinjenja su bile u rasponu od 5 do 10 µg/kg. Slepa proba nije pokazala prisustvo kontaminacije korišćenog posuđa i hemikalija. Efikasnost metode je 65-90% za ispitanih 16 EPA PAH jedinjenja. Analiza svakog uzorka rađena je 2 puta i rezultati predstavljaju srednju vrednost ovih ponavljanja.

3.1.2. Analiza OCC u zemljištu

U istim uzorcima čije sakupljanje je opisano u prethodnom poglavlju (3.1.1), izvršeno je ispitivanje prisustva organohlornih jedinjenja, OCP i indikatorskih PCB (Škrbić i sar., 2007). Ekstrakcija uzorka i prečišćavanje dobijenih ekstrakata izvršeno je u skladu sa metodama EPA 3540,3660, 3665 i 3620 (EPA methods, 1986). Uzorci zemljišta (oko 20 g) ekstrahovani su smesom heksan/aceton (1:1, v/v) u Soxhlet aparatu u toku 12 časova. Nakon uklanjanja acetona i ispiranja dobijene organske faze vodom (destilovana voda prethodno ekstrahovana heksanom), vrši se desulfurizacija ekstrakta, tj. uklanjanje potencijalno prisutnog sumpora pomoću praha bakra, što je neophodno zbog smetnji koje može prouzrokovati sumpor u ekstraktu tokom analize elektron apsorbcionim detektorom. Nakon toga, ekstrakt se deli na dva dela: prvi deo se uparava na rotacionom uparivaču i prečišćava kolonskom hromatografijom sa aktiviranim Florisilom, eluiranjem sa 6%, 15% i 50% etiletrom u heksanu, uz odvojeno sakupljanje sve tri frakcije radi analize prisutnih OCP-jedinjenja različite polarnosti; drugi deo se najpre prečišćava koncentrovanom sumpornom kiselinom (dobija se bezbojni ekstrakt), a zatim se uvodi u kolonu sa Florisilom na čijem vrhu se nalazi bezvodni Na_2SO_4, i eluiranje PCB-frakcije se vrši pomoću petroletra. Svi sakupljani eluenti se uparavaju, najpre na rotacionom uparivaču, a zatim u struji azota skoro do suva, i, pre analize, rastvore se u 1 ml heksana (gravimetrijski proverena zapremina).

Analiza dobijenih rastvora vršena je na gasnom hromatografu HP 6890 sa kapilarnom kolonom HP-5 (dužine 60 m, unutrašnjeg prečnika 0,32 mm, debljine filma 0,25 μm), povezanom sa elektron-apsorpcionim detektorom (ECD). Korišćen je sledeći temperaturni program: 120^{o}C, 2 min, 10^{o}C/min do 180^{o}C, 5^{o}C/min do 290^{o}C. Kao gas nosač korišćen je helijum, protoka 2,2 ml/min. Temperatura injektora je 290^{o}C, a detektora 310^{o}C. Zapremina uzorka koji se unosi u gasni hromatograf je 1 μl. Identifikacija i kvantifikacija OCP-ova i PCB-ova je izvršena metodom spoljašnjeg standarda, na osnovu pet kalibracionih rastvora dobijenih razblaživanjem osnovnog standardnog rastvora PCB smese 6 indikatorskih kongenera (PCB 28, 52, 101, 138, 153, 180).

Granice detekcije za primenjenu metodu za pojedinačna organohlorna jedinjenja su bile u rasponu od 0,04 do 0,1 ng/g. Provera metode i efikasnost su određeni analizom slepe probe i analizom „spajkovanog“ uzorka. Analiza slepe probe pokazala je da nije bilo kontaminacije korišćenog posuđa i hemikalija. „Spajkovan“ uzorak je pripremljen dodavanjem poznate zapremine standardnog rastvora u uzorak koji je sadržao poznati (najmanji) sadržaj organohlornih jedinjenja (uzorak 5). Primenjena su dva nivoa „spajkovanja“, 0,5 i 5 ng/g suve materije (s.m.). Spajkovan uzorak je ostavljen da bi došlo do uravnoteženja dodatih jedinjenja u matriksu, a zatim je preipremljen i analiziran pet puta, po pomenutoj proceduri. Efikasnost je izračunata kao razlika koncentracija u spajkovanom i odgovarajućem uzorku. Efikasnost za OCP-ove je bila u rasponu od 69-90% (relativna standardna devijacija je bila manja od 12%), a za PCB-ove je bila u rasponu od 66-85% (relativna standardna devijacija je bila manja od 15%), što je u saglasnosti sa preporukama Direktive Evropske unije (EC-SANCO/825/00, 2000).

Analiza svakog uzorka je vršena dva puta i rezultati su predstavljeni kao srednja vrednost ovih ponavljanja.

3.1.3. Analiza OCC u biološkim uzorcima

Analiza 7 indikatorskih PCB kongenera (6 kongenera koji ne ispoljavaju toksičnost dioksina („*non-dioxin lika“*), PCB 28, 52, 101, 138, 153, 180, i 1 kongener, PCB 118, po toksičnom dejstvu sličan dioksinu („*dioxin-like*“) u uzorcima humanog mleka izvršena je u saradnji sa istraživačima sa Farmaceutskog fakulteta Univerziteta medicinskih nauka u Poznanu (Škrbić i sar., 2010). Uzorci humanog mleka uzeti su od davaoca, majki-porodilja iz poljskog regiona Wielkopolska. Sve majke-davaoci bile su smeštene na Odeljenju za pedijatriju i ginekologiju Univerzitetske bolnice za ginekologiju u Poznanu. Uzimanje uzoraka i popunjavanje upitnika od strane donora organizovani su u skladu sa protokolom Svetske zdravstvene organizacije (SZO), prema kojem je potrebno ispuniti sledeće kriterijume: neophodno je da majka i dete koji se uključuju u ispitivanje budu zdravi, da je trudnoća prošla normalno, da majka doji samo jedno dete (ne blizance), a da u poslednjih 5 godina nije menjala mesto boravka. Jedina razlika u odnosu na protokol SZO je da su u ovom radu uključene drugorotkinje. Uzorci mleka su uzimani između treće i osme nedelje od porođaja. Majke-davaoci su ispunile dostavljeni upitnik koji se odnosio na njihove fizičke karakteristike, način ishrane i stanovanja. Prikupljanje uzoraka mleka i analiza je potvrđena od strane lokalnog komiteta za medicinsku etiku Univerziteta medicinskih nauka u Poznanu. Od svake majke je uzeto oko 50 mL mleka. Uzorci mleka su čuvani na temperaturi od -20^{o}C pre analize.

Sadržaj lipida u uzorcima mleka je određivan na osnovu metode Honga i sar. (1992). U pet grama mleka u kiveti od 50 ml, doda se 10 ml etanola i 9 ml heksana, centrifugira oko 1 min pri 4000 o/min. Gornji sloj se prebaci u erlenmajer sa bezvodnim Na_2SO_4. Vodeni sloj se ekstrahuje dva puta sa 7 ml heksana. Dobijeni heksanski ekstrakti se spoje i upare do suva, a određivanje sadržaja lipida u ekstraktu se vrši gravimetrijski.

Uzorci mleka su analizirani po proceduri SZO radi određivanja perzistentnih organskih materija (Colles i sar, 2008, Galceran i sar., 1993). Uzorak homogenizovanog mleka (masa oko 20 g) se pomeša sa 12 g florisila i 130 g bezvodnog Na_2SO_4, i dobijeni suvi prah se ubacuje u kolonu. Eluiranje se vrši sa 100 ml smese n-heksan/aceton (2/1, v/v), eluat se uparava do 3 ml i prečišćava dva puta sa koncentrovanom sumpornom kiselinom. Kombinovani ekstrakt se uparava do 0,5 ml i kvantitativno prenese na SPE kolonu sa Florisilom, koji je prethodno bio aktiviran sa 10 ml heksana. Eluiranje je izvršeno sa 5 ml heksana. Analiza je izvršena na gasnom hromatografu sa elektron-apsorpcionim detektorom (Shimadzu GC-14 A-Ni ECD). Korišćene su dve kolone: jedna slabo polarna-DB5 (dužine 60 m, unutrašnjeg prečnika 0,25 mm, debljine filma 0,25 µm), a druga polarna RT-1701 (dužine 60 m, unutrašnjeg prečnika 0,25 mm, debljine filma 0,25 µm). Gas nosač je helijum. Korišćen je sledeći temperaturni program: početna temperatura od 125^{o}C održavana je 2 min, zatim je izvršen kontrolisani temperaturni program od $7{,}5^{o}$C/min do 190^{o}C i 2^{o}C/min do krajnje temperature od 280^{o}C, koja je održavana 15 min. Temperatura injektora je 250^{o}C, a detektora 300^{o}C. Interni standardi (PCB 30 i 209) su dodati u koncentrovani ekstrakt pre gasno-hromatografske analize radi kvantifikacije.

Kontrola metode je izvršena analizom slepe probe, pri čemu se umesto mleka koristila destilovana voda. Provera efikasnosti je izvršena međulaboratorijskim ispitivanjem. Analiza 7 uzoraka mleka je izvršena na Institutu za primenjena istraživanja u oblasti zaštite životne sredine na Univerzitetu u Stokholmu i na Institutu za neorgansku i analitičku hemiju Univerziteta medicinskih nauka u Poznanu. Dobijeni rezultati su poređeni na osnovu statističkih kriterijuma, i pokazanao ja na osnovu t-testa nije bilo značajnih razlika. Granice detekcije indikatorskih PCB primenjenom metode analize su u rasponu 0,004-0,008 ng/ml mleka.

3.1.4. Postojana organska zagađujuća jedinjenja u vazduhu

Za ispitivanje sadržaja postojanih organskih zagađujućih jedinjenja u atmosferi izabrano je šest lokacija na teritoriji Republike Makedonije (Stafilov i sar., 2011). Geografski položaj ovih mesta prikazan je na slici 3.2:

1-U Lazaropolju ($41{,}540^{o}$S, $20{,}696^{o}$I), udaljeno od izvora zagađenja, smeštena je istraživačka stanica u okviru Sistema za automatsko praćenje zagađenja vazduha Ministarstva za zaštitu životne sredine i prostorno planiranje Republike Makedonije. Stanica je smeštena na planini na

1333 m nadmorske visine, okružena livadama i kućama, u blizini sela Lazaropolje, u zapadnom delu zemlje, u nacionalnom parku Mavrovo;

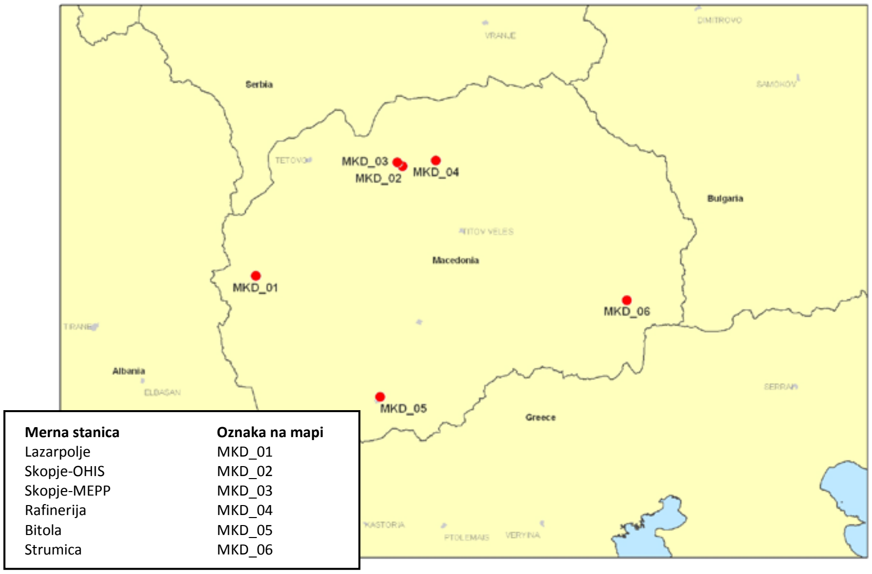
2-Merna stanica Skoplje-OHIS ($41{,}984^{o}$S, $21{,}475^{o}$I) smeštena je u Skoplju, gradu sa oko 550000 stanovnika. Mesto uzorkovanja je smešteno na 236 m nadmorske visine;

3-Merna stanica Skoplje-MEPP ($41{,}998^{o}$S, $21{,}446^{o}$I) smeštena je u centru Skoplja, u oblasti u kojoj je posađeno nisko drveće, a nalazi se na 200 m nadmorske visine, u blizini puta (5 m) sa intenzivnim saobraćajem;

4-Merna stanica Bujkovci ($42{,}005^{o}$S, $21{,}652^{o}$I) smeštena je u seoskom području na 312 m nadmorske visine, udaljeno 25 km od glavnog grada;

5-Merna stanica u Bitoli ($41{,}047^{o}$S, $21{,}356^{o}$I), gradu sa 95000 stanovnika, smeštena je u jugozapadnom delu Makedonije, blizu granice sa Grčkom. Mesto uzorkovanja u ovom gradu je udaljeno 250 m od puta, na 600 m nadmorske visine, u stambenom delu. Termoelektrana Bitola snage 660 MW je na oko 10 km od grada, sa godišnjom potrošnjom oko 8-9 miliona tona lignita.

6-Merna stanica u Strumici ($41{,}442^{o}$S, $22{,}665^{o}$I), najvećem gradu na istoku Makedonije, blizu granice sa Bugarskom, sa ukupnim brojem stanovnika u gradu i okolini od oko 150000, smeštena je na 300 m od puta, u stambenom delu grada, na 232 m nadmorske visine.



Merna stanica	Oznaka na mapi
Lazarpolje	MKD_01
Skopje-OHIS	MKD_02
Skopje-MEPP	MKD_03
Rafinerija	MKD_04
Bitola	MKD_05
Strumica	MKD_06

Slika 3.2. Lokacije mernih stanica u Makedoniji na kojima su uzeti uzorci vazduha radi analize teže isparljivih jedinjenja

Osim izvora zagađenja navedenih za merne stanice 3 (intenzivni saobraćaj) i 5 (termoelektrana), nije bilo drugih izvora zagađenja na mestima uzorkovanja; u stambenim mestima na lokacijama mernih stanica 1, 2, 4 i 6 koristi se drvo za zagrevanje domaćinstava.

Istraživači sa Fakulteta prirodnih nauka Univerziteta Sveti Ćirile i Metodije iz Skopja, zajedno sa kolegama iz Research Centre for Environmental Chemistry and Exotoxicology Masaryk University iz Brna, Češka Republika, su u okviru pilot studije razvoja mreže ispitivanja zagađujućih jedinjenja u Centralnoj i Istočnoj Evropi (MONET_CEEC) 2006, na navedenim lokacijama izvršili uzimanje uzoraka postojanih organskih zagađujućih jedinjenja iz vazduha, periodično u toku četiri meseca u periodu od 14. maja do 3. septembra 2007. godine. Uzeta su četiri uzorka na svakoj stanici (jedan uzorak se odnosi na period od 28 dana) u periodioma od 14.05-11.06.2007, 11.06-09.07.2007, 09.07-06.08.2007, i 06.08.-03.09.2007. Mora se naglasiti da je period od maja do septembra izabran za uzimanje uzoraka, jer je to vreme kada je najmanja emisija iz različitih izvora sagorevanja, odnosno period u godini kada je isparavanje teže isparljivih organskih zagađujućih jedinjenja najizraženije zbog visokih prosečnih temperatura. Za uzimanje uzoraka vazduha korišćen je pasivni uzorkivač sa poliuretanskom penom (PUF), koji se uglavnom koristi za uzorkovanje gasne faze teže isparljivih jedinjenja i deo fine čestične materije. Ovo omogućava informacije o prisustvu dugotrajnog zagađenja na izabranim lokacijama i može da posluži kao metoda za semikvantitativno poređenje u pogledu izvora zagađenja. Pasivni uzorkivač se sastoji od diska (od PUF, prečnika 15 cm, debljine 1,5 cm, gustine 0,03 g/m^3, tip N 3038, Gumotex, Češka Republika), smeštenog u čauru od nerđajućeg čelika. Uzorkivač je tako konstruisan da je disk zaštićen od taloženja materija iz vazduha, naročito krupnije čestične materije i direktne sunčeve svetlosti. Čaure se prvo peru vodom i ispiraju rastvaračem (acetonom) pre instalacije. Svi filteri se takođe peru prvo vodom, zatim ekstrahuju 8 sati u acetonu i 8 sati u dihlormetanu. Nakon toga se umotaju u aluminijsku foliju i ostave u polietilenske vrećice, i drže na niskoj temperaturi do upotrebe. Upotrebljeni filteri se takođe zamotaju u aluminijumsku foliju, ostave u polietilenske vrećice, smeste u mobilni frižider na temperaturi od 5^{o}C, i tako dopreme do laboratorije gde se do analize ostavljaju na temperaturi od -18^{o}C. Prosečna brzina vazduha kroz uzorkivač je 3,5 m^3/dan, što odgovara zapremini uzorka vazduha od 100 m^3 za period od 28 dana. Ovaj podatak je potreban da bi se koncentracija jedinjenja izrazila u ng ili pg po m^3 vazduha. Ovaj protok je u skladu sa prethodnim rezultatima (Shoeib i Harner, 2002). Međutim, i meteorološki uslovi koji vladaju u periodu uzimanja uzoraka utiču na ravnotežnu raspodelu između prisutne gasne faze i uzorkivača. Tako vetar utiče na brzinu uzorkovanja, pa se mogu očekivati veća odstupanja kada je brzina vazduha veća od 5 m/s. Ipak, sveobuhvatno istraživanje Klanove i sar. (2008) pokazalo je da je uticaj temperature i vetra prilikom korišćenja pasivnog uzorkivača mali. Klanova i sar. (2006) su u svojim daljim istraživanjima dokazali da se rezultati o prisustvu PAH, PCB, DDT i HCH u vazduhu dobijeni primenom pasivnog uzorkivača pri ukupnoj zapremini vazduha od 100 m^3 u vremenskom periodu od 28 dana slažu sa rezultatima dobijenim za ista jedinjenja primenom uobičajenim uzorkivača velikih zapremina. Harner i sar. (2006) su takođe pokazali da se pomoću pasivnih uzorkivača sadržaj zagađujućih jedinjenja vazduha može pouzdano proceniti.

Svi uzorci (odnosno poliuretanski diskovi nakon perioda izloženosti od 28 dana) ekstrahovani su pomoću dihlormetana u automatskom ekstraktoru tipa Buchi B-811. Zapremina rastvora nakon ekstrakcije se smanjuje u struji azota na sobnoj temperaturi. Razdvajanje PCB-ova od OCP-ova u ekstraktu se postiže na hromatografskoj koloni sa silika gelom (kiselo modifikovan). Analiza je izvršena na gasnom hromatografu HP 5890 i kapilarnoj koloni (Quadrex) sa elektron-apsorpcionim detektorom za PCB-ove (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 180), kao i OCP-ove (α-HCH, β-HCH, γ-HCH, δ-HCH, p,p'-DDE, p,p'-DDD, p,p'-DDT, o,p'-DDE, o,p'-DDD, HCB, pentahlorbenzen (PeCB)). Gasni hromatograf sa masenim detektorom (HP 6890-HP5972) i kapilarnom kolonom DB-5MS je korišćen za analizu 28 PAH-jedinjenja: naftalena (Naph), acenaftilena (Acy), acenaftena (Ace), fluorena (Flu), fenantrena (Phe), antracena (Ant), fluorantena (Fla), pirena (Py), benzo(a)antracena (BaA), krizena (CHR), benzo(b)fluorantena (BbF), benzo(k)fluorantena (BkF), benzo(a)pirena (BaP), indeno(1,2,3-cd)pirena (IcP), dibenzo(ah)antracena (DahA), benzo(ghi)perilena (BgP), bifenila (Bph), retena (RET), benzo(b)fluorena (BbFLu), benzonafto-tiofena (BNT), benzo(ghi)fluorantena (BgF), ciclopenta(cd)pirena (CPP), trifenilena (Triph), benzo(j)fluorantena (BjF), benzo(e)pirena (BeP), perilena (Per), dibenzo(ac)antracena (DacA), antantrena (Anth) i koronena (Cor)). Kao unutrašnji standard za PAH-ove je korišćen terfenil, dok je za analizu PCB i OCP korišćen PCB 121. Analizom slepe probe proveravan je stepen čistoće korišćenog posuđa i hemikalija, a efikasnost metode je ispitivana dodatkom („spajkovanjem“) surogat standarda u reprezentativni uzorka pre njegove ekstrakcije i to d8-naftalen, d10-fenantren, d12-perilen za analizu PAH-ova, odnosno PCB 30 i PCB 185 za analizu PCB (efikasnost je bila oko 75% za PCB-ove, oko 72% za PAH-ove). Efikasnost metode ispitana je i u odnosu na referentni materijal i dobijene su vrednosti u rasponu 88-103% za PCB, 75-98% za OCP i 72-102% za PAH.

Granica kvantifikacije svih jedinjenja je 0,2 ng/filteru, odnosno 2 pg/m^3.

3.1.5. Analiza teških elemenata u zemljištu

Uzimanje uzoraka površinskog zemljišta izvršeno je tokom 2009. godine na 15 lokacija na području Novog Sada, šest lokacija u prigradskom naselju Veternik i seoskim naseljima u blizini Novog Sada, Ravnom selu i Šajkašu, kao i na dve lokacije u centralnom parku Banja Luke (Škrbić i Đurišić-Mladenović, 2012). Uzorci su uzeti pomoću plastične lopatice, i to sa pet mesta u okviru pravougaone oblasti veličine 20 x 50 m, zatim su pomešani radi dobijanja kompozitnog uzorka od oko 1 kg. Uzorci su stavljeni u plastične vrećice na temperaturi od 4^{o}C do analize. Pre analize uzorci su osušeni na vazduhu, prosejani kroz sito prečnika otvora 2 mm i usitnjeni.

Metoda određivanja teških metala u uzorcima zemljišta zasniva se na EPA metodi 3051, koja se odnosi na mikrotalasnu digestiju sedimenta, zemljišta i otpadnog mulja (Luo i sar., 2007; Škrbić i Mladenović, 2010). Alikvot osušenog i usitnjenog uzorka (0,5 g), podvrgnut je digestiji u mikrotalasnoj peći (CEM MDS 2100) korišćenjem smese 7 ml koncentrovane azotne kiseline i 2 ml vodonik peroksida. Nakon digestije, rastvor je profiltriran (Whatman No.1), a filtrat se sakuplja u normalnom sudu od 25 ml i zatim razblaži do 25 ml ultra čistom vode (stepen čistoće I, električna otpornost 18,2 MΩ/cm; Millipore, France). Koncentracije Cd, CU, Cr, Ni, Pb i Zn određeni su atomskom apsorpcionom spektrometrijom sa grafitnom kivetom (Varian AAS 240/GTA 120) uz korekciju pozadinske apsorpcije korišćenjem deuterijumske lampe. Koncentracije Cd, Cu, Cr, Ni, Pb, i Zn određene su na sledećim talasnim dužinama: 228,8 nm, 324,8 nm, 357,9 nm, 232,0 nm, 283,3 nm, i 213,9 nm. Kvantifikacija teških elemenata je određena na osnovu kalibracione krive dobijene snimanjem apsorbanci kalibracionih standarda pripremljenih sa istom kiselinom, koja je korišćena za digestiju.

Efikasnost metode („recovery“) određena je analizom sertifikovanog referentnog materijala NIST SRM 2711. Koncentracije elemenata, sertifikovane i izmerene, u sertifikovanom materijalu su date u tabeli 3.1, kao i određena efikasnost metode.

Ponovljivost merenja je proveravana analizom rastvora datih elemenata nakon digestije jednog uzorka u šest paralelnih analiza. Preciznost, određena na osnovu standardne devijacije, je između 5% i 6%.

Tabela 3.1. Efikasnost (“recovery”*) primenjene metode pripreme i analize teških metala u uzorcima zemljišta određena u odnosu na sertifikovani materijal NIST SRM 2711 (US Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20 899).*

Teški metal	Izmerena vrednost, mg/kg	Sertifikovana vrednost, mg/kg	“Recovery”, %
Zn	363	350	104
Cu	101	114	89
Cr	43.3	47.0	92
Pb	838	1162	72
Ni	22.1	20.6	107
Cd	39.6	41.7	95

Analiza svakog uzorka je vršena dva puta i rezultat je predstavljen kao srednja vrednost. Koncentracija je izračunata nakon oduzimanja srednje vrednosti dobijene za slepu probu.

Dobijene su sledeće vrednosti granica detekcije i kvantifikacije: 0,6 i 1,98 μg/kg za Cd; 10 i 33 μg/kg za Co; 12,5 i 41,2 μg/kg za Cr; 46 i 13,2 μg/kg za Cu; 1 i 3,3 mg/kg za Fe; 10 i 33 μg/kg za Hg; 0,35 i 1,16 mg/kg za Mn; 20 i 66 μg/kg za Ni; 30 i 99 μg/kg za Pb; i 2 i 6,6 μg/kg za Zn.

3.2. Baze podataka

3.2.1. Policiklični aromatični ugljovodonici u zemljištu

Baza podataka o prisustvu PAH u površinskim uzorcima zemljišta iz različitih delova sveta, pripremljena je na osnovu dostupnih rezultata iz literature, objedinjavajući uzorke sa raznih lokacija Amerike, Australije, Azije i Evrope, uključujući i rezultate analize zemljišta iz Novog Sada (Škrbić i sar., 2005; Tabela 3.3). Pri tome, uzeti su u obzir samo ona PAH-jedinjenja koja su zajednička za sva izabrana istraživanja, a to su: fenantren (PHE), antracen (ANT), fluoranten (FLU), piren (PYR), krizen (CHR), benzo(a)antracen (BAA), benzo(a)piren (BAP), benzo(b+k) fluoranten (BFLU; predstavlja ukupni sadržaj oba izomera[13], benzo(b)fluorantena i benzo(k)fluorantena, s obzirom da u nekim radovima nije ostvareno njihovo hromatografsko razdvajanje) i benzo(ghi)perilen (BGHIP). Na ovaj način, dobijena je matrica veličine 9 promenljivih x 211 uzoraka.

Tabela 3.3. Opis uzoraka zemljišta uzetih iz literature o prisustvu PAH-jedinjenja u zemljištu sa različitih lokacija širom sveta

Lokacija	Broj uzoraka	Opis lokacije	Izvor
		Amerika	
Kosta Rika	1	Seoska sredina	Daly G L, Lei Y D, Castillo L E, Muir D C G, Wania, F, Atmos. Environ., 2007, **41**, 7339-7350
SAD	3	Zemljište zagađeno naftom	Bojes H K, Pope P G, Regular. Toxicol. Pharmacol., 2007, **47**, 288-295.
Brazil	8	Šuma, savana	Wilcke W, Amelung W, Kraus M, Martius C, Bandeira A, Garcia M, Organic Geochem., 2003, **34**, 1405-1417.
		Azija	
Kina	10	Park, seoska sredina, obradivo, industrijski region	Chung M K, Hu R, Cheng K C, Wong M H, Chemosphere, 2007, **67**, 464-473
	3	Gradska i seoska sredina	Zhang H B, Luo Y M, Wong M H, Zhao Q G, Zhang G L, Environ. Poll., 2006, **141**, 107-114
	4	Gradska i seoska sredina, prigradska naselja	Wang Z, Chen J, Qiao X, Yang P, Tian F, Huang L, Chemosphere, 2007, **68**, 965-971
	10	Pirinčano polje navodnjavano otpadnom vodom	Song Y F, Wilke B-M, Song X Y, Gong P, Zhou Q X, Yang G F, Chemosphere,

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[13] pod izomerom se podrazumevaju jedinjenja sa istim brojem prstenova u molekulu, tj. istom molekulskom formulom.

			2007, **65**, 1859-1868.
	43	Obradivo (uzgoj povrća)	Chen L, Ran Y, Xing B, Mai B, He J, Wei X, Fu J, Sheng G, Chemosphere, 2005, **60**, 879-890
Indija	4	Lokacije u blizini aerodroma, udaljene lokacije	Bojes H K, Pope P G, Regular. Toxicol. Pharmacol., 2007, **47**, 288-295.
Japan	4	Pirinčano polje	Honda K, Mizukami M, Ueda Y, Hamada N, Seike N, Chemosphere, 2007, **68**, 1763-1771
Južna Koreja	2	Poljoprivredno (pirinčano polje, brdski predeli)	Nam J J, Song B H, Eom K C, Lee S H, Smith A, Chemosphere, 2003, **50**, 1281-1289
Turska	2	Industrijski region	Bozlaker A, Muezzinoglu A, Odabasi M, J. Hazard. Mater., 2008, **153**, 1093-1102
Australija			
	1	Pored puta	Pathirana S, Connell D W, Vowles P D, Ecotoxic. Environ. Safety, 1994, **28**, 256-269.
Evropa			
Estonija	8	Gradska i seoska sredina	Trapido M, Environ. Poll., 1999, **105**, 67-74.
Francuska	7	Gradska i seoska sredina, prigradska naselja, industrijski region, udaljene lokacije	Motelay-Massei A, Ollivon D, Garban B, Teil M J, Blanchard M, Chevreuil M, Chemosphere, 2004, **55**, 555-565.
Nemačka	11	Nezagađene i zagađene lokacije, zone za rekreaciju, poljoprivredno zemljište, šumsko područje, travnata područja, šumska stelja, park	Franzle O, Krinitz J, Schmotz W, Delschen T, Leisner-Saaber J, Harmonization of investigation methods and evaluation for risk assessment in soil

			protection with the Russian Federation, Report. UBA-FB 95-048, Terytze, K. (Ed.). Umweltbundesamt, Berlin, 1996.
Grčka	29	Industrijski region	Stalikas C D, Chaidou C I, Pilidis G A, Sci. Total Environ., 1997, **204**, 135-146.
Italija	1	Industrijski region	Moretto L M, Silvestri S, Ugo P, Zorzi G, Abbondanzi F, Baicchi C, Iacondini A, J. Hazard. Mater., 2005, **126**, 141-148
Poljska	5	Ukrštanje pruga, kontrolni uzorak	Malawska M, Wilkomirski B, Water Air Soil Pollut., 2001, **127**, 339-349
Rusija	11	Nezagađene i zagađene lokacije, zone za rekreaciju, poljoprivredno zemljište, šumsko područje, travnata područja, šumska stelja, park	Franzle O, Krinitz J, Schmotz W, Delschen T, Leisner-Saaber J, Harmonization of investigation methods and evaluation for risk assessment in soil protection with the Russian Federation, Report. UBA-FB 95-048, Terytze, K. (Ed.). Umweltbundesamt, Berlin, 1996.
Srbija	1	Gradska i seoska sredina	Crnković D, Ristić M, Jovanović A, Antonović D, Environ. Monit. Assess., 2007, **125**, 75-83.
	5	Gradska sredina, poljoprivredno	Škrbić B, Cvejanov J, Đurišić-Mladenović N, J. Environ. Sci. Health A, 2005, **40**, 29-43.
Slovačka	8	Poljoprivredno, šumsko područje	Linkeš V, Kobza J, Švec M, Ilka P, Pavlenda P, Barančikova G, Matuškova L, Soil

			monitoring of Slovak Republic, Present state of monitored soil properties. The Results of Partial Monitoring System-Soil as a part of Environment Monitoring of Slovak Republic for the Period 1992/96., Bratislava, 1997
Španija	4	Gradska sredina, stambeni delovi	Nadal M, Schuhmacher M, Domingo J L, Environ. Poll., 2004, **132**, 1-11.
Švajcarska	23	Obradivo, travnate površine, šumsko područje, gradska sredina	Bucheli T D, Blum F, Desaules A, Gustafsson O, Chemosphere, 2004, **56**, 1061-1076.
Velika Britanija	4	Poljoprivredno	Jones K C, Stratford J A, Waterhouse K S, Furlong E T, Giger W, Hites R A, Schaffner C, Johnston A E, Environ. Sci. Technol., 23, 95-101, 1989

Prikupljeni podaci su podeljeni u tri baze podataka: a) prva baza sa (apsolutnim) vrednostima sadržaja PAH-ova izraženim u ng/g; b) druga sa procentualnim udelom svakog jedinjenja (mas. %) u odnosu na ukupnu koncentraciju svih 9 jedinjenja u uzorku; i c) treća baza sa procentualnim udelom (mas. %) izomera (ukupne koncentracije jedinjenja sa istim brojem benzenovih prstena (3, 4, 5 ili 6) u molekulu) u ukupnom sadržaju svih 9 jedinjenja). Osnovni statistički podaci o ovim bazama podataka prikazani su u tabelama 3.4-3.6.

U analizu glavnih komponenata, uključeni su kako izvorni podaci (izraženi bilo kao apsolutne ili relativne vrednosti), bez prethodnih transformacija, tako i njihove vrednosti dobijene nakon logaritmovanja (sa osnovom 10).

Tabela 3.4. Osnovni statistički podaci o sadržajima 9 PAH-jedinjenja u 211 uzoraka površinskog zemljišta sa različitih lokacija širom sveta (opisani u Tabeli 3.3)

	srednja vrednost, ng/g	medijana, ng/g	SD, ng/g	RSD, %	min, ng/g	max, ng/g
PHE	239	35	1219	509,98	0,2	12000
ANT	116	3,1	1052	909,75	0,006	14800
FLU	235	35	830	354,10	0,05	10310
PYR	502	29	4804	956,40	0,93	69600
CHR	126	34	421	333,71	0,025	4500
BAA	134	15	549	409,53	0,02	5400
BFLU	292	34	1551	531,31	0,075	18700
BAA	183	13	1209	660,31	0,05	13400
BGHIP	195	145	1228	628,43	0,05	14900
UKUPNO	2022	229	11000	544,00	2,9	137851

Tabela 3.5. Osnovni statistički podaci o procentualnim udelima 9 PAH-jedinjenja u 211 uzoraka površinskog zemljišta sa različitih lokacija širom sveta (opisani u Tabeli 3.1)

	srednja vrednost, %	medijana, %	SD, %	RSD, %	min, %	max, %
PHE	21,50	13,81	18,79	87,41	1,00	82,19
ANT	2,46	1,52	3,25	131,77	0,01	30,59
FLU	17,14	16,94	7,46	43,54	0,44	60,40
PYR	13,72	12,68	6,72	48,95	2,55	50,49
CHR	11,52	10,03	7,40	64,28	0,09	28,83
BAA	6,77	6,11	4,63	68,46	0,04	23,58
BFLU	13,97	14,29	7,49	53,60	0,40	51,40
BAA	5,69	5,68	3,36	58,98	0,00	24,01
BGHIP	7,24	5,91	6,35	87,70	0,10	50,97

Tabela 3.6. Osnovni statistički podaci o procentualnim udelima izomera 9 PAH-jedinjenja (sa 3, 4, 5 ili 6 prstena) u 211 uzoraka površinskog zemljišta sa različitih lokacija širom sveta (opisani u Tabeli 3.1)

	srednja vrednost, %	medijana, %	SD, %	RSD, %	min, %	max, %
3-prstena	23,96	16,26	18,97	79,19	2,09	83,96
4-prstena	48,07	49,82	13,15	27,36	12,67	83,84
5-prstena	20,74	20,85	10,57	50,96	0,50	73,28
6-prstena	7,24	5,91	6,35	87,70	0,10	50,97

3.2.2. Organohlorni polutanti u zemljištu

Za analizu prisustva OCC jedinjenja u zemljištu primenom analize glavne komponente korišćeni su podaci iz literature, opisani u tabeli 3.7. Uzorci su uzeti sa različitih teritorija u Evropi i Aziji, uključujući zagađene i nezagađene lokacije. Podaci su se odnosili na sadržaj šest indikatorskih PCB kongenera (PCB 28, 52, 101, 138, 153 i 180), 10 OCP jedinjenja, uključujući i njihove izomere i/ili proizvode njihove degradacije (HCB, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, α-HCH, β-HCH, i γ-HCH). Kao što se vidi iz tabele 3.7, u bazu podataka su uključeni i rezultati analize OCP u zemljištu sa 5 lokacija u Novom Sadu. Međutim, ovi uzorci nisu uneti u bazu podataka sa PCB sadržajima, jer u većini uzoraka nisu detektovane količine ovih zagađujućih jedinjenja iznad granice detekcije (Škrbić i sar., 2007)

Tabela 3.7. Opis uzoraka zemljišta uzetih iz literature o prisustvu polihlorovanih bifenila (PCB) i organohlornih pesticida (OCP) u zemljištu sa različitih lokacija širom sveta

Vrsta uzorka (oznaka)	Broj uzoraka	Lokacija [a] (broj uzoraka na svakoj lokaciji)	Izvor (godina uzimanja uzorka [b])
PCB			
Travnato područje (gl)	12	Nemačka (2), Rusija (2), Švajcarska (8)	Franzle i sar. 1996 (1992-1993) Schmid i sar. 2005 (2002)
Šuma (w)	16	Nemačka (2), Rusija (2), Švajcarska (11), Tenerife-Španija (1)	Franzle i sar. 1996 (1992-1993) Ribes i sar. (2002) Schmid i sar. 2005 (2002)
Obradivo (ar)	8	Nemačka (2), Rusija (2), Švajcarska (2), Tenerife-Španija (2)	Franzle i sar. 1996 (1992-1993) Ribes i sar. 2002 Schmid i sar. 2005 (2002)
Vrt (g)	3	Germany (1), Russia (1), Švajcarska (1)	Franzle i sar. 1996 (1992-1993) Schmid i sar. 2005 (2002)
Rekreaciono područje (rec)	3	Nemačka (2), Švajcarska (1)	Franzle i sar. 1996 (1992-1993) Schmid i sar. 2005 (2002)
Kontrolno-nezagađeno (bcg)	5	Velika Britanija (4), svetska srednja vrednost (1) (uključujući svih 5 kontinenata)	Meijer i sar. 2001 (1944, 1956, 1966, 1980) Meijer i sar. 2003 (1998)
Različito (var)	2	Velika Britanija (2)	Alcock i sar. 1993 Lead i sar. 1997
OCPs			
Travnato područje (gl)	6	Kina (1), Nemačka (2), Rusija (2), Srbija (1)	Franzle i sar. 1996 (1992-1993) Škrbić i sar. 2002 (2001) Zhang i sar. 2006 (2000)
Šuma (w)	8	Kina (1), Nemačka (5), Rusija (2)	Franzle i sar. 1996 (1992-1993) Wenzel i sar. 2002

			Zhang i sar. 2006 (2000)
Obradivo (a)	41	Kina (31), Indija (4), Nemačka (2), Rumunija (1), Rusija (2), Srbija (1)	Kumari i sar. 1996 (1992-1994) Franzle i sar. 1996 (1992-1993) Dumitru 2001 Škrbić i sar. 2002 (2001) Nawab i sar. 2003 Chen i sar. 2005 (2002) Hong i sar. 2005 (2003) Zhang i sar. 2006 (2000)
Vrt (g)	3	Nemačka (1), Rusija (1), Srbija (1)	Franzle i sar. 1996 (1992-1993) Škrbić i sar. 2002 (2001)
Rekreaciona zona (rec)	4	Nemačka (2), Srbija (2)	Franzle i sar. 1996 (1992-1993) Škrbić i sar. 2002 (2001)
Močvarno područje (wt)	1	Kina (1)	Zhang i sar. 2006 (2000)
Meliraciono područje (recl)	1	Kina (1)	Zhang i sar. 2006 (2000)
Nepoznato poreklo (unkn)	4	Indija (3), Kina (1)	Hans i sar. 1999 Zhu i sar. 2005

[a] oznake uzoraka iz različitih zemalja koje su korišćene za ispitivanje geografskih razlika između OCC-profila uzoraka su sledeće: Kina – C, Nemačka – D, Indija – I, Rumunija – Ro, Rusija – R, Srbija – Serb, Španija – S, Švajcarska - Ch

[b] godina kada su uzeti uzorci je prikazana ukoliko je data u literaturi

Podaci su grupisani u tri baze podataka, koje su odvojeno analizirane primenom PCA:

- prva baza sastavljena od 20 promenljive i 16 uzoraka nazvana je „OCC“ baza podataka;

- druga sa 6 promenljivih i 68 uzoraka nazvana je „OCP“ baza podataka; i

- treća sa 6 promenljivih i 49 uzoraka nazvana je „PCB“ baza.

Najopširnija grupa podataka („OCC“) u odnosu na broj posmatranih promenljivih, osim podataka o sadržaju OCC u zemljištu, sadržala je i karakteristike samog zemljišta, a preuzeta je iz projekta Ruske Federacije i Republike Nemačke (Franzle i sar., 1996). Ova baza je iskorišćena kao skup uzoraka za ispitivanje stepena povezanosti (korelacija) između sadržaja posmatranih zagađujućih jedinjenja i osobina zemljišta (sadržaj gline i humusa, gustina i kiselost zemljišta). Uzorci zemljišta uključeni u analizu poticali su iz zagađenih i nezagađenih oblasti, iz dve provincije u Nemačkoj (Stolberg i Borhoved) i dve u Rusiji (Ostashkov i Celyabinsk). Srednje vrednosti merenih sadržaja zagađujućih jedinjenja za date uzorke zemljišta uzetih sa 16 lokacija (poljoprivredno zemljište, šume, livade, dečja igrališta, bašte) korišćene su u analizi. Deskriptivna statistika ovih podataka je data u tabeli 3.8.

Tabela 3.8. Osnovni statistički podaci o varijablama iz grupe „OCC“ ispitani PCA analizom (broj uzoraka: 16)

	Srednja vrednost	Medijana	Min	Max	SD	RSD, %
sadržaj gline u zemljištu, %	24,38	24,33	6,00	48,35	13,42	55,05
gustina zemljišta , g/cm^3	1,26	1,32	0,9	1,58	0,21	16,67
pH zemljišta	4,90	5,07	2,50	6,98	1,09	22,24
sadržaj humusa u zemljištu, %	8,74	6,89	1,83	28,46	7,94	90,85
PCB 28	0,29	0,25	nd	0,58	0,10	34,48
PCB 52	0,28	0,25	nd	0,50	0,09	32,14
PCB 101	0,90	0,442	nd	5,02	1,34	148,89
PCB 138	4,23	2,92	nd	21,71	5,50	130,02
PCB 153	2,76	0,59	nd	24,54	6,09	220,65
PCB 180	1,70	0,25	nd	15,87	3,91	230,00
HCB	2,16	1,03	nd	12,63	3,16	146,30
o,p'-DDE	2,39	0,25	nd	33,46	8,29	346,86
p,p'-DDE	20,32	1,49	nd	270,7	66,88	329,13
o,p'-DDD	0,37	0,25	nd	1,96	0,45	121,62
p,p'-DDD	0,56	0,40	nd	1,66	0,45	80,36
o,p'-DDT	1,67	0,48	nd	11,63	2,96	177,25
p,p'-DDT	6,42	2,10	0,41	29,28	8,72	135,83
α-HCH	0,45	0,25	nd	1,16	0,38	84,44
β-HCH	0,38	0,25	nd	1,66	0,37	97,37
γ-HCH	0,57	0,30	0,25	2,73	0,68	119,30

Statistički podaci za drugu („OCP“) i treću („PCB“) bazu podataka, koje su korišćene radi poređenja raspodele sadržaja PCB i OCP u zemljištu različitih oblasti Evrope i Azije prikazani su u tabeli 3.9. „PCB“ bazu čine podaci o srednjim vrednostima šest indikatorskih PCB kongenera (28, 52, 101, 138, 153 i 180) u uzorcima zemljišta, dok su u „OCP“ bazi sadržaji tri HCH izomera (α-, β- i γ-), kao i p,p'- izomeri DDE, DDD i DDT.

Tabela 3.9. Osnovni statistički podaci o promenljivim iz grupa „PCB“ i „OCP“ ispitanih PCA analizom

Jedinjenje	Broj uzoraka	Srednja vrednost, ng/g	Medijana, ng/g	Min, ng/g	Max, ng/g	SD, ng/g	RSD, %
PCB 28	49	2,48	0,13	0,022	106	15,11	609,27
PCB52	49	0,65	0,175	0,044	21	2,97	456,92
PCB 101	49	0,68	0,302	0,063	7,3	1,29	189,71
PCB 138	49	1,93	0,8	0,01	22	3,54	183,42
PCB 153	49	1,54	0,71	0,017	24	3,60	233,77
PCB180	49	0,94	0,31	0,0065	16	2,35	250,00
α-HCH	68	2,57	0,356	0,04	46	8,00	311,28
β-HCH	68	4,63	0,92	0,04	103	13,61	293,95
γ-HCH	68	3,09	0,296	0,003	47	8,37	270,87
p,p'-DDE	68	18,79	6,9	0,05	271	39,84	212,03
p,p'-DDD	68	4,01	1,2	0,003	60	8,54	212,97
p,p'-DDT	68	27,42	4,4	0,003	778	100,43	366,27

3.2.3. Organohlorna zagađujuća jedinjenja u biološkim uzorcima

Osnovu baza podataka formiranih za ispitivanje korelacija između sadržaja PCB-ova u majčinom mleku činili su uzorci iz Wielkopolska oblasti u Poljskoj u kojima su analizirani sadržaji indikatorskih PCB kongenera uključujući i PCB118 sa toksičnošću sličnom dioksinu (*„dioxin-like“)*. Formirane su dve osnovne baze podataka: tzv. „Wielkopolska“ i „International“.

„Wielkopolska“ baza podataka: sastoji se iz 15 odnosno 14 promenljivih, uključujući sadržaj 7 indikatorskih kongenera (PCB 28, 52, 101, 118, 138, 153, 180) u uzorcima majčinog mleka iz Wielkopolska regiona i nekoliko osobina donora. Šesnaest podataka iz grupe originalnih varijabli je isključeno (PCB 52 nije analiziran u svim uzorcima mleka, a takođe nisu poznati o telesnoj masi svih majki pre porođaja i veličina deteta u vreme uzimanja mleka). Podaci iz upitnika koji se odnose na pozitivan ili negativan odgovor, označene su brojevima 0 i 1; na primer, stanovanje u gradskim sredinama je označeno sa 1, dok u seoskim sredinama 0, s obzirom da se očekuje da gradska sredina utiče na veću izloženost zagađujućim jedinjenjima. Ovaj pristup je ranije primenjen u radovima Schade-a i sar.,1998; Tan-a i sar., 2008. Neki podaci iz upitnika su kombinovani, tako da su dobijeni novi podaci korišćeni u hemometrijskoj analizi; na primer, umesto visine i telesne mase majki, korišćen je indeks telesne mase (BMI; način izračunavanja

prikazan je ispod tabele 3.8), koji uključuje istovremeno oba ova parametra, s obzirom da se lakše može pretpostaviti i objasniti potencijalna veza između sadržaja PCB u mleku i BMI, nego pojedinačno sa visinom ili telesnom masom. Takođe je uveden podatak, koji uključuje procenat povećanja telesne mase majki u toku trudnoće (označen kao MWINC, način izračunavanja prikazan je ispod tabele 3.8). Pored toga, pretpostavljeno je se da se sadržaj PCB-ova u majčinom mleku može povezati sa brzinom rasta deteta, koja je proporcionalna povećanju količine mleka koje dete uzima, te je kao promenljiva korišćena izračunata vrednost nedeljnog povećanja telesne mase deteta u periodu od rođenja do dana uzimanja majčinog mleka (označen sa CWINC; način izračunavanja prikazan je ispod tabele 3.8), a ne direktno podatak o telesnoj masi deteta. Način ishrane (mešovita ili vegetarijanska ishrana) nije uzet u obzir u polaznoj bazi podataka za PCA analizu, jer je samo jedan donor bio vegetarijanac.

S obzirom da se sadržaj OCC jedinjenja u humanom mleku može iskazati na različite načine, na primer, ng/g masnoće (što je uobičajen način), ng/g mleka, mol/g mleka, mas%, mol%, PCA analiza izvršena je nad „Wielkopolska“ bazom podataka u okviru koje su podaci izraženi na različite načine. U slučaju kada je analizirana „Wielkopolska“ baza podataka sa sadržajima OCC jedinjenja iskazanim po masi (g) masnoće mleka, s obzirom da je na ovaj način sadržaj lipida u mleku već uvršten u bazu podataka u vidu normalizovane vrednosti sadržaja jedinjenja (ng/g masnoće), podaci o sadržaju masnoće u mleku u tom slučaju nisu korišćeni. „Wielkopolska“ baza podataka sadrži 22 promenljive, odnosno 21 (u slučaju normalizovane vrednost OCC sadržaja u odnosu na masu lipida, kada nije uvršten sadržaj masnoće u mleku kao promenljiva u bazi podataka) i 24 uzorka (davaoca).

Statistički podaci o prisustvu 7 indikatorskih PCB u majčinom mleku davaoca iz Wielkopolska regiona u Poljskoj prikazani su tabeli 3.10, dok su za razmatrane karakteristike donora u tabeli 3.11.

Tabela 3.10. Srednja vrednost±standardna devijacija (medijana), minimalna-maksimalna koncentracija indikatorskih PCB u humanom mleku donora iz Wielkopolska regiona, Poljska)

Kongener		% >LOD[a]	Prvorotkinje (n=32)	Drugorotkinje (n=18)
PCB 28	ng/g mleka	94[b]	0,040±0,026 (0,035) 0,002-0,110	0,04±0,03 (0,03) 0,01-0,10
	ng/g masnoće		1,36±1,08 (1,00) 0,07-5,06	1,07±0,60 (0,94) 0,07-2,34
PCB 52	ng/g mleka	100[c]	0,156±0,400 (0,042) 0,01-1,62	0,25±0,66 (0,04) 0,02-2,62
	ng/g masnoće		3,75±8,90 (1,14) 0,21-38,30	7,94±19,31 (1,08) 0,77-67,97
PCB 101	ng/g mleka	28[b]	0,011±0,008 (0,008) 0,008-0,03	0,02±0,01 (0,01) 0,01-0,06
	ng/g masnoće		0,41±0,34 (0,28) 0,11-1,55	0,50±0,56 (0,30) 0,14-2,34
PCB 118	ng/g mleka	100	0,194±0,174 (0,146) 0,03-0,992	0,27±0,22 (0,17) 0,02-0,68
	ng/g masnoće		6,36±5,13 (4,95) 0,63-22,15	6,55±4,12 (4,96) 0,60-15,69
PCB 138	ng/g mleka	100	0,873±1,760 (0,494) 0,10-10,38	1,02±1,09 (0,68) 0,07-4,67
	ng/g masnoće		24,26±28,88 (15,56) 2,10-168,78	25,42±23,31 (19,08) 2,10-107,06
PCB 153	ng/g mleka	100	1,099±1,855 (0,715) 0,086-11,001	1,51±1,53 (0,95) 0,12-6,58
	ng/g masnoće		30,50±30,74 (20,34) 2,52-178,88	37,58±32,46 (29,07) 3,55-150,85
PCB 180	ng/g mleka	100	0,602±1,252 (0,345) 0,08-7,365	0,78±0,71 (0,55) 0,19-2,97
	ng/g masnoće		16,59±20,38 (11,94) 1,68-119,76	19,12±14,25 (16,41) 5,31-68,00
Ukupno	ng/g mleka	100	2,938±5,017 (1,794) 0,368-29,887	3,86±3,65 (2,39) 0,51-14,99
	ng/g masnoće		82,288±81,422 (58,757) 7,715-485,967	97,32±76,43 (70,83) 15,27-343,72

[a] Procenat uzoraka u kojima je utvrđena koncentracija PCB iznad granice detekcije (LOD). [b] Pri proračunu srednje vrednosti, standardne devijacije i medijane, za uzorke u kojima nije detektovano prisustvo analiziranog kongenera, uzeta je vrednost jednaka polovini granice detekcije (LOD/2). [c] S obzirom da u 10 od 50 uzoraka nije analizirano prisustvo PCB 52, predstavljena vrednost u procentima predstavlja rezultate dobijene za 40 uzoraka

Tabela 3.11. Karakteristike majki i novorođenčadi uključenih u "Wielkopolska" bazu podataka (srednja vrednost±standardna devijacija (medijana))

Karakteristika (oznaka [a])	Vrednost dodeljena nebrojčanim varijblama	Prvorotkinje	Drugorotkinje
% ukupnog broja donora donors (CORDER)		64	36
Starost majke (MAGE), godina		25,3±3,4 (26)	29,6±5,0 (28,5)
Visina majke, cm		166,5±5,5 (164,5)	165,4±6,0 (164)
Masa majke pre trudnoće, kg		59,0±8,5 (57,5)	57,8±7,8 (57,5)
Masa majke pre porođaja, kg		64,4±8,4 (62)	62,2±8,0 (60)
Indeks telesne mase (BMI [b])		21,3±2,7 (20,7)	21,1±2,8 (20,6)
% neuhranjenih (BMI<18.5)		21,87	11,11
% normalno uhranjenih (18.5<BMI<24.9)		68,75	83,33
% gojaznih (25.0<BMI<29.9)		9,38	5,56
% ekstremno gojaznih (BMI≥50)		-	-
Procenat povećanja mase majke (MWINC [c]), %		10,7±8,5 (10,1)	9,5±7,9 (11,8)

% rođenih dečaka (CGEND)			59,4	44,4
Starost novorođenčeda pri uzimanju uzorka mleka (SAMPLING), nedelja			5,5±1,3 (5,5)	6,1±1,0 (6,0)
Masa novorođenčeda pri rođenju, g			3417,2±418,4 (3410,0)	3310,6±652,3 (3475,0)
Masa novorođenčeda pri uzimanju uzorka mleka, g			4579,3±706,2 (4750)	4755,0±584,9 (4915)
Povećanje mase novorođenčeta u period od rođenja do uzimanja uzorka mleka, %			25,6±38,5 (33,5)	52,3±59,8 (42,6)
Nedeljno povećanja mase novorođenčeta (CWINC ^{d}), %/nedelja			6,0±3,26 (6,4)	8,1±7,2 (6,7)
Područje stanovanja poslednjih 5 godina (RESAR), %	gradsko	1	68,75	72,22
	prigradsko		18,75	16,67
	seosko	0	12,50	11,11
Prethodno područje stanovanja (PRESAR), %	gradsko	1	75,00	61,11
	prigradsko		12,50	22,22
	seosko	0	12,50	16,67
Način ishrane majke, %	mešovita		96,88	100
	vegetarijanska uz korišćenje mleka i jaja		3,13	0,00
	isključivo vegetarijanska		0,00	0,00
Prosečno korišćenje ribe i morskih plodova u ishrani majke, (FISH), %	nikada	0	9,38	5,56
	< 1 nedeljno		46,88	22,22
	1 nedeljno	1	43,75	44,44
	2 nedeljno	2	0,00	27,78
	> 2 nedeljno		0,00	0,00
Prosečno korišćenje mleka i mlečnih proizvoda u ishrani majke (MILK), %	nikada	0	18,75	5,56
	≤ 2 nedeljno		9,38	11,11
	> 2 nedeljno ali ne i svakodnevno	1	15,63	22,22
	svakodnevno		56,25	61,11
Sadržaj masnoće u konzumiranom mleku i mlečnim proizvodima (MILK FAT), %	mali (0.5-1.9%)	1,2	18,75	22,22
	srednji (2.0-2.9%)	2,5	53,13	55,56
	veliki (3.0%ili veći)	3	12,50	16,67
Prosečn korišćenje govedine u ishrani majke (BEEF), %	nikada	0	31,25	38,89
	< 1nedeljno		46,88	22,22
	1 nedeljno	1	15,63	33,33
	2 nedeljno	2	0,00	5,56
	> 2 nedeljno		6,25	0,00
Pušenje (SMOKING), %	nikada	0	68,75	72,22
	bivši pušač		25,00	22,22
	pušač	1	6,25	5,56
Sadržaj			3,31±1,31 (3,15)	3,81±1,42 (3,86)

masnoće u majčinom mleku (FAT%), %				

[a] Skraćenice date u zagradama se odnose na promenljive korišćene u PCA
[b] Indeks telesne mase (BMI) se računa na sledeći način: BMI=[masa (kg)]/[visina (cm)]^2
[c] Procenat povećanja mase majke (MWINC) je izračunat kao procenat u odnosu na masu pre trudnoće: MWINC = (masa majke pre porođaja – masa majke pre trudnoće)/ masa majke pre trudnoće × 100
[d] Nedeljno povećanja mase novorođenčeta (CWINC) je izračunato kao procenat u odnosu na masu novorođenčeta pri rođenju: CWINC = (masa deteta pre uzimanja uzorka majčinog mleka – masa deteta pri rođenju)/masa deteta pri rođenju/starost deteta pri uzimanju uzorka majčinog mleka × 100

„International“ baza podataka: ova baza je korišćena da bi se procenio stepen izloženosti ljudi u Wielkopolska regionu u odnosu na druge regione, kao i da bi se uporedila vremenska i prostorna raspodela sadržaja indikatorskih PCB kongenera u uzorcima majčinog mleka po regionima, prvenstveno iz Evrope i Azije (dostupni radovi iz SAD i Kanade nisu mogli biti uključeni s obzirom da u njima nisu analizirani svi indikatorski kongeneri). Dakle, iz dostupnih radova uzeti su podaci o sadržaju 7 kongenera u humanom mleku (tabela 3.12), koji su sa uzorcima iz „Wielkopolska“ baze podataka uključeni u „International“ bazu podataka.

S obzorom da ljudi mogu biti izloženi PCB-ovima u svakodnevnom direktnom kontaktu sa industrijskim proizvodima, unosom kontaminirane hrane ili ukoliko se nalaze u zagađenoj sredini, unosom preko kože, udisanjem ili oralno, da bi se dobio što sveobuhvatniji uvid u potencijalne izvore prisustva PCB u majčinom mleku i izloženost populacije u Wielkopolska regionu, u „International“ bazu podataka uključeni su i sadržaji 7 indikatorskih kongenera dobijeni za uzoraka kao što su:

- različite namirnice biljnog i životinjskog porekla iz Poljske (margarin, jestivo ulje, kravlje mleko, svinjsko i goveđe masno tkivo) (Lulek, 2002);
- otpadna transformatorska ulja uzeta u Poljskoj u toku 1995 (Lulek, 1998);
- uzorci vazduha uzetih iz radnog i kućnog prostora (Currado i sar., 1998);
- „prosečno“ nezagađeno zemljište iz celog sveta (Meijer i sar., 2003).

Da bi se procenio unos PCB-ova udisanjem, potrebno je razmatrati podatke o kvalitetu vazduha i u zatvorenim prostorijama, pošto ljudi provode veći deo svog vremena u kući i na radnom mestu (Menichini i sar., 2007). Takođe, pošto neka istraživanja ukazuju da sadržaj je PCB-ova izražen po jedinici masnoće sličan u humanom mleku, krvi, masnom tkivu i mišićima (Jensen, 1991), radi poređenja profila PCB u različitim biološkim uzorcima u „International“ bazu podataka uneti su i podaci o sadržaju PCB-ova u uzorcima krvne plazme („izložena plazma“) kod građevinskih radnika, koji su učestvovali u uklanjanju materijala koji je sadržao PCB-ove (Wingfors i sar., 2006),), kao i kontrolni uzorci krvne plazme radnika („kontrolna plazma“), koji nisu bili izloženi uticaju PCB-ova.

Konačna veličina „International“ baze podataka je 7 promenljivih x 90 uzoraka. Analiza ovog seta urađena je na dva načina, analizirajući bazu sa koncentracijama indikatorskih PCB-ova izraženim u ng/g masnoće i u mas%. U tabeli 3.12 predstavljeni su uzorci uključeni u „International“ bazu podataka, dok su osnovni statisticki podaci dobijeni za podatke uključene u ovu bazu iskazani u ng/g masnoće i u mas.% prikazani u tabeli 3.13.

Tabel 3.12. Opis "International" baze podataka o prisustvu 7 indikatorskih PCB kongenera u humanom mleku analizirane primenom PCA

Izvor	Godina uzimanja uzorka [a]	Broj uzoraka [b]	Dete po redu	Starost majke	Sadržaj masnoće u majčinom mleku, %	Starost novorođenčeda pri uzimanju uzorka mleka, nedelja	Lokacija
Ovaj rad	2000-2002	34	1,2	17-36	1.28-7.01	3-8	Wielkopolska region, Poljska
Duarte-Davitson i sar. (1991)		1					Velika Britanija
Bordet i sar. (1993)		1					Francuska
Polder i sar. (1998)	1993	2	1-3	24		≤2	Murmansk i Monchegorsk gradovi, severno-zapadna Rusija
She i sar. (1998)	-	1	1			2-8	Kazahstan
Gladen i sar. (1999)	1993-1994	2	1,2	27-31		1	Kijev i Dnieprodzerzhinsk (visoko industrijalizovani gradovi), Ukrajina
Noren i Meironyte (2000)	1972-1997	11	1,2	27-31			Švedska
Gluszynski (2002)	2001	3	1	23-29		3-7	Brzeg Dolny, Tarnow i Wloclawek (industrijski gradovi), Poljska
Cajka i Hajslova (2003)	2000	2	1,2	18-37			Prag, Češka Republika
Cok i sar. (2003)	1999-2000	1	1	17-39	-	1-4	Ankara,Turska
Herceg Romanić i Krauthacker (2006)	2000	2	≥1	20-43			Zagreb i ostrvo Krk, Hrvatska
Costopoulou i sar. (2006)	2003	1		33.5	4.18	3-8	Atina, Grčka
Zhao i sar. (2007)	2003-2005	2	1			2-6	Pingqiao i Luqiao, Zhejing, Kina
Ingelido i sar. (2007), Abballe i sar. (2008)	1998-2000, 2000-2001	4	1	21-40	2.6-3.1	4-8	Venecija i Rim, Italija
Raab i sar. (2008)	2005	1	1	22-46	1.3-6.5	12, 16	Minhen, Nemačka
Polder i sar. (2008)	2000, 2002	3	1,2	21-30	2.7-3.9	1	Murmansk-grad na Arktičkom krugu, Arkhangelsk-grad na Belom moru, Kargapol-mali grad u unutrašnjosti na severu Rusije
Colles i sar. (2008)	2006	1	1	26		2-8	Belgija

[a] Tačna godina uzimanja uzorka prikazana je ukoliko je data u originalnom radu; u suprotnom, samo je pretpostavljeno da je uzorak uzet pre godine objavljivanja rada (na primer, ako je rad objavljen 1998. godine, a da u njemu nije navedena godina u kojoj su uzeti uzorci, u koloni "Godina uzimanja uzorka" u zagradi je navedeno (<98)). [b] Broj uzoraka podrazumeva broj uzoraka uzetih iz navedenog rada uključenih u "International" bazu podataka.

Tabela 3.13. Osnovni statistički podaci o prisustvu 7 indikatorskih PCB kongenera u uzorcima humanog mleka (izraženi u ng/g masnoće i masenim procentima, mas.%) uključenim u „International" bazu podataka ispitanu PCA analizom

	srednja vrednost	medijana	SD	RSD	min	max
ng/g masnoće						
PCB28	103	2.17	352.73	342.01	0.05	2199
PCB52	309	1.35	1658	535.64	0 [a]	14766
PCB101	123	0.65	606	492.65	0 [a]	5352
PCB118	50.4	7.18	191	379.23	0.005	1709
PCB153	73.6	42.0	109	148.65	0.1	885
PCB138	64.4	30.5	130	202.63	0.15	1134
PCB180	31.1	17.3	36.5	117.34	0.05	215
mas.%						
PCB28	6.87	1.97	11.32	164.63	0.14	51.75
PCB52	9.88	1.65	16.32	165.22	0.00	65.88
PCB101	7.33	7.12	3.67	50.02	0.00	20.22
PCB118	7.33	7.12	3.67	50.02	0.00	20.22
PCB153	31.64	38.41	13.59	42.94	1.61	46.30
PCB138	23.86	27.46	10.02	41.97	0.21	42.51
PCB180	16.24	18.43	8.27	50.95	0.11	30.47

[a] S obzirom da u dva rada iz kojih su preuzeti podaci za formiranje „International" baze podataka (Noren i Meironyte, 2000; Lulek 2002) nisu predstavljeni sadržaji PCB 52 i 101 i to ukupno samo u tri uzorka, uključena u bazu, za njih je usvojena nulta koncentracija kako bi se na ovaj način u analizi zadržali i ovi uzorci.

3.2.4. Postojana organska zagađujuća jedinjenja u vazduhu

Da bi se izvršila hemometrijska obrada podataka dobijenih analizom ekstrakata diskova pasivnih uzorkivača vazduha sa 6 mernih stanica u Makedoniji, formirane su tri baze podataka: u prvoj bazi, nazvanoj „PAH" baza, nalaze se određeni sadržaji PAH jedinjenja; druga baza, tzv. „OCC" baza, sadrži rezultate prisustva OCC-jedinjenja u vazduhu, dok treća, „SVOC" baza, obuhvata sve dobijene podatke. U tabeli 3.14 predstavljeni su sadržaji ove tri grupe jedinjenja. Razdvajanje rezultata o prisustvu PAH-ova i OCC-jedinjenja u dve baze urađeno je zbog različitog porekla ovih zagađujućih jedinjenja. Naime, PAH-ovi potiču iz procesa sagorevanja, dok su PCB-ovi i OCP-ovi sintetičke hemikalije, čija je porizvodnja i upotreba ograničena i/ili zabranjena. Zbog toga, prisustvo OCC-jedinjenja u vazduhu u poslednje 2 decenije se uglavnom objašnjava isparavanjem sa lokacija na kojima se nalaze stari depoziti ovih jedinjenja, zatim usled sagorevanja otpadnog materijala, isparavanja sporednih proizvoda i otpadnog materijala pri proizvodnji hlorovanih rastvarača i pesticida. Zbog razlike u izvorima i intenzitetima njihove emisije postoji i značajna razlika u koncentraciji OCC-jedinjenja u odnosu na sadržaje PAH-ova, koji mogu biti prisutni u vazduhu u koncentracijama većim od koncentracija OCC i do nekoliko redova veličine. „SVOC“ baza podataka, koja uključuje sva ispitivana jedinjenja, uzeta je u obzir da bi se ispitale sličnosti ili razlike izvora zagađenja na mestima sa kojih su uzeti uzorci u odnosu na emisiju ove tri grupe zagađujućih jedinjenja, odnosno da bi se predvideli zajednički izvori zagađenja (na primer, sagorevanje otpadnog materijala kao potencijalni izvor PAH i OCC). Veličine formiranih baza su: 22 (promenljive) x 24 (uzoraka) „PAH“ baza; 19 (promenljive) x 24 (uzoraka) „OCC“ baza; i 41 (promenljive) x 24 (uzoraka) „SVOC“ baza.

Tabela 3.14. Srednje vrednosti (i standardne devijacije) ukupnih atmosferskih koncentracija analiziranih postojanih organkih zagađujućih jedinjenja na šest lokacija u Republici Makedoniji tokom perioda 14. maj-03. septembar 2007

Lokacija	**PAH (ng/m^3)**	**PCB (pg/m^3)**	**HCH[a] (pg/m^3)**	**DDTs [b] (pg/m^3)**	**HCB (pg/m^3)**	**PeCB (pg/m^3)**
Lazaropolje	11.38 ±4.67	23.91 ±5.87	100.99 ±11.4	35.91 ±11.94	45.66 ±2.81	9.69 ±2.43
Skopje-OHIS	46.19 ±1.44	256.62 ±28.05	3033.16 ±552.6	153.83 ±37.56	34.18 ±1.32	8.16 ±1.86
Skopje-MEPP	123.33 ±14.00	277.54 ±21.10	1737.23 ±797.1	245.66 ±10.85	51.02 ±11.21	10.46 ±2.93
Bujkovci	20.33 ±0.69	174.48 ±12.53	182.37 ±14.7	125.51 ±15.07	36.99 ±7.70	11.22 ±1.86
Bitola	24.75 ±11.20	74.21 ±8.72	165.54 ±31.0	206.38 ±4.88	41.07 ±9.69	10.97 ±2.26
Strumica	15.53 ±2.57	75.73 ±14.26	172.17 ±36.7	106.11 ±46.03	34.95 ±4.67	8.67 ±2.43

[a] ukupni sadržaj α-, β-, γ-, i δ-HCH
[b] ukupni sadržaj *o,p'*- i *p,p'*- izomera DDT, DDD i DDE

3.2.5. Teški metali u zemljištu

Raspodela teških metala u zemljištu ispitana je korišćenjem baze sastavljene od podataka o prisustvu šest metala (Zn, Cu, Cr, Pb, Ni, Cd) u uzorcima površinskog zemljišta iz grada Novog Sada, Banja Luke, i naselja u blizini Novog Sada, kao i od relevantnih podataka iz literature, koji se odnose na zemljište iz različitih regiona širom sveta. Ukupno je razmatrano 18 radova; 190

uzoraka je uzeto iz tri rada (Bojinova i sar., 1996; Manta i sar., 2002), uključujući i istraživanje sprovedena na Tehnološkom fakultetu u vezi 23 uzorka iz Novog Sada, sela u njegovoj blizini i Banja Luke, dok je 74 uzorka uzeto iz preostalih 15 radova. Iako postoji neujednačen broj uzoraka uzet iz različitih radova, koji se odnose na različite regione širom sveta, s obirom na raznolikost istraživanja širom sveta, ovo nije smatrano nedostatkom formirane baze, jer je cilj istraživanja iznalaženje opšteg profila izabranih metala u zemljištima širom sveta i identifikacija njihovog dominantnog izvora. Detalji o uzimanju uzoraka u Novom Sadu, selima u okolini Novog Sada i Banja Luci, kao i njihovoj analizi, ranije su opisani u poglavlju 3.1.5, dok su detalji za ostale uzorke uključene u formiranu bazu dati u tabeli 3.15, a na osnovu opisa iz izvornih radova.

Opis mesta uzorkovanja u Novom Sadu, Banja Luci i selima u blizini Novog Sada prikazan je u tabeli 3.16. Uzorkovanje je izvršeno na 15 lokacija na području Novog Sada, na šest lokacija u pomenutim prigradskim i seoskim naseljima u blizini Novog Sada, i na dve lokacije u centralnom parku Banja Luke. Većina uzoraka površinskog sloja zemljišta (0-10 cm) uzeta je sa javnih (uzorci 1-7, 9-12, 14,15, 18, 22, 23) i privatnih (8, 17, 21) zelenih površina (travnjaka). Lokacije 2, 10-12, 22-23 pripadaju rekreativnoj zoni i/ili su dečija igrališta (9, 10). Četiri uzorka su uzeta u baštama za gajenje povrća (13, 16, 19, 20).

Opis podataka koji su sačinjavali celokupnu bazu ispitanu primenom PCA prikazan je u tabeli 3.17.

Da bi se ispitala raspodela metala u zavisnosti od stepena zagađenosti, polazna baza podataka, nazvana “Svi”, podeljena je u dve podgrupe uzoraka u skladu sa SMI (“Soil Metal Indeks”) vrednostima (Škrbić i sar., 2004) izračunatim na osnovu sadržaja metala u njima i u odnosu na referentne vrednosti istih metala u nezagađenom zemljištu prema holandskom standardu (Dutch standards, 2000). SMI ukazuje na ukupno prisustvo metala na datoj lokaciji, tačnije u datom uzorku, a izračunava se na sledeći način:

$$\mathrm{SMI} = \frac{1}{n}\sum_{i-1}^{n} 100 \cdot \frac{V_i}{L_i} \qquad 3.1$$

gde n predstavlja broj ispitivanih metala (u ovom radu n=6); V (u mg/kg) je sadržaj metala u određenom uzorku zemljišta; L (u mg/kg) je referentna vrednost prema holandskom standardu (Dutch standards, 2000) za nezagađeno zemljište, tj. za Zn je 140 mg/kg, Cu 36 mg/kg, Cr 100 mg/kg, Pb 85 mg/kg, Ni 35 mg/kg, i za Cd 0,8 mg/kg. Dakle, ukoliko je izračunata SMI vrednost iznad 100%, može se pretpostaviti da je zemljište zagađeno, jer sadrži ili sve ispitivane metale iznad holandskih referentnih vrednosti, ili je nekoliko metala prisutno u koncentracijama značajno iznad referentnih vrednosti. Isto tako, ako je izračunata vrednost SMI ispod 100% može se zaključiti da je zemljište nezagađeno.

Primenjujući ovaj kriterijum, prvobitno formirana baza sa svim podacima (tzv. “svi” baza) je podeljena u dve podgrupe uzoraka koje se međusobno razlikuju po stepenu zagađenosti: tzv. “iznad 100%” baza sačinjena je od 144 (ili 54,5%) zagađenih uzoraka, tj. sa SMI > 100%; dok je u drugoj bazi nazvanoj “ispod 100%” grupisano 120 uzoraka (45,5%) nezagađenog zemljišta sa SMI < 100%.

Uzorci u okviru polazne baze označeni su u odnosu na način korišćenja zemljišta kao “gradsko”, “poljoprivredno”, “industrijsko”, itd. (Tabela 3.17). Isto tako, uzorci su klasifikovani i u zavisnosti od geografskog porekla, tj. prema zemlji porekla, kako bi se ispitale prostorne sličnosti i razlike u raspodeli teških metala u zemljištu. Razmatrano je i vreme uzimanja uzoraka kako bi se ispitao uticaj uvođenja nove evropske direktive 98/70/EC o zabrani korišćenja benzina sa olovom, te su uzorci podeljeni na dve grupe u zavisnosti da li uzeti pre ili posle 2000. godine (Tabela 3.17). Mora se napomenuti da su sve ove klasifikacije ipak grubo uprošćavanje originalnih opisa uzoraka preuzetih iz citirane literature, s obzirom da je cilj bio da se uzorci grupišu u što manje osnovnih tipova prema načinu korišćenja zemljišta i vremenu uzorkovanja.

Statistički parametri kojim su opisani uzorci iz Novog Sada i okoline, kao i iz Banja Luke prikazani su u tabeli 3.18, dok su parametri celokupne baze, uključujući i podatke iz literature u tabeli 3.19.

Pre izvođenja PCA analize, podaci su transformisani primenom Box-Cox transformacije (Box-Cox, 1964), koja prema nekih autorima predstavlja bolje, univerzalnije rešenje od široko rasprostranjene log-transformacije (Templ i sar., 2008). Na ovaj način se raspodela većine podataka približila normalnoj distribuciji (Filmoser i sar. 2009). Na podacima je primenjen Shapiro-Wilk-ov test za određivanje odstupanja od normalne distribucije Box-Cox transformisanih podataka. Nulta hipoteza o normalnoj distribuciji Box-Cox transformisanih podataka je prihvaćena ukoliko je vrednost verovatnoće (P) veća od 0,05; u suprotnom, nulta hipoteza je odbačena.

Tabela 3.15. Opis metoda uzimanja uzoraka, pripreme i analize teških metala u zemljištima, čiji rezultati su uključeni u baze podataka analizirane PCA

Izvor	**Dubina, cm**	**Krajnja granulacija, mm** [a]	**Metoda pripreme**	**Analitička metoda** [b]	**“Recovery”,%**	**Preciznost, %**
Ovaj rad	0-5	-	$HNO_3+H_2O_2$, mikrotalasna	GFAAS	89-107	<10
Bojinova i sar. 1996	0-30	-	Aqua regia	FAAS/GFAAS	55-94	-
Fränzle i sar. 1995	0-20	-	Aqua regia	FAAS/GFAAS	-	-
Kastori i sar. 2002	-	-	$HNO_3+H_2O_2$	AAS [c]	-	-
Škrbić i Čupić, 2004	0-5	-	HNO_3+HCl	FAAS/GFAAS	-	-
Franco-Uria i sar. 2009	0-20	-	HNO_3, mikrotalasna	ICP-AES	-	-
Dragović i sar. 2009	-	-	Aqua regia	AAS	-	-
Ubavić i sar. 1993	0-30	-	HCl	AAS	-	-
Christiforidis i Stamatis, 2009	0-1	<0.063	HNO_3, mikrotalasna	GFAAS	95.3-97.1	2.5-3.1
Coşkun i sar. 2002	0-10	-	HNO_3, mikrotalasna	FAAS/GFAAS	-	-
Luo i sar. 2007	0-10	-	HNO_3+ H_2O_2, mikrotalasna	ICP-AES	92-108	-
Overesch i sar. 2007	0-50	-	Aqua regia	ICP-AES/GFAAS	-	-
Maiz i sar. 2000	0-10	-	Aqua regia+HF, ultrasonična	FAAS/GFAAS	~95	-
Manta i sar. 2002	0-10	-	Aqua regia, mikrotalasna	GFAAS	-	<10
Gramatica i sar. 2006	0-5	-	Kiselinska digestija (nisu navedene korišćene kiseline), mikrotalasna	ICP-MS	-	-
Salonen i Korkka-Nemi, 2007	0-5	<0.060	HNO_3, mikrotalasna	ICP-AES/GFAAS	-	-
Lee i sar. 2006	0-15	<0.200	HNO_3-$HClO_4$	ICP-AES	80-95	<10
Li i sar. 2004	0-15	<0.200	HNO_3-$HClO_4$	ICP-AES	75-105	<10

[a] U svim radovima, uzorci zemljišta su najpre osušeni, prosejani kroz sito sa otvorima od 2mm i samleveni pre analize. Krajnja veličina čestica (granulacija) je određena u samo nekoliko radova, što je i prikazano u tabeli.

[b] Značenje skraćenica: GFAAS-atomska apsorpciona spektrometrija sa grafitnom kivetom, FAAS-plamena atomska apsorpciona spektrometrija, AAS-atomska apsorpciona spektrometrija, ICP-AES-indukovana spregnuta plazma sa atomskom emisionom spektrometrijom, ICP-MS-indukovana spregnuta plazma sa masenom spektrometrijom; ako su prikazane dve analitičke tehnike, to znači da su obe korišćene u radu za analizu različitih metala, na primer, GFAAS je tehnika korišćena za određivanje malih koncentradcija Cd, a FAAS za ostale metale.

[c] Skraćenica AAS je korišćena ukoliko u radu nije tačno objašnjeno da li je u pitanju plamena ili AAS sa grafitnom kivetom.

- Nije dato u radu.

Tabela 3.16. Opis mesta na kojima je izvršeno uzimanje uzoraka površinskog zemljišta u Novom Sadu i njegovoj okolini

Broj uzorka	Opis
1	Novi Sad: gradska sredina, travnjak, 30 m od prometne ulice
2	Novi Sad: gradska sredina, travnjak (park), blizu železničke i autobuske stanice, 15 m od veoma prometne ulice
3	Novi Sad: gradska sredina, nizak stepen saobraćaja, stambena zona, travnjak
4	Novi Sad: gradska sredina, prometna zona, travnjak, 20 m od glavnog puta, blizu stare željezničke pruge
5	Novi Sad: gradska sredina, nizak stepen saobraćaja, stambena zona, travnjak
6	Novi Sad: gradska sredina, nizak stepen saobraćaja, travnjak, stambena zona, travnjak, blizu dečjeg igrališta
7	Novi Sad: gradska sredina, nizak stepen saobraćaja, travnjak blizu puta, stambena zona, individualno grejanje na gas i ugalj
8	Novi Sad: gradska sredina, nema saobraćaja, travnjak u privatnom dvorištu, stambena zona, individualno grejanje na gas i ugalj
9	Novi Sad: gradska sredina, nizak stepen saobraćaja, dečije igralište blizu parkinga u stambenoj zoni
10	Novi Sad: gradska sredina, travnjak (park i dečije igralište) blizu (ispod) mosta sa intenzivnim saobraćajem
11	Novi Sad: gradska sredina, nema saobraćaja, travnjak (rekreaciona zona) pored šetališta pored reke
12	Novi Sad: gradska sredina, intenzivni saobraćaj, travnjak u rekreacionoj zoni
13	Novi Sad: gradska sredina, nema saobraćaja, stambena zona, bašta udaljena od puta
14	Novi Sad: gradska sredina, nizak stepen saobraćaja, stambena zona, travnjak blizu puta
15	Novi Sad: gradska sredina, industrijska zona, intenzivni saobraćaj prema autoputu beograd-Subotica, travnjak u blizini nedavno zatvorene fabrike veštačkog đubriva
16	Šajkaš: seoska sredina, bašta
17	Šajkaš: seoska sredina, nizak stepen saobraćaja, travnjak između puta i kuće
18	Veternik: seoska sredina, nizak stepen saobraćaja, blizu zemljanog puta
19	Veternik: seoska sredina, nizak stepen saobraćaja, bašta
20	Ravno selo: seoska sredina, nizak stepen saobraćaja, bašta
21	Ravno selo: seoska sredina, nizak stepen saobraćaja, travnjak između puta i kuće
22	Banja Luka: rekreativna zona, centralni park
23	Banja Luka: uz put sa intenzivnim saobraćajem

Tabela 3.17. Opis uzoraka zemljišta koji su uključeni u baze sa sadržajima teških elemenata širom sveta ispitane PCA analizom

Izvor	**Zemlja i period uzimanja uzoraka** [a]	**Klasifikacija prema SMI** [b] **(broj uzoraka)** [c]	**Opis lokacije (broj uzoraka)** [c]	**Ukupan broj uzoraka**
Ovaj rad	Srbija, Republika Srpska, posle 2000.	iznad 100%(2), ispod 100% (21)	poljoprivredno (1), gradsko (9), seosko (6), rekreativno (5), uz put (1), industrijsko (1)	23
Bojinova i sar. 1996	Bugarska, pre 2000.	iznad 100% (37), ispod 100% (13)	poljoprivredno (50)	50
Bojinova i sar. 1996	Bugarska, pre 2000.	iznad 100% (16), ispod 100% (34)	poljoprivredno (50)	50
Fränzle i sar. 1995	Rusija, pre 2000.	ispod 100% (3)	poljoprivredno (2), šumsko (1)	3
Fränzle i sar. 1996	Nemačka, pre 2000.	ispod 100% (4)	poljoprivredno (2), šumsko (1), rekreativno (1)	4
Fränzle i sar. 1996	Nemačka, pre 2000.	iznad 100% (5)	poljoprivredno (3), šumsko (1), rekreativno (1)	5
Fränzle i sar. 1996	Rusija, pre 2000.	iznad 100% (1), ispod 100% (6)	poljoprivredno (4), šumsko (2), rekreativno (1)	7
Fränzle i sar. 1996	Nemačka, pre 2000.	iznad 100% (4)	poljoprivredno (1), šumsko (1), rekreativno (2)	4
Kastori i sar. 2002	Srbija, posle 2000.	ispod 100% (1)	poljoprivredno (1)	1
Škrbić and Čupić, 2004	Srbija, posle 2000.	ispod 100% (5)	gradsko (5)	5
Franco-Uria i sar. 2009	Španija, posle 2000.	ispod 100% (1)	travnato (1)	1
Dragović i sar. 2009	Srbija, posle 2000.	iznad 100% (1)	travnato (1)	1
Ubavić i sar. 1993	Srbija, pre 2000.	ispod 100% (1)	poljoprivredno (1)	1
Christiforidis i Stamatis, 2009	Grčka, posle 2000.	iznad 100% (5), ispod 100% (3)	uz put (8)	8
Coşkun i sar. 2002	Turska, posle 2000.	ispod 100% (1)	nepoznato (1)	1
Luo i sar. 2007	Kina, posle 2000.	ispod 100% (1)	poljoprivredno (1)	1
Overesch i sar. 2007	Nemačka, posle 2000.	iznad 100% (12)	poljoprivredno (2), travnato (8), nepoznato (2)	12
Maiz i sar. 2000	Španija, pre 2000.	iznad 100% (13)	industrijsko (9), uz put (4)	13
Manta i sar. 2002	Italija, posle 2000.	iznad 100% (45), ispod 100% (22)	rekreativno (67)	67
Gramatica i sar. 2006	Italija, posle 2000.	iznad 100% (2)	nepoznato (2)	2
Huang i sar. 2007	Kina, posle 2000.	ispod 100% (1)	poljoprivredno (1)	1
Salonen i Korkka-Nemi, 2007	Finska, posle 2000.	ispod 100% (1)	gradsko (1)	1
Cheng i sar. 2007	Kina, posle 2000.	ispod 100% (1)	poljoprivredno (1)	1
Lee i sar. 2006	Hong Kong, posle 2000.	ispod 100% (3)	gradsko (2), rekreativno (1)	3
Li i sar. 2004	Kina, posle 2000.	ispod 100% (1)	gradsko (1)	1

[a] period uzimanja uzoraka je definisan kao „pre“ i „posle“ 2000. godine, u kojoj je prestalo korišćenje benzina sa dodatkom olova u Evropskoj Uniji u skladu sa Direktivom 98/70/EC; [b] Klasifikacija prema SMI se zasniva na vrednostima SMI (Soil Metal Index) indeksa izračunatih u odnosu na holandske referentne vrednosti za nezagađeno zemljište; uzorak zemljišta u kojem je SMI iznad 100% je klasifikovan kao “iznad 100%”, a ukoliko je SMI < 100% uzorak je klasifikovan kao “ispod 100%”; [c] broj uzoraka u svakoj definisanoj grupi uzoraka

Tabela 3.18. Osnovni statistički podaci o prisustvu teških elemenata u površinskim uzorcima zemljišta iz Novog Sada, Banja Luke i novosadskih prigradskih naselja (izraženi u mg/kg) opisani u tabeli 3.12.

	Srednja vrednost	Medijana	SD	RSD, %	Min	Max
Zn	110	85.6	70.87	64.50	61.3	401
Cu	22.4	19.7	8.62	38.47	8.36	45.7
Cr	3.57	3.48	0.89	24.88	2.08	5.43
Pb	29.4	25.8	14.38	48.83	12.3	74.7
Ni	25.8	25.2	7.02	27.17	16.6	45.6
Cd	1.66	1.73	0.48	29.14	0.75	2.78

Tabela 3.19. Sumarni statistički podaci za celokupnu bazu podataka ("Svi") opisanu u tabeli 3.12., kao i dve podgrupe uzoraka sa vrednostima SMI ("Soil Metal Index") "ispod 100%" i "iznad 100%". P-vrednost Shapiro-Wilk-ovog testa predstavljena je u poslednjoj koloni i odnosi se na Box-Cox transformirane podatke sadržaja teških metala u zemljištu u okviru formiranih baza

Teški metal	**Srednja vrednost (±standardna greška), mg/kg**	**Min, mg/kg**	**Max, mg/kg**	**RDS (%)**	**Shapiro-Wilk test (*P*)**
	"Svi" set (*n* = 266)				
Zn	257.6±34.6	10.6	5518.8	219.4	0.000
Cu	110.8±21.1	6.4	4140.5	310.6	0.002
Cr	69.7±5.0	2.1	927.6	117.8	0.000
Pb	192.0±23.8	0.2	4196.0	202.4	0.000
Ni	41.4±2.6	3.5	320.0	101.7	0.008
Cd	2.03±0.4	0.8	86.6	300.5	0.186
	"Iznad 100%" set (*n* = 144)				
Zn	434.6±60.9	19.0	5518.8	168.2	0.000
Cu	176.8±38.2	8.6	4140.5	258.9	0.000
Cr	90.9±8.5	4.4	927.6	112.6	0.015
Pb	310.7±41.4	22.3	4196.0	159.8	0.005
Ni	53.3±4.4	7.3	320.0	98.7	0.874
Cd	3.2±0.7	0.1	86.6	256.2	0.079
	"Ispod 100%" set (*n* = 122)				
Zn	87.8±3.9	10.6	400.7	48.9	0.000
Cu	32.9±1.9	6.4	114.0	63.8	0.330
Cr	44.6±3.2	2.1	173.0	78.0	0.000
Pb	51.8±4.5	0.2	269.0	96.7	0.000
Ni	27.5±1.4	3.5	78.3	58.2	0.021
Cd	0.62±0.05	0.08	2.1	80.6	0.058

3.3. Hemometrijska analiza

Hemometrijska analiza je urađena primenom programa STATISTIKA 6.0 (StatSoft, Inc, USA) ili R (R Development Core Team. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing. Vienna, Austria. http://www.cran.r-project.org). Ulazne baze podataka su pripremljene tako da kolone sadrže vrednosti posmatranih promenljivih (na primer, sadržaje izabranih zagađujućih materija) određenih u uzorcima, koji se nalaze u redovima. Dakle, ako su tokom merenja sakupljeni podaci za *i* uzoraka, *i*=1,2,...n, i prisustva *j* zagađujućih materija u njima, *j*=1,2,...,p, dobijeni podaci se predstavljaju u vidu matrice podataka sa *n* redova (uzoraka) i *p* kolona (promenljivih), tabela ima izgled:

	Promenljiva 1	Promenljiva 2	...	Promenljiva j	...	Promenljiva p
Uzorak 1:	X_{11}	X_{12}	...	X_{1j}	...	X_{1p}
Uzorak 2:	X_{21}	X_{21}	...	X_{2j}	...	X_{2p}
:	:	:	...	:	...	:
Uzorak i:	X_{i1}	X_{i1}	...	X_{ij}	...	X_{jp}
:	:	:	...	:	...	:
Uzorak n:	X_{n1}	X_{n1}	...	X_{nj}	...	X_{np}

gde (*i,j*) element matrice (baze podataka) predstavlja vrednost *j*-te promenljive merene na *i*-tom uzorku.

Ukoliko nije drukčije naznačeno u prethodnim poglavljima u kojima je dat opis formiranja ulaznih baza podataka, vrednosti promenljivih su transformisane dekadnim logaritmovanjem (logaritmovanje sa osnovom 10). Takođe, ukoliko nije navedeno suprotno, nestandardne opservacije (engleski *outliers*), tj. uzorci u kojima sadržaji posmatranih zagađujućih jedinjenja značajno odstupaju (nekonzistentne su) od preostalih podataka u ulaznoj bazi podataka, nisu uključeni u analizu.

S obzirom da polazne baze podataka moraju biti u potpunosti popunjene, tj. ulazne matrice ne smeju sadržati "prazne" elemente ("ćelije"), kako bi se izvela multivarijaciona analiza, da bi se minimizovao gubitak podataka, ukoliko je sadržaj nekog jedinjenja bio ispod granice detekcije, za dati uzorak uzeta je vrednost, koja predstavljala polovinu granice detekcije (osim u slučaju opisanom ispod tabele 3.13. Ovaj preduslov za popunjenost ulazne baze uticao je i na konačni broj kolona i redova u formiranim bazama, jer u relevantnim radovima dostupnim u literaturi, često su predmet istraživanja slične, ne uvek iste grupe zagađujućih jedinjenja, te su mogli biti izabrani (uključeni u bazu) samo oni koji su predstavili rezultate istih jedinjenja.

3.3.1. Analiza glavnih komponenti

Kao što je ranije spomenuto, analiza glavnih komponenata je metoda smanjenja većeg broja razmatranih promenljivih na manji broj novih promenljivih, koje se nazivaju glavne komponente (engleski - *principal components*). Manjim brojem glavnih komponenti se objašnjava pretežan deo varijanse izvornih (originalnih) promenljivih, što omogućava smanjenje polaznog obima, tj. dimenzionalnosti polaznog skupa uzoraka, izdvajanje i lakše razumevanje informacija sadržanih u podacima, tj. lakšu interpretaciju polazne baze podataka. Osnovni zadatak je konstruisanje glavnih komponenata u vidu linearnih kombinacija originalnih promenljivih, uz uslov da obuhvate što je moguće veći iznos varijanse originalnog skupa promenljivih.

Osnovni koraci u analizi glavnih komponenata su sledeći:

1. Obično se najpre vrši standardizacija promenljivih, što je svakako neophodno u slučaju promenljivih izraženih različitim skalama (redovima veličina); svaki element polaznog seta (matrice) se umanji za srednju vrednost kolone u kojoj se nalazi, a zatim podeli standardnom devijacijom te kolone; na taj način se dobija nulta srednja vrednost svake kolone (tj. promenljive), sa jediničnom varijansom, čime su sve promenljive na istom nivou (skali) pri analizi.

2. Izračuna se matrica korelacija između svih standardizovanih promenljivih.

3. Odrede se svojstvene vrednosti glavnih komponenata.

4. Odbace se one komponente koje opisuju relativno mali udeo ukupne varijanse podataka, tj. zadrži se obično prvih nekoliko glavnih komponenti, koje kumulativno nose bar 70-75% ukupne varijanse. Očigledna je subjektivnost ovog načina određivanja broja glavnih komponenti, jer se on određuje na bazi proizvoljno izabrane vrednosti kriterijuma kumulativne proporcije objašnjene varijanse. Prema Kaiserovom kriterijumu (Kaiser i sar., 1974) zadržavaju se samo one glavne komponente, čiji su vrednosti karakterističnih korena (*eigenvalue*) veće od jedinice.

5. Osnovu za interpretaciju glavnih komponenata čine koeficijenti korelacije („*loadings*“) koji povezuju nove i originalne promenljive. Oni se mogu dobiti bez ili sa primenom rotacije, postupka kojim se transformišu dobijene vrednosti koeficijenata u cilju lakše interpretacije rezultata (u geometrijskom smislu, ovim postupkom se vrši rotacija koordinatnih osa predstavljenih zadržanim komponentama, za određeni ugao, pri čemu njihov međusobni odnos ostaje nepromenjen). Najčešće korišćeni metod rotacije je Varimax metod.

Originalne promenljive za koje su dobijene veće vrednosti koeficijenata korelacije (obično preko 0,7000 ili preko 60% od maksimalne vrednosti koreficijenta dobijene za tu glavnu komponentu) značajno utiču na zadržanu komponentu i važne su za njenu interpretaciju. Vrednosti koeficijenata korelacije u prvoj glavnoj komponenti su, najčešće, relativno ravnomerno raspoređene između većeg broja izvornih promenljivih. U ostalim glavnim komponentama dolazi do veće disproporcije, što omogućava izdvajanje izvorne promenljive (ili nekoliko njih) sa jačim uticajem na zadržanu komponentu i pomaže u objašnjavanju orginalne strukture i, u slučaju interpretacije podataka o prisustvu zagađujućih materija u prirodi, ukazuje na moguće izvore emisije. Na osnovu izračunatih koordinata uzoraka ("*scores*") u koordinatnom sistemu novih promenljivih - glavnih komponenata vrši se grupisanje uzoraka i objašnjenje polazne baze podataka. Naravno, vrednosti dobijene za koeficijente korelacije i koordinate uzoraka u prostoru određenom novim promenljivim (glavnim komponentama) mogu grafički prikazati i na taj način olakšati interpretaciju povezanosti (korelacija između) promenljivih i sličnosti/razlika između uzoraka. Grafički prikaz ovih vrednostima može biti odvojen (čime se dobijaju *"loading"* i *"score"* dijagrami) ili istovremeni kada se na jednom dijagramu tzv. "biplot"-u prikazuju koeficijenti korelacija zajedno sa uzorcima u koordinatnom sistemu određenom glavnim komponentama; na ovaj način, lakše se uočavaju promenljive odgovorne za grupisanje uzoraka, naročito ako se koriste vrednosti koeficijenata i koordinate uzoraka relativno u odnosu na najveću vrednost dobijenu za datu glavnu komponentu, čime su sve vrednosti smeštenu u rasponu od -1 do 1.

Analiza glavnih komponenata je izvršena u okviru svih opisanih baza podataka.

3.3.2. Analiza grupisanja

Analiza grupisanja (ili analiza klastera; engleski *Cluster Analysis)* je multivarijaciona tehnika čiji je primarni cilj klasifikacija uzoraka u grupe ili klastere tako da je (Pacina, 2006):

1. svaka grupa ili klaster homogena (kompaktna) u odnosu na posmatrane promenljive, tj. da su svi uzorci u jednoj grupi slični jedni drugima u odnosu na posmatrane promenljive,

2. svaka grupa različita od druge u odnosu na posmatrane promenljive, tj. da se uzorci u jednoj grupi razlikuju od uzoraka u drugoj grupi u odnosu na posmatrane promenljive.

Kao što je napomenuto u poglavlju 2.2.1.2., pored grupisanja uzoraka iz jedne baze podataka, može se izvršiti i grupisanje polaznih promenljivih, pri čemu je, na primer, jedina razlika između ova dva slučaja u programu STATISTICA, izbor da li će se grupisanje vršiti po kolonama ili redovima ulazne matrice. Grupisanje se vrši na osnovu izabrane mere sličnosti, odnosno načina izračunavanja udaljenosti između tačaka (kojima su predstavljeni uzroci (ili polazne promenljive) u dvodimenzionalnom prostoru, uzimajući u obzir polazne promenljive (ili uzorke u polaznoj bazi podataka)); uzorci koji su najmanje udaljeni jedni od drugih čine jednu grupu, tj. uzorci koji su svrstani u različite grupe su udaljeni jedni od drugih. Najčešće korišćeni način formiranja grupa je Ward-ova metoda, koja je manje osetljiva na prisustvo nestandardnih uzoraka („*outliers*“) u odnosu na metod pojedinačne i potpune vezanosti (videti poglavlje 2.2.1.2). Formirana struktura se prikazuje grafički u obliku dendrograma (hijerarhijskog drveta). Izbor željenog broja grupa moguće je izvršiti povlačenjem zamišljene linije („presecanjem“) dendrograma, čime je dobijeno jedno od mogućih rešenja problema grupisanja.

Analiza grupisanja je izvršena u okviru baza podataka formiranih od podataka ispitivanju sadržaja postojanih organskih zagađujućih jedinjenja u vazduhu na lokacijama 6 mernih stanica u Makedoniji.

3.3.3. Diskriminaciona analiza

Diskriminaciona analiza ima dva osnovna cilja. Prvi je da se utvrdi da li postoji statistički značajna razlika u srednjim vrednostima dve ili više grupa, a zatim da se odredi koja od promenljivih daje najveći doprinos utvrđenoj razlici. Prvi cilj analize naziva se diskriminacija ili razdvajanje između grupa. Drugi cilj odnosi se na utvrđivanje postupka za klasifikaciju uzoraka u dve ili više razdvojenih, unapred definisanih grupa na osnovu vrednosti nekoliko promenljivih. Ovaj cilj analize naziva se klasifikacija ili alokacija uzoraka. U primerima primene diskriminacione analize, ova dva cilja se često preklapaju, te sredstva analize koja se koriste za razdvajanje grupa istovremeno služe i za klasifikaciju uzoraka u unapred definisane grupe. U literaturi, metode diskriminacione analize koje se odnose na prvi cilj – razdvajanje između grupa, označavaju se deskriptivna diskriminaciona analiza, dok se metode za postizanje drugog cilja – alokaciji uzoraka, nazivaju metode klasifikacije (Kovačić 1994).

Diksriminaciona analiza je izvršena nad bazom podataka sa sadržajima teških metala u zemljištu sa različitih lokacija širom sveta radi provere mogućnosti grupisanja uzoraka prema načinu korišćenja zemljišta. U okviru formirane baze podataka („svi“), formirane su sledeće podgrupe uzoraka zemljišta na osnovu opisa datih u originalnim radovima: „poljoprivredno“, „rekreaciono, „travnjak“, „industrijsko“, „urbano“, „ruralno“, „uz put“, „šumsko“, „nepoznato“; opis uzoraka dat je u tabeli 3.17).

3.3.4. Višestruka regresija

Višestruka regresija primenjena je za analizu povezanosti kvantitativnih promenljivih i to: koncentracije postojanih organskih zagađujućih jedinjenja u vazduhu izmerenih na šest lokacija u Makedoniji tokom leta 2007. god. kao zavisne promenljive i više nezavisnih promenljivih u vidu dostupnih meteoroloških podataka (temperatura vazduha, brzina vetra, količina istaloženih materija i osunčanost). Srednje mesečne vrednosti meteoroloških podataka u periodu maj-septembar 2007. god. dobijene su od Hidrometeorološkog zavoda Republike Makedonije. Najniža temperatura vazduha izmerena je na lokalitetu merne stanice Lazaropolje (11,7-19,4^{o}C), gde je brzina vetra bila 2,2-2,7 m/s, slično kao i u Skoplju (2,4-2,8 m/s). U Strumici je zabeležena najviša temperatura (17,7-27,6^{o}C) i osunčanost (232,5-394,7 h/mesec), dok je brzina vetra bila najmanja (0,8-1,3 m/s). U Skoplju temperatura vazduha (17,7-27,1^{o}C) i osunčanost (222,5-386,3 h/mesec) je bila slična kao i za Strumicu. Na lokaciji Bitole bila je najmanja količina padavina (maksimalna količina u avgustu bila je 47,0 mm/m^2), dok je prosečna brzina vetra bila 1,7-1,9 m/s, a temperatura 16,9-25,4^{o}C. Padavine su bile najmanje u julu mesecu, a naviše u maju mesecu: na lokaciji Lazaroplja 10,7-76,6 mm/m^2, u Skoplju 1,2-96,2 mm/m^2, a u Strumici 0,3-107,5 mm/m^2.

Za izučavanje uticaja meteoroloških parametara na sadržaj PAH, OCP i PCB u vazduhu, korišćena je višestruka regresija. Uzete su recipročna vrednost temperature, logaritamska vrednost količine padavina, logaritamska vrednost brzine vetra, kao i logaritamska vrednost osunčanosti kao nezavisne promenljive, dok su logaritamska vrednost sadržaja ispitivanih jedinjenja uzete kao zavisne promenljive. Naime, ako se jedinjenje nađe u vazduhu usled isparavanja iz starih depozita, može se očekivati da logaritamska vrednost koncentracije datog jedinjenja je linearno zavisna od recipročne vrednosti temperature. Čak šta više, ako je smanjenje sadržaja jedinjenja povezano sa količinom padavina, brzinom vetra i periodom osunčanosti, njihov sadržaj se može korelisati sa recipročnom vrednošću ovih veličina. Prema tome, može se očekivati da je logaritamska vrednost koncentracije datih jedinjenja linearno zavisna od recipročnih vrednosti padavina, brzine vetra i perioda osunčanosti. Takođe, ispitivana je semilogaritamska i nelogaritamska zavisnost datih veličina. Uticaj svake od ispitivanih nezavisnih veličina na posmatranu zavisnu promenljivu određen je parcijalnim regresionim koeficijentima. Nagib linije regresije predstavlja vrednost promene zavisne od posmatrane nezavisne veličine (uz pretpostavku da su sve ostale nezavisne konstantne). Takođe, koeficijenti determinacije (R^2) su određeni i sttistički ispitani (F-test).

4. REZULTATI I DISKUSIJA

4.1. Policiklični aromatični ugljovodonici u zemljištu

Analiza glavnih komponenata (PCA) primenjena je na setu sastavljenom od podataka prikupljenih iz relevatnih međunarodnih istraživanja prisustva PAH-jedinjenja u zemljištu sa različitih lokacija, sa ciljem iznalaženja sličnosti i/ili razlika u prostornoj distribuciji ovih zagađujućih jedinjenja, uzimajući u obzir kako geografske razlike tako i razlike usled različitih načina korišćenja (Škrbić i sar., 2009). Istovremeno, formiran set podataka je korišćen za ispitivanje uticaja predtretmana (tj. transformacije logaritomovanjem sa osnovom 10) ulaznih podataka kao i uticaja načina prikazivanja ulaznih podataka (apsolutne vrednosti ili procentualni udeli, tj. kompozicioni podaci) na krajnje rezulatate. Dobijeni rezultati su prikazani u tabelama 4.1-4.3 i na slikama 4.1-4.6.

Tabela 4.1 i slike 4.1 i 4.2. predstavljaju rezultate PCA analize ulazne matrice sastavljene od apsolutnih vrednosti PAH-a u zemljištu bez prethodne transformacije. Dve glavne komponente su izdvojene objašnjavajući veliki procenat ukupne varijanse podataka (~94%). Prva komponenta, PC1, kojom je opisano oko 73% varijanse, značajno (preko 60% maksimalne vrednosti koeficijenta korelacije između posmatranih promenljivih i te komponente) koreliše sa sadržajima sledećih jedinjenja u zemljištu poređanih po opadajućoj koeficijenta korelacije: PYR>ANT>FLU>BFLU>PHE>BGHIP (tabela 4.1a, slika 4.1a). Drugom komponentom, PC2, objašnjeno je oko 21% varijanse podataka i ona je značajno povezana sa BAA>CHR>BAP>PHE>BGHIP (tabela 4.1a, slika 4.1a). Dakle, jedino su dva jedinjenja, PHE i BGHIP, imala značajne koeficijente korelacije sa obe zadržane komponente. Na slici 4.2a dijagramski su predstavljeni rezultati (“skorovi”) glavnih komponenata, čime je omogućen prikaz međusobne sličnosti/razlika ispitivanih uzoraka zemljišta u dvodimenzionom prostoru novih promenljivih (glavnih komponenata), a na osnovu sadržaja 9 posmatranih PAH-jedinjenja u ovim uzorcima. Na slici 4.2a jasno se uočavaju 4 uzorka zemljišta koja po sadržaju ispitanih PAH-jedinjenja značajno odstupaju od ostalih; to su tzv. nekarakteristične vrednosti („*outliers*”): uzorak koji se izdvojio duž PC1 ima u odnosu na sve ostale uzorke izuzetno veliku vrednost PYR, dok su tri uzroka izdvojena duž PC2 uzorci zemljišta sa velikim sadržajima BAA i CHR.

Većina uzoraka se lociralo oko koordinatnog početka prikazanog dijagrama (slika 4.2a), što ukazuje na uniformnu raspodelu PAH-ova u ispitanim zemljištima. Ipak, uveličanjem dela oko koordinatnog početka na 2-D dijagramu na slikci 4.2b, može se uočiti da postoje razlike između uzoraka sa različitih lokacija, tj. da se oni u odnosu na apsolutno prisustvo ispitivanih jedinjenja razlikuju, pri čemu su najmanje razlike uočene za zemljište iz industrijskih urbanih u odnosu na urbane zone i one udaljene od direktnih uticaja zagađivača.

Tabela 4.1. Koeficijenti korelacije („loadings”) glavnih komponenti dobijenih PCA analizom seta sa netransformisanim (a) i log-transformisanim (b) apsolutnim vrednostima prisustva 9 PAH-jedinjenja u 211 uzoraka zemljišta sa različitih lokacija u svetu

a)

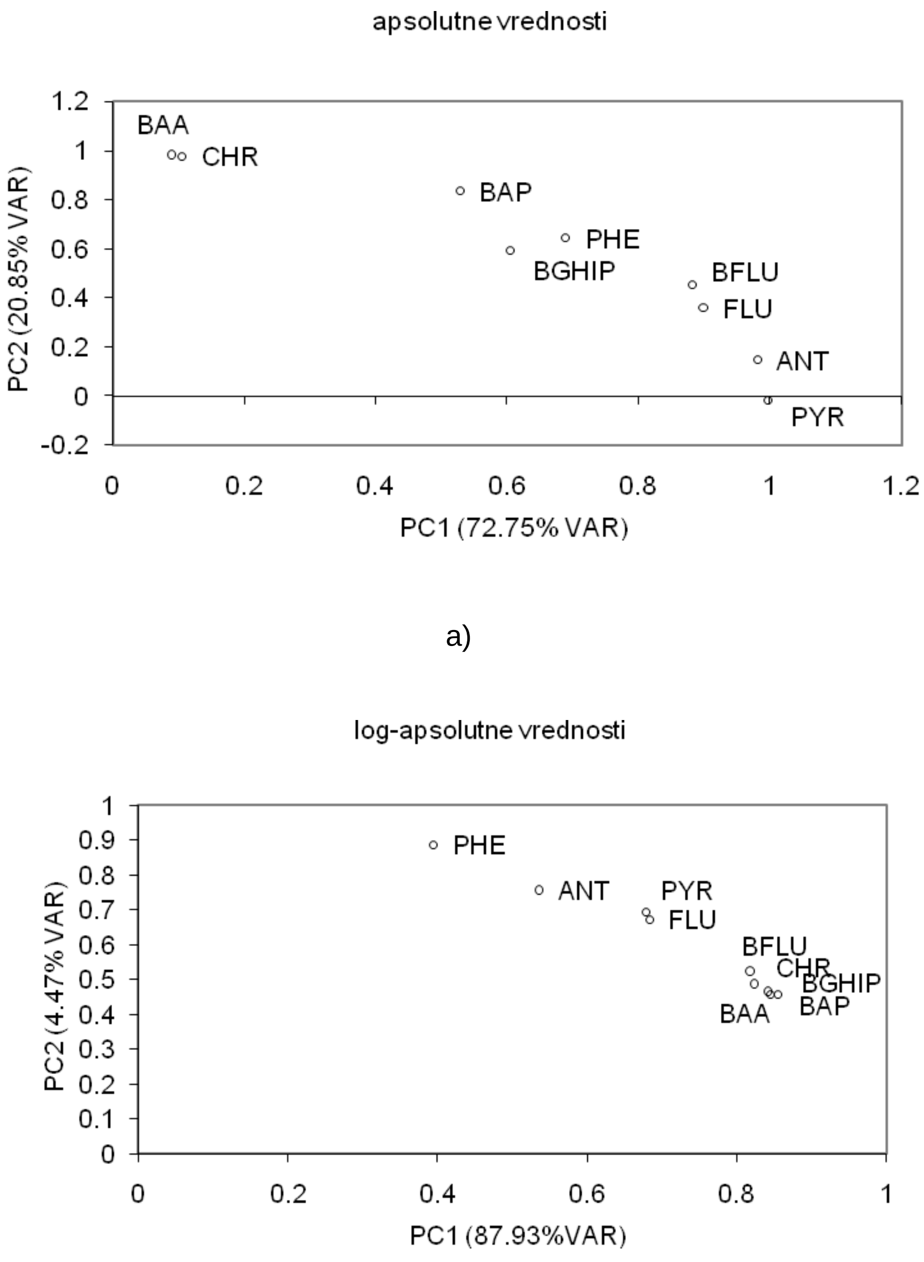
PAH [a]	PC1	PC2
PHE	**0,689236**	**0,643278**
ANT	**0,981414**	
FLU	**0,898723**	
PYR	**0,996980**	
CHR		**0,975783**
BAP		**0,835851**
BFLU	**0,881639**	
BAA		**0,983874**
BGHIP	**0,604981**	**0,593743**
Svojstvena vrednost (eigenvalue)	6,546907	1,876642
VAR% [b]	72,74	20,85

b)

PAH [a]	PC1	PC2
PHE		**0,88714**
ANT	**0,535959**	**0,757365**
FLU	**0,68354**	**0,67247**
PYR	**0,679482**	**0,694077**
CHR	**0,823075**	
BAP	**0,855787**	
BFLU	**0,817732**	
BAA	**0,845516**	
BGHIP	**0,842331**	
Svojstvena vrednost (eigenvalue)	7,913433	0,402411
VAR% [b]	87,93	4,47

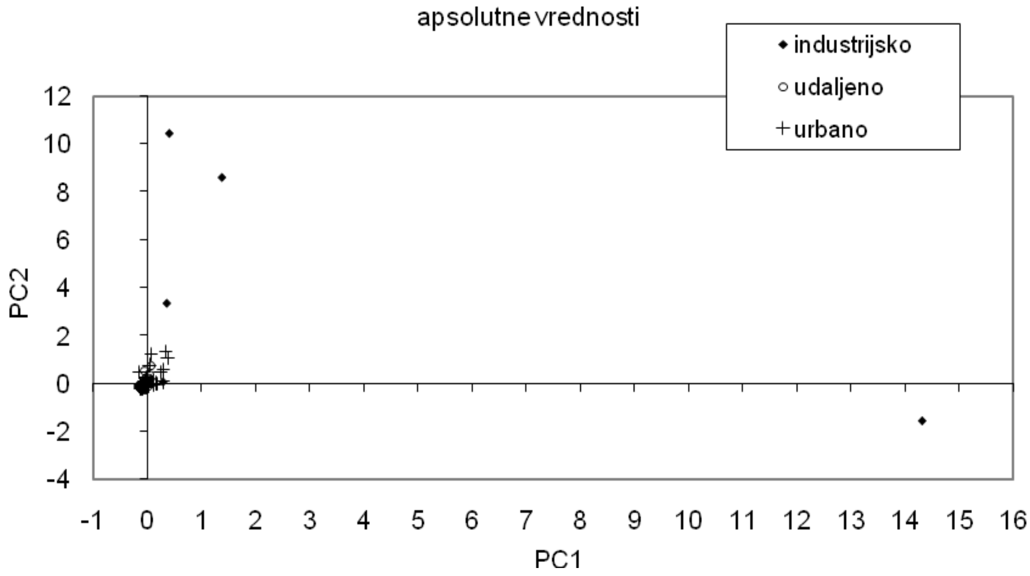
[a] Skraćenica PAH-jedinjenja koje su korišćene za prikazivanje rezultata objašenjene su u poglavlju 2.1.1.2, tabela 2.3.

[b] Procenat ukupne varijanse ulaznih podataka objašnjen svakom od zadržanih glavnih komponenti

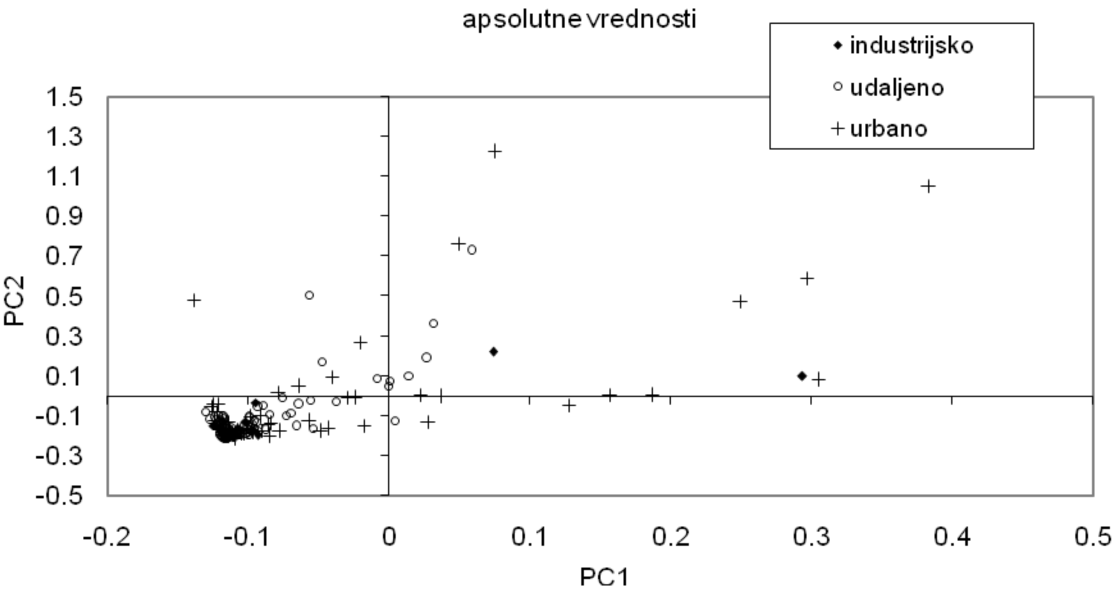


b)

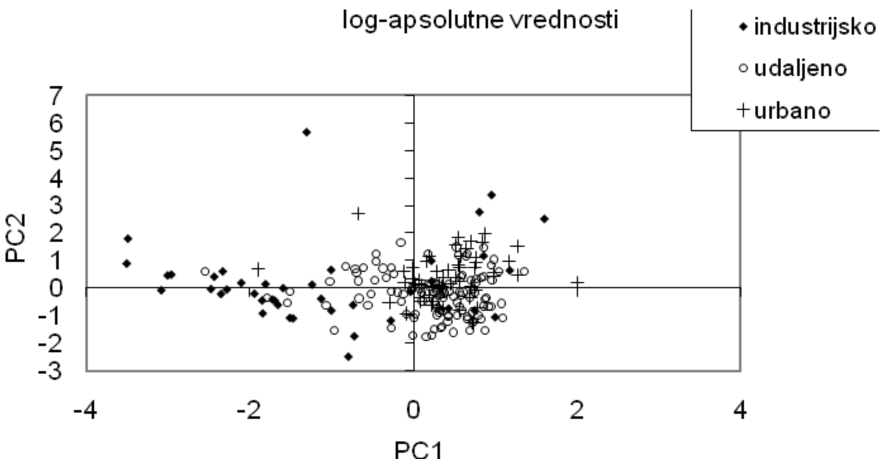
Slika 4.1. Dijagram zavisnosti koeficijenata korelacije prve dve glavne komponente sa netransformisanim (a) i log-transformisanim (b) apsolutnim vrednostima prisustva 9 PAH-a u 211 uzoraka zemljišta sa različitih lokacija u svetu


apsolutne vrednosti
◆ industrijsko
○ udaljeno
+ urbano
PC2
12
10
8
6
4
2
0
-2
-4
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
PC1

a)


apsolutne vrednosti
◆ industrijsko
○ udaljeno
+ urbano
PC2
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
-0.3
-0.5
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
PC1

b)



c)

Slika 4.2. Dijagram rezultata ("scores") prve dve glavne komponente u odnosu na ulazni set podataka sa netransformisanim (a – svi uzorci; b - uveličani deo površine zaokružene na slici pod a)) i log-transformisanim (c) apsolutnim vrednostima prisustva 9 PAH-a u 211 uzoraka zemljišta sa različitih lokacija u svetu

Tabela 4.2. Koeficijenti korelacije ("loadings") zadržanih glavnih komponenti dobijenih PCA analizom seta sa netransformisanim (a) i log-transformisanim (b) masenim procentima (mas.%) prisustva 9 PAH-jedinjenja u 211 uzoraka zemljišta sa različitih lokacija u svetu

a)

PAH [a]	PC1	PC2	PC3
PHE	**-0,90436**		
ANT		**0,828303**	
FLU			**0,625631**
PYR			
CHR		**-0,76587**	
BAP	**0,688347**		**-0,52724**
BFLU	**0,722274**		
BAA	**0,661933**		
BGHIP			**-0,80061**
Svojstvena vrednost (eigenvalue)	2,758028	1,509840	1,349647
VAR% [b]	30,64	16,78	15,00

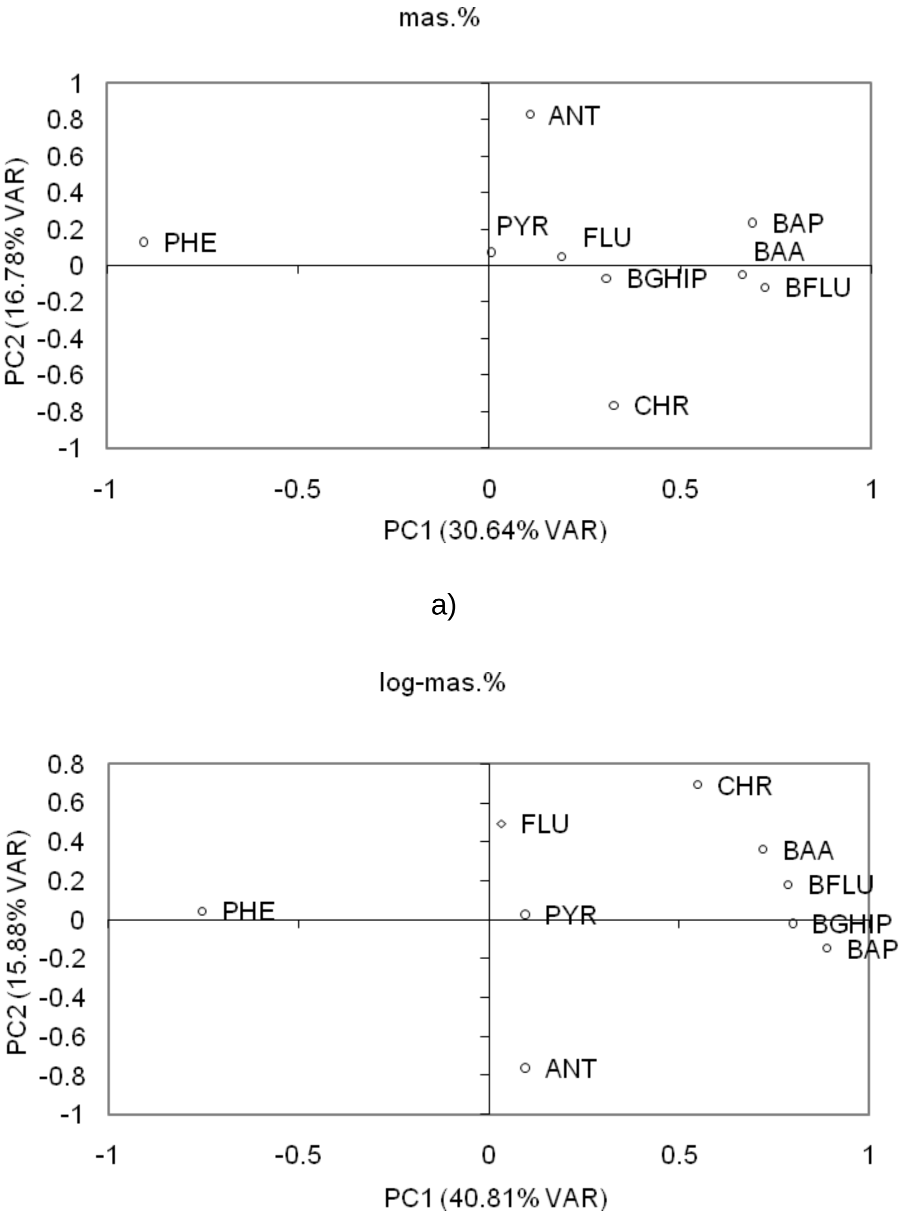
b)

PAH [a]	PC1	PC2	PC3
PHE	**-0,75261**		
ANT		**-0,75982**	
FLU			
PYR			**-0,88112**
CHR	**0,54876**	**0,69178**	
BAP	**0,88854**		
BFLU	**0,78509**		
BAA	**0,72048**		

BGHIP	**0,79860**		
Svojstvena vrednost (eigenvalue)	3,67277	1,35624	1,16804
VAR% [b]	40,81	15,07	12,98

[a] Skraćenica PAH-jedinjenja koje su korišćene za prikazivanje rezultata objašenjene su u poglavlju 2.1.1.2, tabela 2.3.

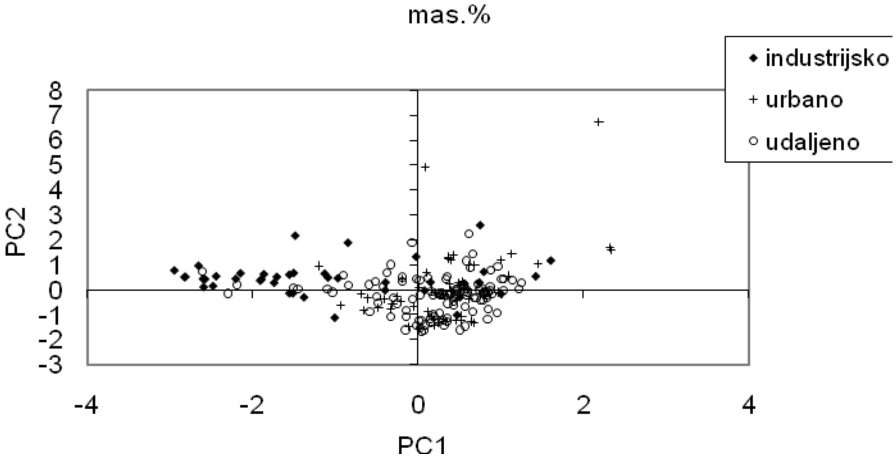
[b] Procenat ukupne varijanse ulaznih podataka objašnjen svakom od zadržanih glavnih komponenti



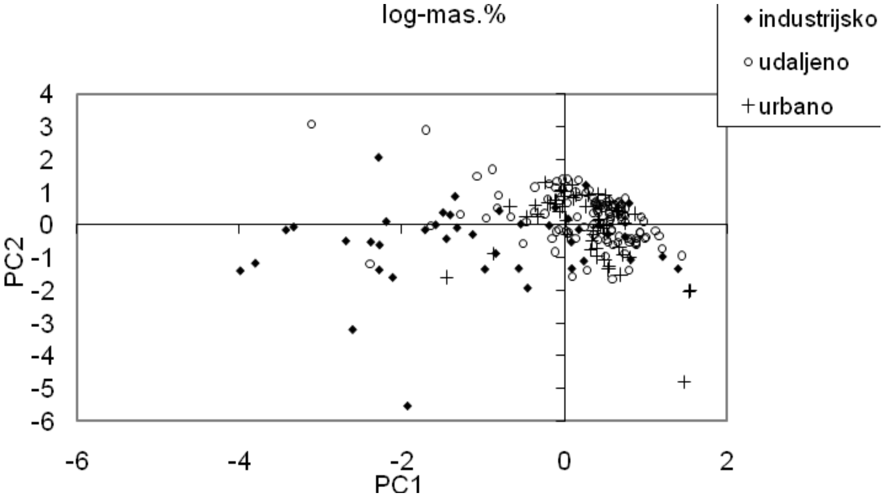
a)

b)

Slika 4.3. Dijagram zavisnosti koeficijenata korelacije prve dve glavne komponente sa netransformisanim (a) i log-transformisanim (b) masenim procentima (mas.%) prisustva 9 PAH-jedinjenja u 211 uzoraka zemljišta sa različitih lokacija u svetu



a)



b)

Slika 4.4. Dijagram rezultata (“scores”) prve dve glavne komponente u odnosu na ulazni set podataka sa netransformisanim (a) i log-transformisanim (b) masenim procentima (mas.%) prisustva 9 PAH-jedinjenja u 211 uzoraka zemljišta sa različitih lokacija u svetu

Tabela 4.3. Koeficijenti korelacije (“loadings”) zadržanih glavnih komponenti dobijenih PCA analizom seta sa netransformisanim (a) i log-transformisanim (b) masenim procentima (mas.%) PAH-izomera u 211 uzoraka zemljišta sa različitih lokacija u svetu

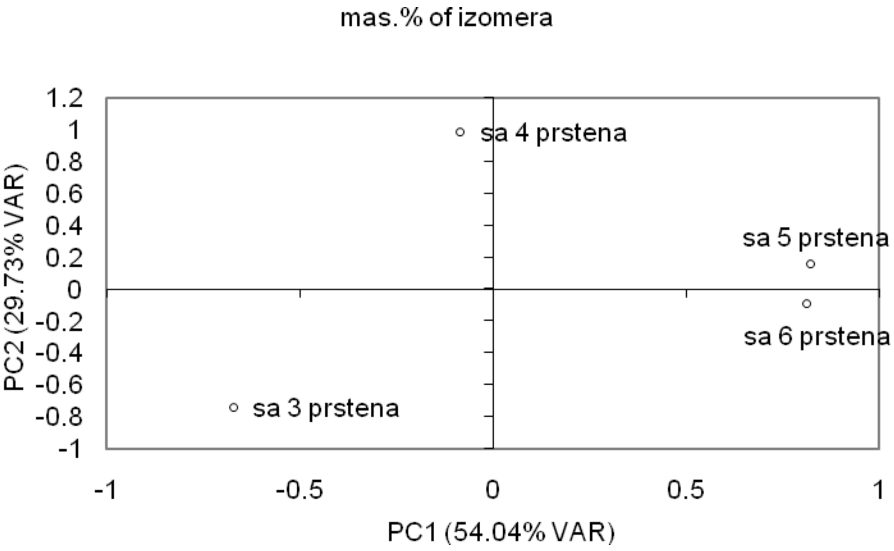
a)

PAH-izomeri	PC1	PC2
Sa 3 prstena	**-0,672003**	**-0,74046**
Sa 4-prstena		**0,98554**
Sa 5-prstena	**0,82366**	
Sa 6-prstena	**0,81328**	
Svojstvena vrednost (eigenvalue)	2,16177	1,18936
VAR% [a]	54,04	29,73

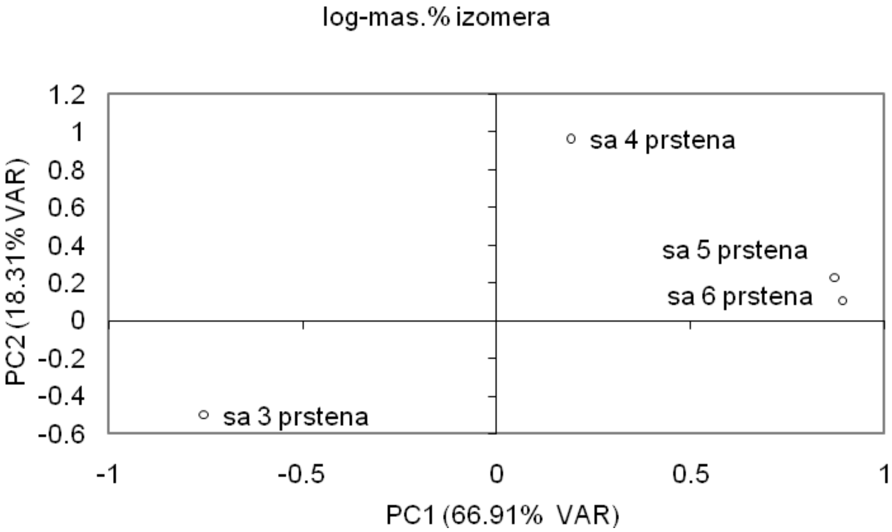
b)

PAH-izomeri	PC1	PC2
Sa 3 prstena	**-0,75536**	
Sa 4-prstena		**0,96567**
Sa 5-prstena	**0,87083**	
Sa 6-prstena	**0,89313**	
Svojstvena vrednost (eigenvalue)	2,67631	0,73260
VAR% [a]	66,91	18,31

[a] Procenat ukupne varijanse ulaznih podataka objašnjen svakom od zadržanih glavnih komponenti.

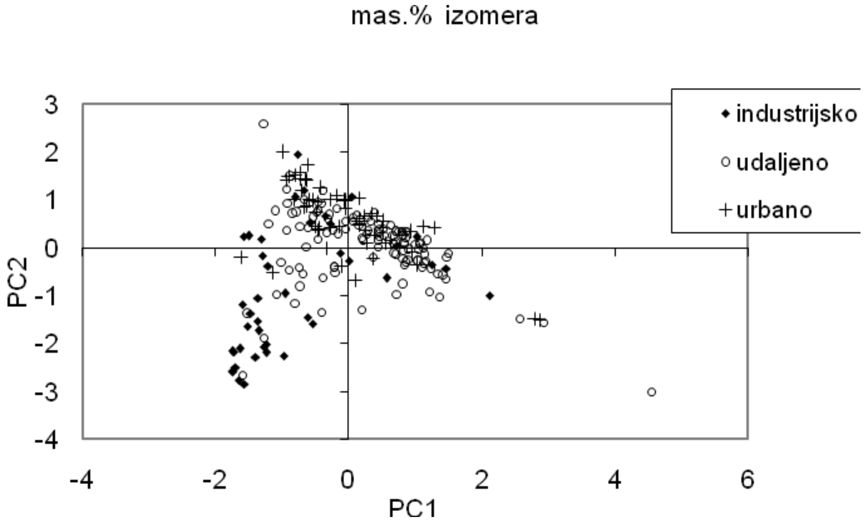


a)

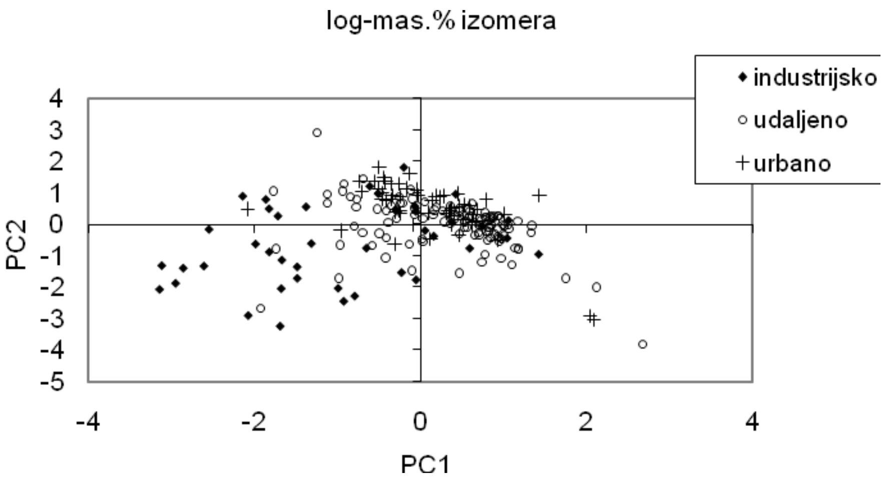


b)

Slika 4.5. Dijagram zavisnosti koeficijenata korelacije prve dve glavne komponente sa netransformisanim (a) i log-transformisanim (b) masenim procentima (mas.%) PAH-izomera u 211 uzoraka zemljišta sa različitih lokacija u svetu



a)



b)

Slika 4.6. Dijagram rezultata ("scores") prve dve glavne komponente u odnosu na ulazni set podataka sa netransformisanim (a) i log-transformisanim (b) masenim procentima (mas.%) PAH-izomera u 211 uzoraka zemljišta sa različitih lokacija u svetu

Prikazani rezultati ukazuju da iako sastav smese emitovanih PAH-jedinjenja u dimnim gasovima zavisi od sastava materijala koji sagoreva, kao i od uslova pod kojima se sagorevanje odvija (Wilcke, 2007; Menichini, 1992), raspodela ovih jedinjenja u većini zemljišta urbanih sredina je slična, pri čemu je prisustvo viših PAH-ova značajno, što je u skladu sa radom Daly i saradnika (Daly i sar., 2007). Uočena sličnost raspodele PAH-jedinjenja u zemljištima urbanih sredina ukazuje da su glavni izvori emisije PAH-ova zajednički za različite urbane sredine sveta i da su to prvenstveno procesi sagorevanja fosilnih goriva za koje je i karakteristično preovlađujuće prisustvo viših PAH-jedinjenja. S druge strane, zemljište sa industrijskih i udaljenih lokacija razlikuju se međusobno po sadržajima i profilima prisutnih PAH-ova, ali je zanimljivo da se njihovi PAH-profili donekle preklapaju. Uočeno preklapanje PAH-profila udaljenog zemljišta sa onim iz industrijskih i urbanih zona nije iznenađujuće, s obzirom da su spomenute kategorije "urbano/udaljeno/industrijsko" pripisano uzorcima zemljišta opisanim u različitim studijama, što predstavlja njihov grubi opis, ne uzimajući u obzir tačnu udaljenost od antropogenih izvora zagađenja. Povećani sadržaj PHE u zemljištu sa udaljenih lokacija može se objasniti većom atmosferskom mobilnosšću lakših PAH-ova, što je u skladu sa zaključkom Chung i saradnika (Chung i sar., 2007). Ovi PAH-ovi prelaze veće udaljenosti te se mogu naći na velikim udaljenostima od njihovog izvora. S druge strane, ovi PAH-ovi su i reaktivniji te su time lakše podložni razgradnji, što takođe može ukazati na postojanje drugih izvora njihovog prisustva u zemljištu udaljenih lokacija. Prethodna istraživanja (Wilcke, 2007) ukazuju da postoje dva karakteristična PAH-profila u zemljištu širom sveta: pozadinski i antropogeni, pri čemu prvi potiče od prirodnih izvora PAH-ova proizvedenih biološkim putem, emitovanih tokom šumskih požara ili vulkanskih erupcija, a uključujući i neminovnu atmosfersku imisiju PAH-ova, koja potiče iz antropogenih izvora. Antropogeni profil PAH-ova potiče iz procesa sagorevanja fosilnih goriva i u njemu preovlađuje prisustvo viših PAH-ova bez obzira na sastav gorive materije i uslove sagorevanja. U nekom zemljištu ova dva tipična profila mogu biti modifikovana u zavisnosti od karakteristika lokalnih izvora, njegove udaljenosti/blizine, i prenosa atmosferskim strijama na koji u velikoj meri utiču vremenski uslovi. Takođe, zemljište može biti i zagađeno izlivenom naftom ili naftnim derivatima, i tada u njemu preovlađuju niži PAH-ovi, prvenstveno naftalen i fenantren (Aislabie, 1999). Na osnovu ovoga, slični PAH-profili zemljišta iz industrijskih zona i sa udaljenih lokacija mogu se objasniti postojanjem ova dva tipična PAH-profila, naročito povećani sadržaj, tj. relativni deo PHE u njima, što je u slučaju “udaljenih” zemljišta posledica pozadinskog profila, tj. prirodnih izvora, dok je u “industrijskom” zemljištu to najverovatnije posledica izlivanja naftnih derivate.

4.2. Organohlorna zagađujuća jedinjenja u zemljištu

Analiza glavnih komponenata je primenjena i radi ispitivanje raspodele indikatorskih PCB i izabranih OCP u uzorcima zemljišta iz različitih zemalja sveta, prvenstveno iz Evrope i Azije (Škrbić i Đurišić-Mladenović, 2007.a; Škrbić i Đurišić-Mladenović, 2007,b).

Najpre, PCA je primenjena radi ispitivanja međuzavisnosti između ove dve klase organohlornih jedinjenja i karakteristika zemljišta, kao što su sadržaj gline i humusa, gustina i kiselost zemljišta, na osnovu rezultata opsežnog istraživanja, koje je uključilo nekoliko ruskih i nemačkih oblasti (Franzle i sar., 1996) Rezultati dobijeni PCA analizom “OCC” seta sastavljenog od sadržaja organohlornih zagađujućih jedinjenja u zemljištu iz nezagađenih i zagađenih oblasti Rusije i Nemačke (opisan u poglavlju 3.2.2) prikazani su u tabeli 4.4. Pet glavnih komponenata objasnilo je 93,9% ukupne varijanse polaznih podataka; sve ispitivane promenljive su povezane sa zadržanim glavnim komponentama. Prva komponenta, PC1, koja je opisala 38,2% ukupne varijanse, značajno je povezana sa sadržajem PCB 52, 101, 138, 153 i 180 (tabela 4.4), čiji su se vrednosti koeficijenta korelacije sa PC1 povećavale sa smanjenjem ispraljivosti i biorazgradljivosti, sa izuzetkom PCB 138 (PCB 52 < PCB 138 < PCB 101 < PCB 153 < PCB 180, pri čemu je PCB 52 najispraljiviji od ispitanih indikatorskih PCB-jedinjenja i najpodložniji je razgradnji u zemljištu). Dakle, prva glavna komponenta opisala je stepen zagađenja zemljišta kongenerima indikatorskih PCB. Odsustvo značajne povezanosti (korelacije) između posmatranih PCB i karakteristika zemljišta (sadržaj gline i humusa, gustina i kiselost zemljišta) verovatno je posledica izraženog mešanja PCB emitovanih iz različitih izvora do kojeg dolazi u vazduhu tako da se nakon taloženja na površinu, smese PCB u zemljištu međusobno ne razlikuju te se ne mogu ni povezati sa ispitanim karakteristikama zemljišta. Do sličnog zaključka došli su Lead i saradnici (1997). Druga glavna komponenta, PC2, opisala je 23,4% varijanse izvornih podataka, i povezana je pozitivno sa većinom DDX jedinjenja (DDT i njegovi metaboliti DDD i DDE) i PCB 28 (tabela 4.4), što ukazuje na njihovo zajedničko poreklo u ispitivanom zemljištu – atmosfersku depoziciju, s obzirom da je PCB 28 najisparljiviji od indikatorskih PCB, a OCP se i dalje rutinski mogu naći u atmosferi. Takođe, koeficijenti korelacije DDX jedinjenja sa PC1, koji se smanjuju u sledećem nizu: p,p'-DDE > o,p'-DDE > o,p'-DDD > o,p'-DDT > p,p'-DDD, ukazuju da na ispitanim lokacijama nije bilo "svežih" unosa DDT. Ispitivane karakteristike zemljišta nisu povezane sa PC2, tako ni sa DDX sadržajem, iako se smatra da se hidrofobni organohlorni pesticide lako adsorbuju na organsku materiju zemljišta. Ovo ukazuje da uključene karakteristike zemljišta nisu dovoljne da bi se ispitala sposobnost zemljišta da vezuje ova organohlorna zagađujuća jedinjenja. Treća glavna komponenta, PC3, kojom je opisano 14,2% varijanse, pozitivno je povezana sa β-HCH, p,p'-DDT i sadržajem humusa, i negativno sa pH (tabela 4.4). Dakle, humus je direktno povezan sa adsorpcijom spomenutih pesticida, što je u skladu sa rezultatima Bollag i Lolla (1983, Chenga i saradnika (1986) i Al-Ghadban i saradnika (1994) dok su niže vrednosti pH doprinele koncentrisanju ovih jedinjenja u zemljištu manje gustine. Pretpostavka o uticaju pH zemljišta na sadržaj ovih pesticide u zemljištu potkrepljena je i rezultatima istraživanja Cartera i Suffeta (1982 koji su pokazali da je DDT vezivanje za humus u vodi povećano u slučaju nižih pH. Dodatno, negativna korelacija uočena između pH i sadržaja humusa ukazuje da je izvor kiselosti u zemljištu razgradnja organske materije, što je u skladu sa rezultatima Jiriesa i saradnika (2002). Četvrta glavna komponenta, PC4, opisala je 11,3% ukupne varijanse prvobitnih podataka i povezana je sa sadržajem -HCH, PCB28 i gline u zemljištu (tabela 4.4). Organohlorni pesticidi se prvenstveno bolje (jače) vezuju za organsku materiju nego za glinu (Stevenson, 1976). Međutim, u zemljištu koje je analizirano dobijeno je da se sadržaji lakše ispraljivih organohlornih pesticida kao što su α-HCH, PCB28, mogu povezati sa sadržajem gline. Peta glavna komponenta, PC5, koja je opisala samo 6,8% varijanse, povezana je sa HCB i γ-HCH (lindan) (tabela 4.4), što ukazuje na njihovo zajedničko poreklo u zemljištu. Istorijski gledano, HCB je kao sporedni proizvod pri proizvodnji nekoliko hlorovanih pesticida, bio i prateća komponenta lindana (Barber i sar., 2005).

Tabela 4.4. Koeficijenti korelacije („loadings“) između zadržanih glavnih komponenata i promenljivih uključenih u “OCC” set (Franzle i saradnici, 1996) (prikazane su samo vrednosti veće od 60% maksimalne vrednosti koeficijenta korelacije u odnosu na svaku od zadržanih glavnih komponenata)

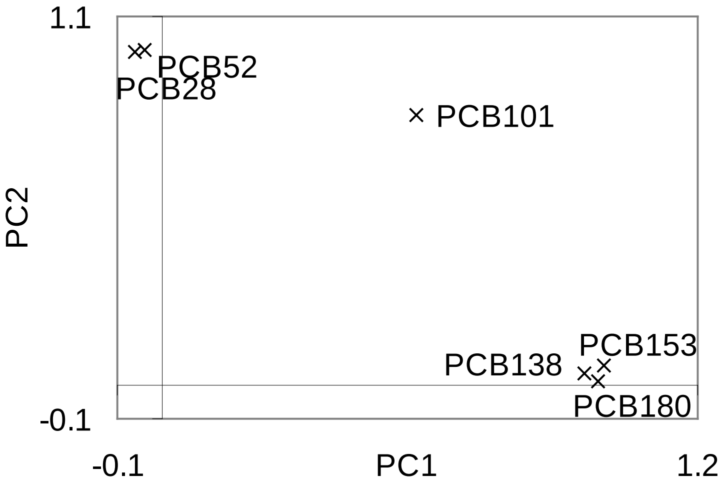
	PC1	PC2	PC3	PC4	PC5
Glina	0.1031	0.2166	-0.2591	**0.8626**	-0.0215
Gustina	-0.4901	-0.3040	**-0.6385**	0.0412	-0.0214
pH	0.4531	0.3445	**-0.7596**	0.1756	0.1574
Humus	0.2959	0.1253	**0.8772**	0.0075	-0.0246
PCB28	-0.0338	**0.7743**	-0.0667	**0.5553**	-0.1950
PCB52	**0.7336**	-0.0190	0.4726	0.4112	0.1275
PCB101	**0.9360**	0.0116	0.2902	0.0434	0.1541
PCB138	**0.9193**	0.2938	0.1347	0.1726	-0.0074
PCB153	**0.9944**	-0.0034	0.0635	-0.0649	0.0258
PCB180	**0.9960**	-0.0157	0.0165	-0.0616	0.0090
HCB	0.0655	-0.1192	-0.0663	-0.1854	**0.9237**
o,p’-DDE	-0.0748	**0.9881**	-0.0355	-0.0085	-0.0279
p,p’-DDE	-0.0680	**0.9905**	0.0029	-0.0240	-0.0264
o,p’-DDD	0.2427	**0.9632**	-0.0632	-0.0103	-0.0497
p,p’-DDD	0.4958	**0.7402**	0.2520	0.1429	-0.1756
o,p’-DDT	0.1001	**0.9203**	0.3563	-0.0192	0.0316
p,p’-DDT	0.4044	0.4008	**0.7851**	-0.0471	0.0899
α-HCH	-0.0099	-0.1170	0.2976	**0.9157**	-0.0769
β-HCH	0.1512	-0.0698	**0.7065**	0.4958	0.2734
γ-HCH	0.1278	-0.0779	**0.5963**	0.2809	**0.7199**
VAR [a], %	38.2	23.4	14.2	11.3	6.8

[a] Procentualni udeo varijanse polaznih podataka objašnjen zadržanim glavnim komponentama

Nadalje, prostorna raspodela organohlornih zagađujućih jedinjenja ispitana je primenom PCA na “PCB” i “OCP” setove sastavljene od podataka dostupnih u literaturi u vezi sadržaja indikatorskih PCB i izabranih OCP u zemljištu različitih zemalja (opis setova je dau poglavlju 3.2.2).

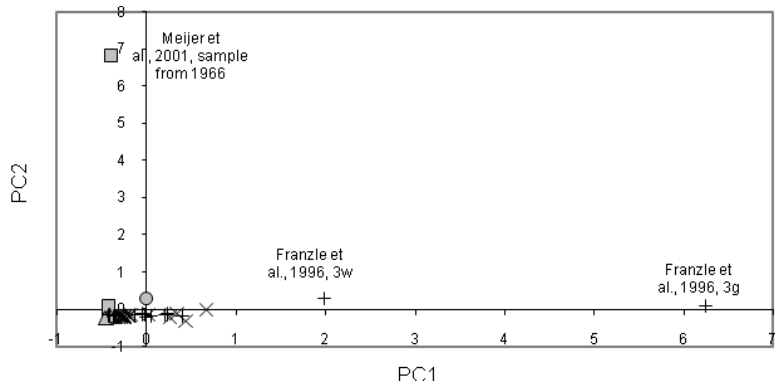
Dve glavne komponente su izdvojene analizom “PCB” seta, koji je sadržao podatke o prisustvu 6 indikatorskih PCB u zemljištu sa različitih lokacija u Evropi i Aziji. Ovim komponentama opisano je čak 96,6% ukupne varijanse ulaznih podataka. Prva komponenta, PC1, opisala je 57,1% varijanse, i bila je značajno povezana sa sadržajem PCB kongenera sa većim sadržajem hlora – PCB 138, 152 i 180 (slika 4.7). Drugom zadržanom komponentom, PC2, objašnjeno je

39,4% ukupne varijanse i ona je povezana sa PCB 28, 52 i 101 (slika 4.7). Dakle, dobijena je značajna povezanost sa jedne strane između kongenera sa manjim sadržajem hlora (PCB 28, 52 i 101), a sa druge strane između onih sa većim sadržajem hlora (138, 153 i 180). Ovo se donekle razlikuje od PCA rezultata dobijenih u odnosu na “OCC” set (Franzle i sar. 1996), ali ipak ostaje činjenica da je grupisanje uzoraka vođeno fizičko-hemijskim osobinama kongenera.

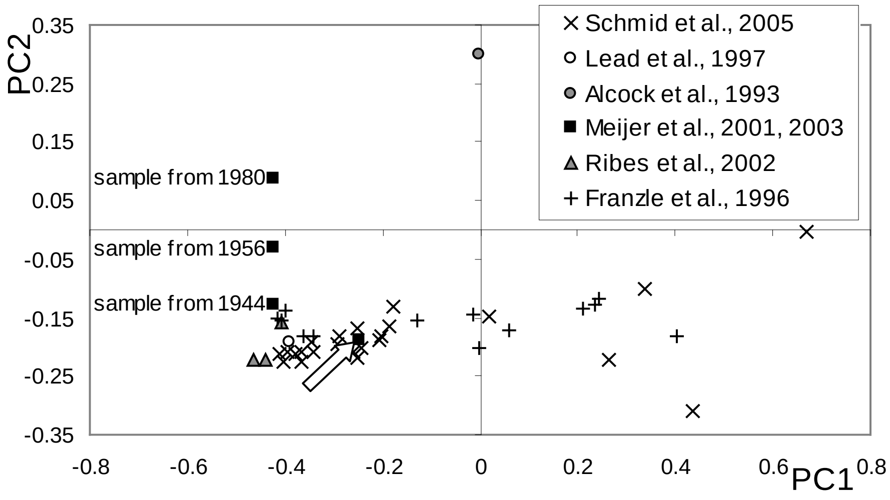


Slika 4.7. Koeficijenti korelacije (“loadings”) duž prve dve glavne komponente zadržane za “PCB” set podataka koji je sadržao podatke iz literature o prisustvu PCB u zemljištu iz Evrope i Azije

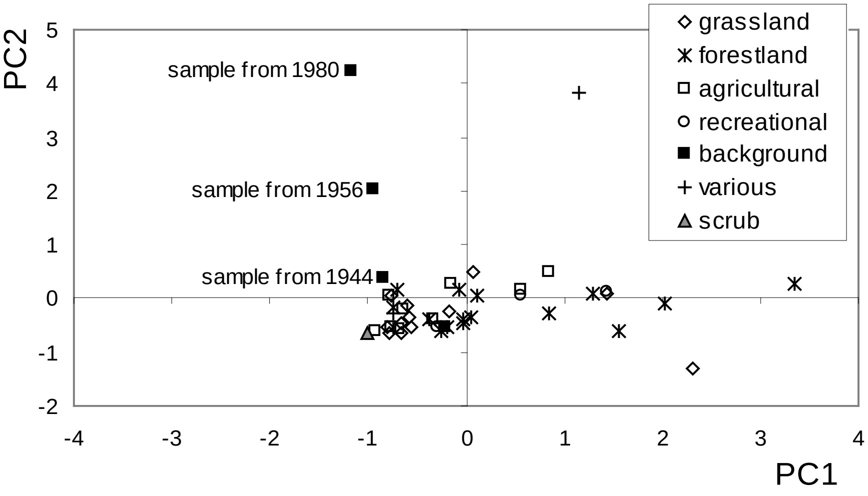
Dijagram rezultata (“*scores*”) PCA, tj. položaja uzoraka u novim koordinatama PC1 i PC2 (slika 4.8) pokazuje da je većina uzoraka smeštena oko koordinatnog početka usled relativno ujednačenih sadržaja PCB u zemljištu sa različitih lokacija, budući da koordinatni početak predstavlja aritmetičku sredinu svih uzoraka. Dalje, ovo govori u prilog da je prisustvo PCB u zemljištu uglavnom posledica njihovog prenosavazdušnim strujama sa velikih razdaljina od samih izvora emisije, a retko posledica direktnih emisija sa malih razdaljina. Uočena su tri nestandardna uzorka (“*outliers*”) sa izrazito velikim sadržajem određenih PCB kongenera: jedan uzorak je imao izrazito veliki sadržaj manje hlorovanih PCB kongenera (106 ng/g PCB28, 21 ng/g PCB52 i 7,3 ng/g PCB101; pogledati tabelu 3.9 u poglavlju 3.2.2), i taj je uzorak uzet u periodu intenzivnog korišćenja PCB (tj. to je uzorak iz 1966. god., (Meijer i sar., 2001), dok su druga dva nestandardna uzorka, uzeta iz nemačke provincije sa izrazitom industrijskom aktivnošću (Franzle i sar., 1996) imala izražen sadržaj kongenera sa većim udelom hlora, a to su uzorci zemljišta iz bašte (21,7 ng/g PCB 138, 24,5 ng/g PCB 153 i 15,9 ng/g PCB 180) i iz šumskog područja (10,2 ng/g PCB 138, 7,52 PCB 153 i 4,15 ng/g PCB 180), verovatno usled blizine lokalnih izvora emisije.



a)



b)



c)

Slika 4.8. Dijagram rezultata ("scores") PCA, tj. položaja uzoraka iz "PCB" seta, koji je sadržao podatke iz literature o prisustvu PCB u zemljištu iz Evrope i Azije, u novim koordinatama PC1 i PC2: svi uzorci (a), uveličani deo oko koordinatnog početka bez nestandardnih uzoraka ("outliers") i sa oznakama uzoraka prema izvoru iz literature (b), nakon izostavljanja 3 uočena nestandardna uzorka i naknadne PCA analize nad smanjenim "PCB" setom (c)

Bolje razdvajanje uzoraka se može uočiti kada se posmatra samo grupa formirana oko koordinatnog početka na dijagramu PC1-PC2 rezultata, bez uočenih nestandardnih uzoraka (slika 4.8b). Većina uzoraka se nalazi oko onog koji predstavlja srednju svetsku "pozadinsku" vrednost (označen strelicom na slici 4.8b; (PCB 28 0,051 ng/g, PCB 52 0,063 ng/g, PCB 101 0,32 ng/g, PCB 138 0,93 ng/g, PCB 153 0,72 ng/g, PCB 180 0,39 ng/g, (Meijer i sar., 2003). Većina uzoraka iz kasnih '90-tih godina prošlog veka i s početka 2000-tih su se našli u trećem i četvrtom kvadrantu ovog dijagrama (slika 4.8b), dok su se uzorci iz '80-tih i s početka '90-tih godina prošlog veka (predstavljeni kompozitnim arhivskim uzorkom iz 1980. god. (Meijer i sar., 2003) i srednjim sadržajem 39 uzoraka iz severno zapadne Engleske (Alcock i sar., 1993) našli u drugom kvadrantu, što govori o značajnom smanjenju sadržaja PCB u zemljištu tokom vremena. Isto tako, može se uočiti da su se PCB profili uzoraka iz kasnih '90-tih i s početka 2000. godina nalaze vrlo blizu onom iz i 1944. godine (Meijer i saradnici, 2001), što predstavlja period pre intenzivne industrijske proizvodnje i primene PCB. Razdvajanje uzoraka u odnosu na geografsko poreklo nije uočeno, što potvrđuje prethodnu pretpostavku o uniformnoj raspodeli PCB-ova usled atmosferske depozicije.

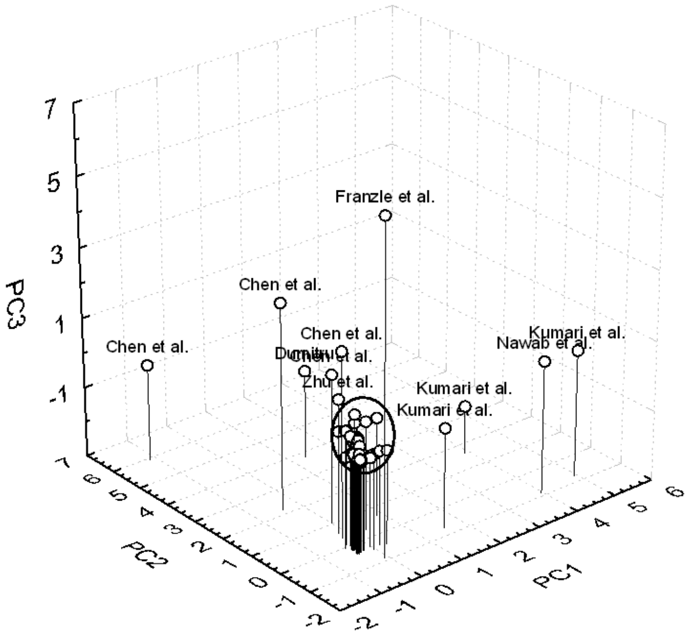
Da bi se eliminisao uticaj nestandardnih uzoraka (“*outliers*”) i proverilo da li su razlike između PCB profila uzoraka uslovljene načinom (vrstom) korišćenja uzoraka, PCA analiza je ponovo izvršena nad “PCB” setom iz kojeg su uklonjena 3 nestandardna uzorka (dakle, smanjeni “PCB” set je sastavljen od 46 uzoraka); dobijeni dijagram rezultata (“*scores*”), tj. položaja uzoraka duž PC1 i PC2 prikazan je na slici 4.8c. Većina uzoraka koji se nalazi na desnoj (pozitivnoj) strani PC1 (42,9%) su uzorci iz šumskih oblasti. Ovi uzorci imaju povećane sadržaje PCB 138, 153 i 180 (svakog iznad 1 ng/g). Horstmann i McLachlan i (1998) su utvrdili da sloj opalog, trulog lišća utiče na povećani sadržaj postojanih zagađujućih jedinjenja u šumskom zemljištu, koje na taj način predstavlja efikasniji način uklanjanja ovih jedinjenja iz vazduha od, na primer, poljoprivrednog zemljišta. PCB kongeneri sa većim udelom hlora, koji su se sa česticama iz vazduha deponovali na površini lišća, talože sa opalom vegetacijom na zemljište i na taj način zaostaju duže u zemljištu od lakših kongenera (sa manjim udelom hlora) koji su podložni isparavanju (Backe i sar., 2004). Dalje razlikovanje tipova zemljišta u odnosu na način njihovog korišćenja ili zonu uzorkovanja nije uočeno.

U odnosu na sadržaj OCP u uzorcima zemljišta iz Evrope i Azije (“OCP” set), tri glavne komponente su zadržane objašnjavajući 79,0% varijanse prvobitnih podataka: prva, PC1 (41,8% ukupne varijanse) povezana je sa HCH izomerima (koeficijenti korelacije sa PC1 su 0,9644 za α-HCH, 0,7219 za β-HCH i 0,9208 za γ-HCH); PC2 (24,3% ukupne varijanse) je povezana sa *p,p’*-izomerima DDD (0,7337) i DDT (0,8203); PC3 (12,9% ukupne varijanse) je povezana sa *p,p’*-DDE (0,9709). Jasno je uočljiva korelacija između α- i γ-HCH, ukazujući da ova dva izomera nose slične informacije, tj. da imaju sličnu sudbinu. Nije uočena značajna korelacija između *p,p’*-izomera DDT i njegovih metabolita, što govori u prilog složenosti degradacionih procesa DDT pod različitim uslovima.

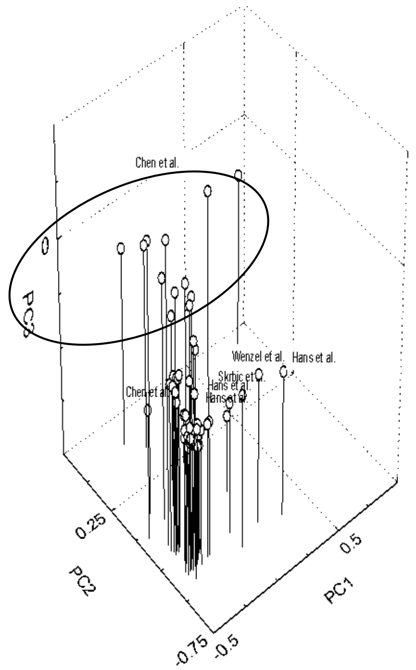
Na trodimenzionalnom dijagramu pozicija uzoraka duž novih koordinata PC1-PC2-PC3 (slika 4.9a) može se uočiti sličnost u OCP profilima većine uzoraka, ali takođe i veći broj nestandardnih uzoraka (“*outliers*”) nego u slučaju PCA analize izvršene nad “PCB” setom (slika 4.8a). Nestandardni uzorci u “OCP” setu su uzorci poljoprivrednog zemljišta iz Kine (Chen i sar., 2005; Zhu i sar., 2005); Rumunije (Dumitru, 2001) i Nemačke (Franzle i sar., 1996) usled velikih sadržaja DDT i njegovih metabolita (ukupni sadržaji ovih jedinjenja u spomenutim uzorcima su u opsegu 112-831 ng/g), što dalje ukazuje ili na ranije intenzivno korišćenje DDT povezano sa usporenom razgradnjom, ili, što je manje verovatno, na njegovu skorašnju upotrebu iako je zabranjena u ovim zemljama. U slučaju uzoraka iz Kine, povećani sadržaji DDT i njegovih metabolita mogu biti posledica korišćenja Dicofol pesticida koji sadrži 5-10% DDT kao nečistoće

(Zhu i sar., 2005), što je dozvoljeno u Kini (Zhang i sar., 2005).Takođe se može uočiti da su nestandardni uzorci i uzorci zemljišta iz Indije (Kumari i sar., 1996; Nawab i sar., 2003) usled povećanih sadržaja HCH-izomera (ukupni sadržaj ovih izomera u indijskim nestandardnim uzorcima se kreće u rasponu 48-144 ng/g) što ukazuje na skorašnje i/ili preterano korišćenje pesticida na bazi HCH na ovim lokacijama.

Na uveličanom prikazu dijagrama sa pozicijama uzoraka u novom sistemu koordinata (PC1-PC2-PC3, slika 4.9b) bez nestandardnih uzoraka, može se uočiti razdvajanje većine uzoraka iz Kine (Chen i sar., 2005), usled povećanih sadržaja DDT i njegovih metabolita. Takođe se može uočiti grupisanje tri uzorka iz Indije (Hans i sar., 1999), jednog iz Nemačke (Wenzel i sar., 2002) i jednog iz Srbije (Škrbić i sar., 2002). Ovi uzorci imaju povećane sadržaje HCH-izomera. Ostala četiri uzorka iz Novog Sada, uzeta 2001. godine (Škrbić i sar., 2002) su se našla u grupi sa ostalim analiziranim uzorcima, što govori o njihovoj međusobno sličnoj raspodeli i profilima OCP jedinjenja.



a)



b)

Slika 4.9. *Dijagram rezultata ("scores") PCA, tj. položaja uzoraka iz "OCP" seta, koji je sadržao podatke iz literature o prisustvu OCP u zemljištu iz Evrope i Azije, u novim koordinatama PC1, PC2 i PC3: svi uzorci (a), uvećani deo grupe zaokružene pod a) bez nestandardnih uzoraka ("outliers")*

4.3. Organohlorna zagađujuća jedinjenja u biološkim uzorcima

Analiza glavnih komponenata je primenjena i u slučaju setova sastavljenih od podataka u vezi prisustva indikatorskih PCB u humanom mleku: „Wielkopolska" set sastavljen je od rezultata analize sadržaja indikatorskih PCB kongenera u 50 uzoraka mleka majki izvršene na Fakultetu za farmaciju Univerziteta medicinskih nauka u Poznanu, (Szyrwinska i sar., 2007; Škrbić i sar., 2010) i podataka o telesnim karakteristikama davaoca i njihovom načinu ishrane i stanovanja;"International" set sačinjen je od podataka iz „Wielkopolska" seta i sadržaja indikatorskih PCB u uzorcima humanog mleka dostupnih u literaturi. Prvi set poslužio je za sagledavanje međuzavisnosti sadržaja ovih postojanih zagađujućih jedinjenja u humanom mleku i karakteristika davaoca, dok je drugi iskorišćen za utvrđivanje razlika i sličnosti u PCB-profilima u zavisnosti od geografskih lokacija, vremena uzorkovanja, načina ishrane i sl.

U tabeli 3.10 u poglavlju 3.2.3 prikazana su osnovni (opisni) statistički podaci o promenljivim uključenim u „Wielkopolska“ set, a podeljenih u zavisnosti da li se radi o prvorotkinjama (*primaparae*) ili drugorotkinjama (*secundiparae*). Medijana ukupne koncentracije indikatorskih PCB je 87,7 ng/g masnoće, što je slično vrednosti za mleko majki iz Finske (91 ng/g masnoće) i manje od onih dobijenih za mleko iz Holandije, Velike Britanije, Nemačke, Slovačke i Češke (116-502 ng/g masnoće; podaci 3. kruga studije izloženosti PCB, PCDD i PCDF putem humanog mleka koordinisane od strane WHO (van Leeuwen i sar., 2002; Kalantzi i sar., 2004). Medijana ukupne koncentracije indikatorskih PCB u mleku dojilja iz Wielkopolske je takođe niža od opsega vrednosti utvrđenih za centralnu Evropu od 200-400 ng/g masnoće (Bake i sar., 2007). Nešto niže vrednosti indikatorskih PCB nađene su u humanom mleku iz Brazila, Australije, Mađarske, Novog Zelanda, Bugarske i Irske (16-61 ng/g masnoće; (Malisch i sar., 2003). Najzastupljeniji kongeneri u mleku Wielkopolskih majki su heksahlorobifenili 138 i 153, zatim heptahlorobifenil 180 i pentahlorobifenil 118. Suma PCB 138, 153 i 180 činila je 84,60±11.22% ukupne PCB koncentracije, dok je relativna suma sadržaja nižih PCB kongenera (PCB 28, 52 i 101) 7,61±11,75%. Ovakva raspodela u kojoj dominiraju kongeneri sa većim sadržajem hlora je tipična za prisustvo PCB u biološkim uzorcima (tj. za „bioakumulirane“ PCB); dobijeni rezultati prisustva i raspodele PCB u mleku Wielkopolskih davaoca slaže se sa prethodnim rezultatima (Ramos i sar., 1997; Noren i sar., 2000; Gluszynski, 2000; Costopoulou i sar., 2006; Ingelido i sar., 2007; Szyrwinska i sar., 2007; Škrbić i sar., 2010; Nakamurai sar., 2008).

Rezultati PCA analize „Wielkopolska“ seta podataka prikazani su u tabeli 4.5. S obzirom da je prema Kaiserovom pravilu veliki broj glavnih komponenata zadržan (8 u odnosu na polazne 22 promenljive), sažeti u dvo- ili tro-dimenzionalni prostor. Ovo takođe govori da se podaci o prisustvu indikatorskih PCB kongenera ne mogu jednostavno povezati sa podacima uzetim iz upitnika o načinu ishrane i života davaoca. Primenom PCA upoređene su strukture baza podataka sa sadržajima PCB u mleku izraženim u različitim jedinicama (ng/g mleka, nmol/g g mleka, ng/g masnoće, nmol/g masnoće, mol.%, mas.%). Utvrđeno je da masene i molske koncentracije nose iste informacije ukoliko su iskazane u odnosu na istu osnovu, tj. po gramu masnoće ili po gramu mleka (tabela 4.5).

Tabela 4.5. Koeficijenti korelacije („loadings“) između zadržanih glavnih komponenata i promenljivih uključenih u “Wielkopolska” set koji sadrži koncentracije indikatorskih PCB kongenera u humanom mleku izražene na različite načine (ng/g mleka, nmol/g mleka, ng/g masnoće, nmol/g masnoće, mas% i mol%) i karakteristike donora. %VAR je procenat ukupne varijanse podataka objašnjenje svakom od zadržanih glavnih komponenata (PC)

Jedinica za izražavanje sadržaja PCB		ng/g mleka (nmol/g mleka)	ng/g masnoće (nmol/g masnoće)	mas% (mol%)
Veličina ulazne matrice (uzorci × promenljive)		34 × 22	34 × 21	34 × 22
PC1	PCB52			0.92588
	PCB118	0.92862	0.92119	
	PCB153	0.96759	0.96857	-0.91229
	PCB138	0.98097	0.98053	-0.94432
	PCB180	0.96099	0.95125	-0.84553
	%VAR	*22.72*	*22.10*	*17.79*
PC2	BMI	0.79219		0.81720
	MWINCR	-0.76574		-0.77270
	MILK		0.88095	
	MILK_FAT		0.80417	
	SMOKING			0.49969
	%VAR	*11.41*	*11.98*	*12.08*
PC3	CORDER	0.86185		0.85266
	MAGE	0.79992		0.84346
	RESAR		0.87266	
	PRESAR		0.91768	
	FISH	0.62709		0.59494
	%VAR	*9.45*	*10.01*	*11.54*
PC4	BMI		0.80130	
	MWINCR		-0.79010	
	RESAR	-0.86694		
	PRESAR	-0.91469		
	SMOKING		0.50384	
	PCB28		0.55674	
	MILK			0.88589
	MILK_FAT			0.81936
	%VAR	*8.82*	*8.88*	*8.83*
PC5	RESAR			0.85955
	PRESAR			0.92449
	MILK	0.89970		
	MILK_FAT	0.77085		
	CORDER		0.86591	
	MAGE		0.72238	
	%VAR	*8.22*	*8.43*	*8.33*
PC6	CGEND	0.83569	0.79494	0.81568
	CWINC	0.65989	0.65914	0.67172
	SAMPLING	0.58750	0.66661	
	%VAR	*7.41*	*7.52*	*7.60*
PC7	FAT%[b]	0.54872		-0.66825
	PCB28	0.57054	0.48807	0.55681
	PCB52	0.80482	0.76205	

	PCB101	0.56413	0.79213	0.86538
	%VAR	*6.19*	*6.15*	*6.45*
PC8	BEEF	0.89678	0.85957	0.87894
	SMOKING		0.53448	
	%VAR	*4.84*	*5.21*	*5.43*
UKUPNO %VAR		79.07	80.28	78.05

[a] Prikazane su samo vrednosti veće od 60% maksimalne vrednosti koeficijenta korelacije u odnosu na svaku od zadržanih glavnih komponenata.
[b] Sadržaj masnoće u humanom mleku je uvršten u PCA kao promenljiva jedino u slučaju ulazne matrice sa podacima o prisustvu PCB u mleku izraženim u ng/g mleka (nmol/g mleka) i mas% (mol%), tj. sadržaj masnoće nije razmatran u slučaju izražavanja sadržaja PCB po gramu masnoće.

Osam glavnih komponenata je zadržano u slučaju kada su PCB sadržaji iskazani po gramu masnoće ili mleka. U oba slučaja, zadržane komponente su opisale oko 80% ukupne varijanse polaznih podataka; prva komponenta je opisala oko 22% varijanse i bila je u korelaciji sa sadržajima najzastupljenijih PCB kongenera: PCB 118, 138, 153 i 180. Ovo istovremeno govori da su sadržaji viših PCB međusobno povezani (korelisani). Niži PCB 28, 52 i 101 su bili značajno povezani sa sedmom glavnom komponentom koja je opisala tek oko 7% varijanse polaznih podataka. Različito „ponašanje“ više i manje hlorovanih kongenera može se pripisati razlikama u njihovoj strukturi koja utiče i na brzinu njihovog nakupljanja (akumuliranja) u masnim tkivima. Naime, veći broj atoma hlora u bifenilnoj strukturi utiče na izraženije koncentrisanje ovih kongenera u živim organizmima, jer ova jedinjenja ne podležu metabolitičkoj razgradnji (Wingfors i sar., 2006). Za razliku od njih, manje hlorovani PCB se lakše razgrađuju tako da se i u manjoj meri akumuliraju.

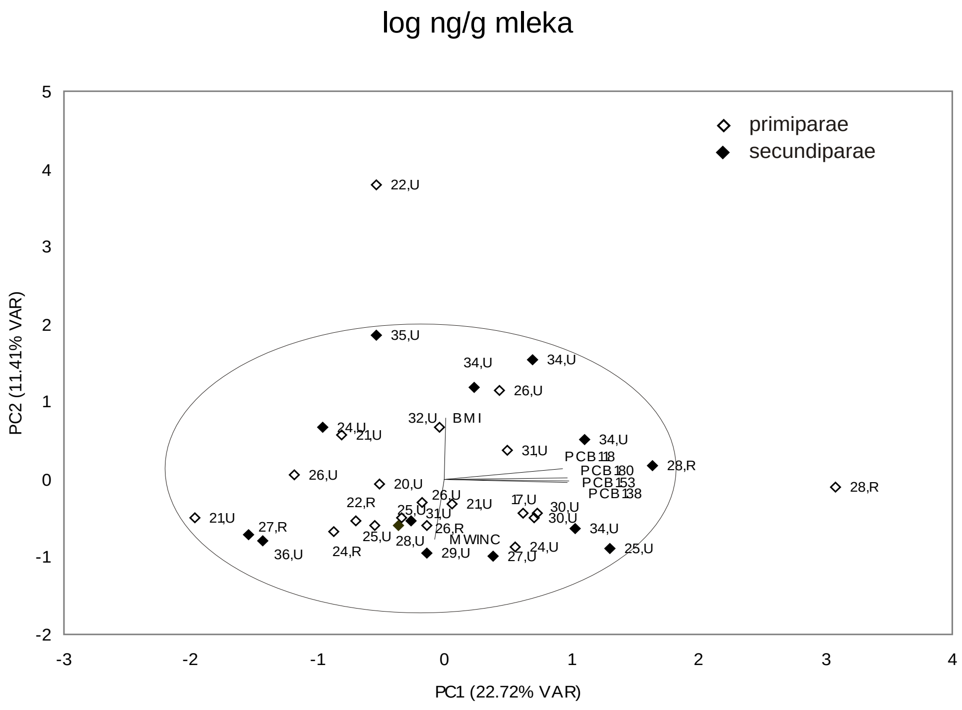
Sadržaj masnoće je značajno povezan jedino sa manje hlorovanim PCB kongenerima, i to duž sedme glavne komponente, PC7 (tabela 4.5). Iako u okviru PC1, međuzavisnost indikatorskih PCB kongenera sa većim sadržajem hlora i sadržaja masnoće nije bila značajna (koeficijent korelacije sadržaja masnoće nije prevazilazila 60% najvećeg koeficijenta korelacije dobijenog za PC7), ona se ipak ne može u potpunosti zanemariti s obzirom da je koeficijent korelacije od 0,54728, veoma blizak graničnoj vrednosti od 0,58858 (60% od maksimalnog koeficijenta korelacije) na osnovu koje su međuzavisnosti podeljena na značajne i neznačajne. Dakle, jedina promenljiva koja je povezana sa sadržajem PCB u mleku je sadržaj masnoće, što ujedno ukazuje da povećani sadržaj masnoća u mleku može biti povezan i sa većim sadržajima PCB.

Preostale glavne komponente bile su značajno povezane sa podacima iz upitnika koji su bili uključeni u „Wielkopolska“ bazu podataka. Na primer, prema ovim podacima, drugorotkinje, koje su očekivano bile u starije od prvorotkinja, u većoj meri koriste ribu u svojoj ishrani; korišćenje mlečnih proizvoda sa velikim sadržajem masnoće (preko 3%) je karakteristično za davaoce koji konzumiraju ove proizvode češće od dva puta nedeljno; kod majki sa većim vrednostima indeksa telesne mase (BMI) pre trudnoće uočen je manji porast mase tokom trudnoće; ženska novorođenčad brže napreduju (u vidu porasta mase CWINC, veličina objašnjena u poglavlju 3.2.3) od muških. Odsustvo značajnih međuzavisnosti koncentracija PCB i godina starosti majki i broja porođaja u skladu je sa ranijim zaključcima (Czaja i sar., 2001; Thomas i sar., 2006). Czaja i saradnici (2001) su utvrdili da ne postoji značajna razlika u koncentracijama PCB u mleku majki nakon drugog porođaja u odnosu na mleko nakon prvog porođaja, ukoliko je razmak između porođaja dve godine, što predstavlja period u toku kojeg dolazi do koncentrisanja (akumuliranja) PCB do nivoa sličnom onom neposredno nakon prvog porođaja. S obzirom da upitnik korišćen za formiranje „Wielkopolska“ baze podataka nije sadržao informaciju o periodu između prvog i drugog porođaja, može se pretpostaviti da je odsustvo korelacija između sadržaja PCB u mleku i broja porođaja posledica perioda dužih od dve godine između porođaja u slučaju drugorotkinja uključenih u studiju.

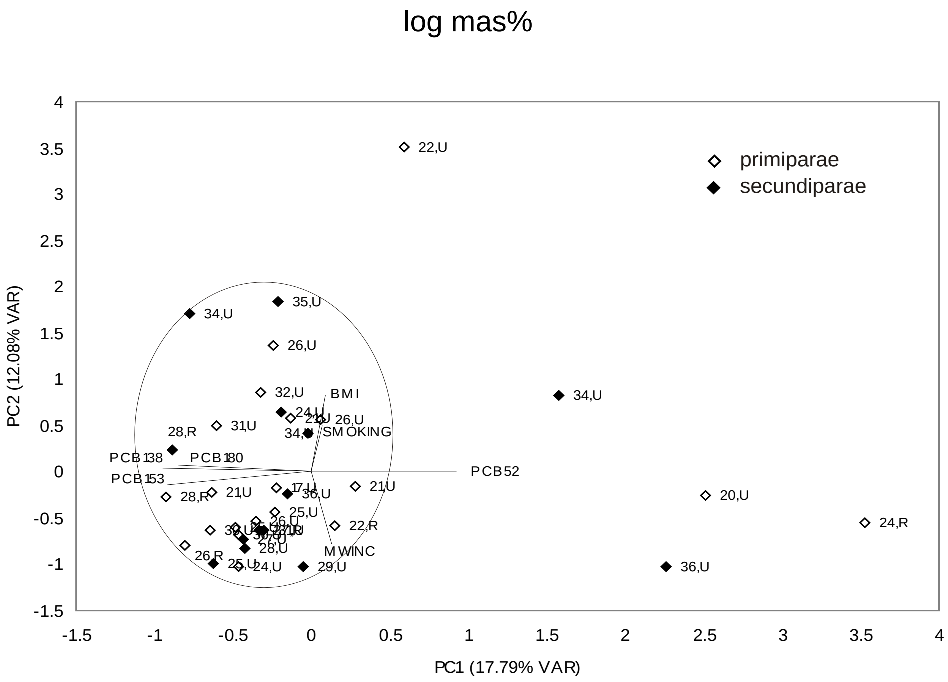
Ostale promenljive kao što je potrošnja ribe i mleka, navika pušenja, područje stanovanja, vreme uzorkovanja, pol deteta i brzina porasta mase nisu značajno povezane sa sadržajem PCB u mleku (tabela 4.5). Slično ovome, Schade i Heinzow (1998) nisu utvrdili značajne veze između sadržaja OCC u humanom mleku sa navikom pušenja niti sa polom deteta, dok Nakamura i saradnici (2008) nisu utvrdili relaciju između potrošnje ribe i koncentracije PCB u mleku.

Rezultati PCA analize masenih (molskih) procenata (tj. relativnog prisustva) indikatorskih PCB u mleku majki-davaoca iz Wielkopolska regiona su nešto drukčiji od prethodno opisanih koji su dobijeni za apsolutne količine izražene u masenim ili molskim koncentracijama (izraženim bilo po gramu masnoće ili gramu mleka). Ukupan broj zadržanih glavnih komponenata (8) je isti, kao i u slučaju apsolutnih koncentracija, i one su objasnile oko 78% ukupne varijanse. Prvom komponentom je opisano samo 18% varijanse polaznih podataka; PC1 je pozitivno povezana sa PCB 52 i negativno sa PCB 138, 153 i 180; PCB 28 i 101 su povezani sa PC7, kojom je opisano tek 6,45% varijanse. Ostale komponente, PC2-PC6 i PC8, su značajno povezane sa karakteristikama opisanim u upitniku i to na sličan način kako je to već opisano u slučaju PCA rezultata u odnosu na apsolutne masene ili molske koncentracije.

Dijagrami sa istovremenim prikazom koeficijenata korelacije i položaja uzoraka (tzv. „*biplot*“-ovi) u koordinatnom sistemu prve dve najznačajnije komponente, PC1 i PC2, zadržane u slučaju promenljivih iskazanih u ng/g mleka i mas.%, prikazani su na slici 4.10. Takođe, s obzirom da su PCB značajno povezani prvenstveno sa PC1, klasifikacija uzoraka je razmatrana jedino u odnosu na ovu glavnu komponentu. U oba slučaja (ng/g mleka i mas.%) uzorci su ravnomerno raspodeljeni duž PC1 bez obzira da li su u pitanju davaoci koji žive u gradskoj ili seoskoj sredini, da li je prvi ili drugi porođaj (slika 4.10), ili su u pitanju starije ili mlađe porodilje. Većina uzoraka se našla oko koordinatnog početka (slika 4.10a i 4.10b), što govori o njihovoj sličnosti u odnosu na količine i raspodelu PCB prvenstveno onih sa većim sadržajem hlora. Ovakvo grupisanje uzoraka je očigledno posledica slične izloženosti davaoca u ispitivanom regionu, što nadalje može dati uvid u prosečnu regionalnu izloženost ljudi. Uočeni su sledeći nestandardni uzorci („*outliers*“): u slučaju podataka izraženih u masenim koncentracijama, to je uzorak mleka 28-godišnje prvorotkinje iz seoske sredine u kojem je značajno povećan sadržaj visokohlorovanih PCB 118, 138, 153 i 180, dok su u slučaju izražavanja normalizovanih masenih (mas.%) koncentracija nestandardni uzorci imali povećani udeo PCB 52 u odnosu na ukupnu koncentraciju PCB (jedna prvorotkinja od 24 godine iz ruralne sredine i dve prvorotkinje (20 i 22 godine) i dve drugorotkinje (34 i 36 godine) iz urbane sredine). Takođe, uočava se ponovo da podaci iz upitnika nisu značajno povezani sa PCB profilima.



a)

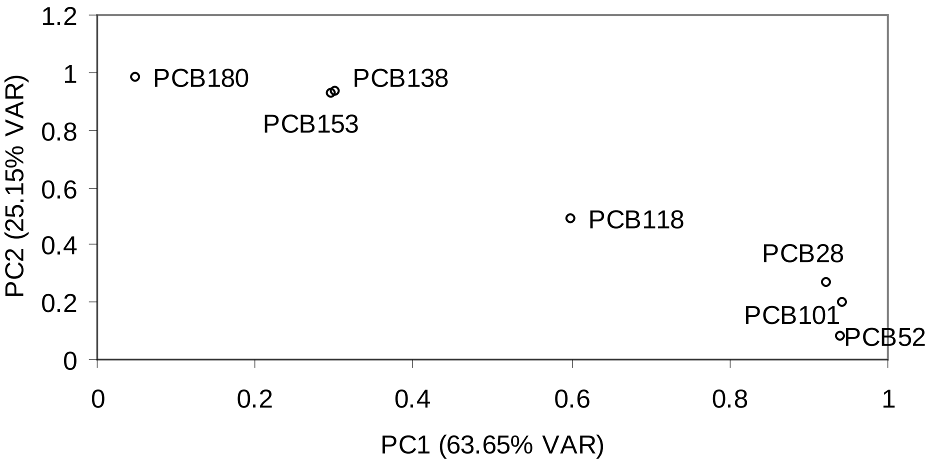


b)

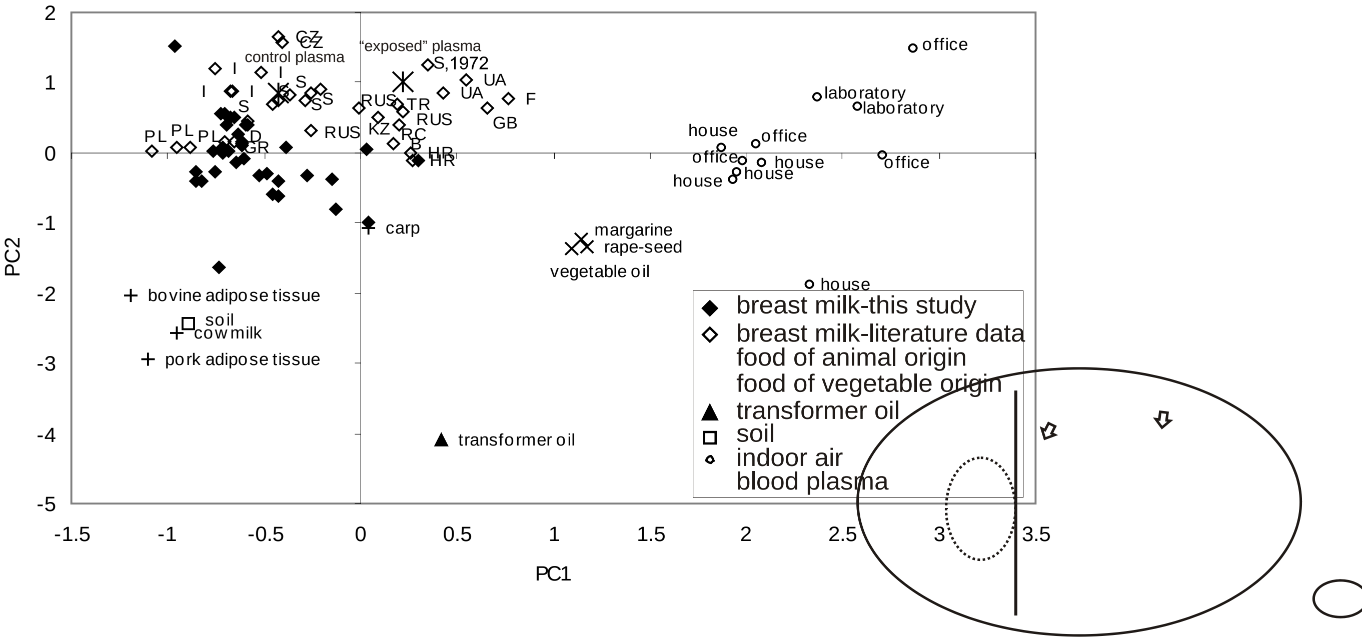
Slika 4.10. Dijagrami koeficijenata korelacija i položaja uzoraka iz "Wielkopolska" seta sa podacima izraženim u ng/g mleka (a) i mas% (b) indikatorskih PCB u koordinatnom sistemu PC1-PC2. Samo promenljive sa značajnim koeficijentima korelacije su prikazane (tabela 4.5). Prikazani brojevi predstavljaju starost majki-davaoca. U i R označavaju uzorke iz urbanih/prigradskih i ruralnih zona stanovanja, redom. %VAR je procenat ukupne varijanse polaznih podataka objašnjen zadržanim glavnim komponentama (PC).

Da bi se dobio bolji uvid u višedimenzionalnu strukturu dobijenih podataka, kao i da bi se ispitale sličnosti, odnosno razlike između prisustva PCB u humanom mleku davaoca sa različitih lokacija, izloženim različitim izvorima, PCA analiza je izvršena i nad „International" bazom podataka (detaljno opisana u poglavlju 3.2.3), i to u odnosu na dva slučaja: kada su količine PCB izražene u ng/g masnoće i kao procentualne masene koncentracije (mas.%). Dve glavne komponente su zadržane u oba slučaja, objašnjavajući 88,93% i 82,28% ukupne varijanse podataka, redom; zadražane komponente su sa ispitivanim promenljivim povezane na različite načine za ova dva načina izražavanja podataka u „International" bazi podataka.

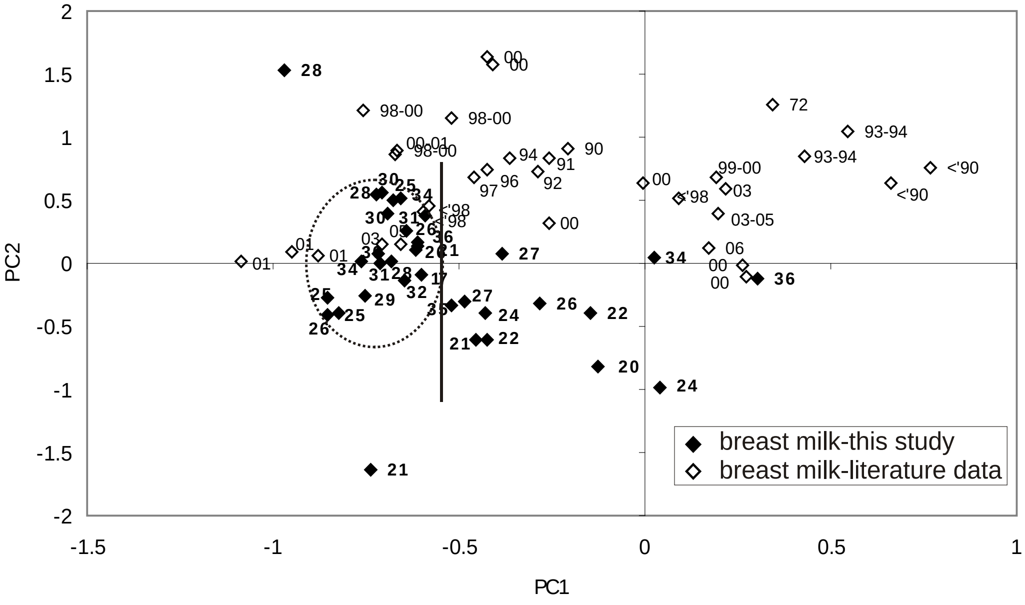
U slučaju izražavanja apsolutnih vrednosti PCB u mleku (ng/g masnoće), značajni koeficijenti korelacije sa PC1 (slika 4.11a) su dobijeni za sledeće PCB kongenere: 101 > 52 > 28 > 118, što ukazuje da su za razlikovanje uzoraka duž PC1 odgovorni od tri- do penta-hloro indikatorskih bifenila. Druga glavna komponenta je značajno povezana sa PCB 180 > 138 ~ 153, što znači da su ovi kongeneri (heksa- i hepta-) odgovorni za raspodelu uzoraka duž PC2. Na PC1-PC2 dijagramu položaja uzoraka na slici 4.11b može se uočiti da su se duž prve glavne komponente razdvojili biološki matriksi (locirani oko koordinatnog početka) i uzorci vazduha iz prostorija (pozitivni deo PC1-ose), što je posledica manjeg prisustva manje hlorisanih PCB kongenera u biološkim uzorcima od njihovog prisustva u vazduhu. Namirnice biljnog porekla u kojima su utvrđene povećane količine PCB 28, 52 i 101 su se grupisale između prethodne dve uočene grupe duž PC1. Uzorci humanog mleka su se razdvojile duž PC2 od grupe namirnica životinjskog porekla i uzorka otpadnog transformatorskog ulja i to u skladu sa njihovim sadržajima PCB 138, 153 i 180. Takođe, može se uočiti da je zbog sličnog PCB profila, uzorak zemljišta grupisan zajedno sa namirnicama životinjskog porekla.



a)


PC2
PC1
2
1
0
-1
-2
-3
-4
-5
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
"exposed" plasma
control plasma
CZ
S,1972
UA
F
GB
RUS
TR
KZ
RC
B
HR
PL
I
S
D
GR
carp
margarine
rape-seed
vegetable oil
office
laboratory
house
bovine adipose tissue
soil
cow milk
pork adipose tissue
transformer oil
◆ breast milk-this study
◇ breast milk-literature data
food of animal origin
food of vegetable origin
▲ transformer oil
□ soil
○ indoor air
blood plasma

b)


PC2
PC1
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-1.5
-1
-0.5
0
0.5
1
28
00
98-00
00-01
72
93-94
<'90
94
90
91
92
97
96
99-00
'98
03
03-05
00
06
30
25
34
31
26
36
01
27
29
32
17
24
22
21
20
◆ breast milk-this study
◇ breast milk-literature data

c)

Slika 4.11. Dijagrami PC1-PC2 dobijeni analizom glavnih komponenata u bazi podataka "International" sa koncentracijama 7 indikatorskih PCB izraženih u ng/g masnoće: a) dijagram koeficijenata korelacije (%VAR je procenat ukupne varijanse polaznih podataka objašnjen određenom glavnom komponentom), b) dijagram položaja uzoraka (sledeće oznake su korišćene da bi se ispitala geografska razlika između uzoraka: Belgija - B, Kina – RC, Hrvatska – HR, Češka Republika – CZ, Francuska – F, Nemačka – D, Velika Britanija – GB, Grčka – GR, Italija – I, Kazahstan – KZ, Poljska – PL, Rusija – RUS, Švedska – S, Ukrajina – UA, Turska – TR) c) uveličana grupa uzoraka lociranih oko koordinatnog početka na slici 4.11b (brojevi prikazani za uzorke analizirane u ovom radu se odnose na starost donora, dok oni koji su prikazano za podatke iz literature se odnose na godinu uzorkovanja u skladu sa tabelom 3.12).

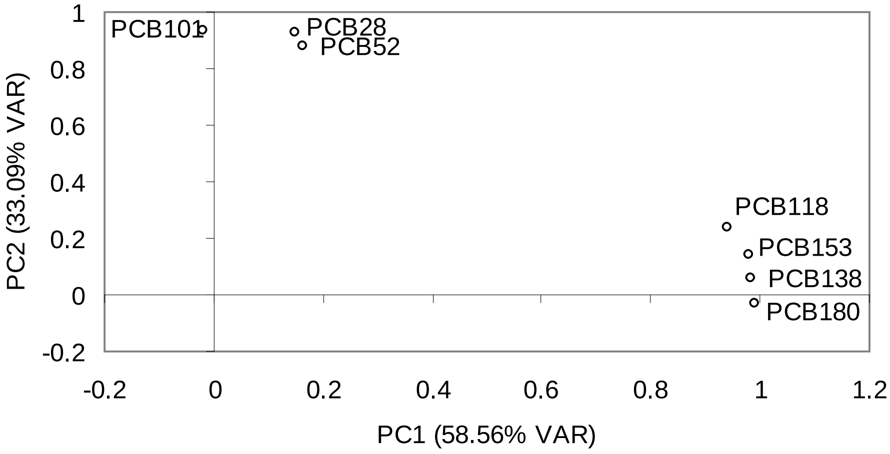
Zanimljivo je uočiti da su kompozitni uzorak krvne plazme građevinskih radnika uključenih u uklanjanje zaptivne mase sa PCB (Wingfors i sar., 2006), označen na slici 4.11b „izložena plazma“, i uzorak plazme radnika koji nisu bili direktno izloženi PCB-ovima („kontrolna plazma“ na slici 4.11b), grupisane zajedno sa ostalim biološkim matriksima, ali ipak međusobno udaljeni jedan od drugog: „izložena plazma“ se našla u pozitivnom delu PC1 u odnosu na „kontrolnu plazmu“ koja se našla u negativnom delu PC1. Ovo govori da direktna izloženost ljudi materijalima na bazi PCB, u ovom slučaju građevinskog materijala u vidu zaptivne mase, dovela do povećanih količina manje hlorovanih PCB kongenera u odnosu na ljude bez direktnog kontakta sa ovakvim materijalima. Uzorak „izložene plazme“ se na dijagramu na slici 4.11b našao blizu tri uzorka humanog mleka uzetih od davaoca iz razvijenih evropskih zemalja u periodu '70- i '80-tih godina 20. veka (slika 4.11b, uzorci „S, 1972“ (Noren i sar., 2000), „GB“ (Duarte-Davitson i sar., 1994); i „F“ (Bordet i sar., 1993), što predstavlja period u kojem su povećane količine PCB određene u životnoj sredini (Škrbić i Đurišić-Mladenović, 2007a). Sve ovo govori da uzorci humanog mleka locirani na pozitivnoj strani PC1 ukazuju na povećani sadržaj PCB u neposrednoj životnoj okolini ovih davaoca. S obzirom da su i PCB-profili uzoraka namirnica biljnog porekla kao i uzoraka vazduha iz prostorija na istoj strani PC1, može se pretpostaviti da su ovi davaoci najverovanije izloženi manje hlorovanim PCB-ovima kroz skorašnji unos namirnica biljnog porekla ili udisanja. Manje hlorovani PCB kongeneri prvenstveno postoje u gasovitoj fazi, jer su lakše isparljivi, a takođe se često mogu naći i u različitim namirnicama, prvenstveno biljnog porekla (Zuccato i sar., 1999; Škrbić i Đurišić-Mladenović, 2007b). Meso riba takođe sadrži manje hlorovane bifenile koji su prisutni i u vazduhu (Schaeffer i sar., 2006), što je u skladu sa dobijenim rezultatima i položajem uzorka mesa šarana na desnoj strani PC1 na slici 4.11b. U organizmu, ovi niži kongeneri postoje vrlo kratko, jer dolazi do njihove brze razgradnje i/ili eliminacije što znači da je njihov doprinos ukupnom sadržaju PCB u ljudskom organizmu veoma mali. Međutim, ako se pretpostavi da su uzorci humanog mleka uzeti nekoliko dana nakon konzumiranja namirnica biljnog porekla, manje hlorovani bifenili će u većoj meri uticati na ukupan sadržaj PCB u telu. U slučaju da su davaoci boravili duže vreme u prostoriji u kojoj je zbog prisustva direktnog izvora PCB i povećan sadržaj manje hlorovanih PCB-ova u vazduhu, može se očekivati da će usled unosa prisutnih PCB disanjem doći i do pojave specifičnog PCB-profila u tkivima. Mora se takođe naglasiti da potencijalna izloženost preko vazduha u prostorijama i konzumiranjem namirnica biljnog porekla nisu uvršteni u upitnik, tako da se može samo pretpostaviti da su ovi putevi izloženosti mogući uzroci povećanih sadržaja kongenera sa manjim sadržajem hlora u 12 uzoraka mleka iz „Wielkopolska“ baze podataka, koji su odvojeni od preostalih uzoraka (zaokruženih isprekidanom linijom) vertikalnom linijom na slici 4.11b. Preostali uzorci (zaokruženi isprekidanom linijom) imaju slične ukupne unose PCB i predstavljaju opštu (nespecifičnu) izloženost ljudi u razmatranom regionu Poljske, koja je u odnosu na ostale zemlje za koje postoje podaci o prisustvu PCB u humanom mleku, prilično mala. Inače, razdvajanje uzoraka iz Evrope i Azije nije uočeno.

Duž PC2, dva nestandardna uzorka („*outliers*“) su jasno odvojena od ostalih uzoraka iz „Wielkopolska“ baze podataka. S obzirom da je PC2 značajno povezana sa više hlorovanim kongenerima (slika 4.11a), može se zaključiti da su ovi nestandardni uzorci imali značajno veće količine (28-godišnja porodilija) i manje količine (21-godišnja porodilja) viših PCB-ova. Jasno je da je stepen izloženosti ova dva davaoca drukčiji od izloženosti većine analiziranih uzoraka iz Wielkopolska regiona, ali se izvori i razlozi drukčije izloženosti ne mogu povezati sa podacima dobijenim iz upitnika.

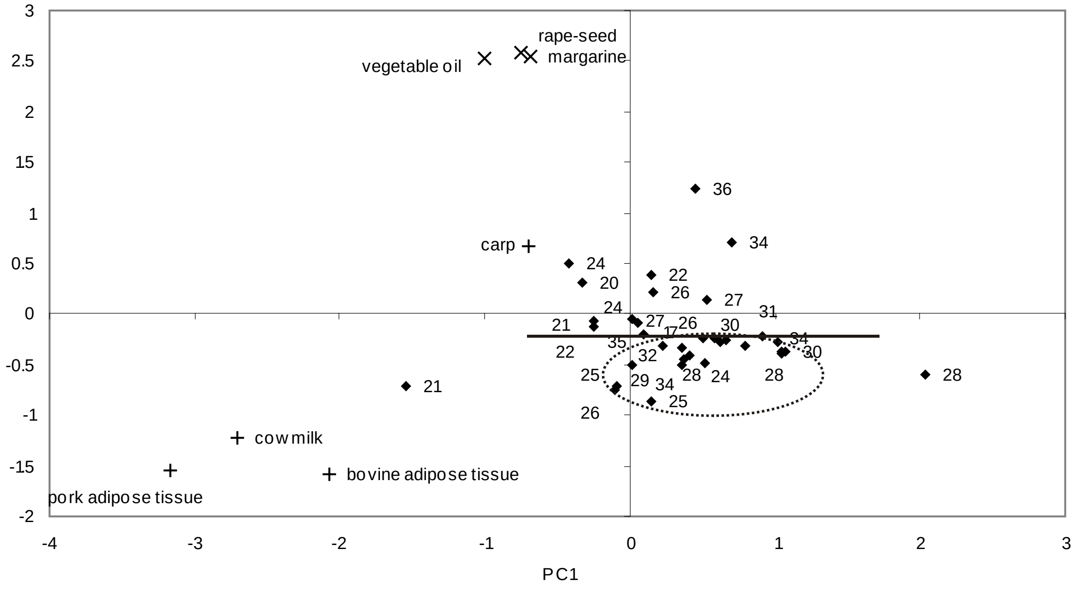
Na uveličanoj centralnoj grupi uzoraka mleka na slici 4.11c ne uočava se razdvajanje na osnovu vremena uzorkovanja.

Da bi se proverilo da li dodatni uzorci (vazduh, krv, i dr.) uključeni u „Internacionalni“ bazu narušavaju grupisanje uzoraka iz Wielkopolska regiona, izvršena je ponovna PCA analiza nad „Wielkopolska“ bazom podataka (matrica 34 x 7) proširenom sa podacima o prisustvu indikatorskih PCB kongenera u 7 reprezentativnih uzoraka namirnica iz Poljske (Lulek, 2002) - čime je formirana matrica veličine 41 x 7. Rezultati (prikazani na slici 4.13) pokazali su da se sličan udeo varijanse objašnjava sa prve dve glavne komponente kao i u slučaju PCA analize „International“ baze podataka (vrednosti VAR% na slikama 4.11a i 4.12a su slične), jedino što su zadržane komponente povezane sa promenljivima na suprotan način: u slučaju poljskih uzoraka („Wielkopolska“ baza veličine 41 x 7), PC1 je povezana sa manje hlorovanim, dok je PC2 povezana sa više hlorovanim PCB kongenerima, dok je obrnuto dobijeno u slučaju

„Internacionalne“ baze podataka (uporediti slike 4.11b i 4.11c sa 4.12b): istih 12 uzoraka sa povećanim količinama PCB 28, 52 i 101 se nalaze van zaokružene grupe, dok ista dva uzorka (21- i 28-godišnja porodilja) su nestandardni uzorci zbog velikih količina PCB-kongenera sa većim udelom hlora u strukturi. Dakle, može se zaključiti da uključenje uzoraka vazduha, krvne plazme, zemljišta i otpadnog transformatorskog ulja nije promenilo strukturu „Wielkopolska“ baze podataka.

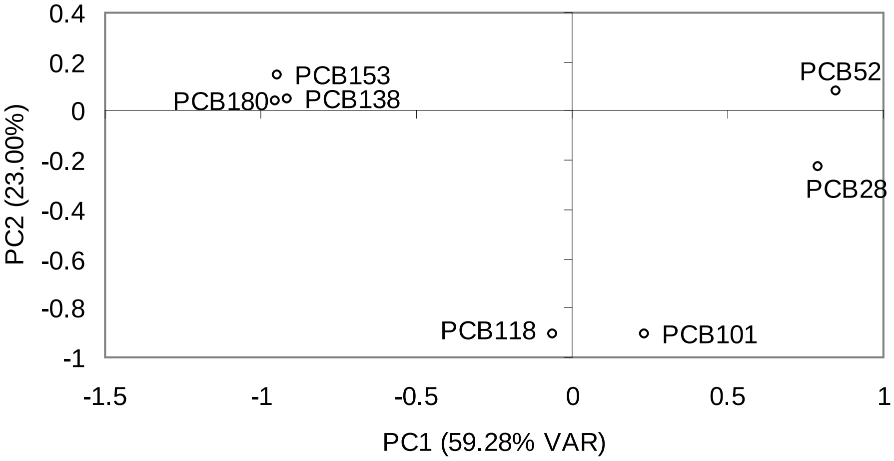


a)

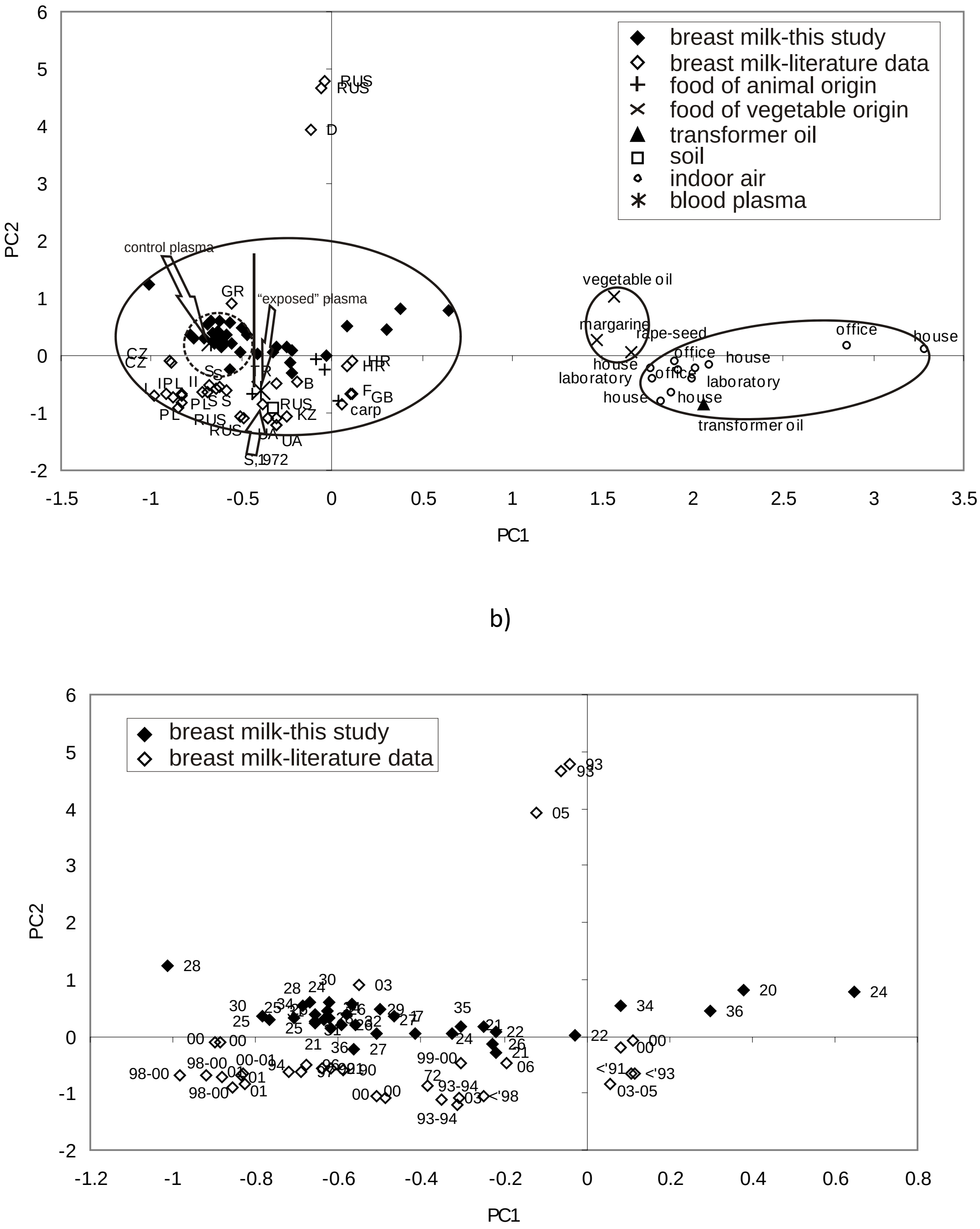


Slika 4.12. Dijagram PC1 - PC2 dobijen analizom glavnih komponenata u bazi podataka sa sadržajima 7 indikatorskih PCB (izraženih u ng/g masnoće) uključenih u "Wielskopolska" bazu podataka proširenoj sa sadržajem PCB u uzorcima hrane iz Poljske (Lulek, 2002): a) dijagram koeficijenata korelacije (%VAR je procenat ukupne varijanse polaznih podataka objašnjen zadržanim glavnim komponentama), b) dijagram položaja uzoraka (prikazani brojevi predstavljaju godine starosti majki-davaoca; isprekidanom linijom su zaokruženi isti uzorci kao i na slikama 4.11b i 4.11c)).

U slučaju „International" baze podataka u kojoj je prisustvo PCB iskazano u masenim procentima, PC1 je pozitivno povezana sa PCB 28 i 52, a negativno sa PCB 138, 153 i 180 (slika 4.13a). Druga glavna komponenta je značajno povezana sa PCB 101 i 118 (kongener koji ima toksično dejstvo slično polihlorovanim dibenzodioksinima), što se može videti na slici 4.13a. Na PCA dijagramu položaja uzoraka (slika 4.13b) može se uočiti razdvajanje uzoraka u dve glavne grupe duž PC1: središnja grupa se nalazi oko koordinatnog početka u kojoj su biološki uzorci koji imaju sposobnost da akumuliraju PCB u masnoj fazi, dok se u "desnoj" grupi nalaze uzorci namirnica biljnog porekla i vazduha prostorija. Ponovo je 12 uzoraka davaoca iz Wielkopolska regiona udaljeno od većine uzoraka koji su zaokruženi isprekidanom linijom (slika 4.13b). Prostorna (slika 4.13b) i vremenska (slika 4.13c) sličnost između donora nije uočena, što govori o specifičnoj izloženosti donora u svakoj od zemalja i/ili perioda uzorkovanja. Dva nestandardna uzorka duž PC2 su ponovo jasno razdvojeni od ostalih uzoraka kao posledica potpuno različitog udela PCB 101 i 118 u ukupnom sadržaju indikatorskih PCB-ova.



a)



b)

c)

Slika 4.13. Dijagram PC1-PC2 dobijeni analizom glavnih komponenata u bazi podataka "International" sa koncentracijama 7 indikatorskih PCB izraženih u mas.%: a) dijagram koeficijenata korelacije, b) dijagram položaja uzoraka (oznake korišćene za ispitivanje geografskih razlika između uzoraka objašnjenje su ispod slike 4.11) c) uveličana grupa uzoraka smeštenih oko koordinatnog početka na slici 4.12b (brojevi prikazani za uzorke analizirane u ovom radu se odnose na godine starost davaoca, dok se oni koji su prikazano za podatke iz literature odnose na godinu uzorkovanja u skladu sa tabelom 3.12).

Dakle, može se zaključiti da je primena PCA nad formiranim bazama podataka ukazala na nizak i prilično ujednačen stepen izloženost PCB-ovima u Wielkopolska regionu (slike 4.11b, 4.11c i 4.13b i 4.13c) bez uočene razlike između prvorotkinja i drugorotkinja ili između donora iz gradskih i seoskih sredina (slika 4.10a i 4.10b). Podaci o načinu života dobijeni iz upitnika popunjenih od strane davaoca nisu povezani značajno sa sadržajima PCB. Iako je ishrana prvenstveno prihvaćena kao glavni način unosa organohlornih polutanata u organizam, podaci o ishrani iz upitnika nisu povezani sa PCB-profilima nađenim u humanom mleku davaoca iz Wielkopolska regiona. Moguću razlozi za ovo mogu se potražiti u sledećem: vrsta namirnica koje koriste davaoci nisu dovoljno razjašnjene u upitniku, na primer, da li se radi o ribi iz slatkovodnih ili slanih voda, da li je ona lokalna ili uvezena (Lakind i sar., 2004) da li spada u vrste bogate masnoćom ili ne (Ingelido i sar., 2007); navike u ishrani opisane upitnikom ne odražavaju stvarni unos PCB-ova; konzumiranje namirnica biljnog porekla uopšte nije razmatrano u upitniku. Takođe, poređenje uzoraka iz Wielkopolskog regiona sa relevantnim podacima iz literature ukazuju na mogućnost da su neki od davaoca bili izloženi PCB iz drugih izvora u svakodnevnom životu, za njih značajnih nego što je unos PCB hranom. S tim u vezi, mora se naglasiti da moguća izloženost udisanjem, tj. prisustvo potencijalnih izvora PCB u zatvorenim prostorima, nije uzeto u obzir kroz upitnike, iako se u poslednje vreme dosta pažnje posvećuje ovome (Tan i sar., 2007; Menichini i sar., 2007). Na primer, neka istraživanja (Currado i sar., 1998; Schade i sar, 1998; Jandacek i sar., 2001; Heinzow i sar., 2004; Hazrati i sar., 2006; Wingfors i sar., 2006; Rudel i sar., 2008) su pokazala da bi postojanje povezanosti (korelacije) između PCB sadržaja u humanom mleku i okruženja u kojem davaoci stanuju i rade moglo biti ispitano ukoliko bi se u upitnike uvrstili podaci o potencijalnim PCB izvorima u zatvorenom prostoru, kao na primer podaci o kupovini nameštaja ili podnih obloga u poslednjoj deceniji, bilo kod kuće ili na poslu, zatim slučajevi poliranja drvenih podloga, godina izgradnje zgrade stanovanja, sezona uzimanja uzoraka (zimi ili leti), frekvencija korišćenja raznih električnih uređaja (u satima po danu), kao što su televizori, mikrotalasne peći, kompjuteri, i dr.

4.4. Postojana organska zagađujuća jedinjenja u vazduhu

Rezultati ispitivanja sadržaja tri grupe postojanih zagađujućih organskih jedinjenja (PAH, OCP i PCB) u vazduhu uzorkovanom na šest mernih stanica u Republici Makedoniji predstavljeni su u tabeli 3.14. Najveće koncentracije sve tri grupe ispitivanih jedinjenja u vazduhu utvrđene su na lokaciji merne stanice Skopje-MEPP (br.3), a zatim na lokaciji stanice Skopje-OHIS (br. 2). Obe ove lokacije (opisane u poglavlju 3.1.4) nalaze se na području Skopja, najvećeg i najnaseljenijeg grada u Makedoniji. Koncentracije PAH-jedinjenja u vazduhu su za nekoliko redova veličine veće od koncentracija OCP i PCB. U poređenju sa koncentracijama koje su odredili Klanova i saradnici (2007) za gasnu fazu analiziranih uzoraka vazduha uzetih na različitim mestima u Srbiji i Bosni i Hercegovini, vrednosti dobijene za Makedoniju su znatno niže. U radu Klanove i saradnika ((2007) ukupna koncentracija PAH-ova u vazduhu u Srbiji kretala se u rasponu 10-1290 ng/m^3, PCB 0,103-39.7 ng/m^3, DDX (suma DDT i njegovih proizvoda DDD i DDE) 0,020-0,519 ng/m^3, i HCB 0,025-0,174 ng/m^3, dok su za Bosnu i Hercegovinu dobijene sledeće vrednosti redom: 3-210 ng/m^3 za PAH-ove, 0,060-5,645 ng/m^3 za PCB-ove, 0,012-0,193 ng/m^3 za DDX i 0,064-0,171 ng/m^3 za HCB. Međutim, srednje ukupne koncentracije HCH-izomera (α-, β-, γ-, δ-) u dva uzorka vazduha uzetih na lokacijama mernih stanica Skopje-OHIS (br. 3) i Skopje-MEPP (br. 2), koje su iznosile 0,758 i 0,434 ng/m^3, redom, značajno su veća u odnosu na vrednosti određene u vazduhu Srbije (0,100-0,321 ng/m^3) i Bosne i Hercegovine (0,025-0,054 ng/m^3). Visoke vrednosti HCH u vazduhu Skopja mogu se pripisati deponiji lindana, sa oko 10000 t otpadnog materijala smeštenog na lokaciji bivše fabrike OHIS (National Waste Management Plan, 2005).

Specifični odnosi određenih jedinjenja, kao što su α-/γ-HCH, *o,p'-/p,p'*-DDT i *p,p'*-DDT/*p,p'*-DDE, koriste se za identifikaciju izvora emisije HCH i DDT. Vrednosti ovih odnosa su takođe izračunate u ovom radu za ispitanih šest lokacija u Makedoniji i dobijeni su sledeći rasponi: 0,15-1,74 za α-/γ-HCH, 0,24-2.43 za *o,p'-/p,p'*-DDT, i 0,08-0,49 za *p,p'*-DDT/*p,p'*-DDE. Da bi se utvrdilo da li je došlo do skorašnje upotrebe HCH (bilo dozvoljene bilo zabranjene), najčešće se poredi odnos koncentracija α- i γ-HCH prisutnih u samom uzorku iz životne sredine (uključujući i uzorke vazduha) sa istim ovim odnosom u dve vrste proizvoda na bazi HCH, koji su se proizvodili (ili se još proizvode) širom sveta: tehnička smesa HCH (pored ostalih izomera sadrži 55-80% α-HCH i 8-15% γ-HCH) i lindan (>99% γ-HCH) (Li i sar.,. 2006). Inače, proizvodnja tehičke smese HCH je zabranjena, dok je primena lindana još uvek dozvoljena u mnogim zemljama. Srednji odnos α-/γ-HCH u tehničkoj smesi HCH je između 3:1 i 7:1, dok se sa dodatkom lindana ovaj odnos smanjuje (Gong i sar., 2010). Male vrednosti odnosa α-/γ-HCH dobijene za vazduh na ispitivanim lokacijama u Makedoniji, naročito one ispod 0,5 koje su dobijene za lokacije Skopje-MEPP, Bujkovci i Bitola, ukazuju na moguće skoro korišćenje lindana. S obzirom da ni za jednu lokaciju nije utvrđen odnos α-/γ-HCH veći od 3 može se reći da nije bilo skorašnjeg korišćenja tehničke smese HCH. Vrednosti odnosa α-/γ-HCH veće od 1 (tj. 1,74 dobijen za Skopje-OHIS) ukazuje na moguće prirodne procese razgradnje („*weathering*") α-HCH prisutnog u životnoj sredini nakon korišćenja dozvoljenog u prethodnom periodu i nastajanje γ-HCH u prisustvu sunčeve svetlosti (Li i sar., 2006). Odnos *o,p'-/p,p'*-DDT se uobičajeno koristi da bi se razlikovali postojeći izvori DDT (stari depoziti ili trenutno dozvoljeni pesticidi koji sadrže male (prateće) količine DDT (kao što je slučaj sa pesticidom Dicofol koji se koristi u Kini) od tehničkog DDT, koji je zabranjen za upotrebu. Tehnički DDT sadrži manje *o,p'*-DDT (oko 15%) nego *p,p'*-DDT (oko 85%), dok je za pesticide kao što je dicofol karakteristična velika vrednost odnosa *o,p'-/p,p'*-DDT (Gong i sar., 2010). U slučaju uzoraka iz Makedonije, najveće vrednosti odnosa *o,p'-/p,p'*-DDT od 2,43 dobijene su za lokaciju u Strumici u periodu 09.07.-06.08.2007., ukazujući da je moguć skorašnji unos pesticida sa tragovima DDT. Odnos *p,p'*-DDT/*p,p'*-DDE se često koristi za razlikovanje "svežih" od "starih" unosa *p,p'*-DDT. S obzirom da su sve vrednosti ovog odnosa bile ispod 0,5, može se pretpostaviti da nije bilo skorašnjih "svežih" unosa *p,p'*-DDT.

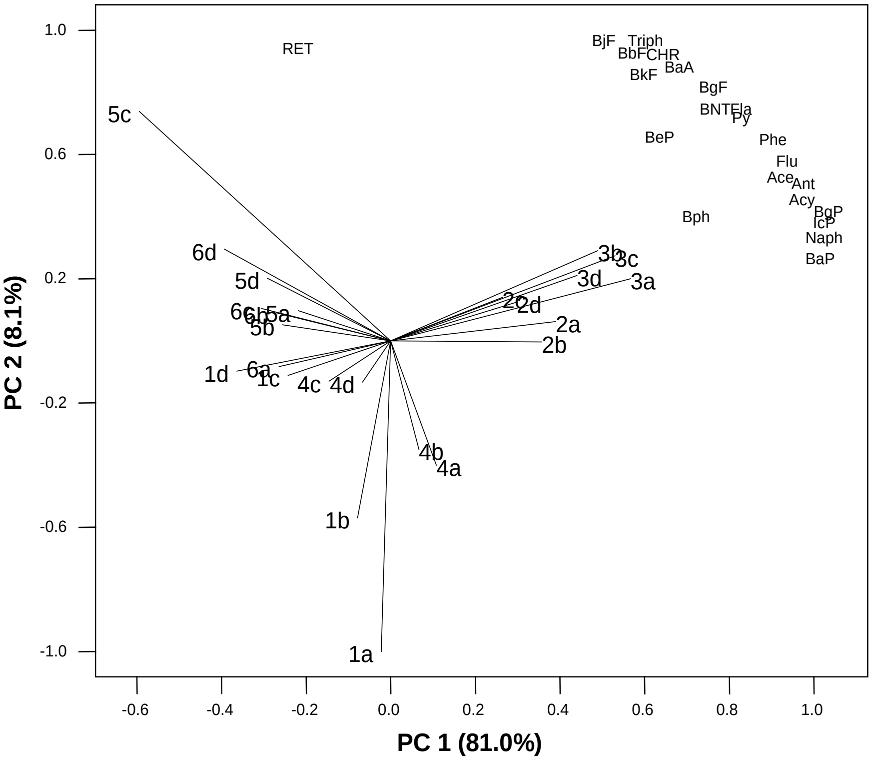
Rezultati PCA analize dobijeni za podatke o prisustvu zagađujućih organskih jedinjenja u vazduhu šest mernih stanica u Makedoniji, svrstanih u tri baze podataka prema grupama jedinjenja (tj. u „PAH", „OCC" i „SVOC" baze podataka) prikazani su u tabeli 4.6 i na slikama 4.14-4.16. U odnosu na „PAH" bazu podataka sa podacima o prisustvu PAH-ova u vazduhu, PC1 opisuje 81,0% varijanse polaznih podataka; ova glavna komponenta je pozitivno povezana sa koncentracijama gotovo svih PAH-ova, osim sa koncentracijom retena. Druga glavna komponenta, PC2, opisala je oko 8,1% varijanse podataka. Iz tabele 4.6 vidi se da su određene promenljive povezane značajno sa obe zadržane glavne komponente. Međutim, za interpretaciju rezultata važnije je posmatrati PAH-ove koji su značajno povezani samo sa jednom glavnom komponentom, jer se tako lakse može pretpostaviti mogući izvor emisije, tj. faktori koji utiču na klasifikaciju uzoraka. Na ovom mestu, potrebno je ponovo napomenuti da se PAH-ovi u životnoj sredini mogu podeliti prema svom poreklu na petrogene (nesagorela nafta ili njeni derivati) i pirogene (nastali sagorevanjem organske materije, bilo fosilnih goriva ili biomase). U pirogenim smesama PAH-ova, preovlađuju nesupstituisani PAH-ovi, prvenstveno oni sa većim brojem prstenova (4 do 6), u odnosu na alkilovane PAH-ove manjih molekulskih masa (sa dva i tri prstena) koji preovlađuju u smesama petrogenih PAH-ova (Ramdahl i sar., 1983). Kako su PAH-ovi i sa manjom i sa većom molekulskom masom značajno povezani sa PC1, može se reći da je ova komponenta ukazala na kombinovane izvore PAH-ova u atmosferi ispitivanih lokacija, a da su najvece koncentracije nađene u stambenom delu Skopja (uzorci br. 2 i 3) povezane sa pirogenim (na primer, sagorevanje fosilnih goriva) i sa petrogenim (na primer, ispravanje iz depozita naftnih derivata na putevima, gubici usled isparavanja tokom punjenja rezervoara motornih vozila gorivom, i sl.) izvorima PAH-ova. Reten je alkilovani fenantren (1-metil-7-izopropil fenantren) koji je indikator sagorevanja biomase (Ramdahl i sar., 1983; McDonald i sar., 2000; Quiroz i sar., 2011) i ovo jedinjenje je značajno povezano sa PC2, zajedno sa još nekim PAH-ovima (nespecifičnim u odnosu na pretpostavljene izvore). Ovo je ukazalo da se PC2 može pripisati sagorevanju biomase.

Tabela 4.6. Koeficijenti korelacije („loadings“) između zadržanih glavnih komponenata i promenljivih uključenih u “PAH” i “OCC” baze podataka koji su sadržali koncentracije 22 PAH-jedinjenja i 19 OCC jedinjenja, redom, izmerenih na šest lokacija u Makedoniji tokom 28-dnevnih uzastopnih perioda od 14. maja do 3. septembra 2007. Istaknute su vrednosti koje su veće od 60% maksimalne vrednosti koeficijenta korelacije dobijene za određenu glavnu komponentu

PAH	**PC 1**	**PC 2**	**OCC**	**PC1**	**PC2**	**PC3**
Naph	**0.878**	0.304	PCB28	**0.637**	**0.652**	0.139
Ace	**0.797**	0.478	PCB52	**0.677**	**0.682**	0.044
Acy	**0.844**	0.414	PCB101	**0.647**	**0.649**	0.069
Flu	**0.816**	**0.525**	PCB118	**0.618**	**0.593**	0.131
Phe	**0.780**	**0.587**	PCB138	0.552	**0.728**	0.063
Ant	**0.849**	0.459	PCB153	**0.727**	0.530	0.206
Fla	**0.719**	**0.675**	PCB180	0.152	0.388	**0.699**
Py	**0.723**	**0.678**	*α*-HCH	0.124	**0.959**	0.011
BaA	**0.580**	**0.796**	*β*-HCH	0.328	**0.808**	-0.006
CHR	**0.541**	**0.832**	*γ*-HCH	0.287	0.460	0.409
BbF	0.481	**0.859**	*δ*-HCH	0.066	**0.846**	0.294
BkF	0.506	**0.812**	*o,p'*-DDE	**0.795**	0.207	-0.162
BaP	**0.878**	0.243	*p,p'*-DDE	**0.924**	0.205	-0.081
IcP	**0.894**	0.359	*o,p'*-DDD	**0.786**	0.099	0.341
BgP	**0.896**	0.357	*p,p'*-DDD	**0.765**	0.525	0.148
Bph	**0.617**	0.364	*o,p'*-DDT	**0.917**	0.109	-0.022
RET	-0.157	**0.849**	*p,p'*-DDT	**0.952**	0.197	-0.067
BNT	**0.654**	**0.674**	PeCB	0.151	-0.150	**-0.784**
BgF	**0.653**	**0.738**	HCB	-0.004	0.079	**-0.806**
Triph	0.502	**0.854**	%VAR^a	57.0	13.8	8.4
BjF	0.435	**0.872**				
BeP	0.538	**0.594**				
% VAR^a	81.0	8.1				

^{a} Udeo ukupne varijanse opisan svakom od zadržanih glavnih komponenata

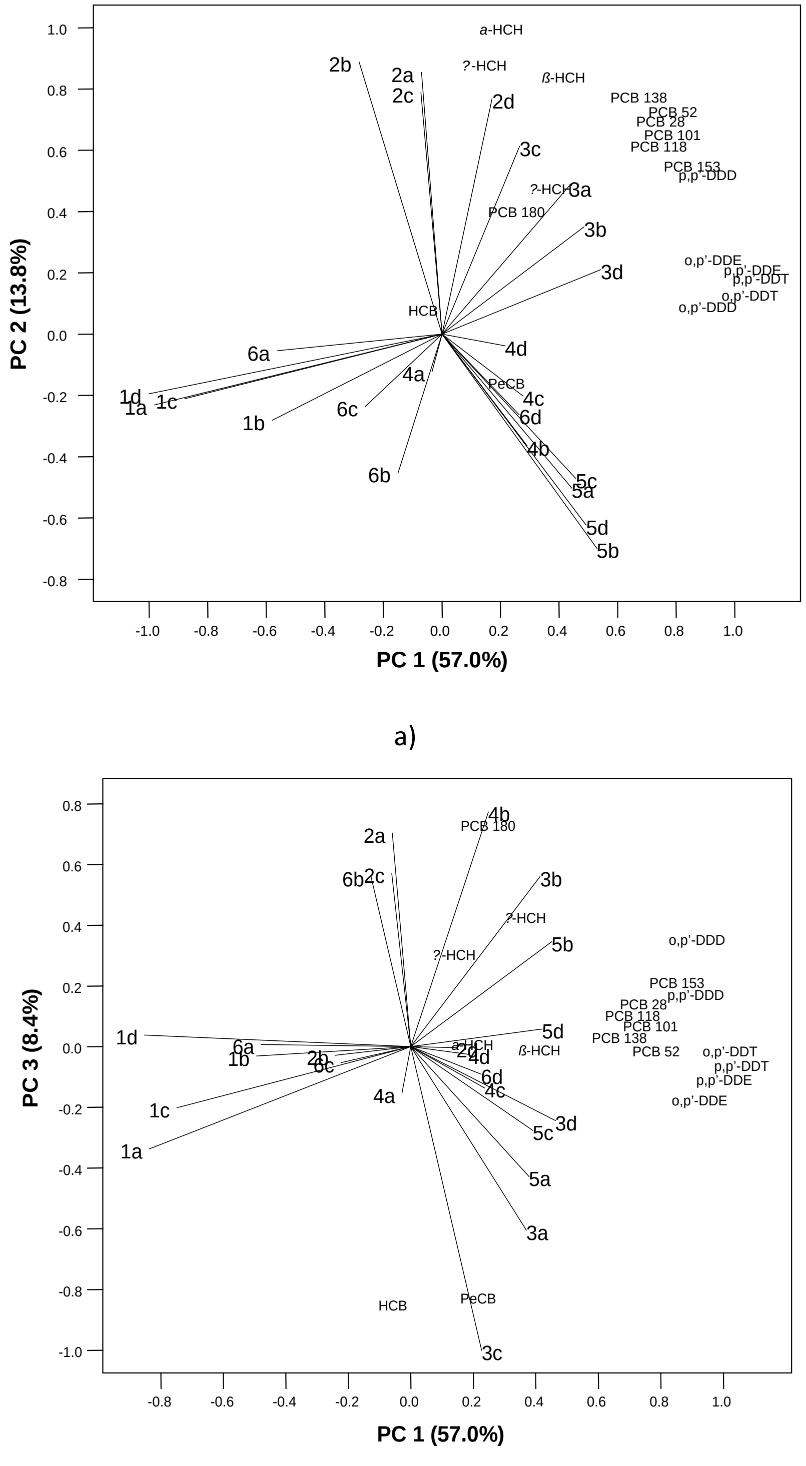
S obzirom da se PC1 može povezati sa ukupnom koncentracijom PAH-ova u vazduhu ispitivanih lokacija, grupisanje uzoraka duž ove glavne komponente je i posledica razlika u prisutnim ukupnim koncentracijama ovih jedinjenja. Raspodela uzoraka duž PC2 može se pripisati razlikama u koncentraciji retena u vazduhu između lokacija. Na „biplotu“ na slici 4.14 mogu se uočiti tri različite grupe uzoraka: grupa 1 obuhvata sva četiri perioda uzorkovanja na dve lokacije u Skopju (br. 2a-2d i 3a-3d) u kojima su utvrđene najveće koncentracije PAH; grupa 2 sastoji se od uzoraka iz seoskih područja Lazapolje i Bujkovci u kojima su utvrđeni srednji sadržaji PAH-ova i najmanji sadržaj retena u prva dva perioda uzorkovanja (uzorci br. 1a, 1b, 4a i 4b); ostali uzorci, koji su imali manje ukupne sadržaje PAH-ova i povećani sadržaj retena svrstani su u grupu 3. Uzorak 5c je nestandardna opservacija („*outlier*“), s obbzirom na izrazito veliki sadržaj retena što se može povezati sa specifičnim antropogenim aktivnostima tokom ovog (trećeg) perioda uzorkovanja, kasni juli-početak avgusta, kao što je, na primer, spaljivanje poljoprivrednog otpada.



Slika 4.14. “Biplot” prve dve glavne komponente (PC1 i PC2) pri analizi “PAH” baze podataka koja sadrži atmosferske koncentracije 22 PAH-jedinjenja na šest lokacija u Makedoniji (1-Lazarpolje, 2-Skopje-OHIS, 3-Skopje-MEPP, 4-Bujkovci, 5-Strumica, 6-Bitola) u četiri perioda uzorkovanja (a: 14.05.-11.06.2007, b: 11.06.-09.07.2007, c: 09.07.-06.08.2007, and d: 06.08.-03.09.2007)

PCA analiza „OCC“ baze podataka sa podacima o prisustvu OCC jedinjenja u vazduhu izabranih lokacija prikazani su u tabeli 4.6 i slici 4.15. Tri glavne komponente su zadržane, koje su objasnile 79,2% ukupne varijanse podataka (tabela 4.6). Vrednosti koeficijenata korelacije između kongenera sa manjim sadržajem hlora (PCB 28, 52, 101, 118) su značajne za prve dve komponente (PC1 i PC2); sadržaj PCB 153 je značajno povezan sa PC1, dok je sadržaj PCB 138 povezan sa PC2. Od ispitivanih indikatorskih kongenera, jedino je PCB 180 povezan sa PC3 (tabela 4.6). Pesticidi iz grupe DDT su značajno povezani sa PC1 (tabela 4.6), dok HCH izomeri sa PC2, osim γ-HCH, za koji nije utvrđena značajna korelacija sa zadržanim glavnim komponenata (tabela 4.6). Pentahlorobenzen (PeCB) i HCB su negativno povezani sa PC3 (tabela 4.6).

Jedinjenja iz OCC grupe koja na slici 4.15 nalaze blizu jedni drugima usled značajne međusobne povezanosti (korelacije) ukazuju na iste izvore emisije i/ili slično ponašanje u životnoj sredini (Ogura i sar., 2004). Na „biplotu“ na slici 4.15 takođe se mogu uvideti specifični profili OCC jedinjenja za ispitane lokacije, kao i da je disperzija (različitost) uzoraka veća od one dobijene u slučaju PAH-jedinjenja (slika 4.14). Raspodela uzoraka duž PC1 je prvenstveno posledica razlika u koncentracijama DDT i njegovih proizvoda, dok je disperzija uzoraka duž PC2 vođena razlikama u koncentracijama HCH izomera. Profili OCC jedinjenja u vazduhu dve lokacije u gradu Skopju (uzorci br. 2 i 3) su se značajno razlikovali, dok su uzorci br. 4 i 5, kao i br. 1 i 6, formirali dve odvojene grupe na „biplotu“ usled međusobno sličnih OCC profila (slika 4.15).



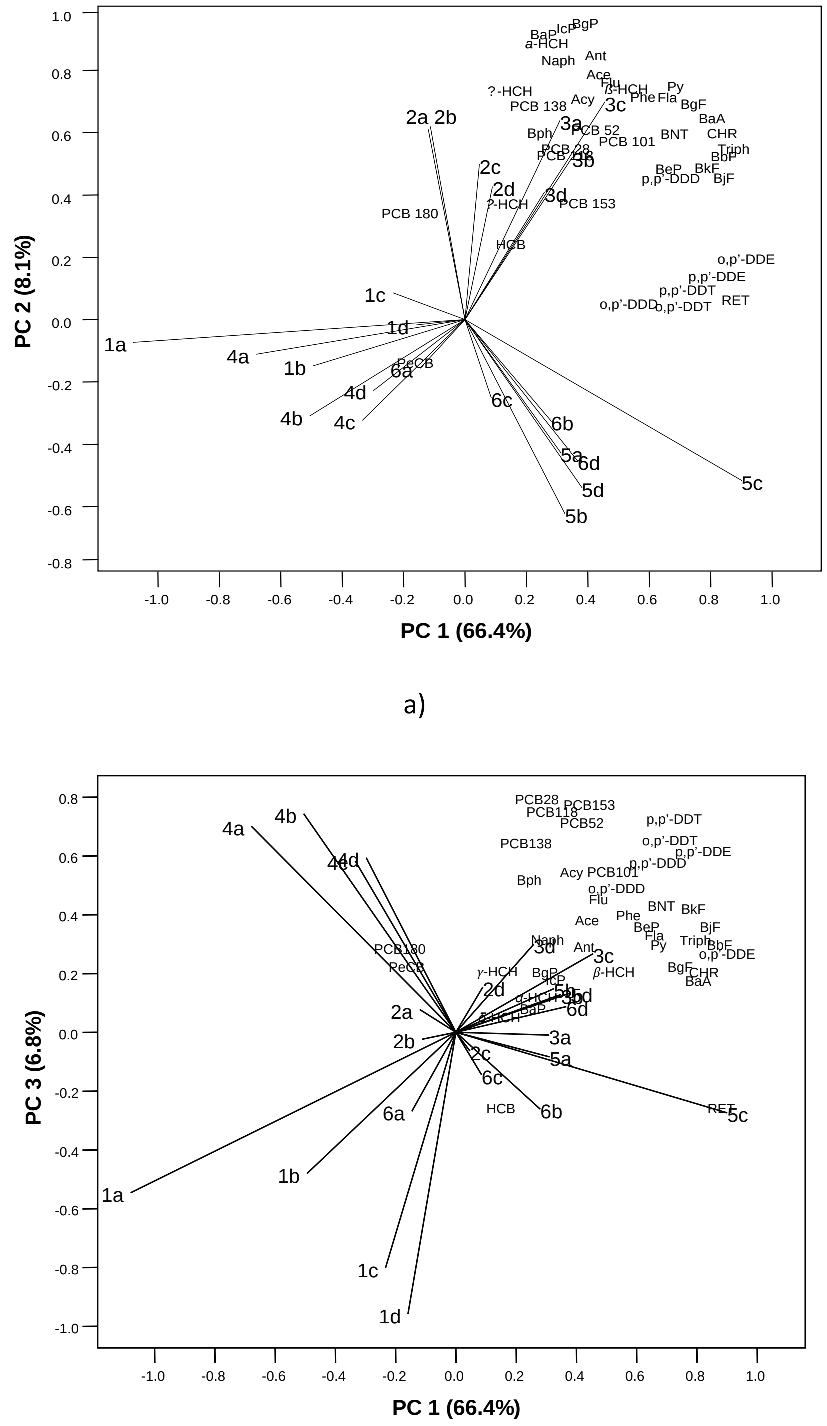
a)

b)

Slika 4.15. "Biplot" prve dve glavne komponente (PC1 i PC2) pri PCA analizi "OCC" baze podataka koja je sastavljena od atmosferskih koncentracija 7 indikatorskih PCB kongenera i 12 OCP na šest lokacija u Makedoniji (1-Lazarpolje, 2-Skopje-OHIS, 3-Skopje-MEPP, 4-Bujkovci, 5-Strumica, 6-Bitola) u četiri perioda uzorkovanja (a: 14.05.-11.06.2007, b: 11.06.-09.07.2007, c: 09.07.-06.08.2007, and d: 06.08.-03.09.2007)

Iako je na treću zadržanu glavnu komponentu, PC3, pripisano samo 8,4% varijanse podataka, interesantno je primetiti da je ova komponenta bila značajno povezana sa PeCB i HCB. U ovom momentu ne postoji industrijska proizvodnja PeCB (Bailey i sar., 2009) u prošlosti ovo jedinjenje je bilo prisutno u smesama hlorobenzena korišćenim u proizvodima na bazi PCB. Trenutne atmosferske koncentracije PeCB u najvećoj meri su posledica spaljivanja čvrstog otpada i sagorevanja biomase (Bailey i sar., 2009). HCB se u prošlosti koristio u različite namene te se njegovo prisustvo u životnoj sredini vezivalo sa primenom fungicida, sredstava za zaštitu drveta, i sl. (Bailey i sar., 2009). Pošto je lokacija br. 3 značajno korelisana sa PeCB i HCB (slika 4.15b) može se pretpostaviti da je izvor ovih OCC jedinjenja isti, i da je to najverovatnije spaljivanje komunalnog otpada.

Da bi se uporedile opšte sličnosti i razlike između atmosferskih koncentracija svih postojanih organskih zagađujućih jedinjenja ispitivanih na posmatranim lokacijama u Makedoniji, PCA analiza je izvršena i nad „SVOC“ bazom podataka kojom su objedinjeni dobijeni sadržaji PAH i OCC; dobijeni rezultati PCA analize prikazani su u obliku „biplota“ prikazanih su na slici 4.16. Tri glavne komponente su zadržane, koje su opisale 81,3% varijanse podataka. Na „biplotu“ PC1-PC2 (slika 4.16a) ponovo se vidi da su lokacije u Skopju (br. 2 i 3) imale izražene koncentracije svih jedinjenja, te su jasno razdvojene od ostalih lokacija. U vazduhu ovih sredina utvrđene su velike koncentracije PAH-ova, HCH-izomera i većine PCB kongenera (osim PCB 180). Većina uzoraka sa lokacija br. 5 (Strumica) i 6 (Bitola) značajno su povezana međusobno osim nestandardnih uzoraka br. 5c i 6a (“*outliers*”): uzorak 5c je imao najveću koncentraciju retena, kao i povećane koncentracije DDT i njegovih proizvoda, dok je uzorak 6a imao raspodelu jedinjenja sličnu lokacijama br. 1 (Lazarpolje) i 4 (Bujkovci). Na slici 4.16b prikazan je „biplot“ PC1-PC3, na kojem se jasno uočava razdvajanje uzoraka sa lokacije 1 i 4 (slično kao što je to dobijeno na slici 4.15a) kao posledica različitih profila OCC jedinjenja, prvenstveno PCB i DDT, promenljivih sa najvećim koeficijentima korelacija sa PC3.



a)

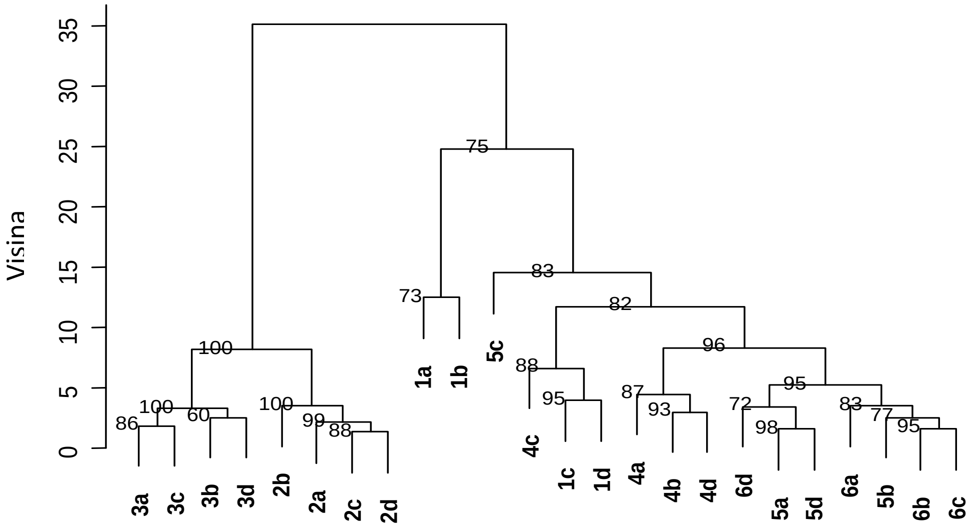
b)

Slika 4.16. "Biplotovi" PC1-PC2 (a) i PC1-PC3 (b) dobijeni pri PCA analizi "SVOC" baze podataka sa atmosferskim koncentracijama 22 PAH jedinjenja, 7 indikatorskih PCB kongenera i 12 OCP na šest lokacija u Makedoniji (1-Lazarpolje, 2-Skopje-OHIS, 3-Skopje-MEPP, 4-Bujkovci, 5-Strumica, 6-Bitola) u četiri perioda uzorkovanja (a: 14.05.-11.06.2007, b: 11.06.-09.07.2007, c: 09.07.-06.08.2007, i d: 06.08.-03.09.2007)

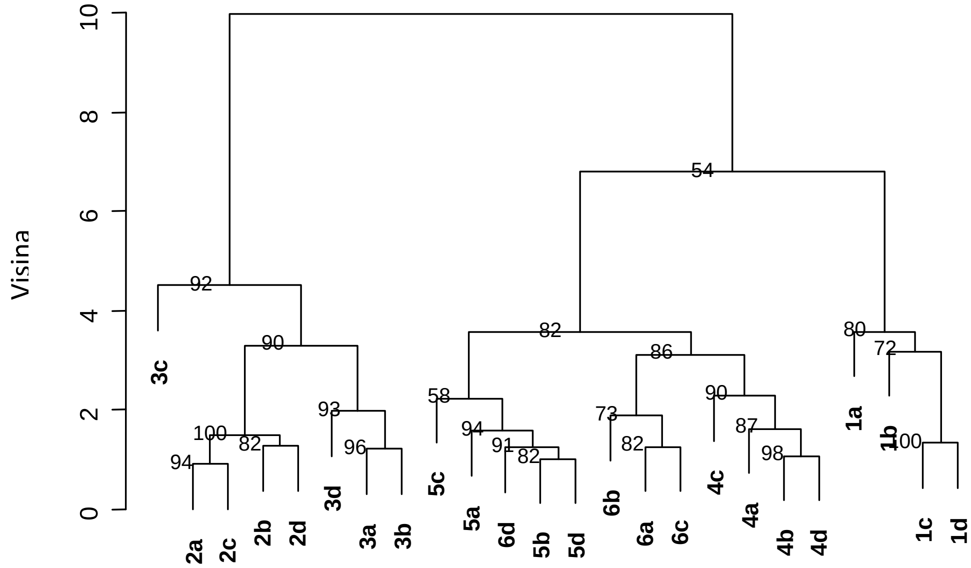
Analiza grupisanja u okviru “PAH” i “SVOC” baza podataka, prikazani su na slikama 4.17 (“PAH” set) i 4.18, redom (dendrogram za “OCC” bazu podataka nije prikazan s obzirom da je dobijeno razdvajanje uzoraka veoma slično onom uočenom za “SVOC” bazu). Uočeno grupisanje uglavnom se poklapa sa onim uočenim na PCA “biplotovima”.

U odnosu na “PAH” bazu podataka, na dendrogramu su dobijene dve “grane” (slika 4.17): jedna povezuje dve lokacije na području Skopja na kojima su uočene najveće koncentracije PAH-ova u vazduhu (lokacije Skopje-OHIS (br. 2) i Skopje-MEPP (br. 3)); dok su drugom “granom” povezane ostale lokacije u kojima su utvrđene manje vrednosti PAH-ova. U okviru ove druge “grane”, tj. grupe uzoraka, može se uočiti dalje podgrupisanje uzoraka: u jednoj od ovih podgrupa nalaze se uzorci iz Lazarpolja uzeti tokom prva dva perioda uzorkovanja (uzorci br. 1a i 1b) dok se u drugoj nalaze ostali uzorci iz Bujkovca (br. 4), Bitole (br. 5) i Strumice (br. 6). Ponovo se može uočiti da su lokacije br. 5 i 6 imale sličnu raspodelu PAH-jedinjenja u vazduhu, osim nestandardnog uzorka 5c, u kojem je utvrđena izrazito velika koncentracija retena.

Rezultati analize grupisanja u ookviru “SVOC” baze podataka (slika 4.18) takođe ukazuju na postojanje dve grupe: u jednoj se nalaze uzorci iz Skopja (br. 2 i 3), dok su u drugoj uzorci sa svih ostalih lokacija (br. 1, 4, 5 i 6), u kojoj je uočeno dalje podgrupisanje uzoraka iz Lazapolja (br. 1) nasuprot onih sa ostalih lokacija (br. 4, 5 i 6), koji su imali slične profile SVOC jedinjenja. Može se reći da se u okviru obe glavne grupe uočava jasno razdvajanje lokacija (jedini izuzetak je uzorak 3c) ukazujući na specifični profil SVOC jedinjenja na svakoj od lokacija. Ovo je takođe uočeno i kod “OCC” baze podataka (podaci nisu prikazani).



Slika 4.17. Hijerarhijsko grupisanje lokacija u Makedoniji na osnovu atmosferskih sadržaja PAH-jedinjenja („PAH" baza podataka) na šest lokacija u Makedoniji (1-Lazarpolje, 2-Skopje-OHIS, 3-Skopje-MEPP, 4-Bujkovci, 5-Strumica, 6-Bitola) u četiri perioda uzorkovanja (a: 14.05.-11.06.2007, b: 11.06.-09.07.2007, c: 09.07.-06.08.2007, i d: 06.08.-03.09.2007)



Slika 4.19. Hijerarhijsko grupisanje lokacija u Makedoniji na osnovu atmosferskih sadržaja PAH, OCC i PCB („SVOC" baza podataka) na šest lokacija u Makedoniji (1-Lazarpolje, 2-Skopje-OHIS, 3-Skopje-MEPP, 4-Bujkovci, 5-Strumica, 6-Bitola) u četiri perioda uzorkovanja (a: 14.05.-11.06.2007, b: 11.06.-09.07.2007, c: 09.07.-06.08.2007, i d: 06.08.-03.09.2007)

U okviru “SVOC” baze izvršena je i višestruka (multipla) regresija (MR) uključujući vrednosti dostupnih meteoroloških uslova. Pre diskusije MR rezultata potrebno je naglasiti da je zavisnost koncentracija postojanih organskih jedinjenja od meteoroloških uslova prethodno bila predmet ispitivanja jedino u slučaju sadržaja određivanih uobičajenim (aktivnim) načinom uzorkovanja (Ogura i sar., 2004; Perez i sar., 2003; Brunciak i sar., 2001), dok su u slučaju pasivnog načina uzorkovanja, parametri sredine razmatrani jedino kao faktori koji utiču na brzinu uzorkovanja (Shoeib i sar., 2002; Thomas i sar., 2006; Tuduri i sar., 2006; Klanova i sar., 2008; Klanova i sar., 2006; Harner i sar., 2006). Može se očekivati da je temperatura vazduha imala kumulativni efekat na koncentracije posmatranih jedinjenja dobijene pasivnim načinom uzimanja uzoraka vazduha tokom perioda od 28 dana, dok su uticaji padavina i vetra zavisili od jačine i frekvencije njihove pojave. Na primer, uticaj uklanjanja čestica iz vazduha kapljicama kiše, pa tako i postojanih organskih jedinjenja kondenzovanih na površini ovih čestica, zavisi od veličine i fizičko-hemijskih karakteristika čestica, veličina kapljica kiše i drugih faktora (Hien i sar., 2007) može se očekivati da retki, ali jaki pljuskovi utiču na smanjenje koncentracije ovih jedinjenja u vazduhu u većoj meri u odnosu na česte i pri tome umerene pojave kiše. Međutim, lokalni vremenski uslovi koji se ne ogledaju u parametrima posmatranim u radu takođe mogu uticati na dobijene sadržaje; na primer, koncentracija aerosola, procesi raspodele materije između čestica i vazduha, pravci vetrova, vlažnost, itd. Gustafson i Dickhut (1997) su uočili da relativno velika vlažnost tokom kišnih sezona utiče na povećanu depoziciju PAH-ova iz gasne faze na čestiče, povećavajući koncentraciju ovih polutanata u čestičnoj materiji. Isto tako, uticaj pravca vetra na koncentracije SVOC jedinjenja je uočen u nekoliko (Bohlin i sar., 2007; Tuduri i sar., 2006). Dakle, može se očekivati da nedostatak ovakvih informacija ograničava izvršenu MR. Isto tako, potrebno je naglasiti da je promenljivost koncentracija posledica ne samo meteoroloških uslova već i različitim doprinosom (emisijom) postojećih izvora na različitim lokacijama i udaljenostima od mernih mesta.

U tabeli 4.7 prikazani su standardizovani parcijalni regresioni koeficijenti i koeficijenti determinacije (R^2) MR modela dobijenih za svako od posmatranih jedinjenja u obliku:

log (sadržaj SVOC) = f (1/t, log (pr), log (ws), log (sh)

Tabala 4.8. Linearni koeficijenti regresije dobijeni za zavisnost logaritamske vrednosti atmosferske koncentracije postojanih organskih jedinjenja na ispitivanim lokacijama u Makedoniji u periodu 14. maj-3. septembar 2007 od recipročne vrednosti temperature (1/t), logaritamske vrednosti količine padavina (log pr), logaritamske vrednosti brzine vetra (log ws) i logarotamske vrednosti osunčanosti (log sh)

SVOC	1/t	log pr	log ws	log sh	R^2
Naph	**-0.877****	0.045	**0.694****	-0.238	**0.687****
Ace	**-1.171****	0.078	**0.552***	-0.630	**0.684****
Acy	**-1.147****	-0.170	**0.717****	**-0.901****	**0.773****
Flu	**-1.110****	-0.034	**0.562***	**-0.872***	**0.615***
Phe	**-1.128****	-0.010	**0.566***	**-0.810***	**0.628***
Ant	**-0.965****	0.105	**0.686****	-0.624	**0.617***
Fla	**-1.120****	-0.017	**0.466***	-0.767	**0.570***
Py	**-1.169****	-0.049	0.444	**-0.835***	**0.602***
BaA	**-1.077****	-0.043	0.295	-0.741	0.487
CHR	**-1.096****	-0.015	0.236	-0.758	0.500
BbF	**-1.055****	-0.090	0.070	-0.714	0.499
BkF	**-1.085****	-0.151	0.074	-0.711	0.549
BaP	**-0.723***	0.197	**0.774****	-0.265	**0.622***
IcP	**-0.920****	0.071	**0.711****	-0.609	**0.613***
BgP	**-0.919****	0.065	**0.712****	-0.612	**0.612***
Bph	-0.785	0.053	0.404	-0.739	0.360
RET	-0.214	0.222	0.032	-0.006	0.050
BNT	**-1.286****	-0.178	0.166	**-0.926****	**0.718****
BgF	**-1.162****	-0.071	0.324	**-0.836***	**0.566***
Triph	**-1.026***	-0.066	0.119	-0.750	0.448
BjF	**-0.935***	-0.185	0.092	-0.655	0.404
BeP	**-1.202****	-0.098	0.112	**-0.687***	**0.684****
PCB28	**-1.304****	-0.137	0.272	**-0.913****	**0.720****
PCB52	**-1.277****	-0.102	0.341	**-0.830***	**0.704****
PCB101	**-1.173****	0.043	0.411	**-0.851***	**0.600***
PCB118	**-1.136****	-0.214	0.370	**-0.981***	**0.564***
PCB138	**-1.139****	-0.182	**0.686****	**-1.100****	**0.771****
PCB153	**-1.201****	-0.338	0.278	**-0.941***	**0.660***
PCB180	-0.669	0.118	0.591*	-0.199	0.423
α-HCH	**-0.833***	0.261	0.511	-0.445	0.440
β-HCH	**-0.968***	-0.205	0.365	-0.768	0.429
γ-HCH	**-1.120****	-0.083	**0.611****	-0.850	**0.654***
δ-HCH	**-0.913****	0.039	**0.712****	-0.640	**0.609***
o,p'-DDE	**-1.059****	-0.507	0.167	**-1.059***	**0.579***
p,p'-DDE	**-1.130****	-0.454	0.042	**-1.108****	**0.647***
o,p'-DDD	**-0.976***	-0.526	0.333	**-1.011***	0.539
p,p'-DDD	**-1.288****	-0.264	**0.394***	**-0.911****	**0.757****
o,p'-DDT	**-1.054****	-0.493	0.265	**-0.891***	**0.605***
p,p'-DDT	**-1.276****	-0.264	0.172	**-1.066****	**0.704****
PeCB	-0.575	**0.625***	0.275	-0.430	**0.583***
HCB	0.132	**0.830****	**0.392***	0.202	**0.741****

* značajno pri $P<0.05$

**značajno pri $P<0.01$

Značajni regresioni koeficijenti su dobijeni za većinu posmatranih jedinjenja osim za BaA, CHR, BbF, BkF, Bph, RET, Triph, BjF, PCB180, α- i β-HCH, i *o,p'*-DDD, za koje koncentracije u vazduhu određene pasivnim načinom uzorkovanja nisu mogle da se statistički značajno povežu (korelišu) sa dostupnim meteorološkim uslovima. Veličina apsolutnih vrednosti regresionih koeficijenata ukazuje na doprinos nezavisnih veličina na promenu koncentracija datog SVOC jedinjenja u vazduhu.

Pored logaritamske zavisnosti, ispitani su i semilogaritamski (log (sadržaj SVOC) = *f* (1/t, pr, ws, sh)) i običan, nelogaritamski (sadržaj SVOC = *f* (1/t, pr, ws, sh)) modeli, ali dobijeni regresioni koeficijenti i koeficijenti determinacije (podaci nisu prikazani) su manji od onih prikazanih u tabeli 4.7, pri tome, najmanje vrednosti su dobijene za nelogaritamski model. Drugim rečima, logaritamski model (log (sadržaj SVOC) = *f* (1/t, log (pr), log (ws), log (sh)) najbolje od ispitanih modela opisuje linearnu zavisnost sadržaja SVOC jedinjenja od meteoroloških parametara, što govori da je logaritmovanje neophodne da bi se uklonili preovlađujući uticaji nestandardnih uzoraka („*outliers*“), koji su verovatno narušili linearnost semi- i ne-logaritmovanog modela.

Uticaj temperature na promenu atmosferskih koncentracija većine ispitanih postojanih organskih jedinjenja pokazao se statistički značajnim pri $p < 0,05$ i $p < 0,01$ (tabela 4.7). Negativni regresioni koeficijenti za recipročnu vrednost temperature ukazuju da se povećanje sadržaja jedinjenja u vazduhu može povezati sa smanjenjem recipročne vrednosti temperature (tj. sa povećanjem temperature). Slična zavisnost atmosferskih koncentracija postojanih organskih jedinjenja od temperature uočena je i u prethodnim istraživanjima (Ogura i sar., 2004; Perez i sar., 2003; Brunciak i sar., 2001; Currado i sar., 2000). Ovo je u skladu sa Clausius-Clapeyron-ovom jednačinom ($\ln P = a_0 + a_1(1/T)$) koja opisuje ponašanje parne faze jedinjenja kroz zavisnost od parcijalnog pritiska (P) i temperature vazduha (T). Ovo dalje ukazuje da je za jedinjenja za koja je dobijen značajan negativni koeficijent za recipročnu vrednost temperature, isparavanje imalo značajan uticaj na njihov sadržaj u vazduhu. Ispravanje iz starih depozita u životnoj sredini se može smatrati današnjim najverovatnijim izvorima OCC, tako da se ovaj poslednji zaključak može direktno pripisati ovoj klasi postojanih jedinjenja, ali ne i PAH-ovim, čiji su glavni izvori procesi sagorevanja. Ipak, relacije uočene za koncentracije PAH-ova i temperaturu vazduha ukazuju na povećanu isparljivost ovih jedinjenja kondenzovanih na česticama, naročito viših PAH-ova (tj. onih sa većom molekulskom masom). Za jedinjenja za koja nisu utvrđeni značajni koeficijenti regresije u odnosu na recipročnu vrednost temperature (kao na primer, bifenil, reten, OCB180, PeCB i HCB), može se pretpostaviti da neki drugi procesi, osim isparavanja, imaju veći uticaj na njihove koncentracije u vazduhu ispitanih lokacija.

U slučaju retena, može se pretpostaviti da su procesi spaljivanja biomase razlog uočenog odsustva zavisnosti njegovog sadržaja od temperature, dok u slučaju PcCB i HCB, to može biti sporadično spaljivanje otpada. Ove pretpostavke su u saglasnosti sa prethodnom diskusijom PCA rezultata. Međutim, objašnjenje potencijalnog izvora PCB180 nije pronađeno u literaturi.

U odnosu na količinu padavina, značajni koeficijenti regresije su dobijeni samo za PeCB i HCB (tabela 4.7). Ovo ukazuje da su specifični izvori čija emisija se može povezati na određeni način sa pojavom kiše, doprineli atmosferskim koncentracijama PeCB i HCB u ispitivanom periodu.

Za ispitivana jedinjenja regresioni koeficijenti dobijeni za brzinu vetra su takođe bili značajni, ukazujući da su se atmosferske koncentracije ovih jedinjenja povećavale sa povećanjem brzine vetra, nasuprot zaključcima nekih drugih studija u kojima je utvrđeno suprotno, tj. da povećanje brzine vetra utiče na razređenje koncentracija postojanih organskih jedinjenja usled mešanja sa strujama „nazagađenog“ vazduha (Ogura i sar., 2004; Reimann i sar., 2000).Postoje i istraživanja u kojima je takođe utvrđena pozitivna korelacija između sadržaja postojanih organskih jedinjenja u vazduhu i brzine vetra, što je objašnjeno pojačanim prelaskom jedinjenja deponovanih na površini zemlje u gasnu fazu., tj. vazduh (Perez i sar., 2003; Brunciak i sar., 2001; Tsapakis i sar., 2005). Pozitivni koeficijenti između koncentracija postojanih organskih jedinjenja u vazduhu i brzine vetre koji su dobijeni u ovom radu mogu se povezati sa mehanizmom pasivnog uzorkovanja. Naime, prethodno je pokazano da se brzine uzorkovanja u slučaju pasivnih uzorkivača menjaju u zavisnosti of brzine vetra (Klanova i sar. 2006). Može se očekivati da veće brzine vetra utiču na brže proticanje vazduha kroz pasivni uzorkivač dovodeći do većih brzina uzorkovanja, a samim tim i do većih sadržaja jedinjenja koji dolaze u kontakt sa diskom od poliuretanske pene na kojima se odvija njihovo zadržavanje u uzorkivaču.

Utvrđeno je da je osunčanost negativno povezana sa koncentracijama nekih postojanih organskih jedinjenja, kao što su DDT i njegovi proizvodi, šest indikatorskih PCB (ne i PCB 180), i iz PAH grupe – acenaftilen, fluoren, piren, benzo-nafto-tiofen (PAH sa atomom sumpora u svom molekulu), BbF i BeP. Ovo je očigledno posledica fotodegradacionih procesa koji su doveli do smanjenja sadržaja ovih jedinjenja u vazduhu.

4.5. Teški metali u zemljištu

Sadržaji teških metala određenih u 23 uzorka zemljišta uzetih iz Novog Sada, njegove okoline i Banja Luke, prikazani su u tabeli 4.8. U odnosu na srednju vrednost i medijanu dobijene za sve uzorke, metali se mogu poređati po sledećem opadajućim redosledu: Zn > Pb ~ Ni > Cu > Cr >Cd. Najveće relativne standardne devijacije od 64% i 49% dobijene su za Zn i Pb, dok se za ostale metale kretala u opsegu od 25% (za Cr) do 38% (za Cu).

U tabeli 4.8 rezultati su upoređeni sa podacima iz literature za prisustvo teških metala u zemljištu iz Srbije (Ubavić i sar., 1993; Kastori i sar.,adnici, 2002 ???? odakle je ovo; Škrbić i sar. 2004); Crnković i sar., 2006; Dragović i sar., 2008 ??? odakle je ova ref; Marjanović i sar., 2009).

Tabela 4.8. Ukupni sadržaj teških metala (u mg/kg) u uzorcima zemljišta iz Novog Sada i Banja Luke analizirani u ovom radu u poređenju sa srednjim vrednostima prethodno određenim za neke lokacije u Srbiji

	Novi Sad, 2009*	Banja Luka, 2009*	Novi Sad, 2001* [a]	Beograd, 2003-2004* [b]	Beograd, 2008* [c]	Vojvodina, obradivo zemljište 1991* [d]	Vojvodina, obradivo zemljište-ogledna polja 2002* [e]	Zlatibor, 2008* [f]
Zn	110		85.45	118	174.2	10.62	70.3	21.8
Cu	22.4		30.86	28.3	46.3	10.82	22.5	8.64
Cr	3.57			32.1		2.41	82.3	46.3
Pb	29.4		10.75	55.5	298.6	14.81	30.0	41.5
Ni	25.8			68		4.26	36.2	320
Cd	1.66		0.15		1.8	0.48	0.37	1.42

* godina uzorkovanja; ukoliko u originalnom radu nije navedena godina uzorkovanja, navedena je godina objavljivanja samog rada

[a] Škrbić and Čupić, 2004

[b] Crnković i saradnici, 2006

[c] Marjanović i saradnici, 2009

[d] Ubavić i saradnici, 1993

[e] Kastori i saradnici, 2002

[f] Dragović i saradnici, 2008

Uočava se da je srednje prisustvo metala u 21 uzorku iz Novog Sada manje u odnosu na zemljište iz Beograda (Crnković i sar., 2006; Marjanović i sar.,2009). Iako se na većini lokacija zemljište nalazi pod uticajem različitih antropogenih aktivnosti, može se pretpostaviti da srednja vrednost sadržaja teških elemenata dobijena za veći broj reprezentativnih uzoraka iz jedne oblasti (regiona), predstavlja dobru osnovu za poređenje sadržaja elemenata sa neke lokacije u tom regionu i procenu stepena antropogenih aktivnosti (Cannon i sar., 2009). Tako, poređenje sa srednjim sadržajem metala u uzorcima zemljišta iz Vojvodine (Ubavić i sar., 1993) pokazuje da su svi metali u približnim ili većim količinama prisutni u ispitivanim uzorcima. Povećanje sadržaja nekih metala tokom vremena takođe se može uočiti i u beogradskom zemljištu (Crnković i sar., 2006; Marjanović i sar., 2009). Zanimljivo je da su zemljište iz Beograda (Crnković i sar., 2006; Marjanović i sar., 2009) i ono sa planine Zlatibor (Dragović i sar., 2008) imali značajno veće sadržaje Ni i Cr, nego što je to dobijeno u ovom radu, a objašenjenje se može naći u prirodnim procesima, s obzirom da se povećani sadržaj Ni može pripisati pedogenim i prirodnim „*weathering*" procesima; najverovatnije, isti razlozi leže iza povećanog sadržaja Cr na ovim lokacijama

U odnosu na domaću regulativu za prisustvo teških metala u zemljištu (Službeni glasnik 1994), nijedan od ispitivanih uzoraka nije imao sadržaj veći od maksimalno dozvoljene koncentracije od 300 mg/kg za Zn, 100 mg/kg za Cu, Cr i Pb (svaki ponaosob), 50 mg/kg za Ni, i 3 mg/kg za Cd. Međutim, u odnosu na holandske referentne vrednosti za nezagađeno zemljište (Dutch standards, 2000), koje se najčešće i citiraju i uzimaju za osnovu poređenja u međunarodnim studijama, u većem broju uzoraka uzetih sa područja Novog Sada, njegove okoline i iz Banja Luke, izmerene količine Cd prevazilaze maksimalno definisanu vrednost. Zanimljivo je primetiti da iako je korišćenje olovnog benzina još uvek dozvoljena na ispitivanim područjima, sadržaj Pb u zemljištu nije prelazio holandske referentne vrednosti. U odnosu na vrednosti SMI (*„Soil Metal Index",* način određivanja objašnjen u poglavlju 3.2.5), izračunate u odnosu na holandske referentne vrednosti za nezagađeno zemljište, u 21 uzorku vrednost SMI je bila ispod 100%, dok je jedino u dva uzorka ona bila iznad 100%. Dakle, većina uzoraka je grupisana u tzv. „ispod 100%" bazu podataka, koja je analizirana hemometrijskim tehnikama. Preostala dva uzorka pripala su bazi „iznad 100%", i to su bili uzorak u neposrednoj blizini puta sa intenzivnim saobraćajem u Banja Luci i uzorak uzet iz okoline Novog Sada.

Rezultati deskriptivne statističke analize formiranih baza podataka („svi", „ispod 100%" i „iznad 100%"), sa sadržajima teških metala u uzorcima ispitanim u ovom radu i podacima iz literature su prikazani u tabeli 3.19 u poglavlju 3.2.5. Setovi „svi" i „iznad 100%" su imali isti redosled metala po opadajućem sadržaju: Zn > Pb > Cu > Cr > Ni > Cd, dok je nešto drukčiji redolsed uočen za set „ispod 100%": Zn > Pb > Cr > Cu > Ni > Cd. Dakle, može se reći da je opšti trend koji postoji u bazi podataka „iznad 100%" uticao i na trend koji je preovladao u setu „svi", maskirajući trend koji postoji u setu „ispod 100%". Kada se uporede sadržaji utvrđeni za 23 uzorka zemljišta u ovom radu (tabela 3.18, poglavlje 3.2.5) sa minimalnim i maksimalnim vrednostima u tabeli 3.19, može se zaključiti da zemljište Novog Sada, njegove okoline i Banja Luke odgovara nižem opsegu svih korišćenih podataka, što govori o njihovom relativno malom opterećenju teškim metalima.

Poznato je da velike koncentracije teških metala u zemljištu u odnosu, na primer, na „pozadinsko“ opterećenje, praćene istovremeno sa velikim standardnim devijacijama, ukazuju na antropogene izvore ovih metala (Manta i sar., 2002). Dakle, velike vrednosti RSD uočene za šest metala u bazi podataka „iznad 100%“ su se i mogle očekivati. U bazi „ispod 100%“, Pb je imalo najveću vrednost RSD (~97%), a kako se Pb često koristi kao indikator izduvnih gasova vozila, uočena velika odstupanja u sadržaju Pb mogu se pripisati različitoj udaljenosti uzoraka svrstanih u bazi podataka „ispod 100%“ od puteva i vozila kao glavnih izvora ovog metala u zemljištu. Vrednosti RSD izračunate za baze „svi“ i „iznad 100%“ su nekoliko puta veće od vrednosti utvrđene za bazu „ispod 100%“, što govori o većem koncentracionom gradijentu, prvenstveno u uzorcima zagađenog zemljišta (svrstanih u bazu „iznad 100%“). U ove dve baze podataka, najveće vrednosti RSD su dobijene za Cu, Cd i Zn (tabela 3.19).

Vrednosti verovatnoće po Shapiro-Wilk-ovom testu korišćenom za proveru raspodele distribucije prikazane su u poslednjoj koloni u tabeli 3.19. Nulta hipoteza u odnosu na Box-Cox transformisane podatke pri nivou značajnosti 0,05 prihvaćena je za Cd za sva tri ispitivana seta podataka; isto je dobijeno za Ni u setu „iznad 100%“ i za Cu u setu „ispod 100%“. P-vrednosti ispod 0,05 (tabela 3.19) ukazale su da značajna asimetrija u raspodeli originalnih podataka nije uklonjena Box-Cox transformacijom. Isto tako, simetrija nije utvrđena za Box-Cox transformisane podatke prisustva Cu u setovima „svi“ i „iznad 100%“, kao i za Ni u setovima „svi“ i „ispod 100%“. Ipak, poređenje EDA dijagrama originalnih i transformisanih podataka (podaci nisu prikazani) ukazuje da je primenjena Box-Cox transformacija poboljšala oblik raspodele dajući simetričnije raspodele: dok su originalni podaci bili asimetrični (u pravcu manjih vrednosti, tj. na levu stranu), Box-Cox transformisani podaci su bili simetrično raspoređeni.

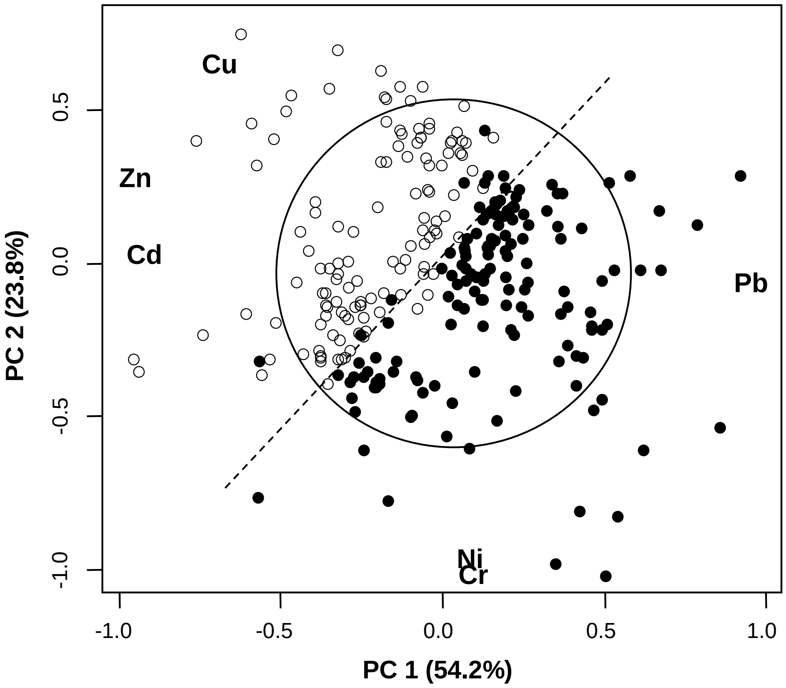
Analiza glavnih komponenata primenjena je na sve tri baze podataka kako bi se ispitala multidimenziona struktura podataka i na taj način izvršila interpretacija raspodele teških metala u zemljištu sa različitih lokacija (iz različitih studija). Rezultati primene PCA u okviru baza podataka „svi“, „ispod 100%“, i „iznad 100%“, sastavljenenih od Box-Cox transformisanih podataka opisanih u tabeli 3.17 i 3.19, predstavljeni su u tabeli 4.9. Rezultati su grafički predstavljeni u vidu “biplota” na slikama 4.19-4.22. Radi lakše istovremene interpretacije uticaja ispitivanih promenljivih na klasifikaciju uzoraka, koeficijenti korelacija originalnih promenljivih sa zadržanim komponentama i koordinate uzoraka u prostoru novih kooridnata (tj. "*loadings*" i "*scores*" vrednosti) normalizovane su u odnosu na najveću vrednost za određenu komponentu, tako da su svedeni na skalu od -1 do 1.

*Tabela 4.9. Koeficijenti korelacije dobijeni primenom PCA u okviru baze podataka "svi" (objašnjenje u poglavlju 3.2.5), kao i baze podataka "iznad 100%" i "ispod 100%" formiranim u skladu sa izračunatim SMI ("*Soil Metal Index*", izračunavanje objašnjeno u poglavlju 3.2.5) vrednostima (%VAR predstavlja procenat od ukupne varijanse polaznih podataka objašenjen određenom glavnom komponentom PC).*

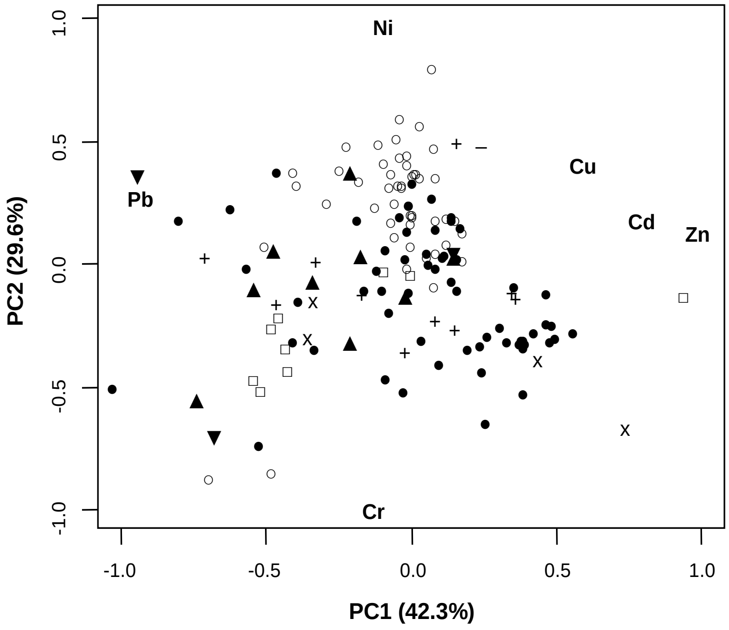
Teški metal	**"svi"**		**"iznad 100%"**		**"ispod 100%"**	
	PC 1	**PC 2**	**PC 1**	**PC 2**	**PC 1**	**PC 2**
Zn	**-0.889**	0.267	**0.919**	0.124	0.180	**0.845**
Cu	**-0.615**	**0.608**	**0.550**	0.380	**0.705**	0.472
Cr	0.103	**-0.913**	-0.113	**-0.912**	**0.879**	-0.208
Pb	**0.885**	-0.042	**-0.851**	0.252	-0.132	**0.661**
Ni	0.093	**-0.865**	-0.081	**0.896**	**0.793**	0.090
Cd	**-0.826**	0.042	**0.736**	0.171	-0.450	**0.651**
% VAR	54.2	23.8	42.3	29.6	35.9	30.8

Prema Kaiserovom pravilu po kojem se zadržavaju samo glavne komponente, koje imaju *eigen* vrednosti (*eigenvalues)* veće od 1, sve tri baze su svedene na dve glavne komponente, PC1 i PC2, pri čemu je najveći udeo varijanse polaznih podataka objašnjen za baze "svi" (78%, tabela 4.9), i "iznad 100%" (71.9%, tabela 4.9), dok je namanji udeo dobijen za bazu "ispod 100%" (66.7%, tabela 4.9). Za baze podataka "svi" i "iznad 100%", PC1 je u korelaciji sa istim elementima: Zn, Cu i Cd, koji su međusobno veoma blisko povezani, dok su negativno korelisani sa Pb (tabela 4.9, slike 4.19 i 4.20a). U istim ovim setovima, PC2 je značajno povezana sa Cr i Ni (tabela 4.9, slike 4.19 i 4.20a). Dakle, ponovo je raspodela teških metala u uzorcima zemljišta iz sveta sa značajnijim stepenom zagađenja (sa SMI > 100%) preovladala nad manje zagađenim zemljištem sa SMI < 100%, utičući i na dominantnu raspodelu u bazi sa svim prikupljenim podacima ("svi").

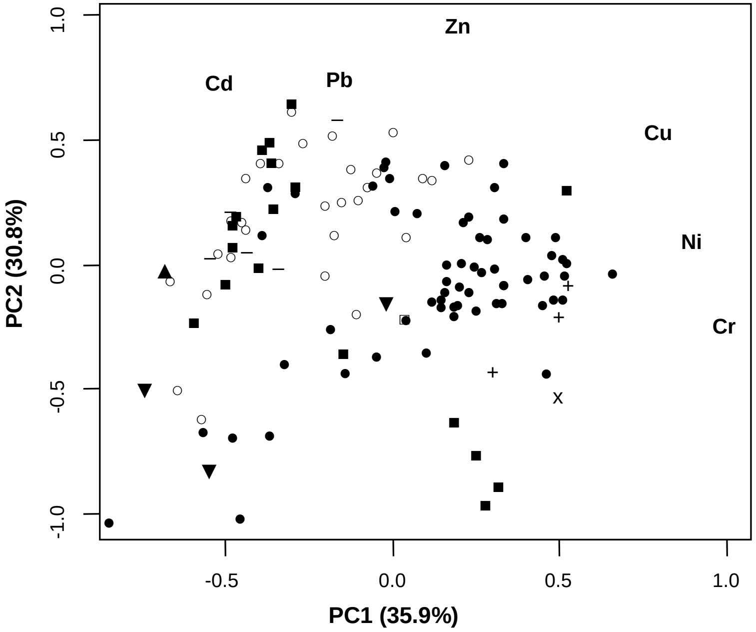
Da bi se ispitalo da li je način pripreme uzoraka (digestije) i analize uticao na PCA rezultate (opisani u tabeli 3.15 u poglavlju 3.2.5), na dobijenom "biplotu" za bazu "svi" izvršena je klasifikacija uzoraka u odnosu na primenjene uslove pripreme i analize (slika 4.20); na osnovu uočene slučajne (nasumične) raspodele uzoraka duž PC1 i PC2 i preklapanje uvedenih kategorija može se zaključiti da nije uočen uticaj eksperimentalnih uslova na postognutu raspodelu uzoraka. Ovo je u skladu sa rezultatima Bojinove i sar., (1996) koji su našli dobru povezanost (korelaciju) između rezultata ispitivanja sadržaja teških elemenata u zemljištu sa ICP-AES i GFAAS/FAAS.



Slika 4.19. PC1-PC2 "biplot" dobijen za bazu podataka "svi", pri čemu su uzorci označeni u skladu sa izračunatim vrednostima SMI ("Soil Metal Index"*) (● označava SMI > 100%, ○ označava SMI < 100%). Procenti u zagradama predstavljaju udele ukupne varijanse objašnjenje svakom od zadržanih glavnih komponenata (PC).*

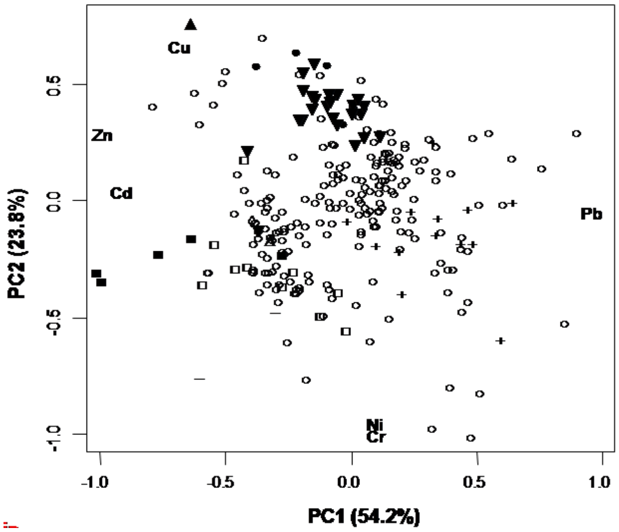


a)

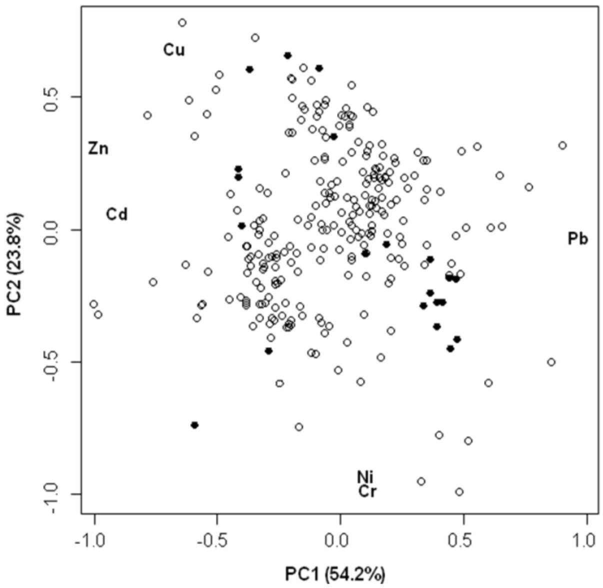


b)

*Slika 4.20. PC1 – PC2 "biplot" dobijen za baze podataka "iznad 100%" (a) i "ispod 100%" (b) formirane u odnosu na izračunate vrednosti SMI ("*Soil Metal Index*"). Različiti načini korišćenja zemljišta su korišćeni kao kriterijum za kategorizaciju zemljišta (● - poljoprivredno; ○ - rekreaciono, □ - travnjak, ▲ - industrijsko, ■ - urbano, – - ruralno, + - uz put, ▼ - šumsko, × - nepoznato). Procent u zagradi predstavlja udeo ukupne varijanse podataka objašnjen svakom od zadržanih glavnih komponentama (PC).*



a)



b)

Slika 4.21. PC1 - PC2 “biplot” dobijen za bazu podataka “svi”, pri čemu su uzorci označeni u odnosu na:

a) kiseline korišćene za digestiju uzoraka: ● – HNO_3+$HClO_4$; ○ – aqua regia, □ – HNO_3, ▲ -HCl, ■ – HNO_3+HCl, – - nije navedena, + - aqua regia+HF, ▼ – HNO_3+H_2O_2

b) instrumentalne tehnike korišćene za određivanje sadržaja teških metala: ● – ICP; ○ – AAS

Da bi se zadržanim glavnim komponentama pripisao fizički značaj, najpre je potrebno sagledati moguće izvore teških metala u zemljištu. Osnovni izvor Pb u sredini su organska jedinjenja olova sa antidetonacionim dejstvom, koja su se intenzivno koristila do ’90-tih godina prošlog veka kao aditivi benzina da bi se sprečili udari pri radu benzinskih motora. Stupanjem na snagu direktive 98/70/EC i amandmana 2003/17/EC, korišćenje „olovnog“ benzina je zabranjeno u okviru Evropske Unije od 2000. god., dok je u Srbiji i Bosni i Hercegovini (zemljama u kojima je izvršeno uzorkovanje zemljišta čiji sadržaji teških metala su takođe predmet ovog rada) njegovo korišćenje još uvek dopušteno. Međutim, s obzirom da je olovo prisutno i u sirovoj nafti, ono je neminovno prisutno i u „bezolovnom“ benzinu (od 0,61 μg/l do 0,04 mg/l, (Kummer i sar., 2009) iako u značajno manjim količinama u odnosu na dodatak tetra-etil olova kao aditiva. Isto tako, utvrđeno je prisustvo olova i u dizelu i to u količinama sličnim onim koje su nađene u „bezolovnom“ benzinu (Frohling i Ludzay, 2002; Kummer i sar., 2009). S druge strane, izvori Cu, Zn i Cd u zemljištu gradskih sredina prvenstveno su saobraćajna vozila usled abrazije guma, ulja za podmazivanje, spaljivanje industrijskog i otpadnog materijala (Markus i McBratney, 1996, Wilcke i saradnici, 1998; Cadle i saradnici (1997) su utvrdili da Cu u prašini sa puteva prvenstveno potiče od motornog ulja. Cink je glavni sastojak automobilskih guma (US EPA, 1979). U prošlosti, Cd je bio prateći element Zn u gumama (US EPA, 1979) i takođe je korišćen u legurama za delove motora (Jeffery, 1998). Sagorevanje goriva (uglja, nafte i njenih derivata) u stacionarnim izvorima takođe je jedan od glavnih izvora Cr i Ni (Pacyna i saradnici, 2007). Dakle, na osnovu ovde opisanih izvora metala u u zemljištu, moguće je objasniti fizičko značenje glavnih komponenti zadržanih u okviru baze podataka sa izrazito zagađenim uzorcima zemljišta iz sveta (sa SMI > 100%). Prva komponenta, PC1, u ovoj bazi podataka očigledno odražava sadržaje Pb, Cu, Cd i Zn u zemljištu širom sveta koji su najverovatnije pod direktnim uticajem saobraćaja bilo preko emisije izduvnih gasova (Pb) ili usled abrazije guma, kočnica, ispuštanja ulja za podmazivanje (Cu, Cd, Zn). Fizičko značenje PC2 može se pripisati najverovatnije istovremenom uticaju prirodnih (pedogenih) i/ili stacionarnih antropogenih izvora Cr i Ni.

Potpuno drukčije objašnjenje se može dati za bazu podataka „ispod 100%“, u kojoj su sadržaji Cr, Ni i Cu značajno povezani sa PC1, dok su Zn, Pb i Cd sa PC2 (tabela 4.9, slika 4.20b). Prva glavna komponenta zadržana za ovu bazu podataka može se opisati posledicom prirodnih i/ili antropogenih izvora osim saobraćaja (kao na primer, sagorevanje goriva u stacionarnim izvorima, poljoprivredna praksa, i sl.), dok PC2 najverovatnije odražava uticaj saobraćaja na raspodelu teških metala u zemljištu. Od svih ispitivanih metala, jedino je Cu značajno povezan sa prvom glavnom komponentom u obe baze podataka, „ispod 100%“ i „iznad 100%“, što ukazuje na kombinovane izvore Cu u nezagađenom i zagađenom zemljištu, na primer, istovremeno iz saobraćaja i poljoprivrednih mera.

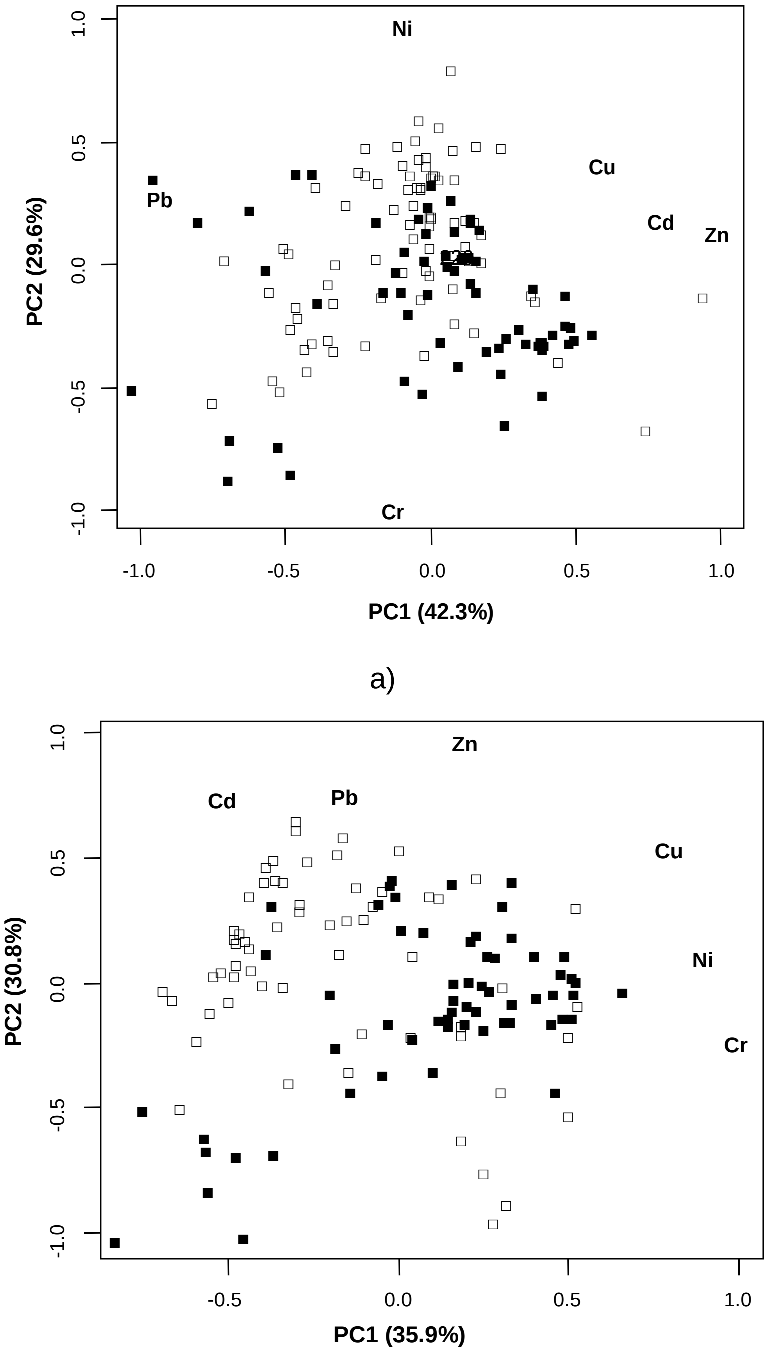
Provereno je i da li geografska lokacija uzoraka utiče na klasifikaciju uzoraka u okviru baza podataka „ispod 100%” i „iznad 100%” (rezultati nisu prikazani), i nisu uočene razlike između uzoraka iz različitih zemalja. Uzorci zemljišta iz Srbije (predstavljeni u tabeli 3.16 i 3.18) nalaze se u različitim delovima biplotova, što se i očekivalo s obzirom da se lokacije sa kojih su uzeti međusobno značajno razlikuju, uzimajući u obzir njihovo poreklo, način korišćenja, udaljenost od direktnih antropogenih izvora i perioda uzorkovanja.

Primenjujući kategorizaciju u odnosu na SMI, postignuto je jasno razdvajanje zemljišta u kojem su SMI vrednosti manje od 100% od onog sa SMI iznad 100% (slika 4.19); samo u nekoliko slučajeva je došlo do preklapanja uzoraka iz ove dve grupe. Linija prikazana na slici 4.19 dijagonalno razdvoja ove dve grupe zemljišta. Uzimajuću u obzir pozicije promenljivih (teških metala) na „biplotu” (slika 4.19) pravac linije razdvajanja ukazuje da su uzorci sa SMI < 100% prvenstveno povezani sa većim količinama Cu, Zn i/ili Cd, dok su oni sa SMI > 100% povezani sa većim sadržajem Pb, Ni i/ili Cr. Ipak, bez obzira na vrednost SMI, može se primetiti da se većina uzoraka nalazi oko koordinatnog početka (zaokruženi na biplotu, slika 4.19), što govori o sličnim sadržajima ispitivanih teških metala u zemljištu bez obzira na stepen njihovog zagađenja. Uzorci van zaokružene površine su nestandardne opservacije („*outliers*“) i oni se podjednako mogu uočiti u obe uvedene kategorije zemljišta u odnosu na SMI vrednosti. Proizilazi da je prisustvo teških metala u ovim nestandardnim uzorcima posledica specifičnih karakteristika tih lokacija, čija identifikacija prevazilazi okvire ovog rada.

Na „biplotovima” dobijenim za baze podataka „iznad 100%“ (slika 4.20a) i „ispod 100%“ (slika 4.20b), uočeno je veoma slabo razdvajanje načina korišćenja zemljišta, s obzirom da se uočava preklapanje različitih kategorija. Ipak, preklapanje je izraženije na slici 4.20a, koja se odnosi na bazu „iznad 100%”. Stoga, može se reći da je profil ispitivanih teških metala u zagađenom zemljištu različite namene očigledno posledica različitih istovremenih uticaja, zbog čega je nemoguće identifikovati dominantni izvor. Grubo razdvajanje poljoprivrednog zemljišta od onog iz urbanih/rekreacionih zona može se uočiti na „biplotu” dobijenom za bazu „ispod 100%” (slika 4.20b), dok se ostale kategije nisu razdvojile. Kada se uzme u obzir položaj većine uzoraka poljoprivrednog zemljišta u setu podataka „ispod 100%“ (slika 4.20b), uočava se da su oni povezani sa većim sadržajem Cr, Ni i Cu, dok je zemljište iz urbanih-rekreacionih zona povezano sa većim sadržajem Zn, Pb i Cd. Ovo je u saglasnosti sa prethodnom pretpostavkom da se PC1 u bazi podataka „ispod 100%“ može pripisati kombinovanom uticaju prirodnih (pedogenih) izvora i/ili antropogenim izvorima osim saobraćaja (na primer, poljoprivrednoj praksi), dok je kroz PC2 reflektovan uticaj saobraćaja kao izvora metala u zemljištu.

Na slici 4.22 prikazan je „biplot” na kojem su uzorci kategorizovani u odnosu na period uzorkovanja (pre ili posle 2000. god., godine kada je benzin sa dodatkom jedinjenja olova zabranjen u okviru EU). Ovom kategorizacijom nije uočeno razdvajanje uzoraka u okviru baze podataka „iznad 100%“ (slika 4.22a). Uočljivije razdvajanje se može videti na „biplotu” dobijenom za bazu podataka „ispod 100%“ (slika 4.22b): većina uzoraka analizirana posle 2000. god. su locirani u gornjem levom delu „biplota”, dok je većina uzoraka analizirana pre 2000. god. u desnom delu „biplota”. Pri tome, interesantno je da je većina uzoraka „posle 2000. god.“ na „biplotu” povezana sa većin sadržajem Pb (pored Cd i Zn), što je bilo za očekivati u slučaju uzoraka analiziranih pre 2000. god. Razdvajanje uzoraka na slici 4.22b poklopilo se sa onim sa slike 4.20b, gde je uočeno grubo razdvajanje poljoprivrednog zemljišta od onog iz urbanih/rekreacionih zona, za koje se može videti u tabeli 3.17 da su uzorkovani u različitim periodima u odnosu na 2000. god., tj. većina poljoprivrednog zemljišta je analizirana pre 2000. god., dok je većina zemljišta iz urbanih/rekreacionih zona analizirana posle 2000. god. Ovo je mogući razlog razdvajanja uočenog na slici 4.22.

Dakle, može se zaključiti da je od svih kategorizacija zemljišta u odnosu na šest posmatranih metala najuspešnija ona koja se zasniva na načinu korišćenja zemljišta, na osnovu koje izvršena razdvajanje profila metala u poljoprivrednom zemljištu od onog u zemljištu urbanih/rekreacionih zona.



a)

b)

*Slika 4.22. PC1 - PC2 "biplotovi" dobijeni za baze podataka "iznad 100%" (a) i "ispod 100%" (b) formiranih u skladu sa izračunatim vrednostima SMI ("*Soil Metal Index*"). Kriterijum za kategorizaciju je period uzorkovanja zemljišta (■ - pre 2000. god., □ - posle 2000. god.). Procenat u zagradi predstavljaju udeo ukupne varijanse objašnjen svakom od zadržanih glavnih komponenti (PC).*

Primenom linearne diskriminacione analize (DA) ispitana je uspešnosti klasifikacije uzoraka zemljišta u odnosu na uvedene kategorije prema načinu korišćenja zemljišta. Rezultati DA za bazu podataka sa svim uzorcima (baza „svi“) prikazani su u tabelama 4.11 i 4.12. U odnosu na Wilks-λ vrednosti, diskriminaciona snaga ispitivanih promenljivih za razdvajanje zemljišta prema načinu korišćenja opada u sledećem nizu: Cu > Zn > Ni > Cr > Cd > Pb. Postignut je ukupan procenat ispravne klasifikacije od 73,3%, pri čemu su procenti ispravne klasifikacije zemljišta iz kategorija „ruralno“, „poljoprivredno“ i „rekreaciono“ zemljište 100%, 90,8% i 75,6%, redom, što je ukazalo na njihovo uspešno razdvajanje.

Tabela 4.11. Rezultati linearne diskriminacione analize baze podataka “svi”

Teški metal	**Wilks' λ**
Zn	0.231
Cu	0.213
Cr	0.247
Pb	0.296
Ni	0.235
Cd	0.266

Tabela 4.12. Rezultati linearne diskriminacione analize baze podataka “svi”: procenti ispravne klasifikacije

Grupa	Broj uzoraka	Procenat ispravne kasifikacije
Poljoprivredno	118	90.8
Rekreaciono	78	60.0
Travnjak	10	30.0
Industrijsko	10	75.6
Urbano	18	61.5
Ruralno	6	100
Uz put	13	20.0
Šumsko	6	16.7
Nepoznato	5	0.0
Ukupno	264	73.3

5. ZAKLJUČAK

- Primena PCA na bazi podataka o prisustvu PAH-ova u zemljištu iz različitih delova sveta pokazala je da je log-transformacija obavezan pretkorak u pripremi podataka za analizu, s obzirom da je utvrđeno da manje od 2% nestandardnih uzoraka (“*outliers”)* u ukupnom broju uzoraka može da dovede do pogrešne interpretacije podataka ukoliko se ne izvrši transformacija ulaznih podataka, zbog preovlađujućeg uticaja ovim ekstremnih vrednosti na krajnjih rezultat. U slučaju analize masenih udela (kompozicionih podataka), dobijeni su slični PCA rezultati sa i bez log-transformacije.
- Najveća varijansa ulaznih podataka o prisustvu PAH u zemljiištu iz različitih regiona širom sveta, izraženih bilo kao apsolutna vrednost ili relativni udeo, vezana je za više PAH-ove i za fenantren.
- Zemljišta sa industrijskih i udaljenih lokacija pokazala su veće rasipanje u koordinatnom sistemu prve dve glavne komponente nego ona sa urbanih lokacija, ukazujući na veliku raznolikost PAH-profila “industrijskih” i “udaljenih” zemljišta, tj. na veću sličnost PAH-profila između “urbanih” zemljišta iz različitih regiona. Uočeno preklapanje PAH-profila zemljišta sa industrijskih i udaljenih lokacija u osnovi ima dva porekla: povećani sadržaj fenantrena u “industrijskom” zemljištu je najverovatnija posledica izlivanja naftnih derivate, dok je povećani sadržaj fenantrena u “udaljenim” zemljištima verovatno posledica prirodnih izvora PAH-ova. Klasifikacija PAH-profila u zemljištima u zavisnosti od geografskog porekla (tj. zemlje u kojoj je uzorkovanje izvršeno) nije uočena.
- Analiza glavnih komponenata baze podataka o prisustvu organohlornih jedinjenja u izabranim uzorcima zemljišta, ukazala je na postojanje međuzavisnosti sadržaja humusa, kiselosti i gustine zemljišta, sa jedne strane, i sadržaja p,p’-DDT, β-HCH i γ-HCH, sa druge, dok je sadržaj gline u zemljištu povezan sa α-HCH i PCB 28.
- Raspodela uzoraka uključenih u bazu podataka prisustva PCB u zemljištu sa različitih lokacija iz Evrope i Azije ukazala je na pretežno male i relativno međusobno slične sadržaje ovih zagađujućih jedinjenja, dok su se kao nestandardni uzorci usled povećanih sadržaja ispitivanih jedinjenja izdvojili arhivski uzorci iz perioda intenzivnog korišćenja PCB.

- Raspodela uzoraka u sistemu zadržanih glavnih komponenata ukazala je da oko 47% ispitanih uzoraka uzetih iz šumskih predela povezana sa povećanim sadržajima PCB; dalje razlike u PCB profilima zemljišta različite namene i sa različitih geografskih lokacija nisu uočene. Takođe, uočene su vremenske razlike u ukupnim sadržajima PCB u ispitivanim uzorcima zemljišta: koncentracije u zemljištu uzorkovanom tokom ’90-tih i nakon 2000. god. slične su onim iz perioda pre intenzivnog korišćenja proizvoda na bazi PCB (ranih ’40-tih), i niže su od onih određenih u uzorcima iz 1956. i 1980. god.

- Analiza glavnih komponeneta baze sa podacima o sadržaju organohlornih pesticide u zemljišta ukazala je na povećane sadržaje DDT i njegovih metabolota u uzorcima iz Kine, kao i povećane sadržaje HCH izomera u uzorcima iz Indije.

- Primena PCA nad formiranim bazama podataka o prisustvu indikatorskih PCB u analiziranim uzorcima humanog mleka davaoca iz Wielskopolska regiona u Poljskoj ukazala na nizak i prilično ujednačen stepen izloženost PCB-ovima u ovom regionu bez uočene razlike između prvorotkinja i drugorotkinja ili između davaoca iz gradskih i seoskih sredina.

- Uvođenjem podataka o PCB profilima u uzorcima namirnica i vazduha iz zatvorenih prostorija u PCA analizu, ukazano je na potrebu proširenja upitnika podacima koji bi dali bolji uvid u potencijalne izvore ovih zagađujućih jedinjenja u uzorcima, naročito u nestandardnim uzorcima („*outliers*“) (na primer, podacima o vrsti namirnica uobičajeno korišćenih u ishrani, tj. da li se radi o ribi iz slatkovodnih ili slanih voda, da li je ona lokalna ili uvezena, da li spada u vrste bogate masnoćom ili ne; podacima o konzumiranju namirnica biljnog porekla, kao i podacima o prisustvo potencijalnih izvora PCB u zatvorenim prostorima (nov nameštaj ili podne obloge, bilo kod kuće ili na poslu, nedavno poliranje drvenih podloga, godina izgradnje zgrade stanovanja, sezona uzimanja uzoraka (zimi ili leti), frekvencija korišćenja raznih električnih uređaja (u satima po danu), kao što su televizori, mikrotalasne peći, kompjuteri, i dr.).

- Analizom glavnih komponenata i grupisanja u okviru baze sa sadržajima postojanih organskih zagađujućih jedinjenja u vazduhu Makedonije, izvršeno je grupisanje izabranih lokacija prema ukupnom stepenu zagađenja, pri čemu nisu utvrđene značajne razlike u profilima ispitanih jedinjenja u odnosu na periode uzorkovanja.

- Višestrukom regresijom dobijenih podataka za uzorke iz Makedonije i dostupnih meteoroloških parametara potvrđen je značajni doprinos temperature na promene atmosferskih koncentracija ispitivanih zagađujućih jedinjenja, kao i uticaj brzine vetra na mehanizam adsorbovanja nekih od jedinjenja na poliuretanskom disku pasivnog uzorkivača. Takođe, dobijeni su pozitivni regresioni koeficijenti između koncentracija pentahlorobifenila i heksahlorbenzena sa količinom padavina, dok su negativni koeficijenti između koncentracija određenih jedinjenja i perioda osunčanosti ukazali na fotodegradacione procese kao mogući način smanjenja njihovog sadržaja u vazduhu.

- Analiza glavnih komponenata baze podataka o prisustvu teških metala u zemljištu sa različitih lokacija širom sveta ukazala je na prisustvo dva glavna, zajednička izvora ovih zagađujućih jedinjenja. U uzorcima zagađenog zemljišta najveća varijansa u podacima pripisana je prisustvu Pb, Cd, Cu i Zn u zemljištu ukazujući da je glavni izvor ovih elemenata saobraćaj, bilo usled emisije izduvnih gasova, abrazije guma, ulje za podmazivanje i sl. U uzorcima nezagađenog zemljišta, prva glavna komponenta, kojom je opisan najveći udeo varijanse ulaznih podataka, povezana je sa Ni, Cr i Cu, ukazujući na pedološke procese i/ili agrotehničke mere kao glavni izvor ovih metala na nezagađenim područjima.
- Diskriminaciona analiza potvrdila je grupisanje uočeno primenom analize glavnih komponenata ukazujući na specifične profile teških metala u uzorcima poljoprivrednog zemljišta, pri čemu promenljiva koja najviše utiče na uočeno grupisanje je sadržaj bakra.

Svi zaključci zasnovani su na bazama podataka, koje su obuhvatile kako eksperimentalne rezultate dobijene u okviru rada tako i međunarodno publikovane podatke. Prvi put je pokušano i verifikovano hemometrijsko tumačenje velikih baza podataka u oblasti postojanih organskih zagađujućih jedinjenja i teških metala u matriksima životne sredine i humanog mleka.

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PRILOG I

Radovi koji su objavljeni na osnovu rezultata istraživanja u okviru rada na doktorskj disertaciji

M21 – Rad u vrhunskom međunarodnom časopisu

1. Stafilov T., Škrbić B., Klanova J., Čupr P., Holoubek I., Kočor M., Đurišić-Mladenović N. *Chemometric assessment of the semivolatile organic contaminants content in the atmosphere of the selected sites in the republic of Macedonia*, J. Chemometr., **25** (2011) 262-274.
2. Škrbić B., Đurišić-Mladenović N. *Chemometric interpretation of heavy metal paterns in soils worldwide*, Chemosphere, **80** (2010) 1360-1369.
3. Škrbić B., Szyrwińska K., Đurišić-Mladenović N., Nowicki P., Lulek J. Principal *component analysis of indicator PCB profiles in breast milk from Poland*, Environ. Int., **36** (2010) 862-872.
4. Škrbić B., Đurišić-Mladenović N. *Principal component analysis for soil contamination with organochlorine compounds*, Chemosphere, **68** (2007) 2144-2152.

M22 – Rad u istaknutom međunarodnom časopisu

1. Škrbić B., Đurišić-Mladenović N. *Distribution of chlorinated organic pollutants in a wide variety of soils from Europe and Asia worldwide: A multivariate statistical approach*, Arch. Environ. Contam. Toxicol., 52 (2007) 466-474.

M23 – Rad u međunarodnom časopisu

1. Škrbić B., Đurišić-Mladenović N. *Distribution of heavy elements in urban and rural surface soils: the Novi Sad city and the surrounding settlements, Serbia*, Environ. Monit. Assess., (2012), DOI: 10.1007/s10661-012-2567-3
2. Škrbić B., Đurišić-Mladenović N. *Levels of PAHs in soil samples from the vicinity of oil refinery Novi Sad-Serbia*, Kuwait J. Sci. Eng., 36 (1A) (2009) 63-75,.
3. Škrbić B., Cvejanov J., Đurišić-Mladenović N. *Organochlorine pesticides and polychlorinated biphenyls in surface soils of Novi Sad and bank sediment of the Danube River*, J. Environ. Sci. Health B, 42 (2007) 311-319.
4. Škrbić B., Cvejanov J., Đurišić-Mladenović N. *Polycyclic aromatic hydrocarbons in surface soils of Novi Sad and bank sediment of the Danube River*, J. Environ. Sci. Health A, 40 (2005) 29-43.

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Chemometric assessment of the semivolatile organic contaminants content in the atmosphere of the selected sites in the Republic of Macedonia

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Data obtained through a pilot study for the development of the monitoring network in the Central and Eastern Europe (MONET_CEEC) 2006, regarding the occurrence of 12 organochlorine pesticides (OCPs), seven indicator polychlorinated biphenyls (PCBs) and 28 polycyclic aromatic hydrocarbons (PAHs) in the air of six locations in the Republic of Macedonia have been interpreted by principal component (PCA) and cluster (CA) analysis. The data structures of three sets organized to contain the atmospheric concentrations of (a) PAHs, the so-called PAHs set, (b) both classes of organochlorine compounds (PCBs and OCPs) grouped in the organochlorinated compounds (OCCs) set and (c) the overall data (the semivolatile organic compounds (SVOCs) set) were compared. The PCA results suggested mixed origin of PAHs, especially dominant in the urban zones of Skopje, the capital of the Republic of Macedonia. Furthermore, it was found that retene had a distinctive source that separated it from the rest of the PAHs, and it was linked to the incidents of biomass burning. The OCC atmospheric patterns differed among the sites more than it was the case with the PAH patterns, implying some site-specific sources or conditions that influenced the OCC atmospheric concentrations. CA coupled with bootstraps confirmed the groupings of samples found by the PCA biplots. The influence of available meteorological parameters on the SVOC atmospheric concentrations has been evaluated by multiple regression analysis (MRA) indicating the positive impacts of temperature and wind speed for majority of analyzed SVOCs. Precipitation was found to be linked proportionally only with pentachlorobenzene and hexachlorobenzene. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: semivolatile organic compounds; atmosphere; urban; rural; multivariate analysis

1. INTRODUCTION

Semivolatile organic compounds (SVOCs) comprise many priority pollutants such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs). All these contaminant classes may pose a threat to terrestrial and aquatic ecosystems and human health once released into the environment. The atmosphere often plays a key role in their transport within the immediate vicinity of SVOCs sources as well as over great distances [1]. In other words, atmospheric transport is the primary distribution pathway for SVOCs, moving them from emission sources to different distances; finally, they are deposited in different environmental compartments (water, soil, biota) through dry or wet deposition [2]. In the atmospheric environment, SVOCs distribute differently in accordance to their physico-chemical properties and intensity of emission sources.

PAHs are formed during the combustion of carbonaceous materials. In the atmosphere they can come from natural sources such as forest fires and volcanic eruptions. However, their presence in the environment has been significantly increased by anthropogenic emissions such as automobile exhausts, domestic heating, biomass burning, industrial activities, oil spillage, etc. Atmospheric PAHs are found in both gaseous and particle phases. Low molecular mass (LMM) PAHs with 2–3 aromatic rings exist predominantly in the gaseous phase. Compounds with four or more rings (high molecular mass, HMM) are presented generally in particulate matter, often in the fine particulate fraction, i.e. in the $PM_{2.5}$ size range, especially in urban areas with heavy traffic [3,4].

Organochlorinated compounds (OCCs) like PCBs and OCPs have been widely used in the world. Both classes are man-made chemicals emitted in the environment through anthropogenic

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activities. PCBs have been utilized as dielectric fluids, flame retardants and industrial lubricating fluids, while OCPs have been spread via dispersion to the soil [5,6]. Although the use of OCCs has been stringently reduced or forbidden in many countries for several decades, they could be still found in the environment representing a mixture of historical residues, fresh inputs from illegal uses and/or as impurities in chlorinated substances legally allowed to be used.

There is a general lack of information on the levels of SVOCs in the countries of Central and Eastern Europe (CEE) [7]. A better situation is in the Czech Republic, Slovakia, Poland, Slovenia, Hungary, Bulgaria and Croatia [7,8], while in the rest of CEE countries, available data on the SVOCs sources and levels are very limited, and there is no systematic monitoring of SVOCs in majority of the countries from former Yugoslavia [7], including the Republic of Macedonia. An interest to monitor the atmospheric SVOCs concentrations in the Republic of Macedonia has been increased significantly during the last decade, primarily through a pilot study for the development of the monitoring network in the Central and Eastern Europe (MONET_CEEC) 2006, under the auspices of Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University, Brno, Czech Republic. Within this study, the results on the occurrence of 12 OCPs, seven indicator PCBs and 28 PAHs in air of six locations in the Republic of Macedonia were generated, including those affected by industrial activities to the more remote areas. However, studies based only on raw data interpretation are rarely satisfactory to assess the multicomponent patterns, pollutants distributions and impact of the potential sources on the analyzed environmental compartment. Thus, a more reliable approach is the application of multivariate analysis to data interpretation and modeling of monitoring. The chemometric tools like cluster [9], principal component [9–11], corresponding [12] and other multivariant analytical techniques provide a higher level of information necessary for better understanding of the contribution of different local sources onto the environmental distribution of the contaminants. Also, understanding the source contributions of SVOCs in the environment is essential for developing effective countermeasures against their pollution.

The aim of this study was to model the structure of a monitoring set of the SVOCs data collected in Republic of Macedonia in order to analyze the variations of the atmospheric patterns and distributions among the sites. The effect of several meteorological parameters like atmospheric temperature, wind speed, precipitation quantity and insolation on the variations in the atmospheric concentrations of the SVOCs was also investigated. In order to elucidate the pattern of SVOCs distribution, relation between the measured variables and to reveal the similarity or dissimilarities among the samples, univariate and multivariate statistical analyses were applied.

2. MATERIALS AND METHODS

2.1. Sampling sites

Six sampling locations were chosen to monitor the atmospheric concentrations of SVOCs in the Republic of Macedonia. The geographical location of the sampling sites is presented in Figure 1. Characteristics of the sampling sites are presented below:

(1) Lazaropole (41.540°N; 20.696°E) is a background environmental station of the Automatic Air Pollution Monitoring System (AAPMS) of the Ministry of Environment and Physical Planning. It is a rural site located on a mountain at 1333 m a.s.l., opposite of the village of Lazaropole in the Western part of the country, in the Mavrovo National Park. The surrounding area is generally open and comprises meadows and residential houses.

Figure 1. Geographical location of six sampling sites.

(2) Skopje-OHIS (41.984°N; 21.475°E) is also a part of AAPMS located in the city of Skopje, capital of the Republic of Macedonia, with about 550 000 inhabitants. The sampling site was located at 236 m a.s.l. and it is an urban residential site, generally open and surrounded by meadows and residential houses.
(3) Skopje-MEPP (41.998°N; 21.446°E) is another sampling site from the urban zone located in the center of Skopje in the open area with small trees (200 m a.s.l.) and it is expected to be affected by heavy traffic, as the nearest road with a high traffic density is only 5 m away.
(4) Bujkovci (42.005°N; 21.652°E) represents a rural site about 25 km away from the capital. It is located at 312 m a.s.l.
(5) Bitola (41.047°N; 21.356°E) is a city with about 95 000 inhabitants in the southwestern part of the Republic of Macedonia near the border with Greece. The chosen sampling site in Bitola was located 250 m from the nearest road, and it represents an open area with residence facilities (600 m a.s.l.). The power plant 'Bitola' of the 660 MW capacity is located about 10 km from the city; its annual consumption rate of coal (lignite) is about 8–9 million tons.
(6) Strumica (41.442°N; 22.665°E) is the largest city in eastern Macedonia, near the border crossing with Bulgaria. About 150 000 people live in the city and the surrounding region. The sampling site was located 300 m from the nearest road, and it represents open area with residence facilities (232 m a.s.l.).

At the sampling sites with no other major emission sources, i.e. at site nos. 1, 2, 4 and 6, wood combustion has been mainly used in households for heating.

2.2. Sampling

Sampling of SVOCs from air was performed consecutively for four months during the period 14 May–3 September 2007. Thus, there were four samples for each sampling site referring to the following 28-day periods: 14.05.–11.06.2007, 11.06.–09.07.2007, 09.07.–06.08.2007 and 06.08.–03.09.2007. It has to be emphasized that the chosen sampling period from May to September represents the season with lowest emissions from various combustion sources [13]. It was also the period in year when the evaporation of SVOCs was the highest due to highest average temperatures. Passive air samplers with polyurethane foam (PUF) were used. These samplers could be regarded as a potential alternative to conventional sampling techniques with high-volume samplers, but it can be used mainly for gas-phase SVOCs and may collect only some parts of fine particles' levels [14–16]. It provides information about long-term contamination at the selected sites and it can be used as a screening method for semiquantitative comparison of different sites having advantage of low sensitivity to accidental short-time changes in concentration of pollutants. The passive samplers used in this study were composed of a foam disk (15 cm diameter; 1.5 cm thick; 0.03 g m^{-3} density; type N 3038; Gumotex Breclav, Czech Republic) positioned in a stainless steel sampling chamber consisting of two domes [7].

This 'flying saucer' design protects the foam disks from direct precipitation, sunlight and coarse particle deposition. Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All filters were prewashed, cleaned (8 h extraction in acetone and 8 h in dichloromethane), wrapped in two layers of aluminum foil, placed into zip-lock polyethylene bags and kept in the freezer prior to deployment. Exposed filters were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported in a cooler at 5°C to the laboratory where they were kept in the freezer at −18°C until the analysis. Air was allowed to flow over the sampling surface through a ~2.5 cm gap between two domes. Average sampling rate was estimated to be 3.5 m^3/day, which roughly corresponds to 100 m^3 for a 28-day sampling cycle. These estimates were used to derive the air concentrations expressed as amounts of SVOCs (ng or pg) per m^3 of air. The estimated sampling rate was in accordance to the previous results [17] from laboratory calibrations of PUF disk samplers and field deployments where depuration compounds were used (these are isotopically labeled chemicals added to the PUF disks prior to exposure and have been used to assess site-specific mean sampling rates). Namely, Shoeib and Harner [17] found that typical sampling rates with PUF passive air samplers were in the range of 3–4 m^3 of air per day. However, the environmental parameters affect the air gas phase-sampler equilibrium partitioning. Wind is an important environmental parameter that can influence the sampling rate [18]. Some studies revealed that larger variation could be expected when ambient wind speeds exceeded approximately 5 m/s [19,20]. The comprehensive study of Klanova *et al.* [21] dealing with effects of environmental parameters like temperature and wind on PUF disks passive air samplers under field conditions revealed that variability in sampling rates for mainly gas-phase compounds is expected to be fairly low (within a factor of about 2) over typical field conditions. Moreover, Klanova *et al.* [22] compared the air concentrations of the same classes of SVOCs estimated from the passive air sampling campaign based on the same type of the PUF samplers providing the sampled air volumes around 100 m^3 per 28 days, with the air concentrations measured during high volume campaigns. They reported that the estimated concentrations of PAHs, PCBs, DDTs and HCH isomers (based on the sampling volume 100 m^3/28 days) were well within the range measured in the same area using conventional high volume samplers. Harner *et al.* [23] stated that at present, passive air samplers can enable the estimation of air concentrations typically within a factor of 2–3 of the 'true' concentrations. So far no comprehensive field calibration has been undertaken, and when greater quantitative power or confidence is required, depuration compounds should be used, making passive air sampling method more complex and expensive.

2.3. Analysis

All samples (PUF disks) were extracted with dichloromethane in a Büchi system B-811 automatic extractor. Volume of extracts after extraction was reduced under a gentle nitrogen stream at ambient temperature. Fractionation of PCB/OCP in extracts was achieved on a silica gel column (a sulfuric acid modified silica gel). Samples were analyzed using GC-ECD (HP 5890) supplied with a Quadrex fused silica column for PCB such as PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180 and OCPs such as α-hexachlorocyclohexane (HCH), β-HCH, γ-HCH, δ-HCH, 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (*p,p*′-DDE), 1,1-dichloro-2,2-bis (p-chlorophenyl) ethan (*p,p*′-DDD), 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethan (*p,p*′-DDT), *o,p*′-DDE, *o,p*′-DDD, hexachlorobenzene (HCB) and pentachlorobenzene (PeCB). Furthermore, 28 PAHs (naphthalene (Naph), acenaphtylene (Acy), acenapthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Py), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)-fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcP), dibenz(ah)anthracene (DahA), benzo(ghi)perylene (BgP), biphenyl (Bph), retene (RET), benzo(b)fluorene (BbFLu), benzonaphtho-thiophene (BNT), benzo(ghi)fluoranthene (BgF), cyclopenta(cd)pyrene (CPP), triphenylene (Triph), benzo(j)fluoranthene (BjF), benzo(e)pyrene (BeP), perylene (Per), dibenz(a-c)anthracene (DacA), anthanthrene (Anth) and coronene (Cor)) were determined in all samples using the GC-MS instrument (HP 6890–HP 5972) supplied with a J&W scientific fused silica column DB-5MS. Terfenyl was used as an internal standard for PAHs and PCB 121 for PCB/OCP analyses. One laboratory blank and one reference material were analyzed with each set of ten samples.

Limit of quantification (LOQ) was 0.2 ng filter^{-1} ($= 2$ pg m^{-3}).

Recoveries were determined by spiking the surrogate standards (d8-naphthalene, d10-phenanthrene, d12-perylene for PAHs analysis, PCB 30 and PCB 185 for PCBs analysis) on the pre-cleaned filter prior to extraction. The amounts were similar to the detected quantities of analytes in the samples. Recoveries were higher than 75 and 72% for all samples for PCBs and PAHs, respectively. Recovery factors were not applied to any of the data. Recoveries of the native analytes measured for the reference material varied from 88 to 103% for PCBs, from 75 to 98% for OCPs and from 72 to 102% for PAHs. Laboratory blanks were very low. Field blanks consisting of pre-extracted PUF disks were taken on each sampling site. They were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 5% of quantities detected in samples for PCBs, 1% for OCPs, 3% for PAHs, indicating minimal contamination during transport, storage and analysis. Previous air sampling studies performed in the laboratory showed a good agreement between samples from duplicate passive air sampling, in which variability ranged from 5 to 20% for all analytes [22].

2.4. Data sets

In order to perform a chemometric assessment of the obtained data, three input matrices with columns containing the variables (contents of SVOCs) and rows referring to the sample sites for particular sampling period were formed. Namely, the first matrix consisting of the results on the PAHs air contents was called 'PAH set'; the second one, called 'OCC set' referred to the OCCs occurrence in air, while the third one containing the overall data on both the PAHs and OCCs presence was named 'SVOCs set'. The separation of the PAHs and OCCs data into two matrices was made in accordance to their different origins in the environment. Namely, PAHs are inevitably emitted from the numerous combustion processes, while the PCBs and OCPs are man-made (synthetic) chemicals, whose production and use have been restricted and/or ceased due to environmental concerns. Therefore, today's presence of OCCs in the air could be explained with the volatilization from old deposits, waste combustion, old disposal sites, by-products and waste materials from the manufacture of chlorinated solvents and pesticides, etc. Consequently there are significant differences in their concentrations, with the concentration of PAHs usually several orders of magnitude higher than the concentrations of PCBs and OCPs [12]. However, the overall SVOCs set was also assessed by the chemometrics in order to examine similarities of the overall SVOC patterns among the sampling sites and to find if there were some similar sources of these two classes of SVOCs over the sites, like combustion of waste or crop residues. For the contents below LOQ, half of LOQ (LOQ/2) was used in the chemometric analysis. If variable was not quantified (<LOQ) in more than 50% of the samples (cases), it was not included in the matrices for the chemometric analysis. Finally, the sizes of the created matrices were as follows: 24 (cases) × 22 (variables) for the PAH set; 24 (cases) × 19 (variables) for the OCCs set and 24 (cases) × 41 (variables) for the SVOCs set.

2.5. Chemometric analysis

The determined SVOC atmospheric concentrations were described by the averages and standard deviations. It is a well-known fact that pollutant contents in the environment, including the SVOCs atmospheric concentrations, varied widely among the samples [24] not following normal distribution. In such cases, it is advisable to transform the skewed data before performing the statistical methods (like ANOVA, PCA, etc.) that are not sensitive to deviations from this kind of distribution [25–27]. Hence, before performing the chemometic analysis, the atmospheric concentrations found in this study were processed by logarithmization [24,28].

The differences in the total content of SVOC classes among the sampling sites were examined by the one-factor analysis of variance (ANOVA) and Tukey's Honestly Significant Difference (HSD) test.

Principal component analysis (PCA) is the multivariate analytical tool used to reduce a set of original variables and to extract a small number of latent factors (e.g. principal components, PCs). In this research, PCA of the data was performed in order to detect similarities, differences and relationships of the variations in the atmospheric concentrations among SVOCs and to evaluate the number of significant factors affecting variations in the atmospheric concentrations. The newly extracted variables, i.e. PCs, are linear combinations of the original ones and are sorted into descending order according to the amount of variance that they account for in the original set of variables. The loadings express how well the new abstracted principal components correlate with the old variables. PCA will show which kinds of compounds are similar to each other, that is, carry comparable information, and which ones are unique. Relationships among the samples are evaluated on the score plots, whereas the loading plots show the extent to which each variable contributes to the sample separation (grouping). Alternatively, variable loadings and sample scores can be combined into unique graphical presentation called biplot. Since the magnitude of loadings and scores are not the same, it is advisable to divide each loading and score values with the respective maximum values obtained for particular PC; thus, the biplot presented the relative positions of the element loadings and the sample scores within the range from -1 to $+1$. In this way, the interpretation of the variables correlation and the influence on the samples' classification could be made more obviously. Number of PCs extracted from the variables was determined by Kaiser's rule [29]. This criterion retains only PCs with eigenvalues that exceed 1. In order to interpret the significance of retained PCs in terms of the original variables, only those loadings (coefficients) whose absolute value was greater than 60% of the maximum coefficient in absolute value for each PC were considered [30]. The variable loadings were varimax rotated for better interpretation of the results [24,31–36]. The algorithm of PCA can be found in the standard textbooks [37].

Additionally, cluster analysis is used to classify sampling sites into groups, i.e. clusters. It can be considered to be an alternative approach to PCA. An important step in clustering is to select a distance measure, which determines the similarity or dissimilarities of the samples. The distance between two points is well defined; the simplest distance measure is the Euclidean distance. However, numerous clustering algorithms exist as to what is considered to be a distance between two groups. It may be defined as the distance of the two closest points or the two farthest points, etc. Weighted schemes are also reliable alternatives. The most popular clustering algorithm is perhaps complete linkage method. Definitions of distance measures and clustering algorithms can be found in standard chemometric textbooks [37]. In this study, complete linkage method as an amalgamation rule and the Euclidean distance as a measure of the proximity between sampling sites are used for the cluster analysis of the input data matrices previously described. Although cluster analysis is frequently applied to environmental data sets, the uncertainty of the results has not been evaluated in practice. One of the most frequently used approaches for this purpose is the bootstrap [38]. This approach generates the large number of input data matrix bootstrap samples in the random way to evaluate the reliability of final outcome of cluster analysis. As a measure of reliability of clusters, approximately unbiased (AU) *p*-value was calculated and expressed in percentages; higher AU percentages imply higher reliability of the formed clusters. In this study, 1000 bootstrap replicates were used to evaluate the results of obtained dendrograms.

In order to analyze the factors affecting variations in the atmospheric concentrations of compounds, ambient temperature, wind speed, amount of precipitations and insolation were selected since they were easily obtainable data and also they were previously considered to affect the atmospheric concentrations of SVOCs [24]. The mean monthly meteorological data for four stations in the period from May to September 2007 were obtained from the Hydrometeorology Agency of the Republic of Macedonia (data not shown). As there was no meteorological station at Bujkovci (site no. 4), the data obtained for the closest meteorological station at Skopje were also attributed to Bujkovci samples. With respect to the meteorological data, Lazarpole was the location with the lowest ambient temperature (11.7–19.4°C) among all sampling sites. Its wind speeds (2.2–2.7 m/s) were similar to those obtained for Skopje (2.4–2.8 m/s). Strumica had the highest temperatures (17.7–27.6°C) and insolation periods (232.5–394.7 h/month) with the lowest wind speeds (0.8–1.3 m/s). Temperature profile (17.7–27.1°C) and insolation periods (222.5–386.3 h/month) in Skopje were similar to those found for Strumica. Bitola was the location with the lowest amount of precipitation (precipitation was not detected in July 2007, while the maximum level of 47.0 mm/m^2 was found in August 2007) with the average wind speeds (1.7–1.9 m/s) and temperatures (16.9–25.4°C) in comparison to other investigated sites. Precipitation levels varied similarly among other meteorological stations with minimum and maximum values found for July and May (2007), respectively, as follows: 10.7–76.6 mm/m^2 at the Lazarpole station, 1.2–96.2 mm/m^2 at the Skopje station and 0.3–107.5 mm/m^2 at the Strumica station.

Multiple regression analysis (MRA) of the data was conducted to analyze the factors affecting variations in the atmospheric concentrations of SVOCs. Reciprocal temperatures (1/*t*), the logarithms of precipitation amount (log pr), wind speed (log ws) and of insolation (log sh) were used as independent variables, and the logarithms of the atmospheric concentrations of SVOCs were used as dependent variables, according to the following considerations. Namely, if a compound is released into the air by volatilization, e.g. from old deposits, it is expected that the logarithms of the atmospheric concentrations of the compound have linear relationship with the reciprocal of the temperature [24]. Moreover, if the dilution rate for the atmospheric concentrations of compounds is correlated with precipitation amount, wind speed and insolation period, the atmospheric concentrations of compounds could be considered to be correlated with reciprocal values of these independent variables. That is, the logarithms of the atmospheric concentrations of compounds are considered to have a linear relationship with the logarithms of precipitation amount, wind speed and insolation. The similar approach was previously used by Ogura *et al.* [24], Perez *et al.* [39] and Brunciak *et al.* [40]. Moreover, semilogarithmic and non-logarithmic regressions were also considered, i.e. the correlations between the log SVOCs concentrations (or SVOCs concentrations without pre-processing) and 1/*t*, pr, ws and sh were examined by MRA. For each particular SVOC variable, separate MRA model was constructed. The effect of each predictor on the SVOC compound was measured by partial regression coefficient. The slope of any partial regression line represents the rate of change (holding all the other predictor variables constant to their respective values). In addition, coefficient of determination of multiple regression model (R^2) was reported and statistically tested by *F*-test.

All the chemometric analyses were performed using functions developed within R software [41].

It has to be emphasized that all statements referring to the chemometric results obtained here are valid within the scope of this study and the samples chosen to be analyzed.

3. RESULTS AND DISCUSSION

3.1. The SVOCs atmospheric concentrations

The averages and standard deviations of the total atmospheric concentrations of the selected SVOCs at the selected sampling locations in the Republic of Macedonia are presented in Table I. It could be easily seen that SKOPJE-MEPP was the site with the highest atmospheric contents of almost all of the analyzed SVOCs classes, followed by SKOPJE-OHIS site. Both of these sites were within the area of the Skopje, the capital and the largest city in the Republic of Macedonia. The observed PAH atmospheric concentrations were several orders of magnitude higher than the concentrations found for OCCs. Data obtained here were generally lower than the averages found by Klanova *et al.* [7] for gaseous phase of the ambient air at different sites in Serbia and Bosnia and Hertzegovina, belonging to the region of the former Yugoslavia as the Republic of Macedonia. Namely, this study reported that total ambiental PAHs contents in Serbia ranged from 10 to 1290 ng/m^3, total PCBs from 0.103 to 39.7 ng/m^3, total DDTs (referring to DDT and its products DDD and DDE) from 0.020 to 0.519 ng/m^3 and HCB from 0.025 to 0.174 ng/m^3, while for the same SVOC types in Bosnia and Hertzegovina the following ranges were found 3–210, 0.060–5.645, 0.012–0.193, 0.064–0.171 ng/m^3, respectively. However, the average total content of HCHs (including its four isomers) found in two Skopje air sample nos. 2 and 3 (3.03 and 1.74 ng/m^3, respectively) was significantly higher in comparison to the data obtained for Serbia

Table I. The averages (and standard deviations) of the total atmospheric concentrations of the analyzed SVOCs at six sampling locations in the Republic of Macedonia during the period 14 May–03 September 2007

Location	PAHs (ng/m^3)	PCBs (pg/m^3)	HCHs[a] (pg/m^3)	DDTs[b] (pg/m^3)	HCB (pg/m^3)	PeCB (pg/m^3)
Lazaropole	11.38 ± 4.67	23.91 ± 5.87	100.99 ± 11.4	35.91 ± 11.94	45.66 ± 2.81	9.69 ± 2.43
Skopje-OHIS	46.19 ± 1.44	256.62 ± 28.05	3033.16 ± 552.6	153.83 ± 37.56	34.18 ± 1.32	8.16 ± 1.86
Skopje-MEPP	123.33 ± 14.00	277.54 ± 21.10	1737.23 ± 797.1	245.66 ± 10.85	51.02 ± 11.21	10.46 ± 2.93
Bujkovci	20.33 ± 0.69	174.48 ± 12.53	182.37 ± 14.7	125.51 ± 15.07	36.99 ± 7.70	11.22 ± 1.86
Bitola	24.75 ± 11.20	74.21 ± 8.72	165.54 ± 31.0	206.38 ± 4.88	41.07 ± 9.69	10.97 ± 2.26
Strumica	15.53 ± 2.57	75.73 ± 14.26	172.17 ± 36.7	106.11 ± 46.03	34.95 ± 4.67	8.67 ± 2.43

[a] The total content of α-, β-, γ- and δ-HCH

[b] The total content of *o,p*′- and *p,p*′-isomers of DDT, DDD and DDE

(0.100–0.321 ng/m^3) and Bosnia and Hertzegovina (0.025–0.054 ng/m^3). Such a high concentration of HCHs in the Skopje air might be attributed to the existence of the lindane landfill with 10 000 t situated in the former producer-OHIS factory [42].

Furthermore, some specific ratios, like α-/γ-HCH, *o,p*′-/*p,p*′-DDT and *p,p*′-DDT/*p,p*′-DDE, widely used to follow the emission sources of HCH- and of DDT-containing pesticides [43–45], respectively, were calculated. The following ranges for all sampling sites and the sampling periods were obtained: 0.15–1.74 for α-/γ-HCH, 0.24–2.43 for *o,p*′-/*p,p*′-DDT and 0.08–0.49 for *p,p*′-DDT/*p,p*′-DDE. Generally, in order to detect recent applications (legal or misuse) of HCH-containing pesticide, the α-/γ-HCH ratio of the environmental (including air) samples is compared with the ratio values characteristic for two types of HCH products manufactured throughout the world: technical HCH (containing among other isomers 55–80% α-HCH and 8–15% of γ-HCH) and lindane (>99% γ-HCH) [44]. It should be mentioned that production and use of technical HCH was banned, while lindane could be legally used for pest control in many countries. Hence, the average α-/γ-HCH ratio in technical HCH should be between 3:1 and 7:1, while the input of lindane will reduce the ratio value [43]. The low α-/γ-HCH values (not shown here), especially those below 0.5 obtained for Skopje-MEPP, Bujkovci and Bitola, suggested possible lindane usage. As there were no ratio values higher than 3, it could be concluded that there were no incidents of the recent misuse of technical HCH. The α-/γ-HCH ratios calculated to be higher than 1 (up to 1.74 at the Skopje-OHIS site) could be most probably attributed to the weathering processes of the old γ-HCH deposits and its transformation into α-HCH by sunlight [44]. The ratio of *o,p*′-/*p,p*′-DDT has been used to distinguish the sources of DDTs from technical DDT, banned to be used, or legal pesticides containing DDT impurities (like dicofol in China). Technical DDT contains less *o,p*′-DDT (about 15%) than *p,p*′-DDT (about 85%), while 'dicofol-type DDT pollution' is characterized by high value of *o,p*′-/*p,p*′-DDT [43]. The highest *o,p*′-/*p,p*′-DDT value of 2.43 found in Strumica in the sampling period 09.07.–06.08.2007 suggested that the input of 'dicofol-type DDT' pesticide might occur in that period. In addition, the ratio of *p,p*′-DDT/*p,p*′-DDE is often used as an indicative of 'fresh' versus 'old' sources of *p,p*′-DDT. Since for all samples the calculated values of *p,p*′-DDT/*p,p*′-DDE ratio were below 0.5, it could be concluded that there were no significant fresh inputs of *p,p*′-DDT.

The *F*-test from one-way ANOVA analysis of the log-transformed total concentrations of the SVOC types, which are presented in Table I, was found to be significant ($p < 0.05$) for all SVOCs except pentachlorobenzene and hexachlorobenzene (data not shown). Pair-wise differences among the sampling sites revealed by the Turkey HSD test are illustrated in Table II. Again, the atmospheric contents of pentachlorobenzene and hexachlorobenzene did not differ among the sites. This implied almost uniform atmospheric concentrations for these two OCCs at the selected sites during May–September 2007. Comparison of the contents of other SVOCs (PCBs, HCHs, DDTs and PAHs) at Lazarpole, the background station, and other sites showed significant differences, especially when it was compared with the Skopje area and nearby Bujkovci village (Table II). Significant differences among all sites were found for PCBs, except for Bitola and Strumica, two cities away from the capital with similar population sizes. The revealed differences indicated the differences in the local emission sources.

Table II. Pair-wise differences among the sampling sites in the Republic of Macedonia concerning the total atmospheric concentrations of seven indicator PCBs, 28 PAHs and 12 OCPs (significant at $p < 0.05$)

Sampling site	Lazarpole	Skopje-OHIS	Skopje-MEPP	Bujkovci	Bitola
Skopje-OHIS	PCBs, HCHs, DDTs, PAHs				
Skopje-MEPP	PCBs, HCHs, DDTs, PAHs	HCHs, PAHs			
Bujkovci	PCBs, HCHs, DDTs, PAHs	PCBs, HCHs, PAHs	PCBs, HCHs, DDTs, PAHs		
Bitola	PCBs, DDTs, PAHs	PCBs, HCHs, PAHs	PCBs, HCHs, PAHs	PCBs	
Strumica	PCBs, DDTs	PCBs, HCHs, PAHs	PCBs, HCHs, DDTs, PAHs	PCBs	DDTs

Table III. Loading values for principal components (PCs) obtained for the PAH and OCC sets containing the atmospheric concentration of 22 PAHs and 19 OCCs, respectively, measured at six sampling sites in the Republic of Macedonia during four 28-day consecutive sampling periods from 14 May to 3 September, 2007. Values in bold are higher than 60% of the absolute maximum loading value of each PC

PAHs	PC1	PC2	OCCs	PC1	PC2	PC3
Naph	**0.878**	0.304	PCB28	**0.637**	**0.652**	0.139
Ace	**0.797**	0.478	PCB52	**0.677**	**0.682**	0.044
Acy	**0.844**	0.414	PCB101	**0.647**	**0.649**	0.069
Flu	**0.816**	**0.525**	PCB118	**0.618**	**0.593**	0.131
Phe	**0.780**	**0.587**	PCB138	0.552	**0.728**	0.063
Ant	**0.849**	0.459	PCB153	0.727	0.530	0.206
Fla	**0.719**	**0.675**	PCB180	0.152	0.388	**0.699**
Py	**0.723**	**0.678**	α-HCH	0.124	**0.959**	0.011
BaA	**0.580**	**0.796**	β-HCH	0.328	**0.808**	−0.006
CHR	**0.541**	**0.832**	γ-HCH	0.287	0.460	0.409
BbF	0.481	**0.859**	δ-HCH	0.066	**0.846**	0.294
BkF	0.506	**0.812**	*o,p′*-DDE	**0.795**	0.207	−0.162
BaP	**0.878**	0.243	*p,p′*-DDE	**0.924**	0.205	−0.081
IcP	**0.894**	0.359	*o,p′*-DDD	**0.786**	0.099	0.341
BgP	**0.896**	0.357	*p,p′*-DDD	**0.765**	0.525	0.148
Bph	**0.617**	0.364	*o,p′*-DDT	**0.917**	0.109	−0.022
RET	−0.157	**0.849**	*p,p′*-DDT	**0.952**	0.197	−0.067
BNT	**0.654**	**0.674**	PeCB	0.151	−0.150	**−0.784**
BgF	**0.653**	**0.738**	HCB	−0.004	0.079	**−0.806**
Triph	0.502	**0.854**				
BjF	0.435	**0.872**				
BeP	0.538	**0.594**				
% VAR[a]	81.0	8.1		57.0	13.8	8.4

[a] Share of the total variance explained by each retained principal component.

3.2. Principal component analysis

The PCA results obtained for the PAH-, the OCC- and the SVOC-sets are shown in Table III and Figures 2–4, respectively.

Concerning the PAH set, it could be easily seen that majority of the data variance (81.0%) was accounted by the first PC, PC1. It was positively loaded with almost all PAH compounds, except retene (Table III and Figure 2). The second principal component, PC2, accounted for additional 8.1% of the data variance. According to the significant loading values given in bold figures in Table III, it could be seen that there were variables with split loadings on both PCs. However, the PAH compounds that loaded significantly only one PC were more important for the interpretation of the PCA results and indication of possible factors responsible for the samples classification. It should be mentioned that PAHs in the environment can come from two types of sources: petrogenic (unburned petroleum products) or pyrogenic (combustion of fossil fuels and biomass). In pyrogenic PAH mixtures, non-substituted or parent HMM PAHs (with four and more benzene rings) are more abundant than alkylated and/or LMM PAHs, whereas petrogenic PAHs include more alkylated LMM PAHs (with two or three benzene rings) [46]. As both low and high molecular mass PAHs had significant loading on PC1, it could be concluded that PC1 reflected the mixed sources of PAHs in the atmosphere of the investigated sites and that the highest

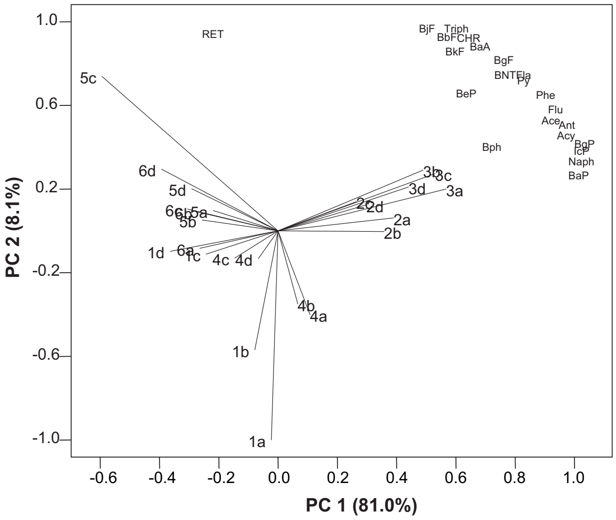

Figure 2. The PC1 vs. PC2 (varimax rotated) biplot of the PAH set containing the atmospheric concentrations of 22 PAHs at six sampling locations (1—Lazarpole, 2—Skopje-OHIS, 3—Skopje-MEPP, 4—Bujkovci, 5—Strumica, 6—Bitola) in four sampling periods (a: 14.05.–11.06.2007, b: 11.06.–09.07.2007, c: 09.07.–06.08.2007 and d: 06.08.–03.09.2007).

concentrations found in the residential areas of Skopje (nos. 2 and 3) originated from both pyrogenic (fossil fuel combustion) and petrogenic (evaporation of fossil fuel drippings on the roadway, evaporative losses during motor vehicle refueling, venting of the restaurant frying oils) sources. Retene, an alkylated phenanthrene (1-methyl-7-isopropyl phenanthrene) that has been suggested as a marker for biomass burning [46–48], significantly loaded PC2 together with some other PAHs not indicative for specific sources, implying that physical meaning of PC2 could be ascribed to the combustion of biomass.

As PC1 described the total PAH burden of the air in the investigated sites, grouping of samples along this axes in the biplot (Figure 2) could be ascribed to the total PAH burden. Dispersion of the samples along PC2 could be attributed to the retene atmospheric contents. Accordingly, three different sample groupings could be found on the biplot: group 1 gathered two urban sites at Skopje (nos. 2a–2d and 3a–3d) that showed the highest PAH contents during all four sampling periods and they had the highest positive scores along PC1 (Figure 2); group 2 consisted of two rural samples at Lazarpole and Bujkovci for which the intermediate PAH contents and the lowest retene concentrations were found for the first two sampling periods (sample nos. 1a, 1b and 4a, 4b); the rest of the samples having the lowest levels of the total PAHs and elevated retene contents formed group 3. The reason for outlying of sample 5c was obviously the highest retene concentration that could be connected to some specific anthropogenic activities during that sampling period, late July–early August, like crop residue burning.

The PCA results for the OCC set are given in Table III and Figure 3. Three principal components were retained explaining the total data variance of 79.2% (Table III). Low chlorinated PCBs (28, 52, 101, 118) had the split loadings on PC1 and PC2; PCB 153 had significant loading on PC1, PCB 138 on PC2, whereas PC 180 on PC3 (Table III). Pesticides from DDT group correlated significantly with PC1 (Table III). In contrast, HCH isomers correlated with PC2 except γ-HCH that failed to load significantly any of the retained PCs (Table III). Pentachlorobenzene (PeCB) and HCB were negatively correlated with PC3 (Table III).

It could be easily seen from Figure 3 that similar compounds belonging to the same type of OCCs correlated among each other reflecting their common sources and/or similar environmental fate [24]. The biplots in Figure 3 also reflected site-specific OCC burdens and patterns with more pronounced dispersion of the samples than in the case of the PAH atmospheric patterns presented in Figure 2. The sample dispersion along PC1 and PC2 was governed primarily by the concentrations of DDT and its products and of HCH isomers, respectively, having the highest loadings, while PCBs had slightly lower loadings split between both PCs. The OCC profiles at two residential sites in Skopje (nos. 2 and 3) differed significantly, while site nos. 4 and 5, and nos. 1 and 6 formed two separate groups on the biplot due to similar OCC patterns (Figure 3a).

Even though PC3 accounted for only 8.4% of variance, it was very interesting to note that it was highly correlated with penta- (PeCB) and hexachlorobenzene (HCB). The former is not known to be manufactured for any commercial uses at present [49]; in the past it was component of a chlorobenzenes mixture used with PCB products, but there are no longer any large scale uses of PeCB. Atmospheric concentrations of PeCB are most closely tied to current emissions of PeCB whereas the other media may be more reflective of past emissions; the largest sources appear to be combustion of solid wastes and biomass burning [49]. HCB has been used in the past for a variety of applications from which it potentially has entered the environment (fungicide, wood preservation, etc.) [50]. Currently, the principal sources of HCB in the environment are estimated to be the manufacturing of chlorinated solvents, the manufacturing and application of HCB-contaminated pesticides and inadequate incineration of chlorine-containing wastes, including municipal waste incineration [50]. Hence, as site no. 3c was highly correlated with the highest concentrations of PeCB and HCB (Figure 3b), it could be assumed that there was a common source for these two OCCs, and it was most probably the incidents of the municipal waste incineration.

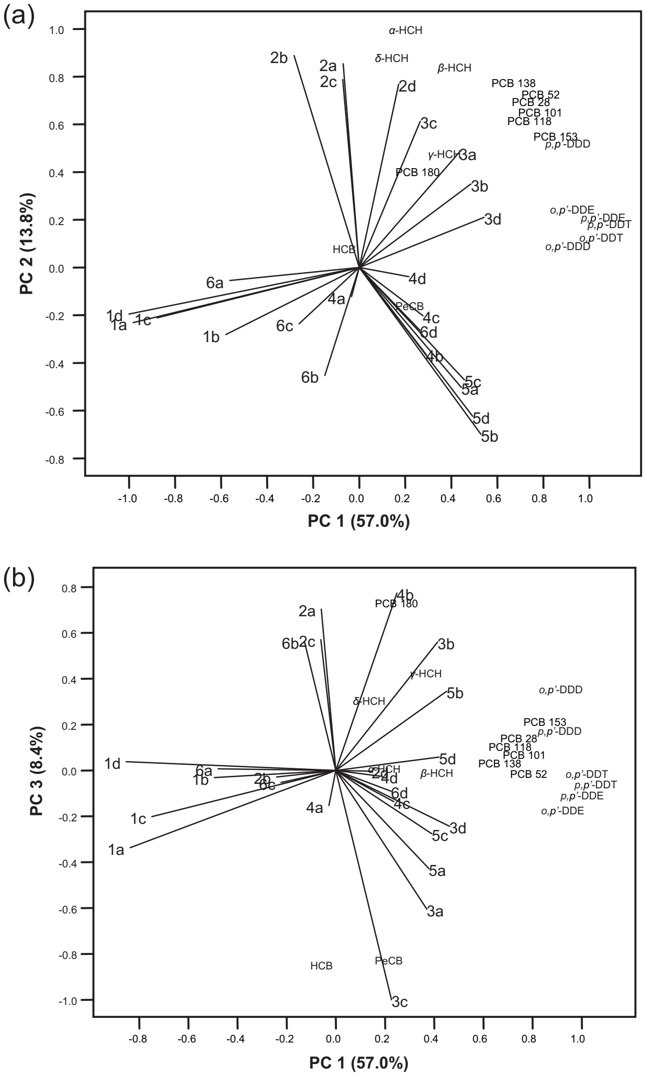

Figure 3. The (varimax rotated) biplots of the OCC set containing the atmospheric concentrations of 7 indicator PCBs and 12 OCPs at six sampling locations (1—Lazarpole, 2—Skopje-OHIS, 3—Skopje-MEPP, 4—Bujkovci, 5—Strumica, 6—Bitola) in four sampling periods (a: 14.05.–11.06.2007, b: 11.06.–09.07.2007, c: 09.07.–06.08.2007 and d: 06.08.–03.09.2007): (a) PC1 vs. PC2, (b) PC1 vs. PC3.

In order to discuss the general similarities/dissimilarities of the SVOCs atmospheric pattern at the investigated sites, the biplots obtained for the SVOCs set are presented in Figure 4. Three principal components accounted for 81.3% of data variance.

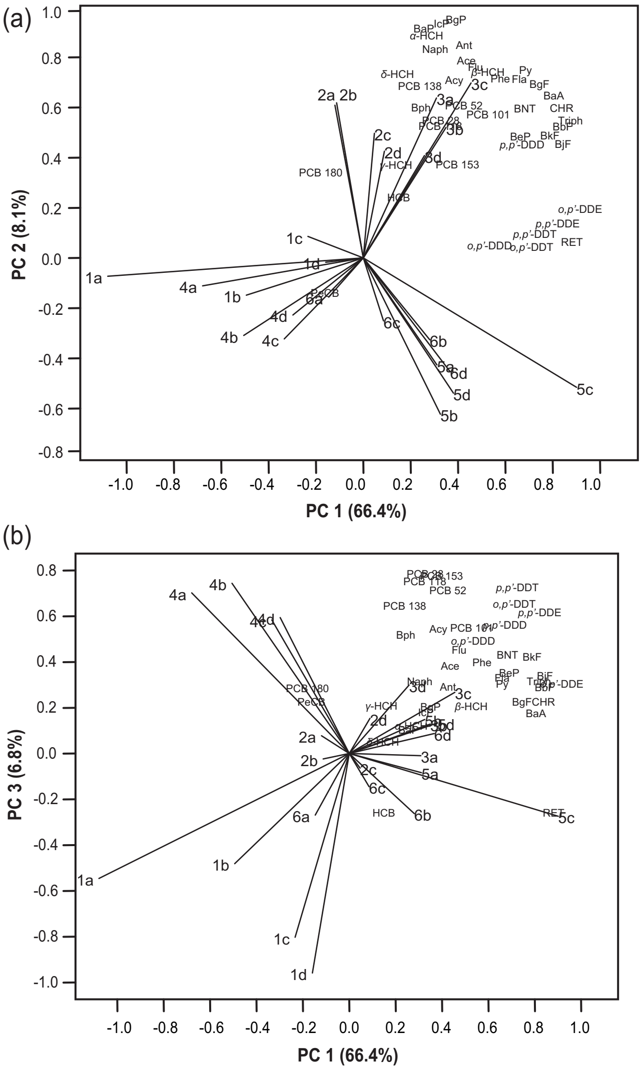

Figure 4. The (varimax rotated) biplots of the SVOCs set containing the atmospheric concentrations of 22 PAHs, 7 indicator PCBs and 12 OCPs at six sampling locations (1—Lazarpole, 2—Skopje-OHIS, 3—Skopje-MEPP, 4—Bujkovci, 5—Strumica, 6—Bitola) in four sampling periods (a: 14.05.–11.06.2007, b:11.06.–09.07.2007, c: 09.07.–06.08.2007 and d: 06.08.–03.09.2007): (a) PC1 vs. PC2, (b) PC1 vs. PC3.

Concerning the PC1 versus PC2 biplot, it could be again seen that residential sites at Skopje (nos. 2 and 3) had distinct SVOC pattern clearly separated from the rest of the sites along PC2 (Figure 4a). Their atmospheric patterns were characterized with highly correlated contents of PAHs, HCH isomers and majority of the indicator PCB congeners (except PCB 180). Furthermore, the sample nos. 5 and 6 were highly correlated between each other with only two outliers: samples 5c and 6a. The former outlier could be related to the highest concentration of retene with elevated contents of DDT and its products, whereas sample 6a had the SVOC pattern similar to the sample nos. 1 and 4. Considering the biplot PC1 versus PC3 (Figure 4b), clear separation of sites no. 1 and 4 along PC3 (similar to those in Figure 3a) could be seen as a consequence of different OCC patterns, primarily of the PCBs and DDTs patterns that had the highest PC3 loadings.

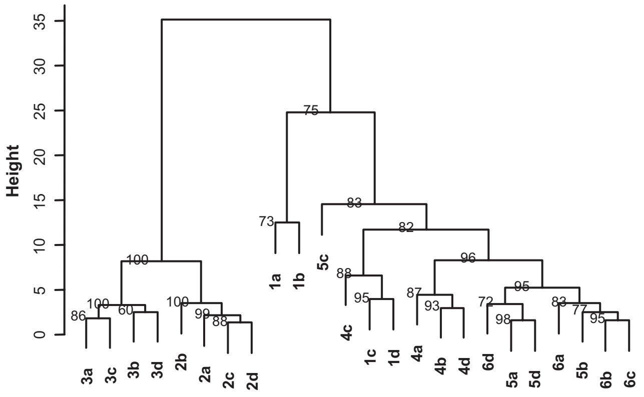

Figure 5. Hierarchical clustering of sampling sites based on the PAH atmospheric concentrations. Values at branches of dendrogram indicate approximately unbiased (AU) *p*-values expressed in %. (1—Lazarpole, 2—Skopje-OHIS, 3—Skopje-MEPP, 4—Bujkovci, 5—Strumica, 6—Bitola) in four sampling periods (a: 14.05.–11.06.2007, b: 11.06.–09.07.2007, c: 09.07.–06.08.2007 and d: 06.08.–03.09.2007).

3.3. Cluster analysis

Dendrograms along with the bootstrap (AU) *p*-values obtained for data sets containing atmospheric concentrations of PAHs, and all SVOCs analyzed at six sites in the Republic of Macedonia are presented in Figures 5 and 6, respectively. The dendrogram for the OCC data set is not presented since it revealed clustering similar to that found for the SVOC data set. Generally, the clustering of the samples obtained by CA coincided with the sample grouping observed at the corresponding PCA biplots.

Concerning the PAH set two branches could be seen in the dendrogram (Figure 5): the one supported with maximum bootstrap value (100) gathered two residential sites from Skopje with highest atmospheric burden of PAHs (nos. 2 and 3), and the other with high bootstrap AU *p*-value (75) connecting all of the remaining sampling sites with lower atmospheric concentrations of the PAHs. Within the latter, further subclustering could be seen making two second-order branches: one with the samples from Lazarpole taken in first two sampling periods (nos. 1a and 1b), and the other supported with higher bootstrap AU *p*-value (83) with the rest of samples located in Bujkovci

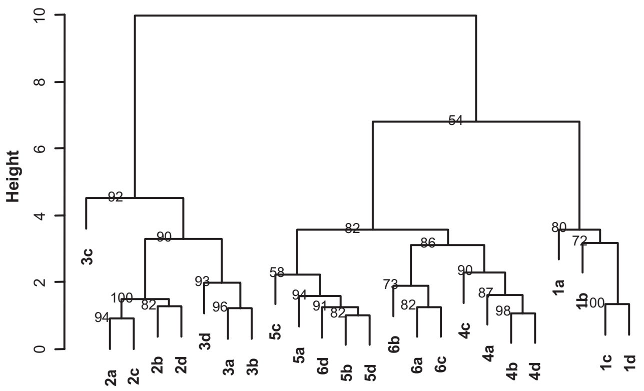

Figure 6. Hierarchical clustering of sampling sites based on the SVOC atmospheric concentrations. Values at branches of dendrogram indicate approximately unbiased (AU) *p*-values expressed in %. (1—Lazarpole, 2—Skopje-OHIS, 3—Skopje-MEPP, 4—Bujkovci, 5—Strumica, 6—Bitola) in four sampling periods (a: 14.05.–11.06.2007, b: 11.06.–09.07.2007, c: 09.07.–06.08.2007 and d: 06.08.–03.09.2007).

(no. 4), Bitola (no. 5) and Strumica (no. 6). Again, it could be observed that site nos. 5 and 6 were similar to each other respecting the PAH air pattern, except the outlying sample 5c that contained the highest content of retene.

The CA results of the SVOC set (Figure 6) also revealed two main clusters indicating differences between the Skopje (nos. 2 and 3) and the other sites (nos. 1, 4, 5, 6). Within the latter cluster, further sub-clustering was observed between background station at Lazarpole (no. 1) and sites nos. 4, 5 and 6 that had similar SVOC pattern. In fact, within both main clusters, clear separation of the sites could be observed (the only exception was sample no. 3c), implying the specific SVOC patterns of each site. This was also the case for the OCC data set (data not shown).

3.4. Multiple regression analysis

Before discussion on the MRA results it should be emphasized that the relation of the atmospheric SVOC concentrations with the meteorological conditions has been previously studied taking into account the contents determined by the active (high-volume) air sampling [24,39,40]. Concerning the passive air samplers, environmental parameters have been evaluated mainly as factors affecting the sampling rate [17,19–23]. Of the available meteorological factors it could be expected that ambient temperature would have cumulative effects on the atmospheric concentrations of pollutants obtained by passive air samplers, while the effect of precipitation and wind speed would depend strongly on their distribution. For instance, the effects of the rain scavenging of particulate matter that carries the condensed phase of the SVOC depend on the size and physical–chemical properties of the particulate matter, raindrop size and other factors [51]: it could be expected that seldom high rainfalls decrease the SVOC air content more than frequent light rains. However, local weather conditions that are not reflected in the available meteorological data may also be important. Complex interactions, such as aerosol concentrations, air–water exchange, wind directions, humidity, etc., may also influence the total atmospheric concentrations. For instance, Gustafson and Dickhut [52] reported that the high relative humidity in the rainy season increased the deposition effects of PAHs emitted in the gas phase onto particulate matter and enhanced the PAH pollution in particulate matter. Furthermore, the importance of wind direction on the SVOC atmospheric concentrations has been observed in several studies [18–20]. Thus, the present lack of information on these effects limits further analysis. Also, it should be emphasized that variability of the concentrations is driven not only by the meteorological data but also by variable contributions from different SVOC sources located at different directions and distances.

The standardized partial regression coefficients and the coefficients of determination (R^2) of MRA models for each SVOC compound (log SVOC content $= f\,(1/t$, log pr, log ws, log sh)) are presented in Table IV. The significant regression coefficients were found for majority of the SVOCs except for BaA, CHR, BbF, BkF, Bph, RET, Triph, BjF, PCB180, α- and β-HCH and o,p'-DDD, for which obviously the atmospheric concentrations could not be correlated significantly with the available meteorological conditions. The magnitude of the absolute values of the regression coefficients indicated the contributions of independent variables to the variation of the atmospheric concentrations for the particular SVOC compound.

The MRA semilogarithmic (log SVOC content $= f\,(1/t$, pr, ws, sh)) and non-logarithmic (SVOC content $= f\,(1/t$, pr, ws, sh)) models had also been examined, but the obtained regression coefficients and the coefficients of determination (not shown here) were less than those given in Table IV; non-logarithmic models gave the lowest coefficients. Thus, the logarithmic model (log SVOC content $= f\,(1/t$, log pr, log ws, log sh)) better described linear dependence of the SVOC contents with the meteorological parameters, implying also that logarithmization was necessary to remove the overwhelming influence of outliers that probably impaired the linearity of semi- and non-logarithmic models.

The contribution of temperature to the variations in the atmospheric concentrations for the majority of SVOCs was significant at $p < 0.05$ and $p < 0.01$ (Table IV). The negative regression coefficients for reciprocal temperature indicated that the atmospheric concentrations of the SVOCs increased as the reciprocal temperature decreased (i.e. as temperature increased). The similar temperature dependence of the atmospheric concentrations of SVOCs has been well documented in the previous reports [24,39,40,53]. This is in accordance to the Clausius–Clapeyron-type expression ($\ln P = a_0 + a_1(1/T)$) that describes vapor phase behavior of the compounds through dependence of the partial pressure (P) and the ambient temperature (T). This finding further implied that volatilization had marked influence on the atmospheric contents of the compounds with significant negative coefficients found for the reciprocal temperature. However, the volatilization from the old environmental deposits could be assigned as today's most probable source for OCCs, so the latest observation could be directly assigned to OCCs, but not to PAH for which the combustion processes are the primary emission sources. Still, the observed relation of the PAH atmospheric concentrations and the ambient temperatures might suggest increased evaporation of the condensed PAHs (particularly HMM PAHs) from the particles to the gas phase. For the compounds for which significant regression coefficients for the reciprocal temperature were not found (e.g. biphenyl, retene, PCB180, PeCB and HCB), it could be speculated that processes other than volatilization had more influence on their atmospheric concentrations. In the case of retene, it could be assumed that the thermal process of biomass burning was behind this observation, while in the case of PeCB and HCB, the waste combustion incidents probably contributed to their atmospheric concentration. These assumptions are in agreement with the previous discussion related to the PCA results. However, the potential emission source of PCB 180 has not been found in the available literature.

Concerning the precipitation level, significant positive standardized partial regression coefficients were found only for PeCB and HCB (Table IV). This observation suggested that some specific sources with emissions related somehow with the rain events contributed to the atmospheric PeCB and HCB concentrations in the examined period.

Furthermore, the significant positive regression coefficients for wind speed were found for some compounds, indicating that the atmospheric concentrations increased with the wind speed. There have been contradictory reports on the influence of wind speed on the ambient concentration of SVOC. In several studies, it was found that an increase in wind speed caused a dilution of the SVOC concentrations due to the advection of background air [24,54]; in some other reports, a significant positive correlation between gas phase ambient concentration of SVOCs and wind speed was measured and explained by

Table IV. Linear coefficients for temperature (*t*), precipitation amount (pr), wind speed (ws) and insolation (sh) with respect to variations in the atmospheric concentrations of SVOCs at the investigated sites in the Republic of Macedonia during the period 14 May–3 September 2007

SVOC	1/*t*	Log pr	Log ws	Log sh	R^2
Naph	**−0.877****	0.045	**0.694****	−0.238	**0.687****
Ace	**−1.171****	0.078	**0.552***	−0.630	**0.684****
Acy	**−1.147****	−0.170	**0.717****	**−0.901****	**0.773****
Flu	**−1.110****	−0.034	**0.562***	**−0.872***	**0.615***
Phe	**−1.128****	−0.010	**0.566***	**−0.810***	**0.628***
Ant	**−0.965****	0.105	**0.686****	−0.624	**0.617***
Fla	**−1.120****	−0.017	**0.466***	−0.767	**0.570***
Py	**−1.169****	−0.049	0.444	**−0.835***	**0.602***
BaA	**−1.077****	−0.043	0.295	−0.741	0.487
CHR	**−1.096****	−0.015	0.236	−0.758	0.500
BbF	**−1.055****	−0.090	0.070	−0.714	0.499
BkF	**−1.085****	−0.151	0.074	−0.711	0.549
BaP	**−0.723***	0.197	**0.774****	−0.265	**0.622***
IcP	**−0.920****	0.071	**0.711****	−0.609	**0.613***
BgP	**−0.919****	0.065	**0.712****	−0.612	**0.612***
Bph	−0.785	0.053	0.404	−0.739	0.360
RET	−0.214	0.222	0.032	−0.006	0.050
BNT	**−1.286****	−0.178	0.166	**−0.926****	**0.718****
BgF	**−1.162****	−0.071	0.324	**−0.836***	**0.566***
Triph	**−1.026***	−0.066	0.119	−0.750	0.448
BjF	**−0.935***	−0.185	0.092	−0.655	0.404
BeP	**−1.202****	−0.098	0.112	**−0.687***	**0.684****
PCB28	**−1.304****	−0.137	0.272	**−0.913****	**0.720****
PCB52	**−1.277****	−0.102	0.341	**−0.830***	**0.704****
PCB101	**−1.173****	0.043	0.411	**−0.851***	**0.600***
PCB118	**−1.136****	−0.214	0.370	**−0.981***	**0.564***
PCB138	**−1.139****	−0.182	**0.686****	**−1.100****	**0.771****
PCB153	**−1.201****	−0.338	0.278	**−0.941***	**0.660***
PCB180	−0.669	0.118	**0.591***	−0.199	0.423
α-HCH	**−0.833***	0.261	0.511	−0.445	0.440
β-HCH	**−0.968***	−0.205	0.365	−0.768	0.429
γ-HCH	**−1.120****	−0.083	**0.611****	−0.850	**0.654***
δ-HCH	**−0.913****	0.039	**0.712****	−0.640	**0.609***
o,p′-DDE	**−1.059****	−0.507	0.167	**−1.059***	**0.579***
p,p′-DDE	**−1.130****	−0.454	0.042	**−1.108****	**0.647***
o,p′-DDD	**−0.976***	−0.526	0.333	**−1.011***	0.539
p,p′-DDD	**−1.288****	−0.264	**0.394***	**−0.911****	**0.757****
o,p′-DDT	**−1.054****	−0.493	0.265	**−0.891***	**0.605***
p,p′-DDT	**−1.276****	−0.264	0.172	**−1.066****	**0.704****
PeCB	−0.575	**0.625***	0.275	−0.430	**0.583***
HCB	0.132	**0.830****	**0.392***	0.202	**0.741****

*Significant at $p < 0.05$.
**Significant at $p < 0.01$.

translocation of SVOCs deposited on the earth surface to the gas phase with increased wind speed [39,40,55]. The positive coefficients between the air SVOCs concentrations and wind speed found in this study could also be linked with a mechanism of passive air sampling. Namely, it was previously shown that sampling rates in the case of passive air samplers fluctuate under the real-field conditions, including fluctuations of the wind speed [22]. It might be expected that higher wind speeds influenced the faster air flow through passive sampler resulting in this way in higher sampling rates and the contents of SVOCs in contact with PUF sampling disk.

Finally, insolation was found to be negatively correlated with some SVOCs, like DDT and its products, six indicator PCB (not including PCB 180) and from the PAHs group—acenaphthylene, fluoren, pyrene, S-containing PAH (benzo-naphtho-thiophene), benzo(b)fluorene and benzo(e)pyrene. This was obviously a consequence of photodegradation process as a way of reducing the SVOC atmospheric contents.

4. CONCLUSION

The chemometric assessment of the results on the SVOC atmospheric concentrations at six sampling sites in the Republic of Macedonia with different impact of anthropogenic sources delivered important information about the potential polluting sources in the regions of interest. Incidents of some specific emissions have been indicated by the principal component analysis (PCA) plots. The SVOC patterns of two sites from the capital city of Skopje were clearly separated from the rest of the samples and they were characterized by highly correlated contents of PAHs, HCH isomers and majority of indicator PCBs. Cluster analysis (CA) coupled with bootstrap confirmed the sample groupings obtained by PCA. Even though the differences between sampling periods were evident, some specific temporal trends were not identified and in order to explore temporal differences in more details, it should be necessary to include autumn/winter months. The SVOC atmospheric concentrations were linked to the available meteorological parameters by MRA confirming their importance for the quantitative understanding of the source information. The significant contribution of temperature to the variations in the atmospheric concentrations for the majority of SVOCs was found, indicating that the SVOCs concentrations increased with temperature. Similarly, the significant positive effect of wind speed was found for some compounds that could be linked to a mechanism of passive air sampling. Concerning the precipitation level, significant positive standardized partial regression coefficients were found only for PeCB and HCB, pointing out some specific sources of these compounds related to the rain events. The negative correlation between insolation and the atmospheric concentration of some SVOC compounds signified the photodegradation process as a potential way for the reduction of their presence.

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Chemometric interpretation of heavy metal patterns in soils worldwide

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ABSTRACT

Principal component analysis (PCA) was applied on data sets containing levels of six heavy metals (Pb, Cu, Zn, Cd, Ni, Cr) in soils from different parts of the world in order to investigate the information captured in the global heavy metal patterns. Data used in this study consisted of the heavy metal contents determined in 23 soil samples from and around the Novi Sad city area in the Vojvodina Province, northern part of Serbia, together with those from the city of Banja Luka, the second largest city in Bosnia and Herzegovina, and the ones reported previously in the relevant literature in order to evaluate heavy metal distribution pattern in soils of different land-use types, as well as spatial and temporal differences in the patterns. The chemometric analysis was applied on the following input data sets: the overall set with all data gathered in this study containing 264 samples, and two sub sets obtained after dividing the overall set in accordance to the soil metal index, SMI, calculated here, i.e. the set of unpolluted soils having SMIs < 100%, and the set of polluted soils with SMIs > 100%. Additionally, univariate descriptive statistics and the Spearman's non-parametric rank correlation coefficients were calculated for these three sets. A Box–Cox transformation was used as a data pretreatment before the statistical methods applied. According to the results, it was seen that anthropogenic and background sources had different impact on the data variability in the case of polluted and unpolluted soils. The sample discrimination regarding the land-use types was more evident for the unpolluted soils than for the polluted ones. Using linear discriminant analysis, content of Cu was determined as a variable with a major discriminant capacity. The correct classification of 73.3% was achieved for predefined land-use types. Classification of the samples in accordance to the pollution level expressed as SMI was necessary in order to avoid the "masking" effect of the polluted soil patterns over the non-polluted ones.

1. Introduction

As heavy metals are non-biodegradable and accumulative in nature, the elevated metal emissions and their deposition over time can lead to anomalous enrichment and the contamination of the surface environment. Soil surface receives deposits from more or less remote sources (vehicle emissions, industrial discharges, domestic heating, waste incineration and other anthropogenic activities) through atmospheric transport as well as from local human activities (Thornton, 1991). If the soil is dedicated to agricultural activities, the application of commercial fertilizers, sewage sludge and pesticides, which usually may contain a wide variety of heavy metals as impurities, have to be considered also as pollution sources (Gimeno-García et al., 1996). The ecological importance of heavy metals in soils is closely related to human health due to their high ecological transference potential (Morton-Bermea et al., 2008).

Although the severity of pollution depends not only on the total heavy metal content, but also on the proportion of their mobile and bioavailable forms, the total content of heavy metal has been used to evaluate the anthropogenic impact (Morton-Bermea et al., 2008). Furthermore, anthropogenically altered soils provide an integrated record of numerous processes over time and record the net effects of human activities over long periods.

Many scientific activities have been devoted to the determination of sources, types and degree of the heavy metal pollution in soils (Manta et al., 2002; Škrbić and Čupić, 2004; Coşkun et al., 2006; Lee et al., 2006; Christoforidis and Stamatis, 2009; Franco-Uría et al., 2009). Their content and the impact upon ecosystems are influenced by many factors such as parent material, climate and anthropogenic activities such as industry, agriculture and transportation. Due to heterogeneity of the soil and often accidental nature of contaminating processes, concentrations of heavy metals can vary remarkably over short distances. Therefore, the high variability of the heavy metals soil concentrations obtained at various sampling sites requires a careful evaluation and interpretation to decide which of contributions, pedogenic or anthropogenic, are of crucial importance for the main distribution patterns

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found in the samples. Accordingly, these tasks have to be addressed by using multivariate statistical procedures typical for chemometrics.

In this work, six heavy metals (Pb, Cu, Zn, Cd, Ni, Cr) were analyzed in surface soils collected in and around the Novi Sad city area in the Vojvodina Province, the northern part of Serbia, and in the city of Banja Luka, the second largest city in Bosnia and Herzegovina. The determined contents were compared with heavy metal burden of soils worldwide reported in literature by principal component analysis (PCA). PCA as the multivariate analytical tool reduces a set of original variables and extracts a small number of latent factors (principal components, PCs) for analyzing relationships between the observed variables and samples. It has been widely used to deliver more information on links among sampling sites, pollutant concentrations, correlation patterns, and latent factors responsible for the data-set structure in the environmental studies (Golobočanin et al., 2004; Škrbić et al., 2005; Škrbić and Đurišić-Mladenović, 2007; Škrbić et al., in press, 2009). The aim of this work is also to clarify the general distribution patterns or similarities of heavy metals occurring in soils collected at various sites worldwide with different contribution of potential sources. In other words, the present study uses the chemometric approach to examine the heavy metal soil burden worldwide and to capture the heavy metal-soil distribution patterns and differences amongst various land-use types. In order to extract as much as possible information from the data set, univariate methods and linear discriminant analysis were also applied and the obtained results were compared with the ones obtained by PCA.

2. Materials and methods

2.1. Determination of heavy metals

Twenty-one surface soil samples were collected from various sites of urban and rural areas in the city of Novi Sad, Serbia, and the nearby villages, in 2009. Novi Sad arose on the left bank of the river Danube, and it is the second largest economic and cultural centre in Republic of Serbia. Novi Sad is the capital of the Autonomous Province of Vojvodina, located in the northern part of Serbia. Together with the outskirts settlements it has about 300 000 inhabitants in total. The city is located between 19°51′ of the east longitude and 45°20′ of the north latitude. Within the city area there are numerous industrial plants and also an oil refinery. Novi Sad is the centre of the most fertile agriculture region in Serbia. It is the seat of the wheat exchange (Official Web Site of the City of Novi Sad).

Two more samples were obtained from the city of Banja Luka, the second largest city in Bosnia and Herzegovina. The Banja Luka's population accounts for 250 000. The city is located at 44°47′ of the north latitude and 17°11′ of the east longitude. Banja Luka's downtown is at 163 m above sea level, surrounded by hills. Due to many of its green surfaces – parks and tree-lined roads, Banja Luka is also known as the city of greenery. Banja Luka used to be a strong economic center with a developed industry (Official Web Site of the City of Banja Luka).

Most of the samples from Novi Sad and Banja Luka were collected from grassland areas either public or private. All samples were collected away from nearby roads in order to avoid direct impact of the vehicle emission of the soil quality. The only exception was a sample collected next to the road with high traffic intensity in Banja Luka, representing in this way a soil under a direct influence of vehicles emission. At each area of sampling four sub-samples were taken within a rectangular of approximately 20 × 50 m (or in the case of the soil with direct influence of vehicle emission in Banja Luka, four sub-samples were taken at 20 m distance between each other along the road) and then mixed up to give bulk sample. Samples were collected with plastic tools and stored in plastic bags at −4 °C prior to analysis. All samples were air dried, sieved through 2-mm sieve and ground.

Metal contents in the soils were analyzed after a microwave assisted digestion of the samples (Luo et al., 2007) using CEM MDS 2100 microwave oven. The procedure was based on Methods 3050B (US EPA, 1996) and 3051A (US EPA, 1998). Aliquot of 0.5 g of each sample was measured and then digested with mix of 7 mL of HNO_3 and 2 mL of H_2O_2. As recommended by the US EPA Method 3051A, the temperature of samples raised to 170 °C in less than 5.5 min and remained between 170 and 180 °C for the balance of the 10 min irradiation period. After digestion, solutions were filtered through Whatman No. 1 filter papers and volumes were adjusted to 50 mL using double deionized water (Milli-Q 18.2 $M\Omega\,cm^{-1}$ resistivity). Further dilutions of the digested samples were made for analyzing the metals presented in quantities exceeding the upper calibration point by 20%, like it was the case for Zn and Pb.

Triplicate soil samples were provided as a part of the quality control procedure. The same procedure (reagents without soil samples) was applied for the blank analysis. Precaution measures were used during the analysis to prevent contamination from air, glassware and reagents, which were all of Suprapur quality (Merck, Germany).

Concentrations of Cd, Cu, Cr, Ni, Pb and Zn were measured by graphite furnace atomic absorption spectrometry using a Varian AAS 240/GTA 120 instrument with deuterium lamp background correction. The wavelengths (in nm) used for the determination of Cd, Cu, Cr, Ni, Pb, and Zn were: 228.8, 324.8, 357.9, 232.0, 283.3, and 213.9, respectively. Each recording was repeated three times. Quantification of metal content was done using calibration curves. Calibration standards were prepared in the same acid matrix used for the soil samples. The repeatability of measurement was checked by the analysis of Cd, Cu, Cr, Ni, Pb and Zn in six parallel aliquots of one soil samples after the microwave digestion applying the described analytical procedure. The analytical precision, measured as relative standard deviation, was routinely between 5% and 6%, and never higher than 10%. The analytical detection limits (3× standard deviation of the baseline noise/sensitivity) for each element were: 0.006 $\mu g\,L^{-1}$ for Cd, 0.04 $\mu g\,L^{-1}$ for Cu, 0.05 $\mu g\,L^{-1}$ for Cr, 0.2 $\mu g\,L^{-1}$ for Ni, 0.06 $\mu g\,L^{-1}$ for Pb and 0.004 $\mu g\,L^{-1}$ for Zn.

As a part of quality control process, the certified material NIST SRM 2711 (US Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20 899) was analyzed in the same way as samples to check the accuracy of the procedure. Certified values, measured concentrations, and recoveries are shown in detail in Appendix A, Table S1. Recoveries ranged from 72% for Pb to 107% for Ni. It is evident that the concentrations of heavy metals determined agreed well with the reported certified values, confirming the accuracy of the procedure applied.

2.2. Data sets

Statistical characterization of the heavy metal contents in soils was performed on data set consisted of the heavy element contents in 23 soils analyzed in this study and those previously reported in the literature. The sources of the used data with short description of the soils are given in Table 1. Only those studies comparable with each other regarding the analyzed heavy metals were taken into consideration. As it was found that Zn, Cu, Cr, Cd, Pb and Ni were the most frequently analyzed metals in soils, the contents of these six metals were taken into account here. In total, 18 studies have been considered; the results for 190 samples were taken from this study and two other studies (Bojinova et al., 1996; Manta

Table 1

Description of the soil samples incorporated in the data sets of heavy metal contents investigated in this study.

Reference	Country, city or region, and period of sampling[a]	SMI classification[b] (number of samples)[c]	Land-use type (number of samples)[c]	Total number of samples
This study	Serbia, Novi Sad, Bosnia and Hertzegovina, Banja Luka, after 2000	Above (2), below (21)	Agricultural (1), urban (9), rural (6), recreational (5), roadside (1), industrial (1)	23
Bojinova et al. (1996)	Bulgaria, Plovdiv-Pazadjik plain, before 2000	Above (53), below (47)	Agricultural (100)	100
Fränzle et al. (1995)	Russia, Ostaskov, before 2000	Below (3)	Agricultural (2), woodland (1)	3
Fränzle et al. (1995)	Germany, Borhoveder, before 2000	Below (4)	Agricultural (2), woodland (1), recreational (1)	4
Fränzle et al. (1995)	Germany, Stolberg, before 2000	Above (5)	Agricultural (3), woodland (1), recreational (1)	5
Fränzle et al. (1995)	Russia, Chelyabinsk, before 2000	Above (1), below (6)	Agricultural (4), woodland (2), recreational (1)	7
Fränzle et al. (1995)	Russia, Karabash, before 2000	Above (4)	Agricultural (1), woodland (1), recreational (2)	4
Kastori et al. (2002)	Serbia, Vojvodina Province, after 2000	Below (1)	Agricultural (1)	1
Škrbić and Čupić (2004)	Serbia, Novi Sad, after 2000	Below (5)	Urban (5)	5
Franco-Uría et al. (2009)	Spain, A Pastoriza, Galicia, after 2000	Below (1)	Grassland (1)	1
Dragović et al. (2008)	Serbia, Zlatibor mountain, after 2000	Above (1)	Grassland (1)	1
Ubavić et al. (1993)	Serbia, Vojvodina Province, before 2000	Below (1)	Agricultural (1)	1
Christoforidis and Stamatis (2009)	Greece, Kavala, after 2000	Above (5), below (3)	Roadside (8)	8
Coşkun et al. (2006)	Turkey, Thrace region, after 2000	Below (1)	Unclassified (1)	1
Luo et al. (2007)	China, Guanting reservoir, Beijing, after 2000	Below (1)	Agricultural (1)	1
Overesch et al. (2007)	Germany, Worlity, Stechley, Sandan, Rogatz, Stechby, after 2000	Above (12)	Agricultural (2), grassland (8), unclassified (2)	12
Maiz et al. (2000)	Spain, Gipuzkoa, before 2000	Above (13)	Industrial (9), roadside (4)	13
Manta et al. (2002)	Italy, Palermo, after 2000	Above (45), below (22)	Recreational (67)	67
Gramatica et al. (2006)	Italy, Piedmont, Aosta Valey, after 2000	Above (2)	Unclassified (2)	2
Salonen and Korkka-Niemi (2007)	Finland, Turku, after 2000	Below (1)	Urban (1)	1
Lee et al. (2006)	China, Hong Kong, after 2000	Below (3)	Urban (2), recreational (1)	3
Li et al. (2004)	China, Hong Kong, after 2000	Below (1)	Urban (1)	1

[a] Period of sampling is defined as “before“ or “after“ 2000, with 2000 taken arbitrary as a year when the usage of leaded gasoline within EU was ceased in accordance to the implementation of the Directive 98/70/EC.

[b] SMI classification was based on the calculated soil metal index (SMI) values relative to the Dutch reference values for unpolluted soils; soils with the SMI values above 100% were classified as “above”, and those with SMI < 100% as “below”.

[c] Number of samples belonging to the particular soil class.

et al., 2002), while the rest of 15 studies provided the results for 74 samples. Thus, size of the created data set, so-called the “all” data set, was 264 (cases) × 6 (variables). The uneven number of the samples from different studies have not been considered as a limitation, as we tried to gather as much as possible data about the occurence of the chosen metals in soils worldwide to elicit information on global metal patterns and to identify dominant sources. In fact, more data gathered, the more reliable statistical results could be obtained. The similar approach was previously applied for the assessment of the distribution pattern of organochlorine compounds (Škrbić and Đurišić-Mladenović, 2007) and polycyclic aromatic hydrocarbons (Škrbić et al., 2009) in soils from different countries.

Details on the soil sampling, preparation and analytical procedure available in the cited literature are summarized in Table S2 (Appendix A). In the majority of chosen studies, composite samples of the surface soils (most often the uppermost 5–30 cm, see Table S2 in Appendix A) were prepared from several sub-samples collected at the investigated sites according to the predefined sampling blocks (grid) of various dimensions. Only Maiz et al. (2000) analyzed individual samples taken randomly from the studied sites in Spain. All the samples were dried, sieved through a 2.0-mm sieve and ground before the digestion. Final soil granulation was indicated only in few studies (see Table S2 in Appendix A). Soil samples were digested most often by aqua regia or concentrated nitric acid used alone or in mixture with hydrogen peroxide or perchloric acid; the exception was the study of Maiz et al. (2000), who used more vigorous acid mixture with hydrofluoric acid. Broad spectrum of acid digestion methods for determination of heavy metals found in the selected studies was not surprising as various nationally and internationally recognized methodological standards have been applied worldwide despite the obvious need for the harmonization and standardization (European Soil Bureau-Scientific Committee, 1999). Previously, it was found that aqua regia gives results for the Cd, Cu, Ni and Zn contents in soil close to the ones obtained by the hydrofluoric acid digestion, while the latter more efficiently recovers Cr than the former, since Cr is bound in soil stable minerals (Bojinova et al., 1996; Chen and Ma, 2001). Considering Pb, Bojinova et al. (1996) found that aqua regia was less efficient than hydrofluoric acid for its recovery from unpolluted soil, in which Pb is presented in stable minerals, not attacked by former. On the other hand, these two digestion methods gave similar results concerning the Pb presence in polluted soils because the anthropogenic Pb is mostly connected with soil organic matter destroyed during both types of acid digestion, leaving the “total” content of Pb in the extract (Bojinova et al., 1996). As can be seen from Table S2, the analytical procedures used for the heavy metal content determination were based on atomic absorption spectrometry with flame (FAAS) or graphite furnace (GFAAS), or inductively coupled plasma with atomic emission (ICP-AES) or mass spectrometry (ICP-MS) detector. Besides differences in the instrumental limits of detection, Bojinova et al. (1996) found a good correlation between the results on heavy metal contents in soils obtained by ICP-AES and GFAAS/FAAS. Thus, considering all the said, it was less expected that differences in digestion or analytical techniques used in the cited studies (Table S2) would influence the statistical results, even in the case of data obtained by hydrofluoric acid taken from the study of Maiz et al. (2000), representing ~5% of total number of the samples analyzed.

All reported data were expressed in mg of metal per kg of dried soil sample. Only in very few cases, mainly for Cd, the reported contents were below the limit of detection (LOD). For these data, half of the limit of detection, LOD/2, was used in statistical analysis.

In order to evaluate a difference in the heavy metal distribution pattern depending on the soil pollution level, the input data set was divided into two sub sets in accordance to the soil metal index, SMI (Škrbić and Čupić, 2004). The SMI reflects the whole soil metal burden of the localities under investigation. For the calculation of SMI for each soil sample, the relative values of metal contents with regard to the Dutch soil standard critical values that represent the maximum metal content in the non-polluted soils (Dutch standards, 2000), were calculated first. These values were then summed up and divided with number of metals investigated in this study for which the Dutch limits were used. The following equation was used for the SMI calculation:

$$\mathrm{SMI} = \frac{1}{n}\sum_{i-1}^{n} 100 \cdot \frac{V_i}{L_i}$$

where n is a number of metals (in this study $n = 6$); V, in mg kg^{-1}, is a content of a metal reported for a particular soil sample; and L, in mg kg^{-1}, is the Dutch reference content of a metal in the unpolluted soil, i.e. for Zn 140 mg kg^{-1}, for Cu 36 mg kg^{-1}, for Cr 100 mg kg^{-1}, for Pb 85 mg kg^{-1}, for Ni 35 mg kg^{-1}, and for Cd 0.8 mg kg^{-1} (Dutch standards, 2000). Hence, it could be accepted that SMI values above 100% pointed out the polluted soils, as they contained all six metals in the levels above the Dutch reference value, or only several metals but in excessively high contents in relation to the reference; contrary, the samples with SMIs below 100% indicated the unpolluted soils.

By applying this criterion, the so-called "all" data set of 264 soil samples was divided into two sub sets with a different levels of the heavy metals pollution. The "above" sub set contained 144 (or 54.5%) samples that could be regarded as polluted soils (SMI > 100%), while the second sub set named "below" consisted of 120 (or 45.5%) non-polluted soil samples (SMI < 100%).

In order to elucidate the relationships between different land-use types, the samples in both sub sets "above" and "below" were categorized in following way: "urban", "agricultural", "industrial", etc. (see Table 1). All 264 samples were also categorized in relation to the geographical origin, i.e. the country where the sampling had been performed (Table 1). In this way, it has been tried to reveal the spatial similarities or differences in the heavy metal soil patterns. Furthermore, in order to examine whether heavy metal soil patterns changed after the implementation of the Directive 98/70/EC that ceased the usage of leaded gasoline within the EU after the 1990s, the samples were divided into two categories depending on whether they were sampled before or after 2000 (Table 1). Nevertheless, all these categories represent a rough simplification of the original descriptions in the cited studies, as the effort was made to classify all the data in as few as possible categories of the land-use types, as well as of the spatial and temporal groups.

2.3. Exploratory statistical analyses

Descriptive statistical parameters such as mean value, median, minimum, maximum values and relative standard deviation were calculated to describe the heavy metal contents in all the samples.

It is well known that classical statistical methods are not sensitive to deviations from normal distribution. Since the geochemical variables often do not follow normal distribution, it is advisable that such skewed data are transformed before any subsequent statistical analysis to a more symmetric distribution (Reimann and Filzmoser, 2000; Templ et al. 2008), to improve the statistical results. In many cases the log-transformation can be successfully used to approach symmetry. However, according to the Templ et al. (2008), a more universal choice is the Box–Cox transformation (Box and Cox, 1964), which brings the data (majority) as close as possible to normality (Filzmoser et al., 2009). In this study, the Box–Cox transformation of the "raw" (analytical) data was also used prior the statistical analyses.

The Shapiro–Wilk's test was used as a measure of departure from normality for the Box–Cox transformed data on the heavy metal contents in soils. The Shapiro–Wilk's test is highly recommended as it has the most power for testing normality against all classes of alternative distributions (Madansky, 1988). A null hypothesis on normal distribution of the Box–Cox transformed data was accepted if probability value (P) is higher than 0.05; otherwise, the null hypothesis was rejected.

Furthermore, exploratory data analysis (EDA) plots were constructed providing deeper insight into the "raw" (non-transformed) and the Box–Cox transformed variables distribution. The EDA-plots combine in one graphical display one-dimensional scatter plot, histogram, probability density plot, and boxplot. The samples are clearly visible in the one-dimensional scatter plot; outliers are flagged by the boxplot; and the form of the distribution is visualized by histogram and density trace (Reimann and Filzmoser, 2000).

In order to quantitatively analyze the relationship among heavy metal contents of soils, the Spearman's non-parametric rank correlation coefficient was calculated. The non-parametric correlation coefficient is a common parameter used to quantify the relation between the pairs of variables when the presumption about normality is violated. Definition of the Spearman's non-parametric correlation coefficient could be found in standard textbook of statistics (Massart et al., 1997).

The principal of PCA is to characterize each sample (named also as object or case) not by analyzing every variable (heavy metal content), but projecting the data in a much smaller sub set of new variables called principal components. These new variables are linear combinations of the initial variables, but highlight the variance within a data set and remove the redundancies. Successive principal components arranged in decreasing order of eigenvalues account for decreasing amounts of variance. The relevant portion of information is carried out by the first principal components (PCs). The coefficients between the old and new variables are called the loadings. They explain how the new PCs are composed from the original variables (Héberger et al., 2005). The PCs are orthogonal (independent), in other words uncorrelated. Further on, they are ordered in such a way that the variance of the first PC (PC1) is the greatest, the variance of the second PC (PC2) is second-greatest, and so on, whereas that of the last one is the smallest. The solution is obtained by an eigenvalue calculation. A basic assumption in the use of PCA is that the score and loading vectors corresponding to the largest eigenvalues contain the most useful information relating to a specific problem and that the remaining ones constitute mainly noise, i.e. for a practical problem it is sufficient to retain only a few components accounting for a large percentage of the total variance (Héberger et al., 1999). In this work, the input data matrix was created by putting the soil samples into the rows and the Box–Cox transformed heavy metal contents in the columns. The matrix was firstly mean-centered (column means subtracted from each matrix element); then each matrix element was divided by the standard deviation of the respective column and the established matrix was submitted to PCA. The number of PCs extracted from the variables was determined by Kaiser's rule (Kaiser and Rice, 1974). This criterion retains only PCs with eigenvalues that exceed one. The algorithm of PCA can be found in the standard textbooks (Vandeginste et al., 1998).

Linear discriminant analysis (LDA) was further used to inspect the correctness of the land-use types predefined and obtained to be most important by PCA. LDA, similarly to PCA, can be considered as a dimension reduction method. In the method of LDA a linear function of the variables is to be sought, which maximizes the ratio of between – class variance and minimizes the ratio of within-class variance. Finally, a percentage of correct classification is given (Héberger et al., 2003). The description of the LDA algorithm can be found elsewhere (Vandeginste et al., 1998).

All statistical data analyses were done with R software (R Development Core Team; http://www.cran.r-project.org).

3. Results and discussion

3.1. Heavy metal contents

The heavy metal contents determined in this study are presented in Table 2. The range of the concentrations was from 0.75 mg kg^{-1} found for Cd to 401 mg kg^{-1} for Zn. According to the mean and median concentrations of all samples analyzed here (Table 2), the metal abundance could be ordered as follows: Zn > Pb ~ Ni > Cu > Cr > Cd. Considering the calculated values of relative standard deviation, RSD, of the metal levels (Table 2), Zn and Pb showed the highest variability in the investigated samples, being approximately 64% and 49%, respectively. The variability of the rest of obtained metal contents was from about 25% (for Cr) to 38% (for Cu).

Comparison of the results with those found in literature for the heavy metals in the Serbian soils (Ubavić et al., 1993; Kastori et al., 2002; Škrbić and Čupić, 2004; Crnković et al., 2006; Dragović et al., 2008; Marjanović et al., 2009) is also given in Table 2. The soils investigated here were less loaded with heavy metals than those from Belgrade (Crnković et al., 2006; Marjanović et al., 2009), the capitol of Serbia that is the only Serbian city with population over 1 million. Although all soils in the region probably bear some imprint of human activities and no longer reflect purely natural conditions, regional soils provide a baseline against which potentially more intense human activity in urban areas can be judged (Cannon and Horton, 2009). Comparison with the average metal contents reported for the samples of regional soils in the Vojvodina Province by Ubavić et al. (1993), showed that all metals analyzed in this study occurred in similar or higher levels; for instance, the contents found were higher that the average of the Vojvodina arable soils (Ubavić et al., 1993) from 1.5 times for Cr, 2 times for Cu and Pb, 3.5 times for Cd, up to 6 and 10 times for Ni and Zn, respectively. Moreover, higher concentrations of Cd and Pb could be seen comparing the results with the 2001 soil metal burden in Novi Sad (Škrbić and Čupić, 2004). For the rest of the analyzed metals, similar contents were found for soils sampled in 2009 (this study) and those from 2001. The increase of some heavy metal contents over the years could be also seen for Belgrade soils (Crnković et al., 2006; Marjanović et al., 2009). It is interesting to note that the soils collected from the Belgrade city area (Crnković et al., 2006; Marjanović et al., 2009) and at the Zlatibor mountain in the central part of Serbia (Dragović et al., 2008) had markedly higher contents of Ni and Cr than those found in this study. The both groups of authors explained the elevated levels of Ni as a natural enrichment by weathering and pedogenesis processes; most probably, the same reason was behind the high contents of Cr at these two locations.

When compliance with national limits (Serbian regulation, 1994) for heavy metals in soils is considered, none of the samples (Table 2) exceeded the limit values set to be 300 mg kg^{-1} for Zn, 100 mg kg^{-1} for each of Cu, Cr and Pb, 50 mg kg^{-1} for Ni, and 3 mg kg^{-1} for Cd. However, considering the Dutch standard reference values for unpolluted soil (Dutch standards, 2000) mentioned before, a great part of the soil samples collected throughout the Novi Sad area and also from Banja Luka seemed to be polluted with Cd as the contents exceeded the respective limit. Interestingly, the Pb contents were higher than the Dutch reference value for the non-polluted soil only for two samples of the Novi Sad soil despite the fact that leaded gasoline is still allowed to be used in Serbia. According to the SMI values calculated for soils analyzed in this study, 21 samples had values below 100%, while only two samples showed SMI higher than 100%. Thus, majority of the samples (21 out of 23) were grouped into the "below" data set formed for the subsequent statistical analyses. The remaining two samples belonged to the "above" group were the soil sampled next to the high traffic road in Banja Luka and the one from the suburban settlement in the vicinity of Novi Sad.

3.2. Univariate characterization of data sets

The descriptive statistics of the data sets consisting from the original values of six heavy metals (Zn, Cu, Cr, Pb, Ni, Cd) in 264 samples ("all" data set) and also for two later sub sets ("above" and "below") were summarized in Table 3. For both the "all" and "above" data sets, the order of heavy metals based on their abundance was: Zn > Pb > Cu > Cr > Ni > Cd. In the "below" data set the rank order was slightly different, e.g. Zn > Pb > Cr > Cu > Ni > Cd. Hence, it could be said that the general pattern observed in the

Table 2
The results of the total heavy metal contents (in mg kg^{-1}) in 23 soil samples analyzed in this study in comparison to the mean values previously published for the Serbian soils.

Element	This study, 2009[A]					Novi Sad, 2001[A]	Belgrade, 2003–2004[A]	Belgrade, 2008[A]	Vojvodina agricultural soils, 1991[A]	Vojvodina agricultural soils-field trials, 2002[A]	Zlatibor mountain, 2008[A]
	Mean	Median	Min	Max	RSD, %	[a]	[b]	[c]	[d]	[e]	[f]
Zn	110	85.6	61.3	401	64.50	85.45	118	174.2	10.62	70.3	21.8
Cu	22.4	19.7	8.36	45.7	38.47	30.86	28.3	46.3	10.82	22.5	8.64
Cr	3.57	3.48	2.08	5.43	24.88		32.1		2.41	82.3	46.3
Pb	29.4	25.8	12.3	74.7	48.83	10.75	55.5	298.6	14.81	30.0	41.5
Ni	25.8	25.2	16.6	45.6	27.17		68		4.26	36.2	320
Cd	1.66	1.73	0.75	2.78	29.14	0.15		1.8	0.48	0.37	1.42

[A] Year of sampling; if it was not originally stated in the cited literature it was taken as a year of the literature publishing.
[a] Škrbić and Čupić (2004).
[b] Crnković et al. (2006).
[c] Marjanović et al. (2009).
[d] Ubavić et al. (1993).
[e] Kastori et al. (2002).
[f] Dragović et al. (2008).

Table 3
Summary statistics on the heavy metal contents (mg kg^{-1}) in soils grouped in “all” data set, containing all data investigated, and in “above” and “below” sub sets formed in accordance to soil metal index (SMI) values. The probabilities of the Shapiro–Wilk’s test presented in the last column refers to the Box–Cox transformed data on heavy metal soil contents in each defined set.

Heavy metal	Mean (±st. error of mean)	Minimum	Maximum	RSD (%)	Shapiro Wilk test (P)
“All” data set (n = 264)					
Zn	257.6 ± 34.6	10.6	5518.8	219.4	0.000
Cu	110.8 ± 21.1	6.4	4140.5	310.6	0.002
Cr	69.7 ± 5.0	2.1	927.6	117.8	0.000
Pb	192.0 ± 23.8	0.2	4196.0	202.4	0.000
Ni	41.4 ± 2.6	3.5	320.0	101.7	0.008
Cd	2.03 ± 0.4	0.8	86.6	300.5	0.186
“Above” data set (n = 144)					
Zn	434.6 ± 60.9	19.0	5518.8	168.2	0.000
Cu	176.8 ± 38.2	8.6	4140.5	258.9	0.000
Cr	90.9 ± 8.5	4.4	927.6	112.6	0.015
Pb	310.7 ± 41.4	22.3	4196.0	159.8	0.005
Ni	53.3 ± 4.4	7.3	320.0	98.7	0.874
Cd	3.2 ± 0.7	0.1	86.6	256.2	0.079
“Below” data set (n = 120)					
Zn	87.8 ± 3.9	10.6	400.7	48.9	0.000
Cu	32.9 ± 1.9	6.4	114.0	63.8	0.330
Cr	44.6 ± 3.2	2.1	173.0	78.0	0.000
Pb	51.8 ± 4.5	0.2	269.0	96.7	0.000
Ni	27.5 ± 1.4	3.5	78.3	58.2	0.021
Cd	0.62 ± 0.05	0.08	2.1	80.6	0.058

“above” data set influenced in fact the pattern of the “all” data set, “masking” at the same time the pattern of the unpolluted soils. Comparing the minimum and maximum values from Table 3 with the ones found for the soils analyzed in this study (Table 2), it could be concluded that the latter belonged to the lower range of all data statistically evaluated here, implying the lower heavy metal burdens of the Novi Sad and Banja Luka areas.

Manta et al. (2002) stated that high concentrations of heavy metals (e.g. in comparison to the background values) coupled with the high standard deviation suggest anthropogenic sources for these elements. Thus, the higher relative standard deviations, RSD, of six studied heavy metals observed in the “above” data set was expected. In the “below” set, Pb was the metal with the largest variability with RSD of almost 100%. Since Pb has been most often used as indicator of vehicle exhausts, this finding reflected most probably variability in distances of the unpolluted sites in the “below” set from the roads where Pb from the vehicular emissions deposited. The RSD values of all metals in two other data sets (“all” and “above”) were several times higher than in the “below” set, implying a great concentration gradient of the metal contents in the investigated soils. In these two sets, the most variable heavy metal contents described with the highest RSDs were Cu, Cd and Zn (Table 2).

The probability values of the Shapiro–Wilk test used as a measure of distributional fit are shown in the last column of Table 3. In all three data sets a null hypothesis of the Box–Cox transformed data symmetry at 5% probability level was accepted for Cd; the same was found for Ni in the “above” set and also for Cu in the “below” set. The probability values below 0.05 (Table 3) indicated that mark asymmetry in the distribution of the original data of the Zn, Cr and Pb contents in all three data sets could not be removed by the Box–Cox transformation. Moreover, the symmetry was not found for the Box–Cox transformed Cu contents in the “all” and in the “above” sets, as well as for the transformed Ni contents in the “all” and in the “below” sets. However, the visual comparison of the original and the transformed data on the heavy metal contents by EDA-plots (shown in Figs. S1a–f of the Supplemental material in Appendix A) indicated that the Box–Cox transformation improved the distributional shape towards the more symmetrical distribution: while the original data were left-skewed, the Box–Cox transformation resulted in a more symmetric image of the data.

3.3. Spearman’s non-parametric correlation test

The Spearman’s correlation matrices were computed and the significant correlations obtained for the criterion values of probability $P < 0.05$ and $P < 0.01$ were presented in Table 4. The high positive values of the Spearman’s correlation coefficient between some heavy metals indicated the existence of similar kind of information in the analyzed data. The most prominent positive and significant ($P > 0.01$) relations in all data sets were observed between Zn and Cu, and between Zn and Cd. In other words, high concentrations of Zn were followed with high concentrations of Cu and Cd, and vice versa, regardless of the pollution status of the soils under investigation. This also implied that these metals in surface soils had probably the same origin. Moreover, Zn was also associated with Pb, but in the “all” and “above” data sets it was negatively signed relation reflecting different origins of these two metals, contrary to the “below” set where their relation was positive indicating the possibility of the same origin. It was also found that Zn was significantly ($P > 0.01$) related with Cr and Ni only in the “all” data set, where negative relation of these metals were found.

Many other significant relations between heavy metals were also observed in the data sets and they were of the same or different signs between the sets (Table 4). Hence, the results of the Spearman’s non-parametric correlation test showed multicollinearity of the data since many relations between heavy metals existed. This further indicated that dimensionality of the underlying data-set structures was in fact lower than the number of the heavy metals used in this study as there were variables that carried out the comparable information.

3.4. Principal component analysis and linear discriminant analysis

PCA was applied to identify the underlying pattern in the data sets, distributional structure of soil samples regarding the heavy metals pollution, and to help the data interpretation. The results

Table 4
Spearman’s non-parametric correlation coefficients among the heavy metal contents in soils (Box–Cox transformed) grouped in “all” data set, containing all data investigated, and in “above” and “below” sub sets formed in accordance to soil metal index (SMI) values.

	Cu	Cr	Pb	Ni	Cd
“All” data set (n = 264)					
Zn	0.622[**]	−0.248[**]	−0.784[**]	−0.284[**]	0.681[**]
Cu		−0.468[**]	−0.566[**]	−0.337[**]	0.322[**]
Cr			0.103	0.733[**]	0.034
Pb				−0.023	−0.503[**]
Ni					−0.213[**]
“Above” data set (n = 144)					
Zn	0.276[**]	−0.179[*]	−0.597[**]	0.117	0.746[**]
Cu		−0.329[**]	−0.355[**]	0.061	0.090
Cr			−0.180[*]	−0.751[**]	−0.097
Pb				0.357[**]	−0.306[**]
Ni					0.231[**]
“Below” data set (n = 120)					
Zn	0.373[**]	−0.057	0.561[**]	0.152	0.396[**]
Cu		0.439[**]	0.227[*]	0.473[**]	−0.005
Cr			0.030	0.634[**]	−0.529[**]
Pb				−0.136	0.279[**]
Ni					−0.117

[*] Significant at the 0.05 probability level.
[**] Significant at the 0.01 probability level.

of the PCA application on three sets formed in this study (“all”, “above”, “below”) after the Box–Cox transformation of the data (described in Table 1) are presented in Table S3 of the Appendix A with the Supplementary material. For the graphical representation of PCA results, biplot graphs were used (Gabriel, 1971) and presented in Figs. 1–3. The scaled heavy metal loadings and sample scores on the (−1.0 to 1.0) interval were used prior the construction of the biplot graphs. In this way, the interpretation of the variables correlation and the influence on the samples classification could be made more easily.

According to the Kaiser rule, all three input data matrices were reduced on two uncorrelated principal components, PCs, with eigenvalues greater than one. The largest percentage of explained variance (as a sum of the variances explained by PC1 and PC2) was observed in the “all” data set (78.0%, see Table S2 in the Appendix A), followed by the “above” set (71.9%, Table S2), while the smallest was found for the “below” data set (66.7%, Table S2). Furthermore, for both the “all” and “above” data sets, the first principal component, PC1, was significantly loaded with the same heavy metals in the same way, i.e. Zn, Cu, and Cd were closely correlated among each other and opposite to Pb (Table S2, Figs. 1 and 2a). Considering the second principal component, PC2, retained for the “all” and “above” sets, it was significantly loaded with Cr and Ni (Table S2, Figs. 1 and 2a). Thus, it could be said again that the polluted soils (with SMIs $>$ 100%) influenced dominantly the general pattern of the “all” data set. In order to inspect whether the digestion methods and analytical techniques influenced the PCA results, the additional sample categorizations were introduced in accordance to the applied acid mixture and the analytical instruments. The corresponding biplots (Fig. S2a and b in the Appendix A) illustrated random distribution of the samples along PC1 and PC2 and the overlapping of the introduced classes regardless of the used techniques for digestion and analysis. Hence, influence of the experimental conditions on the sample classification was not seen, which is in accordance to the above mentioned results of Bojinova et al. (1996).

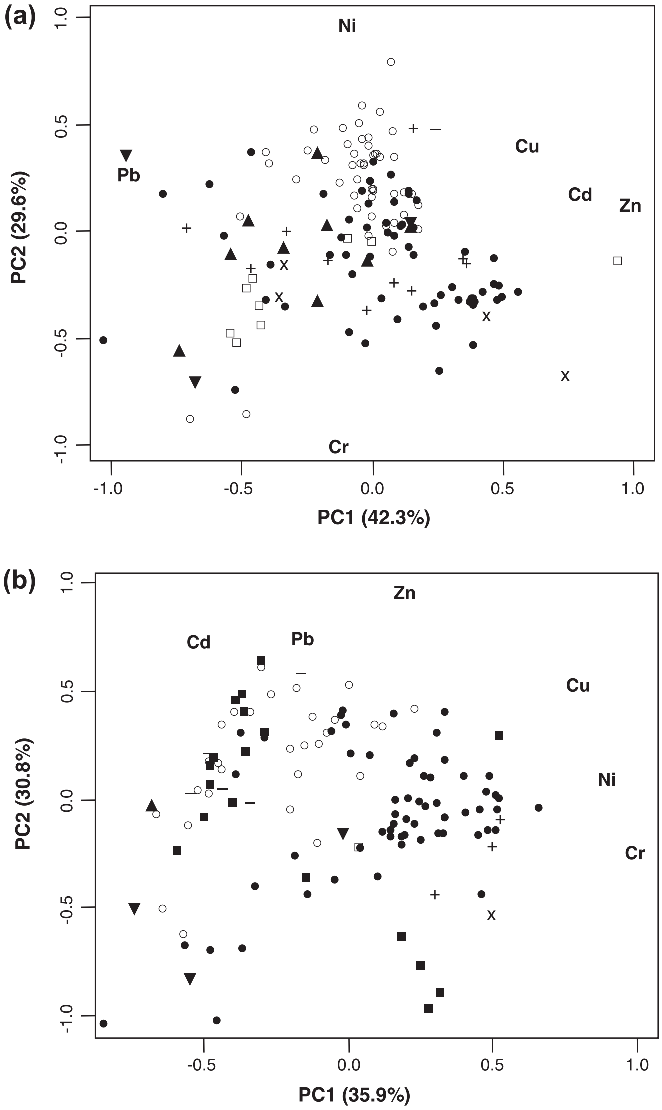

Fig. 2. The PCA biplot PC1 vs. PC2 obtain for the “above” (a) and “below” (b) data sub sets formed in accordance to soil metal index (SMI) values. Different land-use types are used as criteria for the soil sample categorization (●, agricultural; ○, recreational; □, grassland; ▲, industrial; ■, urban, –, rural; +, roadside; ▼, woodland; ×, unclassified). Percentages given in parentheses are the shares of the total variance explained by each PC.

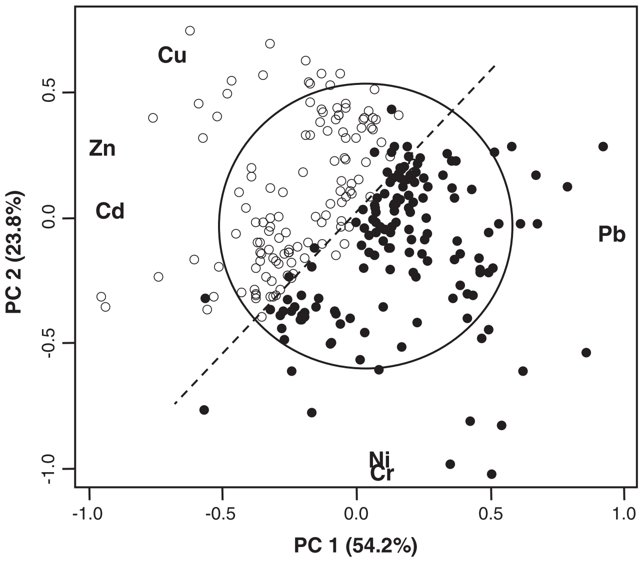

Fig. 1. The PCA biplot PC1 vs. PC2 obtain for the “all” data set containing all data investigated, using soil metal index, SMI, as a criterion for soil sample categorization (● stands for SMI $>$ 100%, ○ stands for SMI $<$ 100%). Percentages given in parentheses are the shares of the total variance explained by each PC.

In order to ascribe the physical meaning to the retained PCs, one should look into the possible sources of these heavy metals in soils. The key product that has contributed especially to the large quantities of Pb into the environment is organo-Pb anti-knock additives to gasoline (Nriagu, 1998). Tetra-ethyl lead was used until the 1990s as an additive in gasoline to prevent the engine from premature detonation (“knocking”) (Kummer et al., 2009). Although leaded gasoline has been banned within the EU from 2000 on following the Directive 98/70/EC and its amendment (Directive 2003/17/EC), some European countries like Serbia and Bosnia and Hertzegovina are still selling the leaded gasoline along with unleaded gasoline. However, unleaded does not mean that there is no lead in gasoline as crude oil contains lead as geogenic impurity: the geogenic Pb content of gasoline fuels sold nowadays in the EU ranges from 0.61 μg Pb L^{-1} to 0.04 mg Pb L^{-1} (Kummer et al., 2009). The same range of the Pb contents was found in diesel fuels (Fröhling and Ludzay, 2002; Kummer et al., 2009). On the other hand, the sources of Cu, Zn and Cd are car components, tyre abrasion, lubricants, industrial and incinerator emissions (Markus and McBratney, 1996; Wilcke et al., 1998). Cadle et al. (1997) indicated that Cu in road dust might originate from motor oil. Zinc is a major

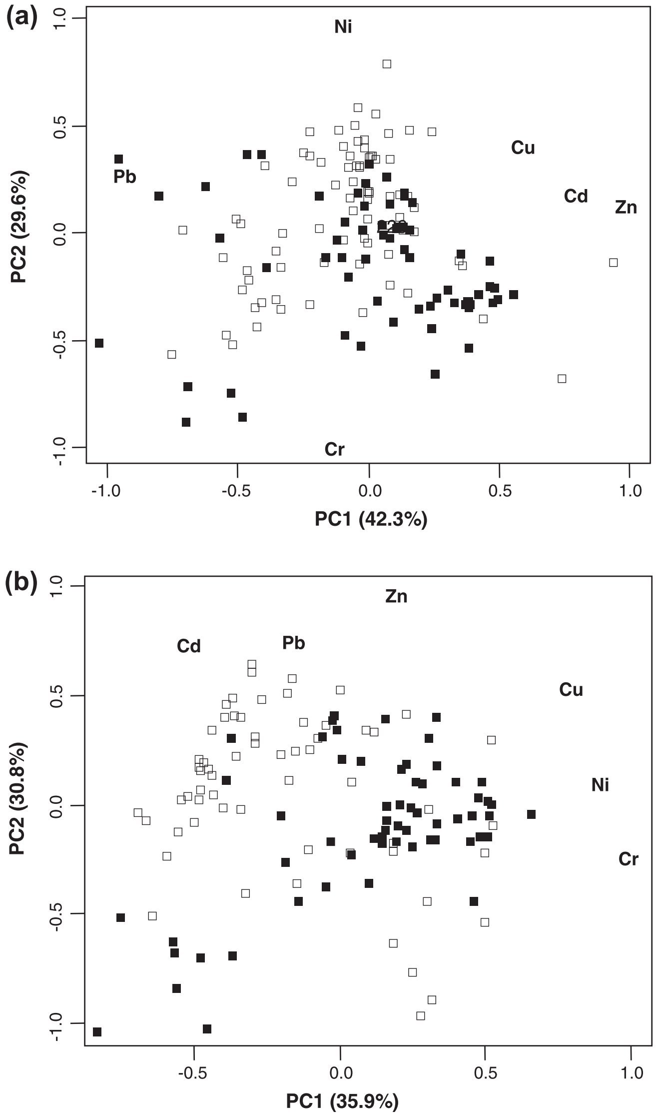

Fig. 3. The PCA biplot PC1 vs. PC2 obtain for the "above" (a) and "below" (b) data sub sets formed in accordance to soil metal index (SMI) values. Sampling period is used as a criterion for soil sample categorization (■, before 2000; □, after 2000). Percentages given in parentheses are the shares of the total variance explained by each PC.

component of rubber tires (US EPA, 1979). In the past, Cd was a trace contaminant of Zn used in tires (US EPA, 1979) and it is also used in alloys to harden engine parts (Jeffery, 1998). Furthermore, combustion of fuel (oil, coal) in stationary sources could be regarded as main emission source for Cr and Ni (Pacyna et al., 2007). These common sources of the heavy metals explained previously may be the basis for the close association observed by PCA in the soils categorized as polluted (with SMIs > 100%) (Fig. 2). Hence, PC1 reflected the variability of the Pb, Cu, Cd and Zn contents in soils worldwide influenced most probably by traffic either through vehicular exhaust fumes (Pb) or non-exhaust emissions (Cu, Cd, Zn) from the abrasion of tyres/brakes and/or from lubricants. The physical meaning of PC2 could be attributed most probably to the combined effects of background (pedogenic) and/or stationary anthropogenic sources of Cr and Ni in soils.

Quite opposite situation was obtained for the "below" data set, in which Cr, Ni and Cu had the highest loadings in PC1, whereas Zn, Pb and Cd loaded significantly PC2 (Table S2 in Appendix A, Fig. 2b). These correlations were also revealed by the product moment correlation analysis (Table 4). The PC1 for the "below" set might be described with a variability of the soil metal burdens as a consequence of differences in background and/or anthropogenic sources other than traffic (combustion of fuel in stationary sources, agricultural practice, etc.), whereas PC2 reflected the traffic as a source of metal pattern variability. Only Cu was the metal significantly loaded PC1 in both data sets, the "above" and "below". This implied mixed origin of Cu in these two sets of polluted and non-polluted soils, respectively, for instance from traffic and agriculture practice simultaneously.

The biplots given in Figs. 1–3 also show discrimination of the sample categories introduced: polluted and non-polluted soils with the SMI values above and below 100%, respectively (Fig. 1); agricultural, urban, industrial, and other land-use types (Fig. 2); and period of sampling (Fig. 3). When the spatial distribution was taken into account (the biplot not shown), there were no marked differences between the countries of origin of soils. The Serbian soils discussed previously (Table 2) were distributed in different parts of the "above" and "below" biplots. This was not surprising as all these soils were collected from locations in Serbia that differed very much among themselves concerning the parent material and the background metal contents, land-use type, distance from the anthropogenic sources, and period of sampling.

It could be easily seen that the application of SMIs clearly differentiated the soils with SMIs higher than 100% from the ones with SMIs lower than 100% (Fig. 1); there were only few overlaps of these two classes. The differentiation was most obvious along the line shown in Fig. 1 that almost diagonally separated two sample categories. Taking into account the variable (heavy metal content) positions in the given biplot (Fig. 1), direction of differentiation line indicated that the "below" samples (with SMIs < 100%) were generally related to the higher contents of Cu, Zn, and/or Cd, while the "above" samples (with SMIs > 100%) were associated to the higher Pb, Ni and/or Cr contents. However, regardless of the SMIs, the majority of samples were located around the biplot origin (within the arbitrary circled area in Fig. 1), reflecting rather uniform heavy metal loading among the soils worldwide regardless of the pollution level. Dispersion of the samples outside the circled area, i.e. outliers, could be seen in both sample categories characterized either with SMI values higher or lower than 100%. It was obviously that the heavy metal burden of the outlying soil samples was influenced by some specific features of the particular locations, which identification is out of the scope of this study.

Fig. 2a and b give the biplots obtained for the "above" and "below" data sets divided into different land-use type categories. Very little discrimination between different land-use types could be seen in both figures as different soil types were overlapped across the plots. Still, the overlapping is slightly more evident in Fig. 2b than in Fig. 2a. Thus, it could be said that the pattern of six commonly analyzed heavy metals in polluted soils of different land-use types obviously presented a mixed signature of the wide variety of factors involved in the formation and conservation of the metals, making impossible the identification of dominant sources. Rough separation of the agricultural and urban/recreational soils could be seen in Fig. 2b, while other soil categories failed to be grouped. Respecting the positions of the majority of agricultural soils in the "below" set (Fig. 2b) it is worth noting that they were correlated with the higher contents of Cr, Ni, and Cd, whereas the urban/recreational soils were correlated with Zn, Pb, and Cd. This coincided with previous assumption that PC1 in the "below" data set could be attributed to the combined effect of pedogenic sources and/or non-traffic anthropogenic sources (for instance, agricultural practice), while PC2 reflected the traffic as a metal source.

The biplot of samples categorized in accordance to the period of sampling, i.e. before or after 2000 when leaded gasoline has been banned within the EU, could be seen in Fig. 3. This categorization did not reveal clear discrimination concerning the "above" data set (Fig. 3a). Slightly more obvious discrimination could be seen within the "below" set (Fig. 3b): majority of the samples analyzed after 2000 were located in the upper left part of the biplot, while the most of those analyzed before 2000 were in the right part. It was rather surprising to find that the position of majority of the "after 2000" samples in the biplot (Fig. 3b) was associated to the higher content of Pb (besides of Cd and Zn), which was expected to be the situation with the "before 2000" samples. It should be also emphasized that discrimination observed in Fig. 3b coincided with the one in Fig. 2b where rough separation of agricultural and urban/recreational soils was seen. Closer inspection of the years of sampling for these two classes (Table 2) revealed that the majority of agricultural soils were sampled before 2000, while urban/recreational soils were taken after 2000. This was the reason of the discrimination seen in Fig. 3. Hence, it could be concluded that of the all soil categorizations introduced in this study, the one that was most successful in accordance to six heavy metals discussed, was based on the land-use types, showing discrimination of the metal patterns of the agricultural and urban/recreational soils.

Finally, LDA was also used for differentiation of soil samples according to the predefined land-use types. The results for the "all" data set are presented in Table S4 in the Appendix A. The variables most important for the discrimination function are the ones with the smallest values of Wilks' Lambda. Thus, the following variables had the highest discrimination power for differentiation of land-use types: Cu, Zn, Ni, Cr, Cd, and Pb (ordering in decreasing significance). The total percentage of correct classification achieved 73.3%. It could be seen that rural, agricultural, and recreational soils were easy to discriminate as the correct classification was 100%, 90.8%, and 75.6%, respectively.

4. Conclusions

The application of PCA to the data set consisting of the contents of six heavy metals commonly analyzed in soils worldwide revealed the general distribution patterns and identified two specific compositional trends that appear to record different types of polluted and unpolluted soil. In the case of the polluted soils, the very strong correlation of the first principal component with Pb, Cd, Cu and Zn in soils suggested an anthropogenic causative factors, primarily traffic emissions as exhausts, tyre abrasion, lubricants, etc. as likely sources; the second principal component was correlated with Ni and Cr, reflecting most probably the combined sources (pedogenic and stationary anthropogenic). Contrary, for the unpolluted soils the majority of variance was explained by the principal component significantly correlated with Ni/Cr and Cu, indicating most probably the influence of pedogenic processes and/or agricultural practice, respectively, while the second component implied the traffic as a second source of data variability. The most obvious discrimination of the samples seen in the PCA biplots was the one based on the land-use types with roughly separated agricultural soils on one side and urban/recreational on the other. This was confirmed by the use of LDA. In general, the associations between metals observed by the Spearmen non-parametric correlation test were also graphically identified by PCA biplots allowing easier interpretation. Finally, it has to be emphasized that classification of the samples in accordance to the pollution level, for instance defined by soil metal index, as it was made in this study, was necessary in order to avoid the "masking" effect of the polluted soil patterns over the non-polluted ones. Naturally, all of these statements are valid within the scope of this study and the samples chosen to be analyzed here.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.06.010.

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Principal component analysis of indicator PCB profiles in breast milk from Poland

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ABSTRACT

Principal component analysis (PCA) was applied to a data set containing the levels of indicator polychlorinated biphenyls (PCBs) in human milk of mothers living in the Wielkopolska region, Poland, in order to investigate the information captured in the PCB patterns and to elucidate the relationship between PCB concentrations in milk and donor characteristics. According to the obtained PCA results milk fat content was the most influential factor affecting the PCB levels in milk of the Wielkopolska cohort. The lifestyle data collected from the questionnaire completed by the donors appeared to have no influence on PCB concentrations in breast milk. The score plots revealed the PCB contents of milk were quite low and uniform with a few outliers, without discrimination observed either between the primipareous and secundipareous females or between donors from the urban and rural areas. Comparison of the PCB levels and profiles of human milk from the Wielkopolska region and from various European and Asian locations made by PCA reflected a generally low background exposure and indicated the possible reasons for the outlying of some samples. In order to enhance the chances of observing the relationship between donor habits and PCB levels in breast milk it was suggested that the questionnaire be redesigned to gather information about vegetable product consumption and indoor air exposure.

1. Introduction

Human milk is a complex mixture of endogenous substances produced by the mother that provides breastfed infants with the necessary nutrients (i.e. proteins, amino acids, and carbohydrates) and non-nutritive factors (i.e. enzymes, hormones, and immunoglobulins) all of which are essential for proper development (LaKind et al., 2004). Breast milk is also a source of lipophilic environmental contaminants, which accumulate in the fatty tissues of the mother over time. The levels of lipophilic contaminants in breast milk can be correlated to the levels in plasma, serum lipids and adipose tissue, reflecting the body burden of these contaminants (Costopoulou et al., 2006; Nakamura et al., 2008). Therefore breast milk monitoring is a non-invasive means of determining the levels of lipophilic chemicals in humans. Breast milk monitoring also provides a means of examining exposure times and related trends in environmental contamination, and of hypothesizing on determinant factors and potential perinatal exposures for breastfeeding infants.

Polychlorinated biphenyls (PCBs) are persistent organic pollutants and have been identified worldwide as human fat tissue contaminants (Cok and Satiroglu, 2004; Vaclavik et al., 2006; Szyrwinska and Lulek, 2007; Polder et al., 2008; Tan et al., 2008). Several studies have concluded that consumption of meat and dairy products, as well as processed foods and fish, contributes significantly to overall intake of PCBs, accounting for more than 90% of the human body burden of PCBs (Wolff et al., 2005; Yu et al., 2007), with inhalation contributing the majority of the remainder (Duarte-Davitson and Jones, 1994). However, only a few investigations (Currado and Harrad, 1998; Rudel et al., 2008) have suggested that the indoor microenvironment could contribute more significantly than diet to the overall PCB exposure.

Variables such as mothers' age, parity, body weight, dietary pattern, lifestyle and demographics have been investigated to identify the most influential factors in the accumulation of PCBs in breast milk (Czaja et al., 2001; Nakamura et al., 2008). The methods applied in these studies were restricted to bivariate linear correlation test, i.e. the effect of a single factor on PCB concentrations, and they were based on the assumption that the X-variables were independent of each other. However, in the case of large number of variables, the problem of multicollinearity may exist. The interpretations of large data sets can be successfully performed by multivariate data analysis techniques that successfully deal with strongly collinear and numerous X-variables. Furthermore, the multivariate approach provides an initial overview of the data and classification of groups, and is also useful for outlier detection where deviating exposures efficiently can be identified. Principal component analysis (PCA) as the multivariate analytical tool reduces a set of original variables and extracts a small number of latent factors (principal components, PCs) for analyzing relationships between the observed variables and samples. It has been widely used to deliver more information on links among sampling sites, pollutant concentrations, correlation patterns, and latent factors responsible for the data-set

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structure in the environmental studies (Golobočanin et al., 2004; Škrbić et al., 2005; Škrbić and Đurišić-Mladenović, 2007a; Vives et al., 2008). Unfortunately, only a few applications of this technique were employed in the investigation of breast milk contamination by persistent organic contaminants (Rachdaawong and Christensen, 1997; Kalantzi et al., 2004).

In this work, PCA was performed on a data matrix consisting of concentrations of indicator PCBs in human milk samples collected in the period 2000–2002 from the mothers living in the Wielkopolska region, Poland, and the variables from the questionnaire completed by the milk donors, in order to investigate the relationship between the PCB level/profiles and donor demographic characteristics, lifestyle factors and some variables reflected in the infants development. Moreover, PCB-accumulation features of the Wielkopolska cohort were compared with the data from the relevant international studies also by applying PCA.

2. Materials and methods

2.1. Chemicals

Individual chlorobiphenyls used as primary standards (PCBs 28, 52, 101, 118, 138, 153, and 180), and as internal standards (PCB 30 and 209) were purchased from Dr. Ehrenstorfer, Germany. The different working standard solutions were prepared by adding the appropriate weight amounts of primary standards to isooctane (Baker ® Ultra-resi analyzed quality) or to acetone (Baker ® Ultra-resi analyzed quality). Concentrated H_2SO_4 (Merck®), n-hexane (Mallinckrodt Nanograde®), granulated anhydrous sodium sulphate ("Baker Ultra-resi Analyzed") and Florisil® (for residue analysis; Baker Analyzed) were also used. Florisil was activated at 650 °C for 4 h, stored in a desiccator and kept at 130 °C for 2 h before use. Isooctane, 2-propanol and diethyl ether anhydrous (Ultra-resi analyzed®), formic acid (6 M) and NaCl 0.9%, Baker analyzed® were purchased from J.T.Baker.

2.2. PCB levels in human milk

Previously, 7 indicator PCBs (IUPAC Nos.: 28, 52, 101, 118, 138, 153, and 180) had been quantified in 27 human milk samples from the Wielkopolska region in Poland and the results were published elsewhere (Szyrwinska and Lulek, 2007). A short description of the sample collection method, materials and the method used for the analysis of an additional 23 breast milk samples from the Wielkopolska region follows.

All mothers (typical women from Poland) were recruited from the Department of Perinatology and Gynaecology in the University Hospital of Gynaecology and Obstetrics in Poznan. The sampling and individual interviews of donors were organized according to the World Health Organization's (WHO) protocol. According to this protocol the inclusion criteria for the recruitment of study participants were as follows: both mother and child were apparently healthy and the pregnancy was normal; the mothers were exclusively breastfeeding one child (i.e. no twins); mothers were residing in the same area for about 5 years; at least 50 ml of milk was collected from each mother; the interviews with all donating mothers were performed including also the completion of the distributed questionnaires. The individual milk samples were analyzed in consistency to the latest WHO protocol of the fourth survey of human milk for persistent organic pollutants, which was recently expanded to include individual milk samples contrary to the previous three surveys that were based on the pooled samples (Colles et al., 2008). In contrast to the WHO protocol, which further implies that donors should be primiparae, in this study 18 mothers nursing their second child were included besides 32 primiparae mothers. The sample collection and analysis was approved by the local committee of medical ethics — the Institutional Review Board at the Poznan University of Medical Sciences. After delivery to the laboratory, the collected milk samples were stored at −20 °C until the analysis.

Informed consent was completed by each donating mother, giving information on age, height, weight before pregnancy and after delivery, sampling time, duration of residence in the locality, smoking status, dietary habits (frequency of food consumption of animal origin — fish, beef, milk and its products, cheese), occupation history, newborn's sex, and weight at birth. The cohort under study is described in detail in the supplementary Table S1. Donors were aged between 17 and 36 with an average age of 25.3 and 29.6 for primipareous and secundipareous, respectively. The mean body mass index (BMI) was almost the same for these two subgroups of the Wielkopolska cohort with the average value of 21. According to BMIs, 9 donors were underweight, 4 were overweight while the rest of them had normal weight before pregnancy. The questionnaires documented a diminished consumption of fish and beef, i.e., never or less than once a week in ~90% (primipareous) and ~70% (secundipareous).The majority of donors consumed milk and dairy products two or more times per week (72% of primipareous and 83% of secundipareous). Only two primipareous and one secundipareous mothers were smokers, while the remaining were either nonsmokers or former smokers. With the exception of 6 donors who lived in rural areas, donors were from urban/suburban areas. None of the donors had been occupationally exposed to PCBs. All the mothers performed milk sampling between the third and the eighth week from delivery.

The lipid content in milk samples was determined according to the method of Hong et al. (1992). 5 g of milk sample was weighed in a 50 mL centrifuge tube. 10 mL of ethanol and 9 mL of hexane were added to the centrifuge tube, shaken vigorously for 1 min and centrifuged at 4000 rpm for 10 min. The upper layer was transferred to an Erlenmeyer flask containing anhydrous Na_2SO_4. The aqueous residue was extracted twice with 7 mL hexane. The combined extracts were used for a gravimetric lipid determination.

Congener-specific analysis was performed by the modified method of Galceran et al. (1993). The homogenized milk sample (about 20 g) was placed in a mortar and then 12 g of Florisil and 130 g of anhydrous sodium sulfate were added. This was mixed to yield a dry powder and placed on a column previously filled with a small plug of glass-wool. After elution with 100 ml of n-hexane/acetone (2:1, v/v), the eluate was concentrated to less than 3 ml and cleaned up two times with concentrated H_2SO_4. The combined extract was concentrated to about 0.5 ml and quantitatively transferred to a Florisil SPE cartridge (500 mg) that had previously been activated with 10 ml of hexane. The PCB congeners were eluted with 5 ml of hexane. The cleaned up extract was analyzed by the Shimadzu GC-14 A gas chromatograph equipped with a ^{63}Ni ECD and split/splitless injector. Two chromatographic columns were used: slightly polar — DB5 (60 m, 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific), and more polar — RT_x®-1701 (60 m, 0.25 mm i.d., 0.25 μm film thickness, Restek Corporation) with helium carrier gas and nitrogen make-up gas. The temperature program of the column was 2 min at 125 °C; 7.5 °C/min to 190 °C and 2 °C/min to 280 °C, held for 15 min. The injector temperature was at 250 °C, and the detector temperature was 300 °C. The relative retention times were measured with an accuracy of 0.01. The internal standards (PCB 30 and 209) were added to concentrated extracts before analysis by gas chromatography. The quantification was made by a peak-by-peak height comparison and a calibration curve for each analyte.

Before PCB analysis the linear range of the ECD detector was determined according to Wells et al. (1992). The analysis was carried out in three runs. The GC analysis of the cleaned up extracts was performed in triplicate. Procedural blanks, which consisted of water instead of milk, were included within each sample batch. The multi-level calibration curves, which included the whole concentration range of analytes found in the samples, were created for the quantification. The quality of the results was verified in an interlaboratory exercise. The analyses of seven breast milk samples were performed simultaneously at the Institute of

Applied Environmental Research of Stockholm University and at the Department of Inorganic and Analytical Chemistry of the Poznan University of Medical Sciences. The results obtained were compared on the basis of statistical criteria. A Student's paired *t*-test did not show significant differences between the analytes levels determined in the two laboratories. A detailed description of the validation of the method used for determination of 7 indicator PCBs in human milk samples can be found elsewhere (Lulek et al., 2003).

2.3. Principal component analysis

PCA as the multivariate analytical tool was used to reduce a set of original variables and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables and classification of samples. In fact, the principal of PCA is to project the variations in a multivariate data matrix X with n rows (samples or cases or objects) and k columns (variables) into a few uncorrelated (orthogonal) principal components (PCs). The principal components are linear combinations of the original variables and vice versa. Basically, the systematic variation of the X matrix is extracted into the smaller matrices, the score T and the loading P' matrices. The first PC is oriented to explain as much variation in the data as possible and presents the best linear summary of X. The second PC is orthogonal to the first, and explains the next largest variation in the data, and so forth. The PCs of the T matrix can be plotted in two (or three)-dimensional space to produce score plots. In a score plot, the relationship between samples is visualized, hence, the samples close to each other in the score plot are similar and vice versa. The loading plots of the P' matrix are produced in the same way and visualize how the variables are related to each other. In fact, the loadings express how well the new abstract principal components correlate with the old variables. The higher the loading of a variable the more that variable contributes to the variation accounted for by the principal component. The sign of loading value indicates whether the particular variable is in positive or in negative correlation with the principal component. Comparing the score and loading plots reveals the relationship between the samples and the variables, e.g. which individual PCBs are present in high or low concentrations in the samples positioned in different parts of the score plot. More precisely it could be said that higher principal component scores are the results of lower concentrations of the variables with a negative loading and higher concentrations of the variables with a positive loading. It is also possible to view for possible presence of outliers using the PC score plots. Outliers are in fact the measurements which are far removed from the others in the plot because they have exceptionally high concentrations of the variables (Smeyers-Verbeke et al., 1984). The algorithm of PCA can be found in the standard textbooks (Massart et al., 1997).

The analysis was carried out after logarithmic transformation of the PCB contents in order to correct the skewness of data typical for environmental contaminants. Principal components were computed via the correlation matrix: first, the data were mean-centered (column means subtracted from each matrix element). Then each matrix element was divided by the standard deviation of the respective column. In this way, the data were centered to zero mean and scaled to unit variance. Varimax orthogonal rotation was applied to get as many as possible positive loadings and to achieve a more meaningful and interpretable solution. The number of PCs extracted from the variables was determined by Kaiser's rule (Kaiser and Rice, 1974). This criterion retains only factors with eigenvalues that exceed one. According to Morrison (1967) principal components should account for approximately 75% of the total variance. In order to interpret the significance of retained PCs in terms of the original variables, only those loadings (coefficients) whose absolute value was greater than 60% of the maximum coefficient in absolute value in each PC were considered (Jolliffe, 1986). Relationships between the samples were evaluated on the score plots, whereas the loading plots showed the extent to which each variable contributed to the sample separation (grouping). Throughout the study STATISTICA for Windows program package (version 6.0, StatSoft Inc., Tulsa, OK, USA) was used.

We analyzed the correlation between PCBs content in human milk and the questionnaire data as well as the spatial and temporal trends in the PCB-accumulation pattern by applying PCA on two input data sets (matrices) denoted as “Wielkopolska” and “International”. While preparing input data for PCA we tried to collect a sufficient number of suitable samples in order to provide reliable estimations of the correlations among variables. Detail description of the sets building is given below.

2.3.1. The “Wielkopolska” set

This set was used as the most comprehensive available for assessing the links between the contents of indicator congeners in milk and the donors' characteristics. It consisted of breast milk concentrations of 7 indicator PCBs and the 15 variables (or 14, see the explanation of the chosen variables below) from the questionnaires completed by milk donors from the Wielkopolska region. As PCB52 was not analyzed in all the samples and as there were missing data on the mother's weight before delivery and on the child's weight in the moment of sampling, 16 samples out of 50 analyzed were excluded from PCA.

In order to include the nominal variables provided by the questionnaire into the “Wielkopolska” matrix, such as current and previous residential area, smoking habits, etc., variables were dichotomized by assigning scores of 0 and 1 (see Table S1). For instance, considering the residential area, the urban and suburban areas were scored with 1, whereas the rural with 0. This approach was previously used in the study of Schade and Heinzow (1998) and Tan et al. (2008). In addition, we combined several original variables from the questionnaire into the new ones (as it is presented below Table S1), and these calculated variables were further included into the input matrix analyzed by PCA to obtain more meaningful PCA results. For example, instead of using mothers' height and mass we combined them into the body mass index (BMI) presuming that eventual link of the PCB milk-levels with BMI as a reliable indicator of body fatness would be more interpretable than the link with the height or the mass. Similar reasoning was behind the inclusion of the percentage of mothers' body mass increase during pregnancy-MWINC into the input matrix. Additionally, it was assumed that PCB content would be associated with the rate of child growth (expressed as a weekly rate of child mass increase from birth to sampling-CWINC) rather than to absolute infant body mass, as the former could indicate the breast milk consumption rate and thus the rate of excretion of chemicals (depuration). Type of diet was discarded as a variable in the input matrix for PCA as the donors under the study consumed a generally mixed diet (except one female who was vegetarian eating fish, milk and eggs; Table S1).

Taking into consideration that the results of the analysis of PCBs in biological samples have been expressed on different ways, i.e. ng/g fat (the most common way), ng/g milk (Craan and Haines, 1998), mol/g (Wingfors et al., 2000)), mol%, mass% (Yang et al., 2002; Borrell et al., 2007) several PCAs were performed for each metric in order to identify the latent data structure and to obtain the most interpretable PCA solution concerning the correlation of the PCB pattern and donors' characteristics. As variations in lipid levels had been accounted for, milk fat content was not included when the lipid normalized contents were subjected to PCA, nor it was discussed as a determinant factor.

Finally, 22 variables (abbreviation given to the donors characteristics used as variables are given in Table S1), or 21 variables in the case of the lipid normalized contents, and 34 samples making the “Wielkopolska” set were investigated by PCA.

2.3.2. The “International” set

This data set was used to compare the spatial and temporal accumulation patterns of the indicator congeners in the milk samples from different regions. It contained the results on the concentrations of 7 indicator congeners collected from the relevant international studies (Duarte-Davitson et al., 1991; Bordet et al., 1993; Polder et al., 1998; She et al., 1998; Gladen et al., 1999; Noren and Meironyte, 2000; Gluszynski, 2002; Cajka and Hajslova, 2003; Cok et al., 2003; Costopoulou et al., 2006; Herceg Romanić and Krauthacker, 2006; Ingelido et al., 2007; Zhao et al., 2007; Abballe et al., 2008; Colles et al., 2008; Polder et al., 2008; Raab et al., 2008) combined with the 34 × 7 (samples × variables) matrix obtained after excluding the questionnaire data (i.e. by keeping only the data on the PCB levels) from the “Wielkopolska” set. These studies are mainly originated from Europe and Asia. Considering the data on the PCB levels of human milk from other parts of the world, only few studies have been available for the U.S. and Canadian population (Korrick and Altshul, 1998; Craan and Haines, 1998; Kostyniak et al., 1999; LaKind et al., 2001; She et al., 2007). However, they were not comparable to the majority of collected data as they reported the results only for some of the indicator congeners (not for all 7) or presented the total PCB concentration. It has to be emphasized that only those studies comparable with each other regarding 7 analyzed PCBs were taken into consideration. The sources of the data with short descriptions are given in the Table S2 in the supplemental material.

In this set we also included the contents of the indicator PCBs in the various matrices (samples of different foodstuffs from Poland (Lulek, 2002), waste transformer oil collected in Poland in 1995 (Lulek, 1998)), air sampled within a variety of workplace and domestic indoor environments (Currado and Harrad, 1998), and composite soil sample representing the average background level of the sites worldwide (Meijer et al., 2003), in order to provide further insight into the potential sources of PCB exposure of the Wielkopolska donors. The reason behind the inclusion of these samples into the matrix analyzed by PCA lies in the well known fact that human may be exposed to PCBs by direct contact with industrial products, accidental contamination of foodstuffs or from contaminated environmental components, either orally, dermally or via inhalation. In assessing PCB exposure by inhalation, it has been proven that indoor air quality may be more important than outdoor air quality as people spend most of their time at workplaces and homes (Menichini et al., 2007). Furthermore, as many studies indicated that PCB levels calculated on a lipid basis are about the same in milk, blood, adipose tissue and muscle (Jensen, 1991), the PCB levels in the composite blood plasma sample of the construction workers involved in the abatement of PCB-containing sealants (Wingfors et al., 2006) was also included representing the human tissue after recent high occupational exposure through inhalation. In addition, the control blood plasma of the workers without previous occupational PCB exposure was incorporated into the matrix to compare the PCB profiles (Wingfors et al., 2006).

Finally, the size of “International” matrix was 90 × 7. Within the data set, ng/g fat and mass% concentrations of indicator PCBs were considered creating two subsets that were subsequently examined by PCA.

3. Results and discussion

3.1. PCB levels in human milk

Table 1 shows the descriptive statistics on the concentrations of indicator PCBs analyzed in 50 individual human milk samples from the Wielkopolska region divided into two groups according to a number of breastfed infants born to one mother. In statistical calculations, concentrations below the LOD were assigned a value of LOD/2. The median sum of indicator PCBs obtained for all samples ($n = 50$) analyzed in this study (87.7 ng/g fat) was similar to the value measured in Finnish human milk (91 ng/g fat) and was lower than in Dutch, UK, German, Slovakian and Czech human milk samples (116–502 ng/g fat) (van Leeuwen and Malisch, 2002; Kalantzi et al., 2004). It was also below the total concentration of 6 indicator PCB compounds in Central Europe of 200–400 ng/g fat according to WHO research data (Bake et al., 2007). Somewhat lower concentration of PCB indicators in human milk was found in Brazil, Australia, Hungary, New Zealand, Bulgaria, and Ireland (16–61 ng/g fat) (Malisch and van Leeuwen, 2003).

The most abundant congeners in the analyzed samples were hexachlorobiphenyls 138 and 153, followed by heptachlorobiphenyl 180 and pentachlorobiphenyl 118. PCB 138, 153 and 180 accounted for 84.60 ± 11.22% of the total milk PCB concentrations, while the relative sum of PCB 28, 52, and 101 was 7.61 ± 11.75%. This kind of congener distribution is a typical characteristic of bioaccumulated PCBs, with high degrees of chlorination in the biphenyl rings and a lack of vicinal hydrogen atoms (Wingfors et al., 2006). Our results agree with the results published on PCB levels in human milk (Ramos et al., 1997; Noren and Meironyte, 2000; Gluszynski, 2002; Costopoulou et al., 2006; Ingelido et al., 2007; Szyrwinska and Lulek, 2007; Nakamura et al., 2008).

Table 1
Concentration of indicator PCBs in breast milk of donors from Wielkopolska region, Poland (mean ± standard deviation (median) minimum–maximum).

Congener		% >LOD[a]	Primaparae ($n = 32$)	Secundiparae ($n = 18$)
PCB 28	ng/g milk	94[b]	0.040 ± 0.026 (0.035) 0.002–0.110	0.04 ± 0.03 (0.03) 0.01–0.10
	ng/g fat		1.36 ± 1.08 (1.00) 0.07–5.06	1.07 ± 0.60 (0.94) 0.07–2.34
PCB 52	ng/g milk	100[c]	0.156 ± 0.400 (0.042) 0.01–1.62	0.25 ± 0.66 (0.04) 0.02–2.62
	ng/g fat		3.75 ± 8.90 (1.14) 0.21–38.30	7.94 ± 19.31 (1.08) 0.77–67.97
PCB 101	ng/g milk	28[b]	0.011 ± 0.008 (0.008) 0.008–0.03	0.02 ± 0.01 (0.01) 0.01–0.06
	ng/g fat		0.41 ± 0.34 (0.28) 0.11–1.55	0.50 ± 0.56 (0.30) 0.14–2.34
PCB 118	ng/g milk	100	0.194 ± 0.174 (0.146) 0.03–0.992	0.27 ± 0.22 (0.17) 0.02–0.68
	ng/g fat		6.36 ± 5.13 (4.95) 0.63–22.15	6.55 ± 4.12 (4.96) 0.60–15.69
PCB 138	ng/g milk	100	0.873 ± 1.760 (0.494) 0.10–10.38	1.02 ± 1.09 (0.68) 0.07–4.67
	ng/g fat		24.26 ± 28.88 (15.56) 2.10–168.78	25.42 ± 23.31 (19.08) 2.10–107.06
PCB 153	ng/g milk	100	1.099 ± 1.855 (0.715) 0.086–11.001	1.51 ± 1.53 (0.95) 0.12–6.58
	ng/g fat		30.50 ± 30.74 (20.34) 2.52–178.88	37.58 ± 32.46 (29.07) 3.55–150.85
PCB 180	ng/g milk	100	0.602 ± 1.252 (0.345) 0.08–7.365	0.78 ± 0.71 (0.55) 0.19–2.97
	ng/g fat		16.59 ± 20.38 (11.94) 1.68–119.76	19.12 ± 14.25 (16.41) 5.31–68.00
Sum PCB	ng/g milk	100	2.938 ± 5.017 (1.794) 0.368–29.887	3.86 ± 3.65 (2.39) 0.51–14.99
	ng/g fat		82.288 ± 81.422 (58.757) 7.715–485.967	97.32 ± 76.43 (70.83) 15.27–343.72

[a] Percentage of samples above the limit of detection (LOD).

[b] In the calculation of mean, standard deviation and median, LOD/2 was used for concentrations below LOD.

[c] 10 of 50 samples were not analyzed for PCB52, thus, presented percentage of detection reflects the results on the PCB52 presence in 40 samples analyzed.

3.2. Principal component analysis

3.2.1. The “Wielkopolska” set

There was a large number of PCs retained in the analysis (Table 2) indicating that the data did not compressed well. This further implied that the PCB levels in milk samples could not be easily described nor correlated to the data obtained from the questionnaires.

The same results (Table 2) were obtained in the cases when the PCB levels were expressed as ng/g milk and nmol/g milk; ng/g fat and nmol/g fat, as well as when they were presented as normalized mass% and mol%. In the frame of this study, these findings suggested that the mass and molar concentration carried the same level of information in so far as the same basis for PCB concentrations was used.

8 PCs were retained when PCB contents were expressed on milk and milk fat basis and they correlated with the original variables in a similar way. In both cases, the retained PCs explained ~80% of the total variance and the first PC (PC1) accounted for ~22% of the variance, correlating significantly with the contents of major contributing congeners in breast milk: PCB 118, 138, 153 and 180. In other words, it could be said that the occurrence of these higher chlorinated indicator PCBs in milk were closely related to each other. Loading of fat percentage of breast milk (FAT%) in PC1 (0.54728, this value is not given in Table 2 in accordance to the table footnote [a]) could not be rejected as negligible, being slightly lower than the value (0.58858) used for discriminating significant from non significant loadings in PC1. This finding implied that the contents of higher chlorinated PCBs might be also positively associated with the milk fat content, meaning that higher fat contents might be indicative for elevated amount of these congeners in the human milk. PCB 28, 52 and 101, had high loadings in PC7 that explained only ~7% of the total variance. Additionally, fat content of the sampled breast milk correlated significantly with PC7 (Table 2) and thus with PCB 28, 52 and 101 contents in milk, coinciding with the observation previously explained for the link between the content of milk fat and higher chlorinated congeners. The different

Table 2

Varimax normalized loadings[a] obtained by PCA after applying the Kaiser's rule for the ng/g milk, nmol/g milk, ng/g fat, nmol/g fat, mass% and mol% content of indicator PCB congeners in investigated breast milk samples and donors' characteristics — the “Wielkopolska” set (%VAR is the percentage of the total variance explained by the particular PC).

Metrics used for expression of PCB contents		ng/g milk (nmol/g milk)	ng/g fat (nmol/g fat)	mass% (mol%)
Input matrix size (cases × variables)		34 × 22	34 × 21	34 × 22
PC1	PCB52			0.92588
	PCB118	0.92862	0.92119	
	PCB153	0.96759	0.96857	−0.91229
	PCB138	0.98097	0.98053	−0.94432
	PCB180	0.96099	0.95125	−0.84553
	%VAR	*22.72*	*22.10*	*17.79*
PC2	BMI	0.79219		0.81720
	MWINCR	−0.76574		−0.77270
	MILK		0.88095	
	MILK_FAT		0.80417	
	SMOKING			0.49969
	%VAR	*11.41*	*11.98*	*12.08*
PC3	CORDER	0.86185		0.85266
	MAGE	0.79992		0.84346
	RESAR		0.87266	
	PRESAR		0.91768	
	FISH	0.62709		0.59494
	%VAR	*9.45*	*10.01*	*11.54*
PC4	BMI		0.80130	
	MWINCR		−0.79010	
	RESAR	−0.86694		
	PRESAR	−0.91469		
	SMOKING		0.50384	
	PCB28		0.55674	
	MILK			0.88589
	MILK_FAT			0.81936
	%VAR	*8.82*	*8.88*	*8.83*
PC5	RESAR			0.85955
	PRESAR			0.92449
	MILK	0.89970		
	MILK_FAT	0.77085		
	CORDER		0.86591	
	MAGE		0.72238	
	%VAR	*8.22*	*8.43*	*8.33*
PC6	CGEND	0.83569	0.79494	0.81568
	CWINC	0.65989	0.65914	0.67172
	SAMPLING	0.58750	0.66661	
	%VAR	*7.41*	*7.52*	*7.60*
PC7	FAT%[b]	0.54872		−0.66825
	PCB28	0.57054	0.48807	0.55681
	PCB52	0.80482	0.76205	
	PCB101	0.56413	0.79213	0.86538
	%VAR	*6.19*	*6.15*	*6.45*
PC8	BEEF	0.89678	0.85957	0.87894
	SMOKING		0.53448	
	%VAR	*4.84*	*5.21*	*5.43*
TOTAL %VAR		79.07	80.28	78.05

[a] Only loadings higher than 60% of the maximum absolute value in each PC are presented.

[b] Fat content of the human milk is taken into account only when PCA was performed on ng/g milk (nmol/g milk) and mass% (mol%), i.e. it was not used for PCA of the PCB contents expressed per fat content.

“behavior” of higher and lower chlorinated congeners found in this study could be ascribed to dissimilarity of their structure influencing the accumulation rate in lipid tissues eventually. Namely, high degrees of chlorination in the biphenyl rings usually favor enrichment in biota, as such congeners are resistant to metabolism (Wingfors et al., 2006). Similarly, less chlorinated PCBs are easily metabolized and thus they are accumulated to a lesser extent that more persistent congeners.

Remaining PCs were correlated significantly with the questionnaire data revealing the general structure of the cohort under the study (see Table 2). For example, the secundipareous females that were older than primipareous, ate more fish. The residential areas of the donors correlated with previous ones as most of them did not change the area where they lived. The consumption of high-fatty dairy products (with fat content above 3%) was characteristic for donors that notably consumed dairy products (more than twice a week). Mothers with higher BMI values before pregnancy showed a lower weight increase during pregnancy. Baby girls gained in weight more rapidly than boys.

Absence of a significant correlation between PCB concentrations and mothers' age/parity coincided with the previous findings (Czaja et al., 2001; Thomas et al., 2006). Czaja et al. (2001) revealed that for the donor who gave birth to the second child after 2 years, there were no statistically significant differences in the concentrations of the PCBs in milk of the first and the second breastfeeding period. Since the questionnaire did not provide the information about the period between the deliveries for secundipareous females under the study, we could only speculate that it had been long enough for PCBs to have been supplemented in the fat tissues of the donors.

Other variables such as fish and milk consumption, smoking habit, residential area, sampling time, child's gender and rate of mass weight increase did not turn out to be significantly associated with PCB levels in breast milk (see Table 2). Similarly, Schade and Heinzow (1998) did not find significant links between level of organochlorine compounds (including PCBs) in human milk and smoking and gender of the child, while Nakamura et al. (2008) did not observe a relation between fish intake and the concentrations of PCBs in breast milk.

Use of mass% (mol%) normalized concentration of indicator PCBs in the “Wielkopolska” data set analyzed by PCA gave results something different from PCA in which the absolute mass (or molar) PCB concentrations were used as variables (Table 2). Again 8 principal components with eigenvalues higher than 1 were extracted, but they explained slightly less of the total data variance (~78%). PC1 accounted for ~18% of the variance. It reflected the PCB (non-)persistency as the less stable (less chlorinated) congener (i.e. PCB 52) had significant positive loadings in PC1, while PCB 138, 153 and 180 had the negative ones (see Table 2). PCB 28 and 101 correlated with PC7 explaining 6.45% of the data variance. PC2–PC6 and PC8 were significantly correlated with the questionnaire data in a similar way (Table 2) as it was previously explained in the case of PCA of the “Wielkopolska” matrices with absolute PCB contents (ng/g milk and ng/g fat).

Scores of the first two the most informative components (PC1 and PC2) retained in the case of ng/g milk- and mass%-contents are plotted in Fig. 1a) and b), respectively, together with the variables with most significant loadings (in accordance to data given in Table 2). As the other PCs explained less of data variation giving us the additional but not main information, they were not plotted. Moreover, since PCBs significantly correlated with PC1, the classification of samples was further considered only with respect to their position relative to this component. In both cases (ng/g milk- and mass%-contents), the samples were distributed uniformly along PC1, without differentiation between those coming from urban and rural areas nor between the primipareous and secundipareous mothers (Fig. 1). Moreover, there was neither discrimination of samples according to the mothers age (Fig. 1). In other words, majority of the samples grouped in the circled cluster around the plot origin (see Fig. 1a) and b)) had the similar levels or the similar profiles (i.e. relative percentage to the total PCB content) of higher chlorinated indicator PCBs. Such grouping phenomenon could be explained by homogenous general exposure of the donors. The following outlier in the first component (PC1) emerged: in the case of PCA with mass concentrations it was the 28-years old primiparae from the rural area due to significantly enhanced content of highly chlorinated congeners (PCB 118, 138, 153, and 180), whereas in the case of PCA with mass% normalized concentrations, the outliers were the ones with highly elevated percentage of PCB 52 relative to the total concentration (one primipara (24 years) from rural location as well as two primiparas (20 and 22 years) and two secundipars (34 and 36 years) from urban locations). However, the information provided by the questionnaire could not explain why these samples had significantly different PCB patterns.

3.2.2. The “International” set

To gain a better insight into the latent structure (hidden regularities) of the obtained data and to investigate similarities or dissimilarities of the PCB loads of human milk from various locations and with respect to different source of exposure, we applied PCA to the “International” data set previously described. Two PCs were retained explaining 88.93% and 82.28% of total variance in the data expressed as ng/g fat and mass%, respectively, each carrying different kinds of information.

With regard to the absolute values of PCBs in milk (ng/g fat), the significant loadings in PC1 (Fig. 2a) ordered congeners as follows: 101 > 52 > 28 > 118 implying that tri- to penta-indicator biphenyls would be responsible for the sample discrimination along PC1. PC2 was considerably correlated with PCB 180 > 138 ~ 153, which governed the distribution of the samples along PC2. The score plot (Fig. 2b) revealed that PC1 was responsible for the discrimination of biological matrices (around the plot origin) and indoor air samples, as a consequence of the lowest levels of the less chlorinated congeners found in the former and the highest levels in the later. Foodstuffs of vegetable origin with elevated contents of PCB 28, 52 and 101 formed intermediate cluster along PC1. Along PC2 human breast milk samples were separated from the food of animal origin and the waste transformer oil in accordance to the levels of PCB 138, 153 and 180. Because of the similarity in the levels of these congeners the soil sample was located in the cluster of the food of animal origin.

It is interesting to note that the pooled sample of blood plasma (Wingfors et al., 2006) taken from the Swedish construction workers involved in abatement of PCB-containing sealants (“exposed” plasma, see Fig. 2b)) and the one (Wingfors et al., 2006) from the Swedish workers non exposed to PCBs (control plasma, Fig. 2b)) were also grouped in the cluster of biological matrices. However, they located distantly from each other, i.e. “exposed” plasma situated in the positive part of PC1 reflecting the more elevated levels of lower chlorinated PCB congeners in contrast to the control plasma that is in the negative part of PC1. Furthermore, the “exposed” plasma is located near to three breast milk samples from developed European countries in the period 1970/80s (see

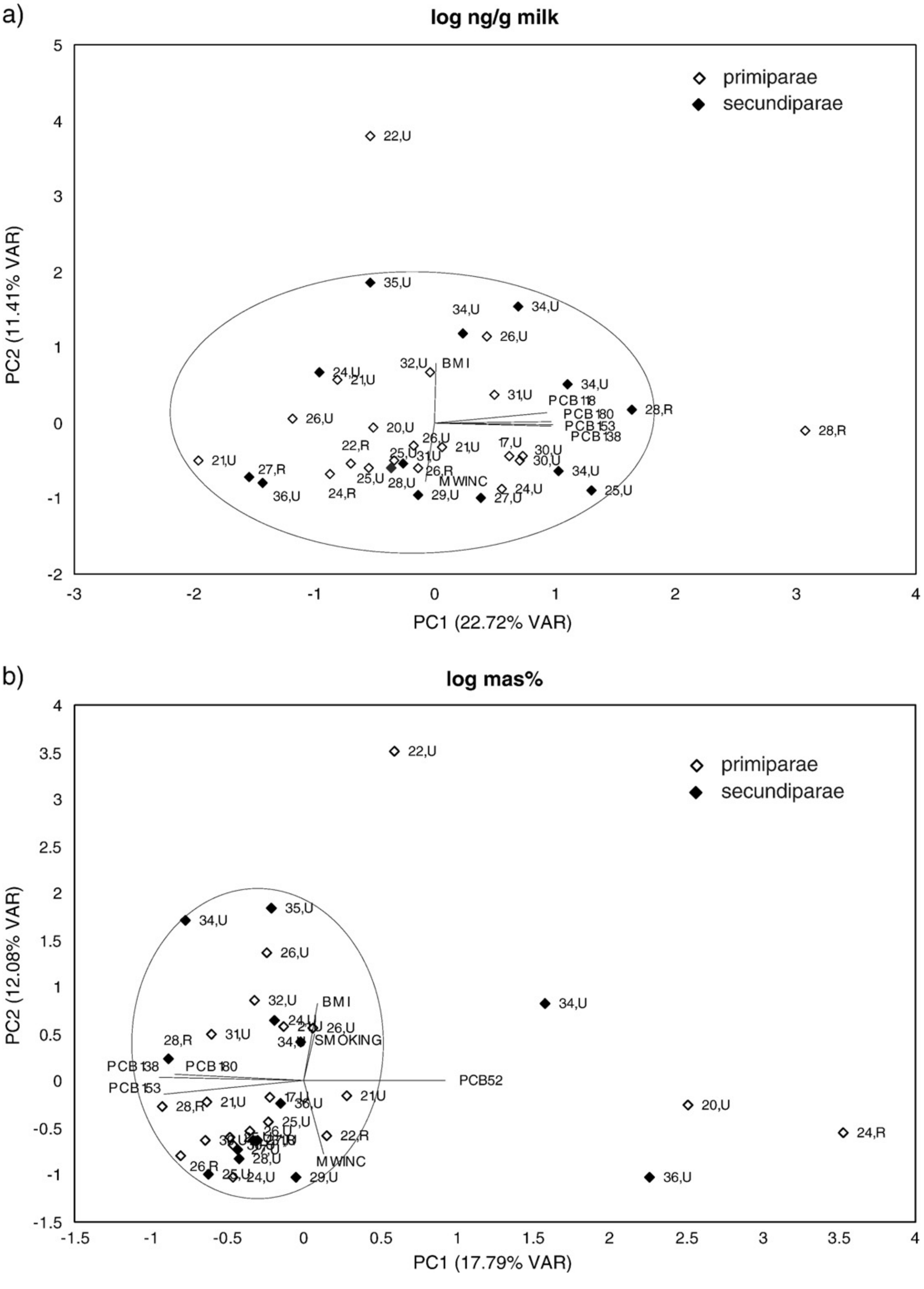

Fig. 1. Biplots PC1 vs. PC2 for the "Wielkopolska" set with a) mass (ng/g milk) and b) mass%-normalized concentrations of the indicator PCBs. Only the variables with significant loadings (Table 2) are shown. Numbers indicate the mother's age. U and R denote samples from the urban/suburban and rural residential areas, respectively. %VAR is the percentage of the total variance explained by the particular PC.

Fig. 2b: "S, 1972", "GB" and "F" samples taken from Noren and Meironyte (2000), Duarte-Davitson et al. (1991), Bordet et al. (1993), respectively), which could be considered as the period of the elevated level of the environmental pollution with PCBs (Škrbić and Đurišić-Mladenović, 2007a). All this suggested that the milk samples positioned on the positive side of PC1 could reflect the elevated PCB levels in the donors' microenvironments. As the plant food matrices and the indoor air samples were also on this side of PC1, it could be further assumed that these donors were most likely exposed to the sources of less chlorinated congeners either through recent ingestion of some plant foodstuffs or inhalation. The less chlorinated congeners exist mainly in vapor phase as they are more volatile, and also they could be found in various foodstuffs, including vegetables (Zuccato et al., 1999; Škrbić and Đurišić-Mladenović, 2007b). Fish also contain many of the non-persistent, lower chlorinated PCB congeners that are present in the atmospheric vapor phase (Schaeffer et al., 2006), which is consistent with our results and the location of "carp" sample on the right side of PC1 in Fig. 2b). Once ingested by humans, these PCBs persist only for brief periods because of their rapid metabolism and/or elimination and consequently they contribute very little to the total PCB body (milk) concentrations. However, assuming that the human milk sample is taken several days after the last consumption of plant based food, the less chlorinated PCBs would contribute more to the total PCB contents in the body. In the case of the indoor microenvironment with the PCB source, the elevated contents of the more volatile

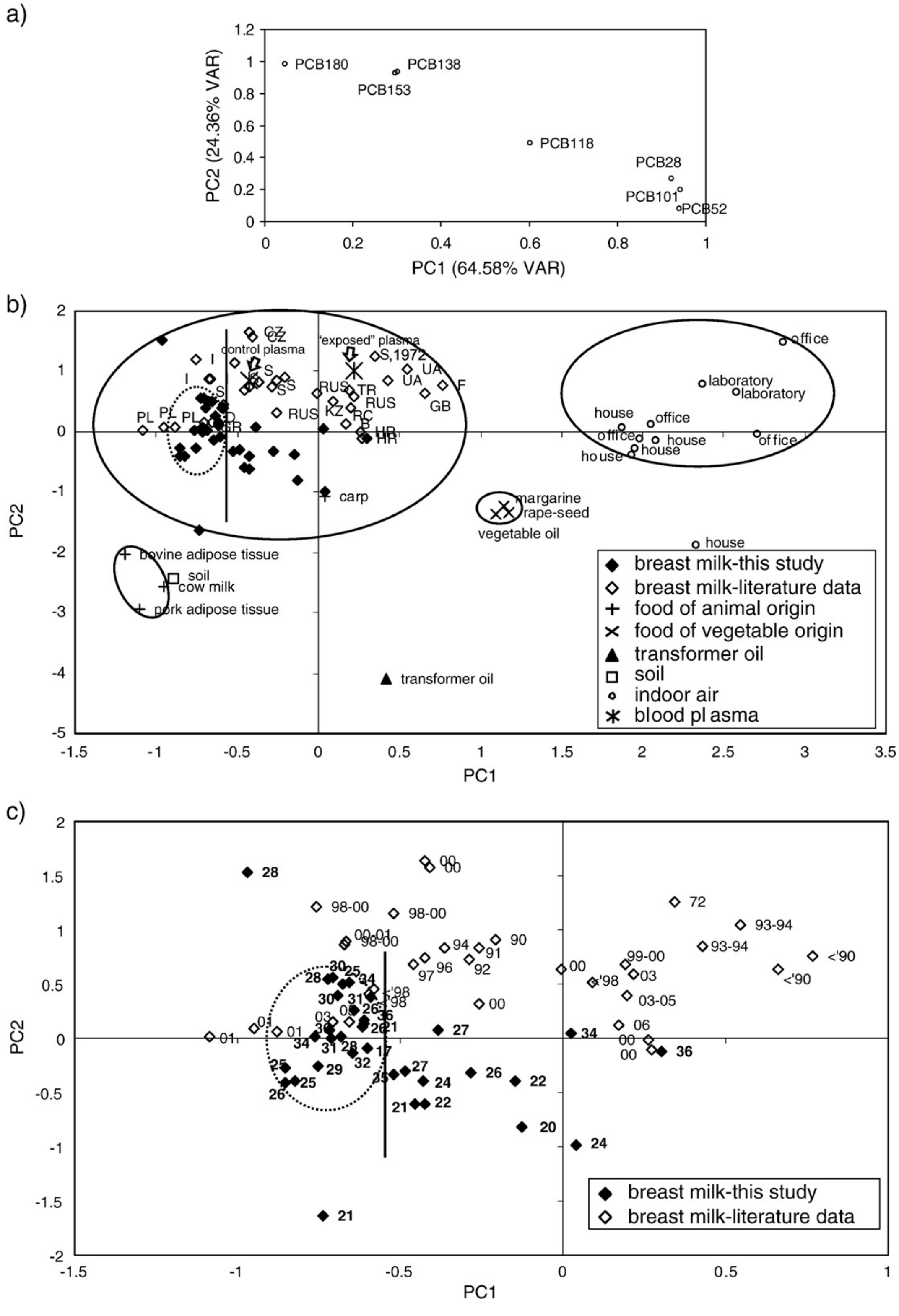

Fig. 2. PC1 vs. PC2 plots after performing PCA to the "International" data set consisting of 7 indicator PCB contents expressed in ng/g fat: a) the loading plot (%VAR is the percentage of the total variance explained by the particular PC), b) the score plot (the labels of milk samples from different countries used to examine the geographical differences are as follows: B — Belgium, China — RC, Croatia — HR, Czech Republic — CZ, France — F, Germany — D, Great Britain — GB, Greece — GR, Italy — I, Kazakhstan — KZ, Poland — PL, Russia — RUS, Sweden — S, Ukraine — UA, Turkey — TR) c) the close up of the cluster of breast milk samples located around the origin in panel b) (numbers given to the samples from this study are the mothers' age, while those given to the literature data refer to the year of the sampling according to Table S2).

congeners in the air could be expected and, consequently, such constant exposure through inhalation would eventually lead to the specific PCB profile. It must be emphasized that potential exposure via the indoor environment and consumption of plant based foodstuffs was not been included in the questionnaire, so we could only presume that these pathways are likely explanation for the elevated levels of lower chlorinated indicator congeners in 12 milk samples from the "Wielkopolska" set separated by vertical line in Fig. 2b). The rest of the Wielkopolska donors situated in the dashed circle on the left side of vertical line in Fig. 2b) reflected the similar overall intake of PCBs also indicating that the general human exposure to indicator PCBs in this Polish region was quit low in comparison to other regions represented by milk samples from majority of other countries. With respect to the regional differences, clear discrimination in the PCB exposure of donors from the European and Asian countries included in this study could not be seen.

Along PC2 two outlying samples (21- and 28-years old mothers) clearly separated from the remaining samples of the Wielkopolska set could be seen. As PC2 was correlated significantly with the content of highly chlorinated indicator PCBs (see Fig. 2a) it could be concluded that these two outliers had considerably higher and lower levels of these congeners. It was obvious that the factors driving the exposure levels in these outlying Wielkopolska samples were quite different from those affecting the PCB levels in milk from the majority of the cohort, but these factors were not included in the questionnaire.

A close up of the central cluster of the milk samples shown in Fig. 2c) did not reveal temporal discrimination neither within the “Wielkopolska” nor the “International” set.

In order to check if additional samples (air, blood, etc.) included in the “International” set distort the classification of the Polish samples, separate PCA of the “Wielkopolska” data (34 × 7 matrix) extended by 7 samples of food representative for Poland (Lulek, 2002), forming the 41 × 7 matrix, were also performed. The results revealed that very similar share of the data variance was explained by the first two PCs in these cases (compare VAR% in Figs. 2a) and 3a)), whereas the PCs correlated with congeners in opposite way, i.e. in the case of the Polish samples PC1 correlated with less chlorinated congeners while PC2 with higher chlorinated ones, and vice versa was obtained for the “International” set. Nevertheless, the positions of the Wielkopolska breast milk samples relative to the Polish foodstuffs of different origin were the same as they were within the “International” set (compare Figs. 2b) and c) with 3b)): the same 12 samples with elevated content of PCB 28, 52 and 101 positioned outside of the dashed circled cluster, while the same two donors (21- and 28-years old) had outlying positions because of the substantially different content of the higher chlorinated congeners. Hence, it could be concluded that incorporation of air, blood, soil, and waste transformer oil samples did not change the data structure captured in the PCB profile of the “Wielkopolska” set.

The results of PCA applied to the “International” data set with mass%-normalized contents of 7 indicator PCBs, revealed that PC1 was positively correlated with PCB 28 and 52, and negatively with PCB 138, 153 and 180 (Fig. 4a). PC2 was considerably correlated with PCB 101 and dioxin-like PCB 118 (Fig. 4a). Inspection of the corresponding score plot (Fig. 4b) revealed discrimination of samples into two major clusters along PC1: the “central” cluster around the plot origin gathered the samples that have the ability to accumulate PCBs in the lipid phase, while the “right” cluster formed of two subclusters (plant origin foodstuffs and indoor air samples) ring rounded the samples with the PCB patterns reflecting direct air (diffuse) pollution. Again, 12 samples from the “Wielkopolska” set were distant from the majority that were rounded with the dashed circle. Spatial (Fig. 4b)) and temporal (Fig. 4c)) similarity between the donors could not be seen suggesting the specific exposure sources in each of the country and/or the period of sampling, respectively. Two outlying samples located along PC2 were distinctively dislocated from the rest of the samples as a consequence of the quit different share of PCB 101 and 118 in the total PCB concentration.

In summary, principal component analysis (PCA) showed that the general PCB exposure within the Wielkopolska cohort was low in comparison to the available literature data and fairly uniform (Figs. 2b), c), 4b) and c)) without observed discrimination either between the primipareous and secundipareous females or between donors from the urban and rural zones (Fig. 1a) and b)). The lifestyle data collected from the questionnaire completed by the donors was not found to correlate with the levels of contaminants measured. Although food is generally accepted as the major source of organochlorine compound intake, dietary habits included in the questionnaires did not correlate significantly with the found PCB profiles of breast milk samples from the Wielkopolska region. The possible reasons for this may include the following: the type of the food consumed was not sufficiently classified, for example, whether fish was from fresh or seawater, domestic or imported (LaKind et al., 2004), lean or fat (Ingelido et al., 2007); the dietary information collected from the questionnaires did not adequately reflect the donors' actual daily intake of PCBs; consumption of vegetable products was not considered in the questionnaire. Additionally, the comparison of the Wielkopolska milk samples with the relevant literature data by PCA suggested that some people may be exposed in their

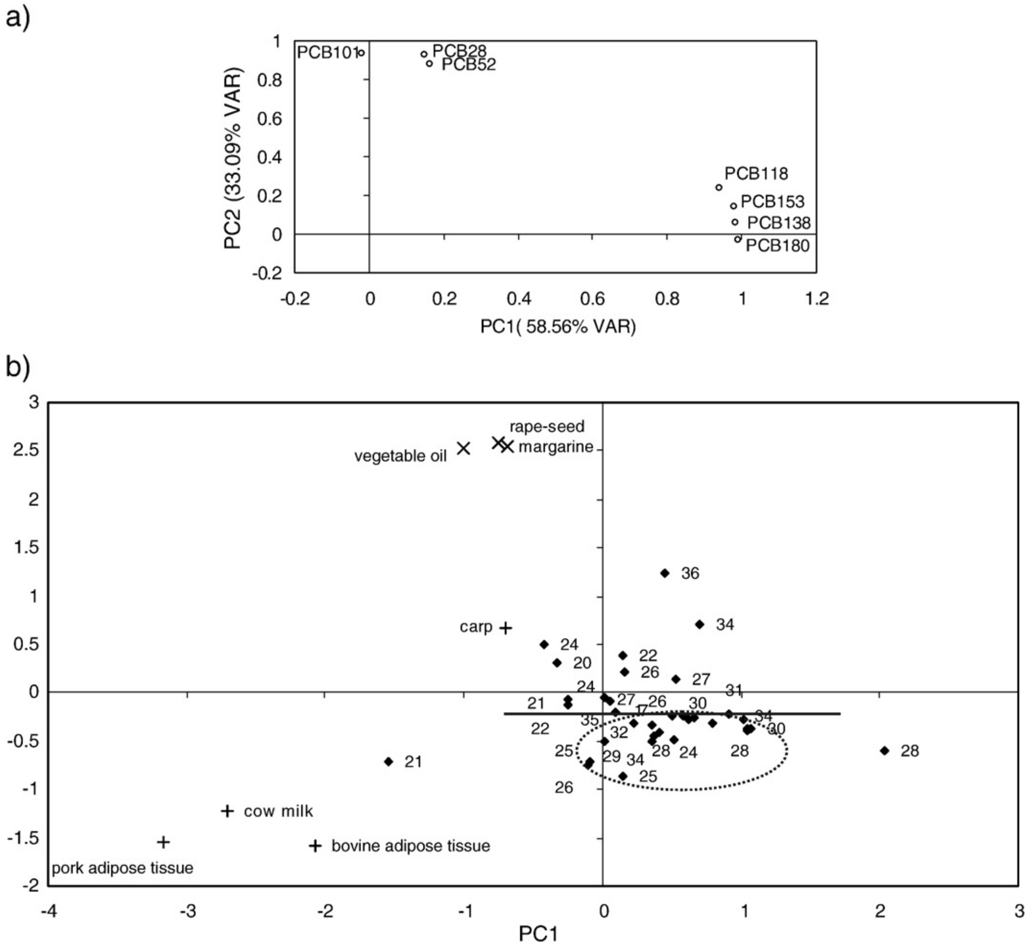

Fig. 3. PC1 vs. PC2 plots after PCA of the set containing the contents of 7 indicator PCB (expressed in ng/g fat) in the Wielkopolska human milk samples and in Polish food samples (Lulek, 2002): a) the loading plot (%VAR is the percentage of the total variance explained by the particular PC), b) the score plot (numbers given to the samples from this study are the mothers' age; dashed line rounded the same samples as in Fig. 2b) and c)).

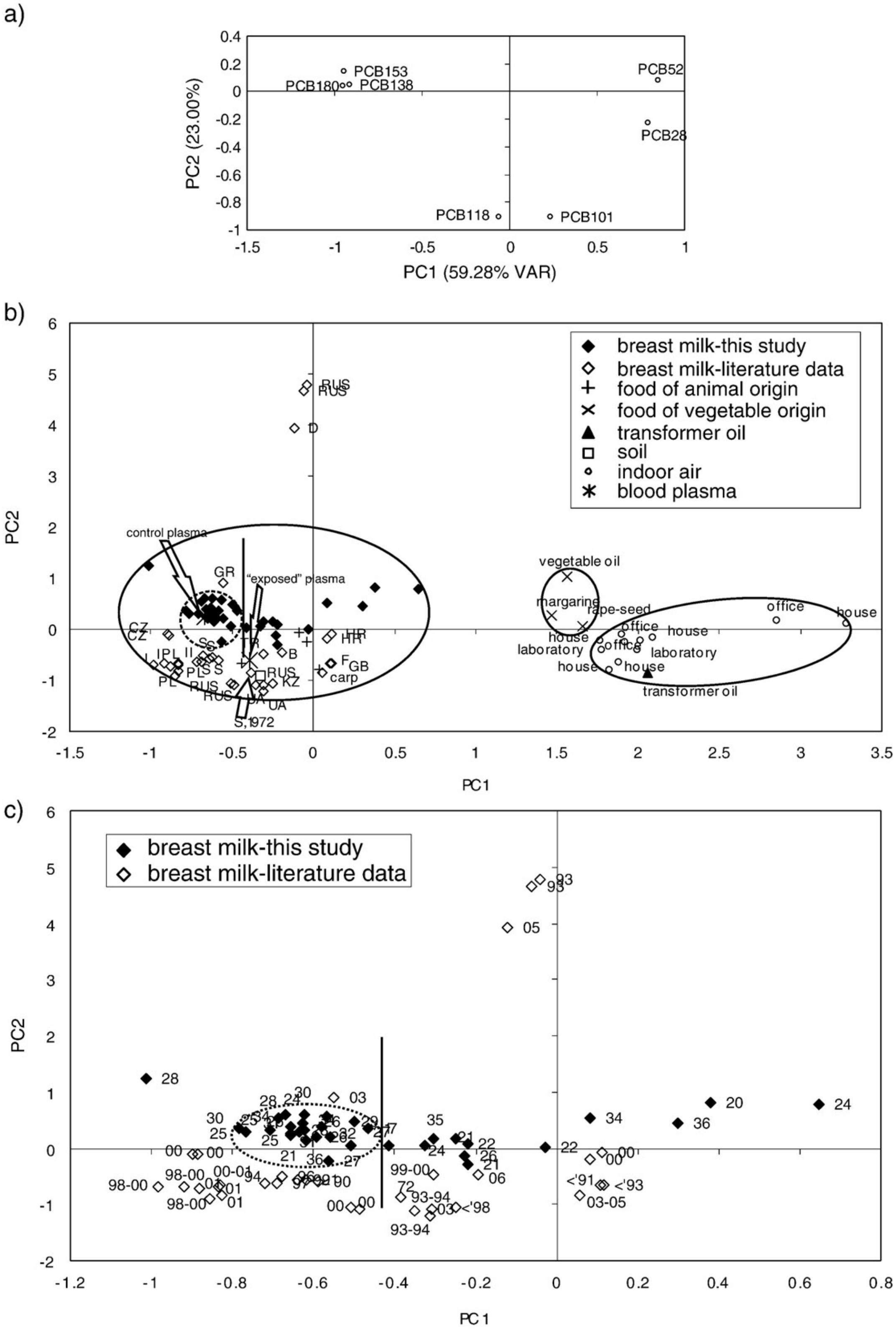

Fig. 4. PC1 vs. PC2 plots after performing PCA to the "International" data set consisting of 7 indicator PCB contents expressed in mass%: a) the loading plot, b) the score plot (the labels of milk samples from different countries used to examine the geographical differences are explained below Fig. 2), c) the close up of the cluster of breast milk samples located around the origin in panel b) (numbers given to the samples from this study are the mothers' age, while those given to the literature data refer to the year of the sampling according to Table S2).

homes to PCBs originating from more significant contributors (sources) than diet. It must be emphasized that potential exposure via indoor environment has not been included in the questionnaire even though in recent years greater attention has been given to it (Tan et al., 2007; Menichini et al., 2007). Some previously published data (Currado and Harrad, 1998; Schade and Heinzow, 1998; Jandacek and Tso, 2001; Heinzow et al., 2004; Hazrati and Harrad, 2006; Wingfors et al., 2006; Rudel et al., 2008) indicated that chances of observing relationships between PCB levels in breast milk and donors habits/characteristics might be enhanced designing the questionnaire in a way to assess also indoor exposure besides the nutritional one, including new furniture/carpet purchases (e.g. in the last decade) either at home or work, cases of recent wood floor sanding, date of the residence building construction, various electronic equipment usage (hours per day) such as computers, microwaves, VCRs, TVs, etc., the season of sampling, etc.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.envint.2009.04.008.

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Principal component analysis for soil contamination with organochlorine compounds

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Abstract

In order to investigate the distribution pattern of individual organochlorine compounds in soil samples collected from the sites (Canary Island – Spain, China, Germany, India, Romania, Russia, Serbia, Swiss, UK) affected by industrial activities to the more remote areas, principal component analysis was performed on the data taken from literature. Loading plots pointed out the strong correlation among the variables. Score plots revealed similar PCB- and OCP-soil patterns for majority of the investigated sites. Nevertheless, the temporal differences of PCB-soil loads have been identified: the late 1990s and early 2000s concentrations are similar to those of the early 1940s, and they are below the levels existed in 1980. The most pronounced PCB concentrations characterized the soil from 1966. For OCPs the influence of sites location on the detected concentration has been revealed: China and India were characterized by comparably higher loads of DDX (DDT and its metabolites) and of HCH-isomers, respectively.

Keywords: Polychlorinated biphenyls; Organochlorine pesticides; Soil; Principal component analysis

1. Introduction

Organochlorine compounds (OCCs) such as polychlorinated biphenyls (PCBs) and pesticides (OCPs) are highly persistent organic pollutants (POPs) that have been identified in diverse environmental matrices worldwide. They have become a major issue of environmental research in order to investigate the level of their occurrence in environmental compartments (Manz et al., 2001; Škrbić and Miljević, 2002; Backe et al., 2004; Chen et al., 2005; Zhang et al., 2005), human exposure and health risk assessment (Hans et al., 1999; Barber et al., 2005).

Soils could be regarded as natural sinks for POPs representing rather a long-term archive for the atmospheric deposition than an indicator for the actual input of these compounds (Schmid et al., 2005). Certain soils receive inputs of such chemicals at contaminated sites (e.g. from pesticide usage, sewage sludge disposal), but on a global scale, very little of the soil surface receives such direct inputs. In contrast, all soils, even in remote areas, receive inputs of POPs from atmospheric deposition.

A number of factors appear to control the fate and behavior of OCCs in the soil matrix: soil physico-chemical properties (e.g. texture, structure and porosity (Cousins et al., 1999; Backe et al., 2004), organic matter content (Backe et al., 2004), moisture content (Hippelein and McLachlan, 2000)), as well as physico-chemical properties of the compounds (e.g. vapour pressure, water solubility (Walker et al., 1996)), meteorological factors (e.g. air temperature (Jury et al., 1987), wind direction (Backe et al., 2004)), proximity to the pollutant sources and, in the case of OCPs, application history and agricultural practices (Boul et al., 1994; Spencer et al., 1996; Backe et al., 2004).

The high variability of the OCCs concentrations determined at various sampling sites and in a range of environment (urban, rural, coastal, remote) requires a very careful evaluation and interpretation. The multivariate statistical

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approaches seem to deliver more substantial information on links among sampling sites, pollutant concentrations (Škrbić et al., 2005; Zhang et al., 2005), latent factors responsible for data set structure and pollutant sources allocated (Goloboćanin et al., 2004).

The aim of the present work is to employ a chemometric method, principal component analysis (PCA), to clarify the general distribution patterns or similarities of individual OCC components occurring in soil collected at various sites with different contribution of potential sources in high set of data and improve the environmental methodology for assessment of the degree of pollution.

2. Materials and methods

2.1. Methods

Multivariate characterization was performed using data for OCCs deposited in soils by a wide variety of natural and anthropogenic sources, previously reported in the literature. Preparing input data for a factor analysis we tried to collect sufficient number of suitable samples in order to provide reliable estimations of the correlations among variables. In principle, the more and better the data are available, the more accurate prediction is possible.

The sources of the data with short description are given in Table 1.

2.1.1. OCCs content vs. soil characteristics

The most comprehensive data set of the available (published) ones was analyzed in order to reveal the correlation between OCCs soil content and soil characteristics. The cooperation project between the Russian Federation and the Federal Republic of Germany in the field of soil protection in connection with soil pollutants provided these results (Franzle et al., 1996).

PCA was performed using previously assayed results on content of six indicator PCB congeners (28, 52, 101, 138, 153 and 180), OCPs (hexachlorobenzene (HCB), *o*,*p*′-DDE, *p*,*p*′-DDE, *o*,*p*′-DDD, *p*,*p*′-DDD, *o*,*p*′-DDT, *p*,*p*′-DDT, α-HCH, β-HCH, and γ-HCH) and soil characteristics (percentage of clay and humus, soil density and the acidity) for soil samples taken at various sites occurring both in areas without direct pollution sources and the ones affected by industrial activities. Half of the determination limit value was accepted as content of investigated OCP and PCB components in the case where their values were below the reported limit of determination.

Soils were sampled across four provinces from both uncontaminated and contaminated areas in Germany and Russia. The average values of the variables determined in the soil samples collected at 16 locations including agricultural fields, forestlands, grasslands and recreational zones were used in this study. Descriptive statistics on data taken from the study of Franzle et al. (1996) are presented in Table 2.

2.1.2. OCC-soil pattern distribution

The second and third groups of data used to compare the PCB- and OCP-pattern distribution in different soil samples, respectively, were compiled from the results gathered from different published studies: the former consisted of data on content of six indicator PCBs (28, 52, 101, 138, 153, 180), while the later one on levels of three HCH-isomers (α-, β-, γ-) and *p*,*p*′-isomers of DDE, DDD and DDT. Due to providing reliable data for PCA half of detection limit value was substituted for sample results that were below the detection or quantitation limit (Helsel, 1990). Considering PCBs, total number of samples analyzed was 49, while for OCPs it was 68. Descriptive statistics of data used to investigate PCB- and OCP-soil pattern by PCA are shown in Table 3.

2.2. Statistical analysis

2.2.1. Principal component analysis

PCA as the multivariate analytical tool is used to reduce a set of original variables and to extract a small number of latent factors (principal components, PCs) for analyzing relationships among the observed variables. Data submitted for the analysis were arranged in matrix. For analysis of correlation between OCCs and soil characteristics 20×16-correlation matrix was established, while for the investigation of OCP- and PCB-soil pattern distribution 6×68- and 6×49-correlation matrices, respectively, were prepared. Data matrices were evaluated through PCA (Massart et al., 1997) allowing the summarized data to be further analyzed and plotted.

The number of factors extracted from the variables was determined by Kaiser's rule (Kaiser and Rice, 1974). This criterion retains only factors with eigenvalues that exceed one. According to Morrison (1967) principal components should account for approximately 75% of the total variance. Throughout the study the software packages STATISTICA 5.0, SPSS 10.0, and S-PLUS 2000 were used. Our intention was to perform data processing in the same way for all cases preferring such a way of the factors rotation to get as many as possible positive loadings to achieve a more meaningful and interpretable solution. In order to interpret the significance of retained PCs in terms of the original variables, only those loadings (coefficients) whose absolute value was greater than 60% of the maximum coefficient in absolute value in each PC were considered (Jolliffe, 1986).

3. Results and discussion

3.1. OCCs content vs. soil characteristics

Five principal components explained 93.9% of the total variance. Loading values and the explained variance mapped to each component after PCA are shown in Table 4. Loadings whose absolute value was greater than 60% of the maximum value in each PC are marked throughout the Table 4 in boldface.

Table 1
Source of data investigated by PCA in this study to obtain PCB- and OCP-soil pattern distribution

Reference	Sample location, year[a]	Description of soil	Number of samples
PCBs			
Alcock et al. (1993)	Northwest England	0–5 cm, a range of land uses such as pasture grassland, forestlands, upland bog, recreational, in rural, semiurban and urban locations	1
Franzle et al. (1996)	Ostashkov and Chelyabinsk provinces in Russian Federation, Bornhoved and Stolberg provinces in Germany, 1992–1993	0–20 cm, agricultural fields, forestlands, grasslands, recreational zones	16
Lead et al. (1997)	Throughout the UK	0–25 cm	1
Meijer et al. (2001)	Semirural location 42 km north of London, UK	0–23 cm, archived soils without direct addition of pesticides, used to assess background pesticide concentration, taken in 1944, 1966, 1980 and 1986	4
Ribes et al. (2002)	Teide Mountain, Tenerife, Canary Island	0–5 cm, soils from three altitudes in the range of 10–2500 m above sea level: agricultural fields, forestlands, scrub	3
Meijer et al. (2003)	Worldwide sites from all five continents, 1998	0–5 cm, remote from potential sources to ensure that they were representative of background levels	1
Schmid et al. (2005)	National soil monitoring network (NABO) sites throughout Swiss, 2002	0–10 cm, topsoil including the organic top layer, forestlands, grasslands, arable lands, pasture, city park	23
OCPs			
Franzle et al. (1996)	Ostaskov and Chelyabinsk provinces in Russian Federation, Bornhoved and Stolberg provinces in Germany, 1992–1993	0–20 cm, agricultural fields, forestlands, grasslands, recreational zones	16
Kumari et al. (1996)	Hisar, Sirsa and Rohtak districts, India	0–15 cm, rice growing areas	3
Hans et al. (1999)	The River Ganga, Kanpur, India	2–15 cm, fields of dry bed of the River Ganga	3
Dumitru (2001)	Romania	The upper layer, agricultural land	1
Škrbić et al. (2002)	Novi Sad, Serbia, 2001	0–5 cm, grassland, recreational zones, agricultural soils	5
Wenzel et al. (2002)	Rosa, Taura, Menz areas, central Germany	0–5 cm, pine forest locations in the vicinity of industrial centers and one is the remote site	3
Nawab et al. (2003)	Aligarh City, UP, India	0–15 cm, agricultural fields	1
Zhu et al. (2005)	Vicinity of Beijing, China	0–30 cm, sandy loam and silt loam	1
Zhang et al. (2005)	Three villages around Guanting Reservoir, Hebei, Beijing, China	0–20 cm, farmland soils	1
Chen et al. (2005)	Guangzhou, China, 1999–2000	0–20 cm, vegetable soils	29
Zhang et al. (2006)	Hong Kong, China, 2000	0-10 cm, forestlands, grasslands, arable lands, wetland, reclamation land	5

[a] Year of sampling are given if it was stated in the article.

Table 2
Descriptive statistics of data on OCCs soil contents (ng g^{-1}) taken from Franzle et al. (1996) study investigated by PCA (number of samples: 16)

Compound	Minimum value	Maximum value	Mean value	Median value	Standard deviation	Skewness
Clay (%)	6.00	48.35	24.38	24.33	13.42	0.34
Density (g cm^{-3})	0.9	1.58	1.26	1.32	0.21	−0.40
pH	2.50	6.98	4.90	5.07	1.09	−0.39
Humus (%)	1.83	28.46	8.74	6.89	7.94	1.91
PCB 28	nd	0.58	0.29	0.25	0.10	1.85
PCB 52	nd	0.50	0.28	0.25	0.09	1.85
PCB 101	nd	5.02	0.90	0.442	1.34	2.64
PCB 138	nd	21.71	4.23	2.92	5.50	2.42
PCB 153	nd	24.54	2.76	0.59	6.09	3.48
PCB 180	nd	15.87	1.70	0.25	3.91	3.60
HCB	nd	12.63	2.16	1.03	3.16	2.70
o,p′-DDE	nd	33.46	2.39	0.25	8.29	3.99
p,p′-DDE	nd	270.7	20.32	1.49	66.88	3.98
o,p′-DDD	nd	1.96	0.37	0.25	0.45	3.31
p,p′-DDD	nd	1.66	0.56	0.40	0.45	1.23
o,p′-DDT	nd	11.63	1.67	0.48	2.96	2.92
p,p′-DDT	0.41	29.28	6.42	2.10	8.72	1.68
α-HCH	nd	1.16	0.45	0.25	0.38	1.11
β-HCH	nd	1.66	0.38	0.25	0.37	3.18
γ-HCH	0.25	2.73	0.57	0.30	0.68	2.79

Table 3
Descriptive statistics of data on OCC contents (ng g^{-1})[a] in soils taken from literature sources presented in Table 1 and analyzed by PCA in order to investigate PCB- and OCP-soil pattern distribution

Compound	Number of samples	Minimum value[b]	Maximum value	Mean value	Median value	Standard deviation	Skewness
PCBs							
PCB 28	49	0.022	106	2.48	0.13	15.11	6.98
PCB 52	49	0.044	21	0.65	0.175	2.97	6.95
PCB 101	49	0.063	7.3	0.68	0.302	1.29	3.99
PCB 138	49	0.01	21.713	1.93	0.8	3.54	4.18
PCB 153	49	0.017	24.54	1.54	0.71	3.60	5.77
PCB 180	49	0.0065	15.875	0.94	0.31	2.35	5.67
OCPs							
α-HCH	68	0.04	46	2.57	0.356	8.00	4.41
β-HCH	68	0.04	103	4.63	0.92	13.61	6.15
γ-HCH	68	0.003	47.35	3.09	0.296	8.37	4.23
p,p′-DDE	68	0.05	270.7	18.79	6.93	39.84	4.60
p,p′-DDD	68	0.003	60	4.01	1.20	8.54	4.69
p,p′-DDT	68	0.003	777.71	27.42	4.425	100.45	6.74

[a] The data are expressed in ng g^{-1} retaining all the figures originally presented.

[b] In statistical analysis, half of detection limit value was substituted for sample results that were below the detection or quantitation limit.

It can be observed that the PC model represented all the variables.

The first PC (PC1), accounting for 38.2% of the total variance, correlated significantly with the contents of PCB 52, 101, 138, 153 and 180. Thus, PC1 substantially described the PCB-contamination of the studied areas. It is interesting to note that the PCB congeners were distributed along PC1 in accordance with the decreasing volatility and biodegradability, i.e. their loading values raised from tetra- to hepta-biphenyl. The only exception was pentabiphenyl (PCB 101), which had higher correlation coefficient (loading value) than hexabiphenyl (PCB 138). Namely, volatility and biodegradability vary significantly among these six congeners, PCB 52 and 101, which are more volatile, easier deposited from the atmosphere, but are also much more readily degraded (Erickson, 1997).

No relationship seemed to be among the PCB-levels and soil characteristics what is in accordance with the results of Lead et al. (1997). The possible reason for this could be thorough environmental mixing of PCBs, so that differences can no longer be seen.

PC2 explained 23.4% of the variance in the original data with *p,p′*-DDE having the major loading. The least chlorinated PCB congener of the analyzed ones, PCB 28, loaded significantly on PC2 together with the pesticides from DDX group (*o,p′*-DDT, *p,p′*-DDD, *o,p′*-DDD, *p,p′*-DDE, *o,p′*-DDE) indicating their same origin – the atmospheric deposition, since PCB 28 is the most volatile

Table 4
Factor loading (varimax rotated) for organochlorine compounds and soil characteristics (Franzle et al., 1996) (marked loadings are higher than 60% of maximum loading on each PC in absolute value)

	PC1	PC2	PC3	PC4	PC5
Clay	0.1031	0.2166	−0.2591	**0.8626**	−0.0215
Density	−0.4901	−0.3040	**−0.6385**	0.0412	−0.0214
pH	0.4531	0.3445	**−0.7596**	0.1756	0.1574
Humus	0.2959	0.1253	**0.8772**	0.0075	−0.0246
PCB 28	−0.0338	**0.7743**	−0.0667	**0.5553**	−0.1950
PCB 52	**0.7336**	−0.0190	0.4726	0.4112	0.1275
PCB 101	**0.9360**	0.0116	0.2902	0.0434	0.1541
PCB 138	**0.9193**	0.2938	0.1347	0.1726	−0.0074
PCB 153	**0.9944**	−0.0034	0.0635	−0.0649	0.0258
PCB 180	**0.9960**	−0.0157	0.0165	−0.0616	0.0090
HCB	0.0655	−0.1192	−0.0663	−0.1854	**0.9237**
o,p′-DDE	−0.0748	**0.9881**	−0.0355	−0.0085	−0.0279
p,p′-DDE	−0.0680	**0.9905**	0.0029	−0.0240	−0.0264
o,p′-DDD	0.2427	**0.9632**	−0.0632	−0.0103	−0.0497
p,p′-DDD	0.4958	**0.7402**	0.2520	0.1429	−0.1756
o,p′-DDT	0.1001	**0.9203**	0.3563	−0.0192	0.0316
p,p′-DDT	0.4044	0.4008	**0.7851**	−0.0471	0.0899
α-HCH	−0.0099	−0.1170	0.2976	**0.9157**	−0.0769
β-HCH	0.1512	−0.0698	**0.7065**	0.4958	0.2734
γ-HCH	0.1278	−0.0779	**0.5963**	0.2809	**0.7199**
Explained variance	7.6383	4.6890	2.8467	2.2525	1.3621
Proportion of total variance (%)	38.2	23.4	14.2	11.3	6.8

congener, while OCPs are still routinely found in the atmosphere. Examined soil characteristics did not influence PC2 as the degradation of DDX in soil is a very complicated reaction. This finding suggested that the used soil characteristics are insufficient to assess the soil ability to sorb these pesticides.

Accounting for 14.2% of the variance, PC3 substantially described the soil characteristics at the examined locations. Apparently, *p,p*′-DDT, β-HCH and γ-HCH seemed to respond to such variation with positive effects from humus and negative with pH and density. In other words, the organic component of soil was responsible for the adsorption of aforementioned pesticides, which is in agreement with previously published data (Bollag and Loll, 1983; Al-Ghadban et al., 1994), while lower values of pH and density favors the accumulation of the ones. The latter presumption concerning the soil pH is supported by a study done by Carter and Suffet (1982), who showed that DDT binding to humus increased as pH decreased. In addition, the observed negative correlation between soil pH and humus indicated that the source of soil acidity was from organic matter decomposition coinciding with literature data (Jiries et al., 2002). The higher loading value of β-HCH to γ-HCH can be explained by the isomeration of later one to β-HCH, which is energetically more favorable (Manz et al., 2001).

In PC4, which explained 11.3% of the variance, the absolute loadings of α-HCH, PCB 28 and clay content of the soils were significant. Apparently, in the soil samples investigated here, the most volatile compounds regarding the analyzed ones, i.e. α-HCH and PCB 28, seemed to be dependent on clay content. This is in agreement with the finding of Bollag and Loll (1983), who showed that the adsorption of OCCs depends on the type of compounds and the kind of clay.

The fifth principal component, PC5, describing a residual, yet important 6.8% of the variance, correlated well with HCB and γ-HCH (lindane) suggesting the same origin of these pesticides in soils. Historically, HCB has been found as an impurity in several chlorinated pesticides including lindane, due to its formation as a by-product during production process (Barber et al., 2005).

Naturally, all of these statements are valid within the scope of the investigated data set (Franzle et al., 1996). Soils from other regions might behave differently.

3.2. *OCC-soil pattern distribution*

The distribution of the investigated pollutant classes was subsequently examined by applying the PCA to two sets of data related to PCB and OCP soil contents, respectively, obtained in various studies (Table 1). The applications of PCA permitted to draw the following:

(a) Two underlying factors explaining 96.6% of the original data variance governed the distribution of indicator PCBs in the studied soils: PC1 (accounting for 57.1% of the total variance) was influenced by more chlorinated congeners PCB 138, 153, 180 having loadings 0.9480, 0.9880, 0.9765, respectively; PC2 (accounting for 39.4% of the total variance) was related to the content of the lower chlorinated congeners PCB 28 and 52 (loadings were: 0.9948 and 0.9976, respectively), as well to the PCB 101 (0.8049), which loading on PC1 could not be rejected as negligible (0.5680, i.e. 57% of the maximum loading on PC1 in absolute value). A good correlation (Fig. 1) existed between less chlorinated congeners (28 and 52) on one

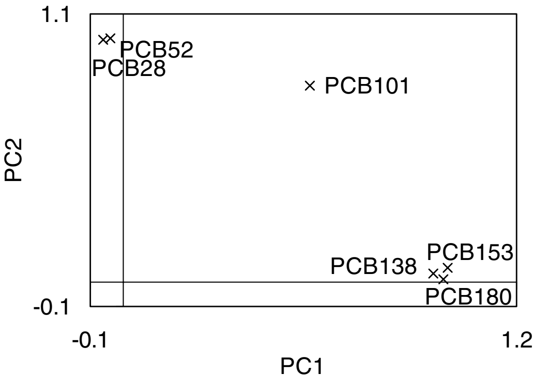

Fig. 1. Loadings plot of PC1 vs. PC2 from the data set containing information on indicator PCBs presence in soils.

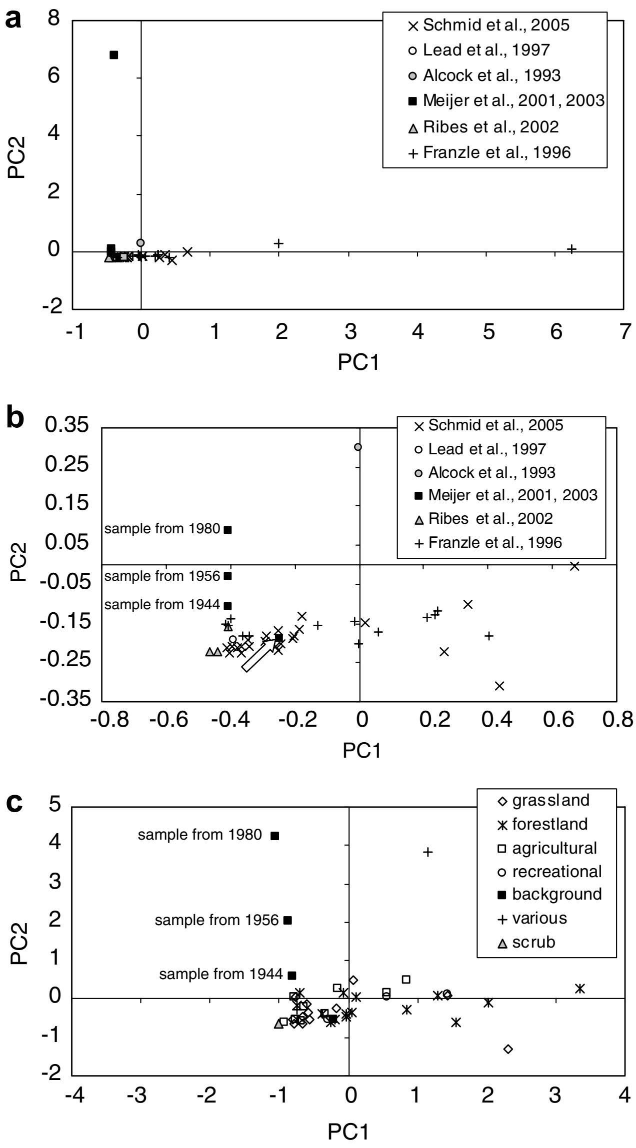

Fig. 2. Score plot of the first two principal components from the data set containing information on indicator PCBs presence in soils: (a) all samples included; (b) close-up of the cluster formed in (a) (arrow points out the position of the soil representing the average background level of the sites worldwide (Meijer et al., 2003)); (c) after the elimination of three outliers and subsequent PCA on 6 × 46-correlation matrix.

hand and on the other between those more chlorinated (138, 153, 180). Such results clearly differentiated indicator congeners of different volatility: more volatile ones represented by PCB 28 and 52 on one hand and those less volatile like PCB 138, 153 and 180 on the other, with PCB 101 of intermediate volatility in between. This finding suggested that the clustering of samples was governed by physico-chemical properties of the congeners, indicating that PCA may be useful in discrimination between samples based on the compound properties.

The sample sites on the PCA-score plot are shown in Fig. 2a with most of the sites located near the origin. The results reflected the relatively low concentrations of PCBs in most of the soils, as the origin represents the mean concentration of all samples. These have probably been subjected to long-range transport of PCBs rather than short-range transport from local sources. Three outlying samples could be observed: one is the sample with the highest loads of lower chlorinated PCBs (106 ng PCB 28 g^{-1}, 21 ng PCB 52 g^{-1} and 7.3 ng PCB 101 g^{-1}; see Table 3) from the period of intense PCBs usage (i.e. sample from 1966, Meijer et al., 2001) and two with pronounced loads of more chlorinated PCBs, which represented the average PCB contents in the gardens and forests located in German province affected by enhanced industrial activities (21.7 and 10.2 ng PCB 138 g^{-1}, 24.5 and 7.52 ng PCB 153 g^{-1}, 15.9 and 4.15 ng PCB 180 g^{-1}, respectively (Franzle et al., 1996)), probably due to proximity to local emission sources.

The close-up of the formed cluster in the score plot of PC1 vs. PC2 without aforementioned outliers (Fig. 2b) offered a better projection of the discrimination between the samples. Majority of the samples were around the one representing the average background level of the sites worldwide (Meijer et al., 2003; see Table 2). Regarding the late 1990s and early 2000s (majority of the samples in the third and fourth quadrant of score plot, Fig. 2b) the PCB soil contents have declined substantially since their elevated levels in the 1980s and early 1990s (points in the second quadrant, Fig. 2b, represented by the composite archived sample from 1980 (Meijer et al., 2001) and the average content of 39 samples in northwest England (Alcock et al., 1993)). As well as, the PCB-loads in samples from late 1990s-early 2000s coincided with the ones from 1956 and 1944 (Meijer et al., 2001), which represent the period before intense industrial manufacture and application of PCBs. Differentiation according to the geographical origin of the samples could not be seen confirming previously assumption of the uniform distribution pattern of PCBs at various locations due to atmospheric deposition.

In order to examine whether discrimination of the samples could be assign to a landuse difference, subsequent PCA was performed. Knowing that outliers can mask the structure of the other data, they were eliminated before

PCA was applied again. Score plot of 46 points remaining after the elimination of the outliers is shown in Fig. 2c. It is interesting to note that majority of the samples (42.9%) on the positive (right) side of PC1 were from the forestlands. These samples had increased contents of PCB 138, 153 and 180 (above 1 ng of each g^{-1}). It has been previously shown by McLachlan and Horstmann (1998) that decaying leaf litter will increase the supply of POPs in forest soils, which may be more effective sinks than agricultural soils. The heavier PCBs deposited by decaying vegetation will probably remain in the soil while the lighter PCBs are subjected to volatilization (Backe et al., 2004). Further discrimination of the PCB loads on the base of a landuse differences could not be seen.

(b) Two underlying components explaining 66.1% of the original data variance governed the distribution of DDX and HCHs. However, in order to describe more of the total variance without considerable loss of information three PCs were retained accounting for 79.0% of the variance: PC1 (accounting for 41.8% of the total variance) was dominated by HCH-isomers (loadings were 0.9644 for α-HCH, 0.7219 for β-HCH, 0.9208 for γ-HCH); PC2 (accounting for 24.3% of the total variance) was related to the content of the *p*,*p*′-isomers of DDD and DDT having loadings as follows: 0.7337 and 0.8203, respectively; PC3 (accounting for 12.9% of the total variance) was dominated by *p*,*p*′-DDE with loading 0.9709. The correlation between α- and γ-HCH was unambiguous and significant; thus, α- and γ-HCH carried out almost the same information. There were no correlation observed between *p*,*p*′-isomers of DDT and the metabolites implying the complexity of DDT degradation behavior under various conditions.

Score plot (Fig. 3a) revealed resemblance among the majority of the analyzed soils but more outlying samples emerged than in the case of PCB-soil pattern analysis (Fig. 2a). Outliers were the agricultural soils from China (Chen et al., 2005; Zhu et al., 2005), Romania (Dumitru, 2001) and Germany (Franzle et al., 1996) due to high DDX-loads (the sum contents were in the range 112–831 ng g^{-1}), suggesting most likely a combination of heavy historical use of DDT and the retarded degradation in soils, or less likely its recent use even though it has been illegal in these countries. Moreover, in the case of China the elevated DDX levels might result from the possible use of Dicofol containing 5–10% DDT as impurity (Zhu et al., 2005) and which use is still allowed (Zhang et al., 2005). Also the samples from India (Kumari et al., 1996; Nawab et al., 2003) emerged as outliers due to pronounced HCH-loads (the sum HCH-contents were in the range of 48–144 ng g^{-1}) pointing out recent and/or excessive use of HCHs in those locations.

The close-up of the score plot (Fig. 3b) without outliers revealed subclustering of the majority of soils collected in China (Chen et al., 2005), due to pronounced content of DDX compounds. Also, another subcluster could be seen, consisting of three sites from India (Hans et al., 1999), one from Germany (Wenzel et al., 2002) and one from Serbia (Škrbić et al., 2002). These sites had elevated contents of HCH-isomers. The rest (four) of the samples representing the soils from urban area in Serbia (Novi Sad, the capital of the Vojvodina Province, at the north of Serbia) in 2001 (Škrbić et al., 2002) were similar to the other analyzed in this study, coinciding with the existing OCP soil pattern distribution.

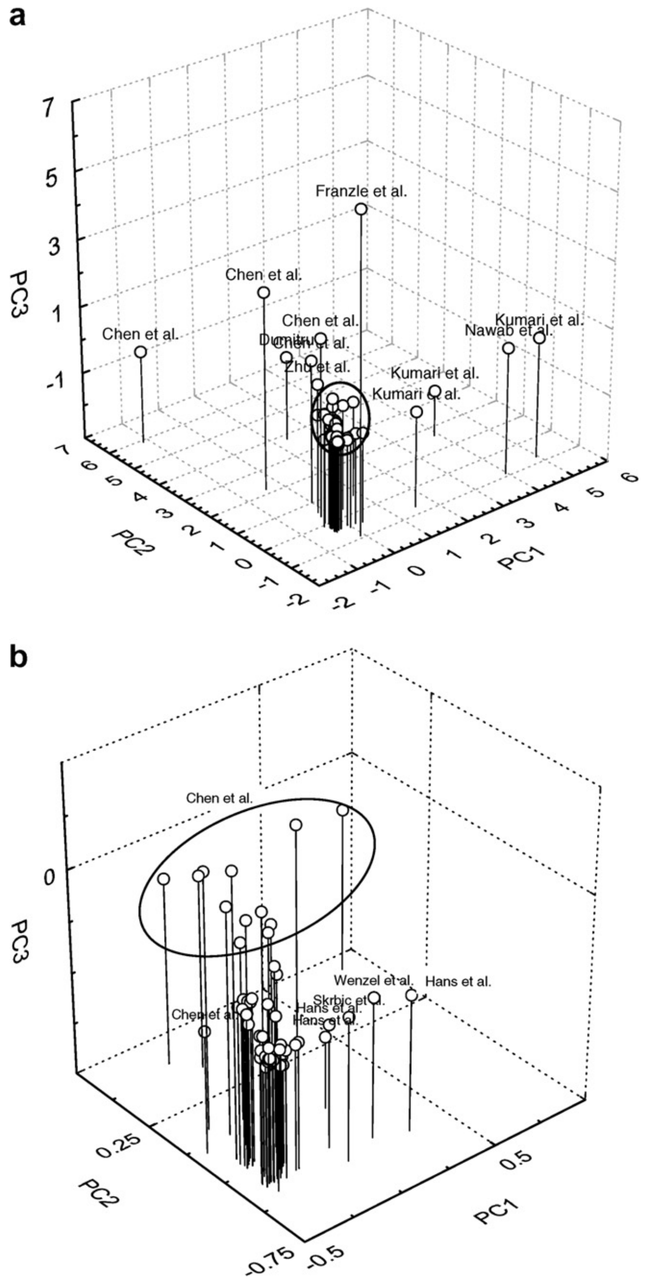

Fig. 3. Score plot of three principal components from the data set containing information on selected OCPs presence in soils: (a) all samples included; (b) without outliers.

4. Conclusions

Principal component analysis (PCA) was used to provide an overview of PCB- and OCP-soil pattern distribution in soils collected from various countries. Most sample sites were located near the origin of the PCA score plots, reflecting a low concentration of investigated organochlorine compounds in the late 1990s and early 2000s. The outliers were the sites from Germany, Romania, China and India.

The investigation also illustrated the correlations between some soil characteristics and OCCs presence. Nevertheless, while progress continues to be made in understanding issues related to OCCs, further investigation is needed to better comprehend the behavior of OCCs under various soil conditions.

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Distribution of Chlorinated Organic Pollutants in a Wide Variety of Soils from Europe and Asia: A Multivariate Statistical Approach

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Abstract. Principal component analysis was used to interpret the levels of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) previously determined in a wide variety of soils from Europe and Asia to (1) examine the interdependencies among them and chosen soil charaeteristics and (2) reveal PCB– and OCP–soil patterns throughout Europe and Asia. Loading values suggested correlations between the levels of certain compounds and soil characteristics, revealing the underlying structure of analyzed data; humus content, pH, and density correlated with the contents of p,p'-DDT, β-hexachlorocyclohexane (HCH) and γ-HCH, and clay content correlated with the concentrations of α-HCH and PCB 28. Component scores reflected relatively low concentrations of six "marker" PCBs in most of the soils, pointing out the outliers in the proximity of the local PCB sources. PCB loads in the 1990s and early 2000s were lower than the ones in 1980 and 1956, and they coincided with the soil levels in 1944. PCBs 138, 153, and 180 had the greatest influence of the six investigated congeners on soil-pattern differences. In relation to the OCP soil loads, the score plot revealed regions with recent and/or enhanced application of DDT and HCH.

Soils are important reservoirs for many persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), representing rather a long-term archive for atmospheric deposition rather than an indicator for the actual input of these compounds (Schmid *et al.* 2005). POPs are very persistent in soils (Mackay 2001). Hence, as POPs are released or escape into the environment, the burden in soils worldwide becomes a complex function of the balance between inputs and losses. The distribution of POPs in surface soils worldwide is a complex function of proximity to source regions, the long-range atmospheric transport potential of the POPs in question, environmental and climatic conditions, and properties of the overlying vegetation and soil-type system (Meijer *et al.* 2003).

The high variability of the organochlorine compound (OCC) soil concentrations obtained at various sampling sites requires a careful evaluation and interpretation. Multivariate statistical approaches, such as principal component analysis (PCA), seem to deliver more information on links among sampling sites, pollutant concentrations, correlation patterns, and latent factors responsible for the data-set structure. Application of PCA proves to be a useful task for the interpretation of large sets of data.

In this work, PCAs were performed on data matrices consisting of information gathered from the relevant published data to find out which soil characteristics had influence on the presence of OCPs and PCBs in soils; to clarify the soil-distribution patterns of these compounds; and to evaluate their spatial distribution throughout Europe and Asia to determine their regional variability.

Materials and Methods

The extent of the present investigation was limited by consistency among many studies that have been focused on the presence of OCCs in soils concerning the number of the analyzed compounds. In this work, only those studies comparable with each other regarding the analyzed compounds were investigated. Also, by seeking comparable analyte profiles, the number of PCB congeners reported were necessarily limited; therefore, for PCB soil profiles, only six indicator congeners were used. Furthermore, information on soil characteristics in those studies is mostly incomparable and often missing, making impossible direct comparison of them. For this reason, three groups of data were analysed by PCA to investigate correlation between PCB and OCP soil loads and soil characteristics and to reveal PCB and OCP soil patterns throughout Europe and Asia.

To reveal the correlation between OCC soil content and soil characteristics, the most comprehensive data set of the ones available was analyzed. The cooperation project between the Russian Federation and the Federal Republic of Germany in the field of soil protection in connection with soil burden of OCCs provided these results (Franzle *et al.* 1996).

PCA was performed using previously assayed results on content of six "marker" PCB congeners (28, 52, 101, 138, 153, 180) and OCPs (hexachlorobenzene, o,p′-dichlorodiphenyldichloroethylene [DDE], p,p′-DDE, o,p′-(dichlorodiphenyldichloroethane) [DDD], p,p′-DDD, o,p′-DDT, p,p′-DDT, α-hexachlorocyclohexane [HCH], β-HCH, and γ-HCH) in soil samples taken at various sites occurring both in areas

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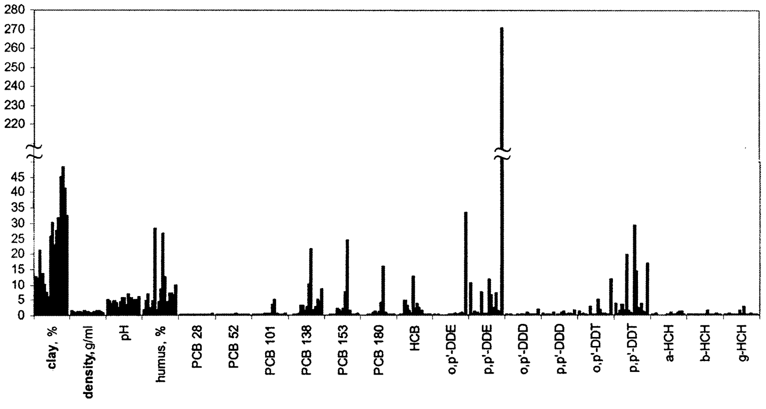

Fig. 1. The range of data (Franzle *et al.* 1996) (compound contents are in ng/g) used in PCA to examine correlations between OCCs and soil characteristics

without direct pollution sources and in areas affected by industrial activities. Censored data were replaced with the half of the corresponding analytic determination limits ranging from 0.25 to 0.5 ng/g dry weight (Franzle *et al.* 1996), to minimize the loss of information. Percentage of clay and humus in the soil samples, soil density, and acidity (pH) were also included in the input matrix because these parameters are known to affect both current concentrations in the soil system and possible adsorption on various soil characteristics (organic substance and sometimes also clay).

Soils were sampled across two German (Stolberg and Borhoved) and two Russian (Ostashkov and Celyabinsk) provinces. Average values of the variables determined for the soil samples—collected from various locations at 16 sites, including arable fields, woodlands, grasslands, children playgrounds, and gardens—were used in this study.

(Figure 1) shows the range of soil parameters and OCC soil loads according to data taken from Franzle *et al.* (1996) and expressed as ng/g dry weight.

The second and third groups of data map which were compiled of the results from different studies, were used to compare PCB and OCP patterns in different soil samples across Europe and Asia, respectively: the former consisted of data on the content of six indicator PCBs (28, 52, 101, 138, 153, and 180), whereas the latter one consisted of levels of six OCPs (three HCH-isomers [α-, β-, γ-] and p,p'-isomers of DDE, DDD, and DDT). Because the detection limits and the expression of the undetectable contents of the analyzed compounds were different (*e.g.*, "not detected" or below the value of the detection limit) depending on the laboratory, for statistical analysis a nil concentration for these ones to avoid discrepancies between the studies was assumed. Considering OCPs, the total number of samples analyzed by PCA in this study was 68, and for PCBs was 49. The sources of the data and short descriptions are listed in Table 1.

(Figures 2a and 2b) show the range of PCB and OCP soil loads at investigated sites according to data taken from studies listed in Table 1.

Data Analysis

PCA as the multivariate analytic tool is useful in reducing a set of original variables to extract a small number of latent (underlying) components called "principal components" (PCs). It has been widely used for exploratory data analysis as well as for explaining the correlation among variables (Meglen 1992; Golobočanin *et al.* 2004; Zhang *et al.* 2005; Lead *et al.* 1997; Manz *et al.* 2001, Montes-Botella & Tenorio 2003; Sanders *et al.* 2002; Škrbić *et al.* 2005b, 2005c; Škrbić and Onjia 2006; Zhao *et al.* 2005). The algorithm of PCA can be found in the standard textbooks (Vandeginste *et al.* 1988; Otto 1999). The Statistica for Windows program package (version 5.0, StatSoft Inc., Tulsa, OK, USA) was used for PCA.

OCC contents were taken as variables (column of the input matrix), and soil samples from various locations were taken as mathematic–statistic cases (rows of the matrix). Some variables are expressed on a different scale. So that certain variables did not dominate the solution, PCA was carried out on the correlation matrices of the data established in the following manner: first, the data were mean centered (column means were substracted from each matrix element). Then each matrix element was divided by the SD (standard deviation) of the respective column. Thus, the data were centered to zero and scaled to unit variance. For analysis of correlations between OCCs and soil characteristics, the 20×16 correlation matrix was obtained and investigated by PCA, whereas for the investigation of OCP and PCB soil patterns 6×68 and 6×49 correlation matrices respectively, were analyzed.

The number of relevant PCs extracted from the variables was determined by applying Kaiser's rule. This criterion retains only PCs with eigenvalues >1. According to Morrison (1967), PCs should account for approximately 75% of the total variance.

Varimax rotation was performed to get as many positive loadings as possible to achieve a more meaningful and interpretable solution. To interpret the significance of retained PCs in terms of the original variables, only those loadings (coefficients) whose absolute value was >60% of the maximum coefficient in absolute value in each PC were considered (Joliffe 1986).

Results and Discussion

PCA was used to investigate the correlations among the OCC content and characteristics of soil (data from Franzle *et al.* 1996), This method also allowed the identification of the different groups of OCCs that correlated and therefore can be considered as having similar behaviour and/or a common origin along the studied areas. The essential feature of PCA is to reduce a large number of original variables to a smaller number of PCs. In this study, 93.9% of the total variability of 20 variables (6 PCBs, 10 OCPs, and 4 soil characteristics) was explained by 5 PCs. Graphic representations of these results are shown in Figures 3a through 3e. The following results can be observed:

1. The first PC (PC1) was significantly associated with PCBs (see Fig. 3a), the loadings of which increased in accordance with decreasing volatility and biodegradability; among these congeners both PCBs 52 and 101 are more volatile, more easily deposited from the atmosphere, and much more readily degradated. The absence of correlation between PCB loads and soil characteristics could be the consequence of thorough environmental mixing of PCBs such

Table 1. Data investigated in this study by PCA to obtain PCB and OCP soil patterns

Sample type (label)	No. of samples	Sample location (number of samples each location)[a]	Reference (year of sampling)[b]
PCBs: Grassland (g1)	12	Germany (2), Russia (2), Swizerland (8)	Franzle *et al.* 1996 (1992–1993) Schmid *et al.* 2005 (2002)
PCBs: Woodland (w)	16	Germany (2), Russia (2), Swizerland (11), Tenerife Island, Spain (1)	Franzle *et al.* 1996 (1992–1993) Ribes *et al.* (2002) Schmid *et al.* 2005 (2002)
PCBs: Arable (ar)	8	Germany (2), Russia (2), Swizerland (2), Tenerife Island, Spain (2)	Franzle *et al.* 1996 (1992–1993) Ribes *et al.* 2002 Schmid *et al.* 2005 (2002)
PCBs: Garden (g)	3	Germany (1), Russia (1), Swizerland (l)	Franzle *et al.* 1996 (1992–1993) Schmid *et al.* 2005 (2002)
PCBs: Recreational (rec)	3	Germany (2), Swizerland (1)	Franzle *et al.* 1996 (1992–1993) Schmid *et al.* 2005 (2002)
PCBs: Background (bcg)	5	UK (4), worldwide, *i.e.*, across all of the 5 continents (1)	Meijer *et al.* 2001 (1944, 1956, 1966,1980) Meijer *et al.* 2003 (1998)
PCBs: Various (var)	2	UK (2)	Alcock *et al.* 1993 Lead *et al.* 1997
OCPs: Grassland (g1)	6	China (1), Germany (2), Russia (2), Serbia (1)	Franzle *et al.* 1996 (1992–1993) Škrbić *et al.* 2002 (2001) Zhang *et al.* 2006 (2000)
OCPs: Woodland (w)	8	China (1), Germany (5), Russia (2)	Franzle *et al.* 1996 (1992–1993) Wenzel *et al.* 2002 Zhang *et al.* 2006 (2000)
OCPs: Arable (ar)	41	China (31), India (4), Germany (2), Romania (1), Russia (2), Serbia (1)	Kumari *et al.* 1996 (1992–l994) Franzle *et al.* 1996 (1992–1993) Dumitru 2001 Škrbić *et al.* 2002 (2001) Nawab *et al.* 2003 Chen *et al.* 2005 (2002) Zhang *et al.* 2005 (2003) Zhang *et al.* 2006 (2000)
OCPs: Garden (g)	3	Germany (1), Russia (1), Serbia (1)	Franzle *et al.* 1996 (1992–1993) Škrbić *et al.* 2002 (2001)
OCPs: Recreational (rec)	4	Germany (2), Serbia (2)	Franzle *et al.* 1996 (1992–1993) Škrbić *et al.* 2002 (2001)
OCPs: Wetland (wt)	1	China (1)	Zhang *et al.* 2006 (2000)
OCPs: Reclamation (rec1)	1	China (1)	Zhang *et al.* 2006 (2000)
OCPs: Unknown (unkn)	4	India (3), China (1)	Hans *et al.* 1999 Zhu *et al.* 2005

[a] Labels of samples from different countries used to examine the geographic differences are as follows: China–C, Germany–D, India–I, Romania–Ro, Russia–R, Serbia–Serb, Spain–S, Swiss–Ch

[b] Year of sampling is given if it was stated in the article.

that differences could no longer be seen. A similar finding was obtained by Lead *et al.* (1997).

2. The second PC (PC2) had large positive coefficients for the majority of the DDX compounds (DDT and its metabolites DDD and DDE) and PCB 28 (see Fig. 3b), pointing out their same origin: atmospheric deposition. Loading values of DDX compounds decreased in the following order—p,p′-DDE $\sim$ o,p′-DDE $\sim$ o,p′-DDD $\sim$ o,p′-DDT $\sim$ p,p′-DDD—indicating that DDT residues were from ‘‘old’’ sources. Examined soil characteristics did not influence PC2, even though hydrophobic OCPs are considered to be easily adsorbed by soil organic matter. This suggests that residue levels were a reflection of DDT application history and dissipation rates rather than air–soil equilibrium, which is similar to soils from China (Zhu *et al.* 2005), Alabama (Harner *et al.* 1999), Georgia, and South Carolina (Kannan *et al.* 2003).
3. The third PC grouped β-HCH, p,p’-DDT and humus, and a negative load for pH (Fig. 3c). In other words, humus was responsible for the adsorption of the aforementioned pesticides,which is in agreement with previously published data (Bollag & Loll 1983; Cheng *et al.* 1986, Al-Ghadban *et al.* 1994), whereas lower pH values favored accumulation of the ones in lower-density soils. The presumption concerning soil pH is supported by a study by Carter and Suffet (1982), who showed that DDT binding to aquatic humus increased as pH decreased.
4. The fourth PC (PC4) corresponded to α-HCH, PCB28, and clay content (see Fig. 3d). Because PCB28 was also loaded on PC2, PC4 accounted for only part of the variation in PCB 28 content that was left unexplained by PC2. OCCs in general seem to preferentially adsorb to organic matter rather than clay, but this depends on the type of compounds and the kind of clay (Stevenson 1976). Apparently, in the soil samples investigated here, the presence of the most volatile compounds of the analyzed OCCs, *i.e.*, α-HCH and PCB28, seemed to be dependent on clay content.
5. The fifth PC correlated well with HCB and γ-HCH (lindane) (see Fig. 3e), suggesting the possibility of the

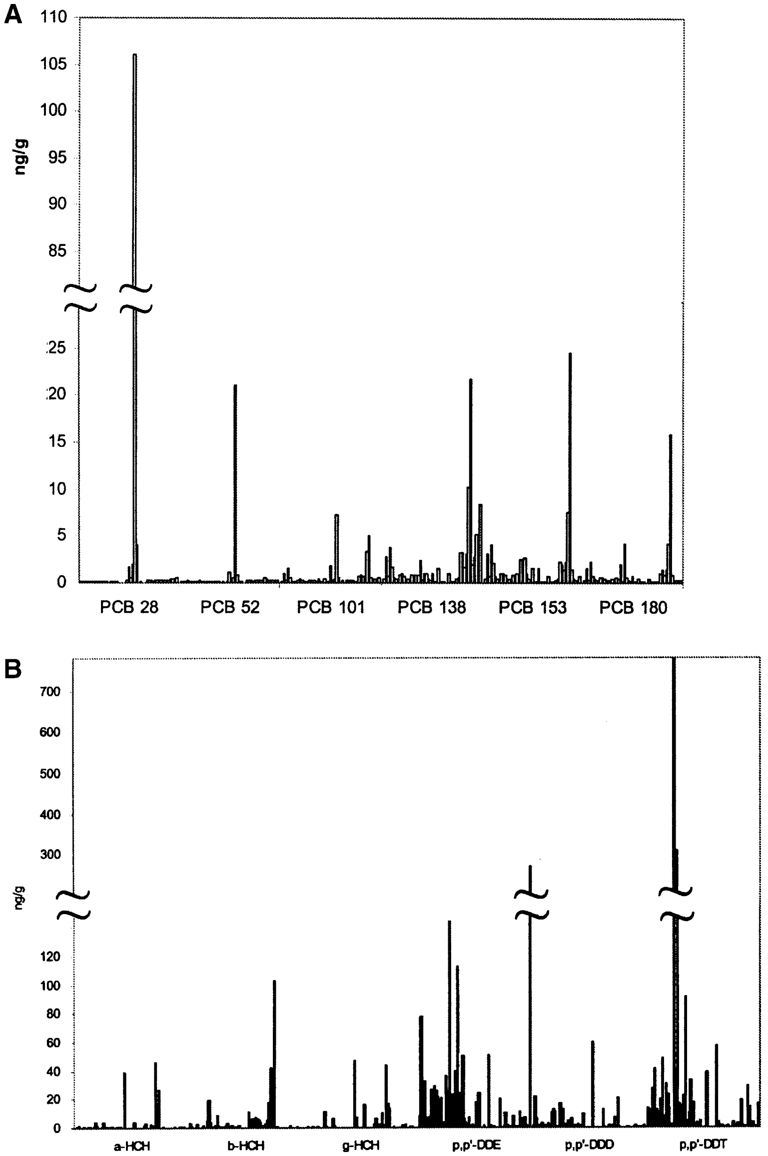

Fig. 2. The range of data taken from various studies (details presented in Table 1) used in PCA to examine soil pattern of PCBs (a) and OCPs (b) throughout Europe and Asia

identical origin of these pesticides in soils. Historically, HCB has been found as an impurity in several chlorinated pesticides, including lindane, because of its formation as a by-product during the production process (Barber *et al.* 2005).

Naturally, all of these statements are valid within the scope of the investigated data set (Franzle *et al.*1996); soils from other regions might behave differently.

The spatial distribution of the investigated pollutant classes was subsequently examined by applying PCA to the datasets obtained in various studies for a wide variety of soils from Europe and Asia (Table 1). To assess the effect of different land use and geographic origin of soils on OCC loads, the samples were labeled as listed in Table 1, taking into account their landuse type and the country where samples were collected.

The applications of PCA to the PCB data set showed the following: two underlying factors explaining 96.6% of the original data variance governed the distribution of six indicator PCBs in the investigated soils: PC1 (accounting for 57.1% of the total variance) was influenced by more chlorinated congeners *i.e.*, PCBs 138, 153, and 180, with loadings of 0.9480, 0.9880, and 0.9765, respectively; PC2 (accounting for 39.4% of the total variance) was related to the content of the lower-chlorinated congeners, i.e., PCBs 28 and 52 (loadings were 0.9948 and 0.9976 respectively) as well to PCB 101 (loading 0.8049), whose loading on PC1 could not be rejected as negligible (loading 0.5680, *i.e.*, 57% of the maximum absolute value of loading on PC1). A good corelation (loading plot not shown) existed between less-chlorinated congeners (PCBs 28 and 52) on one hand and between those more chlorinated on the other hand (PCBs 138, 153, and 180). Such results clearly differentiated indicator congeners of different volatility: more volatile ones represented by PCBs 28 and 52 and those less volatile such as PCBs 138, 153, and 180 with PCB 101 of intermediate volatility in between. This finding differed slightly from the results of the analysis performed on Franzle *et al.* data (Fig. 3), but nonetheless it still remains that the clustering of samples was governed by physicochemical properties of the congeners, indicating that PCA may be useful

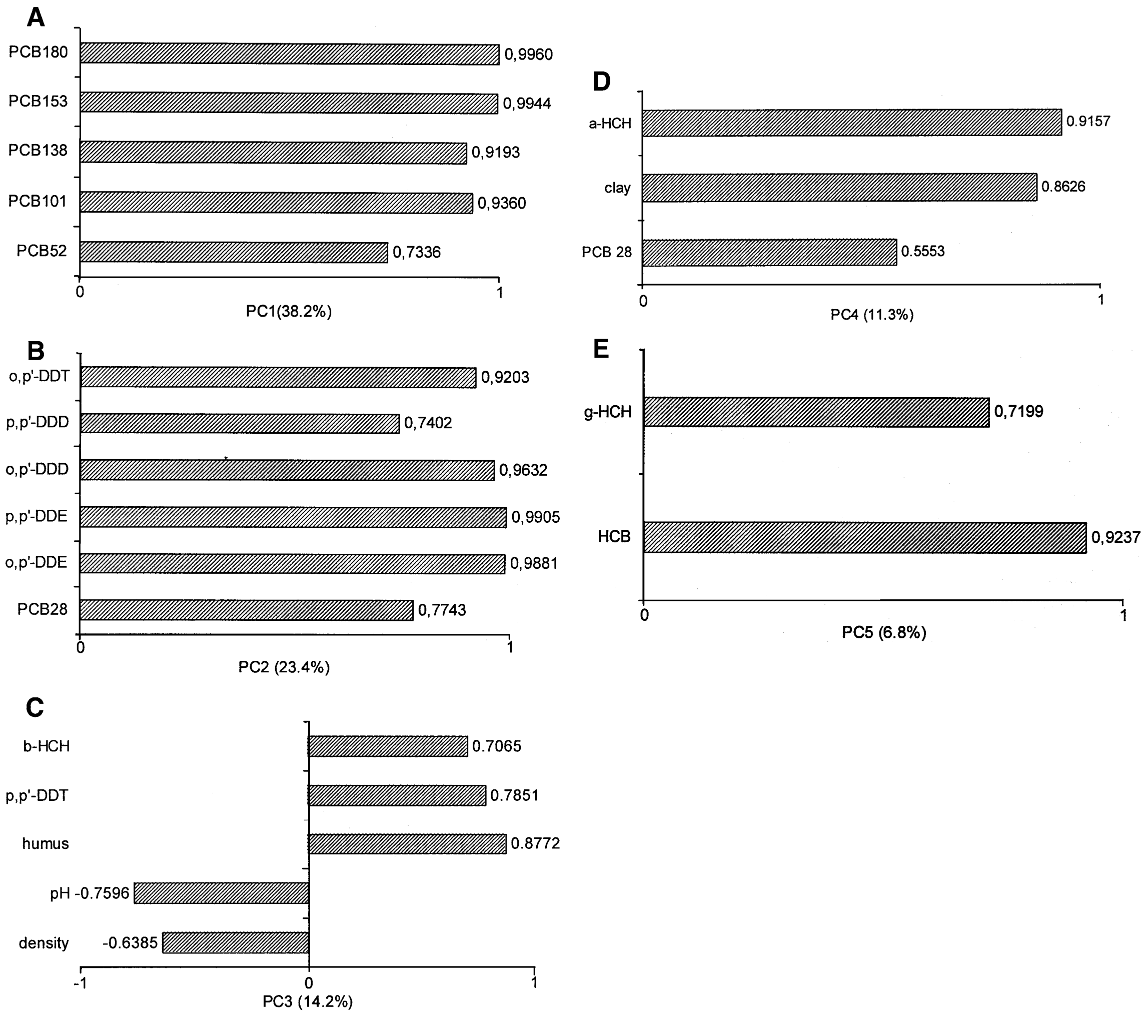

Fig. 3. Results of PCA for dataset of Franzle et al. (1996): graphic representation of loadings on PC1(A), PC2(B), PC3(C), PC4(D), and PC5(E). The percentages of each PC are show in parentheses

in discriminating between samples based on the compound properties.

The sample sites on the PCA score plot are shown in Figure 4a, with most of the sites (93.9%) located near the origin. Because the origin represents the mean concentration of all samples, this reflected the relatively low concentrations of PCBs in most of the soils (van Wijngaarden *et al.* 1995), which have probably been subjected to long-range transport of PCBs rather than short-range transport from local sources. Three outlying samples could be observed. One was the sample with the highest loads of lower-chlorinated PCBs (106 ng PCB 28/g, 21 ng PCB 52/g, 7.3 ng PCB 101/g) was from the period of intense PCB use (*i.e.*, archived sample taken in 1966; Meijer *et al.* 2001). Two pronounced loads of more-chlorinated PCBs, which were taken from the gardens and woods located in Germany (PCB 138: 21.7 and 10.2 ng/g; PCB 153: 24.5 and 7.52 ng/g, and PCB 180: 15.9 and 4.15 ng/g, respectively [Franzle *et al.* 1996]). All were probably outliers because of the proximity of local emission sources.

Knowing that outliers can mask data structure, they were eliminated before subsequent PCA was carried out. Again, two PCs were retained that explained 77.7% (44.1% and 33.6%, respectively) of total variance with a similar distribution of the PCB congeners between them: PC1 was significantly associated with more-chlorinated congeners (PCBs 101, 138, 153, and 180), whereas PC2 represented less-chlorinated PCBs 28 and 52. A score plot of 46 points remaining after the elimination of the outliers is shown in Figure 4b. In interpreting the diagram, following points should be noted:

1. There was no observed land-use difference among the samples. However, it is interesting to note that 46.6% of the woodland samples were on the positive (right) side of PC1 with slightly elevated PCB loads, particularly PCBs 138, 153, and 180. These were from Swizerland (Schmid *et al.* 2005) and Russia (Franzle *et al.* 1996). Thus, it could be concluded that PCBs 138, 153, and 180 had the greatest influence on the soil-pattern difference among various soil types analyzed in this study. Numerous studies have shown that a wide range of semivolatile organic compounds accumulate in forest vegetation (Gaggi & Bacci 1985; Herrmann & Baumgartner 1987; Hinkel *et al.* 1989; Frank & Frank 1989; Horstmann & McLachlan 1998).

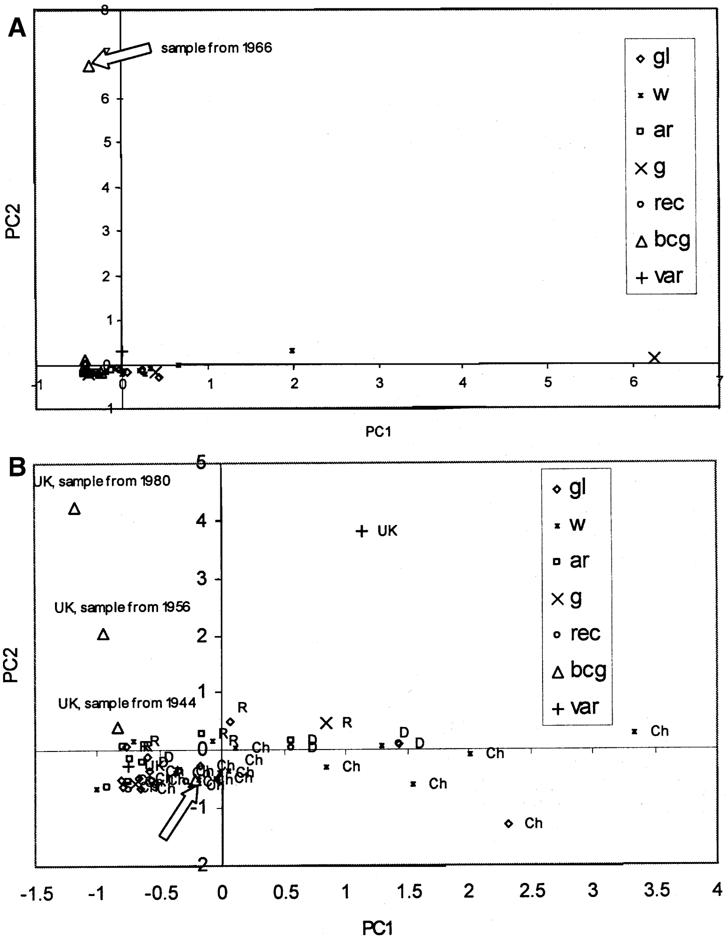

Fig. 4. Results of PCA for data on PCB soil loads taken from different studies (See Table 1): score plots of two PCs (sample labels indicating soil type and origin used to examine land-use and geographic differences, respectively, are explained in Table 1). (a) All samples included. (b) Subsequent PCA without three outliers observed in Fig. 4a (arrow points to the position of the soil representing the average background level of the sites worldwide (Meijer *et al.* 2003)

Decaying plant material can account for the input of PCBs to the soil. The heavier PCBs deposited by decaying vegetation will probably remain in the soil whereas lighter PCBs are subjected to volatilization (Backe *et al.* 2004).

2. Differentiation according to the geographic origin of the samples could not be observed, pointing out the uniform pattern of PCBs at various locations because of their similar source (atmospheric deposition).
3. The majority of the samples were near the one representing the average background soil level obtained for 191 sites from all of the world (Meijer *et al.* 2003; the arrow on Fig. 4b points out this sample).
4. Regarding PCB soil contents in the 1990s and early 2000s (represented by the samples located on the score plot in Figure. 4b along PC2 in the range of (−1, 1)) a substantial decrease could be observed having occurred since the elevated levels in the 1980 and 1956 samples (Meijer *et al.* 2001), and they coincided with the soil levels in 1944 (Meijer *et al.*, 2001), representing the period before intense industrial manufacture and application of PCBs. The only exception was the archived sample from the UK analyzed by Alcock *et al.*, (1993), but this could be the consequence of experimental errors as explained by Meijer *et al.* (2001), who analyzed the same sample as part of the quality control/quality assurance procedure in his study.

Concerning OCP soil patterns, the following was observed. Two underlying components, explaining 66.1% of the original data variance, governed the distribution of DDX and HCHs. However, to describe more of the total variance without considerable loss of information, three PCs were retained that accounted for 79.0% of the variance: PC1 (accounting for 41.8% of the total variance) was dominated by HCH-isomers (loadings were 0.9653 for α-HCH, 0.7199 for β- HCH, 0.9217 for γ-HCH); PC2 (accounting for 24.3% of the total variance) was related to the content of the p,p'-isomers of DDD and DDT with loadings as follows: 0.7406 and 0.8137, respectively; and PC3 (accounting for 12.9% of the total variance) was influenced by p,p'-DDE with a loading of 0.9683.

A score plot (Fig. 5a) revealed that the majority of the samples could be grouped into three clusters. The first consisted of soils characterised by a high DDX load, particularly DDT, which originated from China. The second consisted of samples from India that had high HCHs loads (α- and γ-isomers). The third (central) one consisted of samples with average content of both classes of OCPs. Moreover the plot suggested the presence of two outliers: arable soil sampled in China, with a maximum content of p,p'-DDT (777 ng/g; Chen *et al.* 2005) and soil taken from a garden in Russia which had the highest content of p,p'-DDE (271 ng/g; Franzle *et al.* 1996).

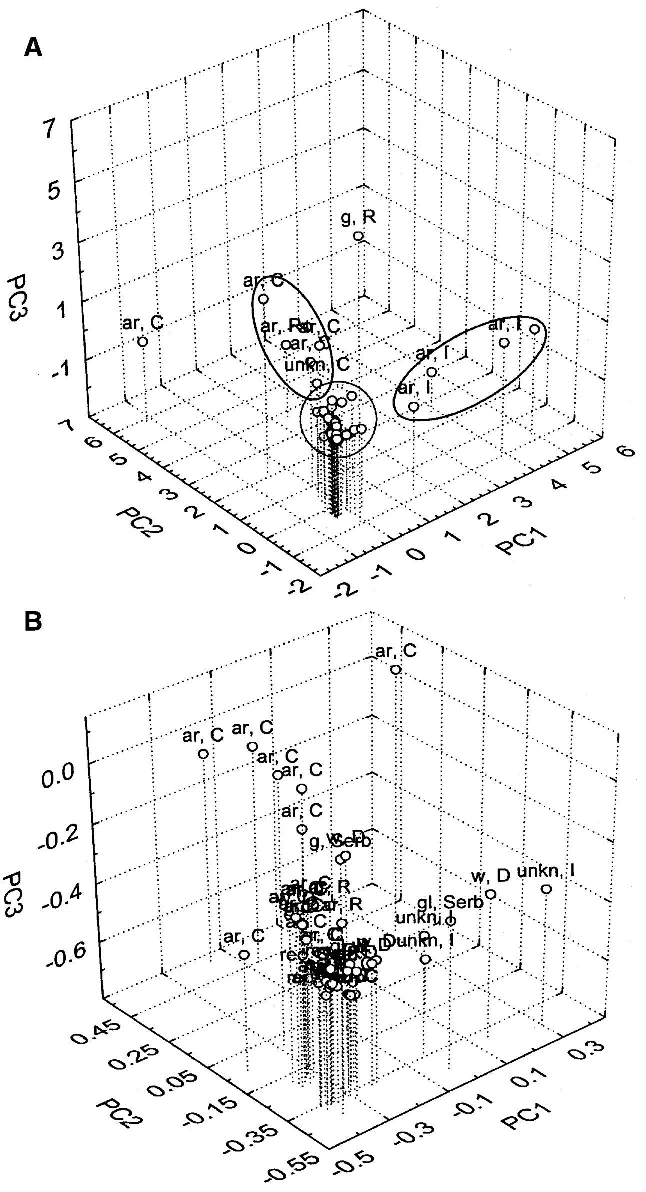

Fig. 5. Results of PCA for data on OCP soil loads taken from different studies (See Table. 1): score plots of three principal componets (sample labels indicating soil type and origin used to examine land-use and geographic differences, respectively, are explained in Table 1). (a) All samples included. (b) Closeup of the central cluster representing average OCPs soil loads

Of all the samples included in OCP-soil pattern analysis 83.8% was grouped in the third cluster. This cluster is shown in Figure 5b; the trend of increased DDX loads in soils from China and HCH loads in India can be seen. These findings suggest most likely a combination of heavy historic use and retarded DDT degradation in soils from China and retarted HCH degradation in soils from India, or, less likely, from their recent and/or excessive use even though such use is illegal in these countries. Moreover, in the case of China, the increased DDX levels might have resulted from the possible use of Dicofol containing 5% to10% DDT as impurity (Zhu *et al.* 2005) and the use of which is still allowed (Zhang *et al.* 2005).

Regarding the soils collected in the urban zone of Serbia (Novi Sad, capitol of Vojvodina, northern Serbian province) at various sites covering different land-use types (Škrbić *et al.* 2002), all of them were clustered with samples characterised by average OCP loads (the third-central cluster), coinciding with the European and Asian OCP soil patterns.

Conclusion

PCAs were used to examine the interdependencies among OC contaminants and chosen soil characteristics in PC space and also to reveal the spatial difference of PCB and OCP concentrations in a wide variety of collected soil samples.

Within the scope of the investigated data set, soil properties—such as humus content, pH, and density—influenced the adsorption of p,p'-DDT, β-HCH, and γ-HCH, whereas clay content influenced α-HCH and PCB 28 soil contents.

The loadings revealed the existence of the correlation of some OCCs, particularly of heavier PCB congeners, implying that the clustering of samples was governed by physicochemical properties of PCBs, indicating that PCA may be useful in discriminating between samples based on compound properties.

Considering PCB soil patterns, score plots showed relatively low PCB loads in most of the soils, which coincided with the worldwide background level, implying that the uniform PCB patterns at various locations are the consequence of their long-range transport; outliers were the archived sample from the period of intense PCB usage and those collected in woods and gardens of Germany province with intense industrial activities, probably because of the closed proximity of local pollutant sources. There were no observed geographic or land-use differences among the samples; however, 46.6% of the examined woodland samples had slightly elevated PCB loads. PCBs 138, 153, and 180 had the greatest influence on the soil-pattern differences. The temporal differences of PCB soil loads have been identified: the 1990s and early 2000s concentrations were similar to those of the early 1940s, and they were below levels in 1956 and 1980.

In the case of OCPs, the influence of sites' location on the detected concentration has been revealed: China and India were characterized by comparably higher loads of DDX compounds (DDT and its metabolites) and HCH isomers, respectively, because of heavy historical and/or recent use.

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Distribution of heavy elements in urban and rural surface soils: the Novi Sad city and the surrounding settlements, Serbia

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Abstract Concentrations of ten heavy elements (Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn), as well as the pH values, organic matter contents, and electrical conductivities were measured in the surface soil samples collected from 21 sites of urban areas in the city of Novi Sad, the second largest city in Serbia, its suburban settlement and the nearby villages. Range of the heavy element concentrations was from 0.16 mg/kg (for Hg) to 18,994 mg/kg (for Fe). Significantly higher Hg and Mn concentrations were observed in subgroups with rural and market garden samples in comparison to the subgroups with urban and grassland samples, respectively, while the contents of Pb found in the grasslands subgroup were significantly higher than in the subgroup with market garden soils. Only one sample of urban soil exceeded the maximum permissible value for Zn set by the relevant Serbian legislation. According to the Dutch soil quality standard, the Cd and Co concentrations in majority of the examined soils were higher than the target values for unpolluted soil. The content of Hg was above the target value in 52% of the samples, most of them belonging to the subgroup of market garden soils. The results for the Novi Sad city area were compared to the relevant data available for other cities in the Western Balkan Countries. Principal component analysis of data revealed seven outlying samples, while the rest of the analyzed samples were grouped together indicating similar heavy element patterns most probably due to mixed emission sources.

Keywords Heavy elements · Soils · Pollution · Principal component analysis · Serbia

Introduction

Urban soils act as a sink for heavy elements and other pollutants. Trace elements as well as other inorganic and organic pollutants are known to accumulate in surface soils as a result of both contaminations from point sources and from long-range aerial transport. Due to their characteristics, soils of urban areas are recognized as being different from agricultural and natural soils (Bretzel and Calderisi 2006). They are known to have peculiar characteristics such as highly variable composition, poor structure, modified soil reaction (in most cases higher pH values), low organic matter content and typically contain higher loadings of contaminants than those from rural settings due to the higher density of anthropogenic activity in urbanized areas (Kabata-Pendias and Pendias 2001; Bretzel and Calderisi 2006; Davidson et al. 2006). Heavy elements

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in urban soils may originate from various human activities, such as industrial and energy production as well as vehicle exhaust (Cannon and Horton 2009; Christoforidis and Stamatis 2009; Maas et al. 2010). In this way, heavy metals are emitted into the air and then subsequently deposited into soil as the metal containing dust. In addition, if the soil is dedicated to agricultural activities, other emission sources have to be considered, like the application of commercial fertilizers, sewage sludge and pesticides, which usually may contain a wide variety of heavy metals as impurities (Gimeno-García et al. 1996). Hence, there is an increasing need to monitor the pollution in order to control the quality of urban environment.

The ecological importance of heavy elements in soils is closely related to human health due to their high ecological transference potential (Morton-Bermea et al. 2009). The prolonged presence of heavy elements in the environment, particularly in urban soils, and their close proximity to human population can significantly amplify the exposure of the urban population to these contaminants via inhalation, ingestion, and dermal contact (Wong et al. 2006). Other indirect consequences of metal contamination of the environment include their subsequent migration to receiving bodies of water via urban runoff, affecting the quality of aquatic ecosystems and increasing the body loadings of aquatic organisms through bioaccumulation and biomagnifications, potentially causing metal contamination of the food chain (Zyadah and Abdel-Baky 2000; Ip et al. 2005; Vinodhini and Narayanan 2008).

Interest in the different factors influencing the presence of trace elements in the urban environment has been rapidly increasing as a consequence of the high levels of contamination measured in a number of cities (Cal-Prieto et al. 2001; Šajn 2001; Manta et al. 2002; Imperato et al. 2003; Madrid et al. 2004; Davidson et al. 2006; Lee et al. 2006; Yay et al. 2008; Cannon and Horton 2009; Christoforidis and Stamatis 2009; Sollito et al. 2010; Maas et al. 2010; Stafilov et al. 2010). There has been very limited research on urban topsoil in Serbia due to lack of strict application of environmental protection legislation (Škrbić and Čupić 2004; Crnković et al. 2006; Marjanović et al. 2009). In this study, the concentrations of ten heavy elements: cadmium (Cd), copper (Cu), cobalt (Co), chromium (Cr), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) were determined in 21 composite soil samples collected from different urban, suburban, and rural locations in and around the city of Novi Sad, Serbia. The aim was to investigate the spatial distribution of heavy elements in order to identify the possible sources of pollutants and to improve their monitoring, since there is an absence of basic data about possible heavy element pollution in analyzed area. Human and environmental risks were assessed by comparing the results with the Serbian and the Dutch soil quality references and also with available literature data, including the urban soils from the Western Balkan region and elsewhere.

Materials and methods

Description of the study area

The samples analyzed in this study were taken from the city of Novi Sad, its suburban settlement Veternik and the villages Šajkaš and Ravno Selo located within a radius of up to 40 km.

Novi Sad is arisen on the left bank of the river Danube, approximately 80 km northwest of Belgrade, the Serbian capital. It is the capital of the Autonomous Province of Vojvodina, the most fertile agriculture region in Serbia, located in its northern part. Together with the outskirt settlements, it has about 300,000 inhabitants in total. Novi Sad is a center of economic and industrial activities and a crossroad of major land and water ways. The city is located between 19°51′ of the east longitude and 45°20′ of the north latitude. Novi Sad has a moderate continental climate, with an average annual air temperature of 11°C. The average annual rainfall in Novi Sad and its surroundings is 600 mm. Potential sources of pollutants for soils in the city are related to industrial, commercial, agricultural activities, and automobile exhaust.

Veternik is suburban settlement adjacent to Novi Sad with intensive traffic between them as majority of the population is directed occupationally towards Novi Sad. Šajkaš and Ravno Selo are villages with about 3,500 to 5,000 inhabitants. Houses with individual fossil fuel heating are dominant in all three settlements with developed infrastructures, as they are not strictly dedicated to the agricultural production but also to small manufactories and services.

Sample sites and sampling

The description of the sampling sites is given in Table 1. Soil sampling was performed on 15 locations within the

Table 1 Description of composite soil sampling sites

Sample no.	Sample description
1	Novi Sad: urban soil, grassland, 30 m from the high traffic street
2	Novi Sad: urban soil, grassland (park-recreational zone) next to the bus and railway station, 15 m from high traffic street
3	Novi Sad: urban soil, low traffic zone, residential area, grassland
4	Novi Sad: urban soil, high traffic zone, grassland, 20 m from the main road, near the old railway
5	Novi Sad: urban soil, very low traffic zone, grassland, residential area
6	Novi Sad: urban soil, very low traffic zone, grassland, residential area, near the kindergarden
7	Novi Sad: urban soil, low traffic zone, grassland near the road, residential area with the domestic heating by gas and solid fuel
8	Novi Sad: urban soil, no traffic, grassland in private backyard, residential area with the domestic heating by gas and solid fuel
9	Novi Sad: urban soil, low traffic zone, children's playground near the parking in the residential area
10	Novi Sad: urban soil, grassland (park-recreational zone and children's playground) near (under) the bridge with high traffic
11	Novi Sad: urban soil, no traffic, grassland (recreational zone) beside the walking path by the river
12	Novi Sad: urban soil, high traffic zone, grassland near recreational zone
13	Novi Sad: urban soil, no traffic, residential area, market garden distant from the road
14	Novi Sad: urban soil, low traffic zone, residential area, grassland near the road
15	Novi Sad: urban soil, industrial area, high traffic zone towards the highway Belgrade/Subotica, grassland in the vicinity of the recently closed fertilizers factory
16	Šajkaš: rural soil, market garden
17	Šajkaš: rural soil, low traffic zone, grassland between the road and house
18	Veternik: rural soil, very low traffic zone near the earthen road
19	Veternik: rural soil, very low traffic zone, market garden
20	Ravno Selo: rural soil, very low traffic zone, market garden
21	Ravno Selo: rural soil, very low traffic zone, grassland between the road and house

Novi Sad city area (see supplementary material, Fig. S1) and on six locations in the surrounding settlements. Most of the samples (0–10 cm) were collected from grassland areas either public (samples nos. 1–7, 9–12, 14, 15, 18) or private (8, 17, 21). Some of the grassland areas from the Novi Sad city have been used as recreational zones (samples nos. 2, 10, 11, 12) and/or as children playgrounds (nos. 9, 10). Four samples out of 21 were market gardens (13, 16, 19, 20) devoted to growing edible plants (small private allotments for the domestic cultivation of vegetables). At all locations, samples of surface soil were taken at depth from 0 to 10 cm with plastic tools. At each area of sampling, five subsamples (~1 kg) were taken within the rectangular area of approximately 20×50 m and then mixed up to give a bulk sample. This was done to avoid the possibility of the spot contamination by urban waste that was not clearly identified.

Samples were stored in plastic bags at −4°C prior to analysis.

Soil characterization

The composite soil samples were air-dried and sieved through 2-mm sieve, ground, and then analyzed for the following chemical parameters: pH, electrical conductivity, and organic matter content. The pH was measured in solution of soil and water with the ratio of 1:5, according to ISO 10390 method using a Lutron YK-2001 pH meter device. Electrical conductivity (EC) was measured in solution of soil and water with the ratio of 1:5 according to ISO 11265 by a Hanna EC 214 conductivity meter. The content of organic matter (OM) was determined as the loss on ignition after heating 1 g soil at 550°C for 2 h (Škrbić and Čupić, 2004).

Heavy element determination

The method applied for heavy metal determination is previously used by Luo et al. (2007) and Škrbić and Đurišić-Mladenović (2010). It is based on EPA method 3051 for microwave assisted acid digestion of sediments, sludge, soils, and oils, which is initially based on the EPA method 3050B.

Subsamples (about 0.5 g) of each air-dried, sieved, and ground soil sample were digested in triplicate in a CEM MDS 2100 microwave oven, using a mixture of 7 ml of HNO_3 and 2 ml of H_2O_2. After digestion, solutions were filtered through Whatman No.1 filter paper and volumes were adjusted to 25 ml using double deionized water (Milli-Q, 18.2 MΩcm[1] resistivity). Concentrations of Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, and Zn were measured by graphite furnace atomic absorption spectrometry using a Varian AAS 240/GTA 120 instrument with deuterium lamp background correction, while Hg concentrations were determined by cold vapor atomic absorption spectrometry using the same instrument. The wavelengths in nanometer, used for the determination of Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, Zn, and Hg were 228.8, 324.8, 240.7, 357.9, 248.3, 279.5, 232.0, 283.3, 213.9, and 253.7, respectively. Quantification of heavy element content was done using adequate calibration curves. Calibration standards were prepared in the same acid matrix used for the soil samples. Each recording was repeated three times. The measured data were not corrected for recoveries obtained by analyzing the soil certified reference material NIST SRM 2711 in the same way as the samples. Certified and measured heavy element concentrations with recoveries in soil reference material are shown in Table 2.

Reagent blanks were provided to assess contamination. Precaution measures were used during the analysis to prevent contamination from air, glassware and reagents, which were of ultra pure quality. The repeatability of measurement was checked by the analysis of Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, Zn, and Hg in six parallel aliquots of one soil samples after the microwave digestion applying the described analytical procedure. The analytical precision, measured as relative standard deviation, was routinely between 5% and 6%, and never higher than 10%. The instrumental detection (LOD_{ins}) and quantification (LOQ_{ins}) limits were determined as three and ten times standard deviation of the baseline noise/sensitivity for each element, respectively, and according to them the following values for the method LOD (LOD_{met}) and the method LOQ (LOQ_{met}) were calculated, 0.6 and 1.98 μg/kg for Cd; 10 and 33 μg/kg for Co; 12.5 and 41.2 μg/kg for Cr; 4 and 13.2 μg/kg for Cu; 1 and 3.3 mg/kg for Fe; 10 and 33 μg/kg for Hg; 0.35 and 1.16 mg/kg for Mn; 20 and 66 μg/kg for Ni; 30 and 99 μg/kg for Pb; 2 and 6.6 μg/kg for Zn.

Table 2 The measured contents and recoveries of the heavy metals obtained by the method applied in this study with respect to the certified material NIST SRM 2711

Elements	Certified concentration (mg/kg)	Measured concentration (mg/kg)	Recovery (%)
Cd	41.7	39.6	95
Co	10.0	10.8	108
Cr	47.0	43.3	92
Cu	114	101	89
Fe	28900	24420	84
Hg	6.25	4.88	78
Mn	638	502	79
Ni	20.6	22.1	107
Pb	1162	838	72
Zn	350	364	104

Statistical analysis

The following statistic parameters were used to describe the data obtained for 21 composite soil samples analyzed in this study: mean, median, standard deviation, relative standard deviation, minimum, maximum, kurtosis and skewness. Descriptive statistic parameters were also determined for the subgroups of the same samples taking into account the sampling locations and the land-use types. Namely, samples originating from the Novi Sad urban area formed the “urban” subgroup of samples, while the ones taken from the chosen nearby settlements made the “rural” subgroup. However, this is very simple sample grouping made roughly in accordance to sizes of the population and the land areas of the chosen settlements. Furthermore, analyzed samples were divided into the “grassland” and “market garden” subgroups in accordance to the type of their usage regardless if they were located in urban or rural areas: “grassland” subgroup gathered

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[1] MΩcm (Mega ohm centimeter)

the samples taken from the areas covered with grass, either from the city parks, children playgrounds or private backyards, while the "market garden" subgroup consisted of the soils from private gardens devoted to the vegetables cultivation.

Shapiro–Wilk's test was used for detection of departure from the normal distribution of the heavy metal contents. The non-parametric Mann–Whitney's test was used to compare the differences in heavy element contents for the above-mentioned soil subgroups, i.e., differences between the "urban" and "rural" subgroups and between the "grassland" and "market garden" subgroups of soil samples. The *P* value for each element was calculated by both tests. If the *P* value is higher than 0.05, the null hypothesis, is accepted; if *P* value is lower than 0.05, the null hypothesis is rejected. The null hypothesis for the Shapiro–Wilk's test means the distribution of the element contents is normal, while for the Mann–Whitney's test, it states that there is no significant difference between the heavy element contents in two soil subgroups.

As an multivariate pattern recognition tool principal component analysis (PCA) was used to extract as much as possible information from the presented dataset. The main objective of PCA was to characterize each soil sample by projecting the data in a much smaller sub set of new variables called principal components (PCs). These new variables are linear combinations of the initial variables, but highlight the variance within a data set and remove the redundancies. Successive principal components arranged in decreasing order of eigenvalues account for decreasing amounts of variance. The relevant portion of information is carried out by the first principal components. The coefficients between the old and new variables are called the loadings. They explain how the new PCs are composed from the original variables (Škrbić et al. 2010). The PCs are orthogonal, in other words, uncorrelated. Further on, they are ordered in such a way that the variance of the first PC (PC1) is the greatest, the variance of the second PC (PC2) is the second greatest, and so on, whereas that of the last one is the smallest. The solution is obtained by an eigenvalue calculation. A basic assumption in the use of PCA is that the score and loading vectors corresponding to the largest eigenvalues contain the most useful information relating to a specific problem and that the remaining ones constitute mainly noise, i.e., for a practical problem, it is sufficient to retain only a few components accounting for a large percentage of the total variance (Škrbić and Đurišić-Mladenović 2010). Since the geochemical variables often do not follow normal distribution (Stafilov et al. 2011), the log transformation of data was performed prior PCA. For the purpose of this work, the input data table was created by putting the soil samples into the rows and the log-transformed heavy metal contents in the columns. The number of PCs extracted from the variables was determined by Kaiser's rule (Kaiser and Rice 1974), which retains only PCs with eigenvalues that exceed one. To get the better interpretation of the results of PCA, a Varimax rotated PC were produced. The algorithm of PCA can be found in the standard textbooks (Varmuza and Filzmoser 2009). Examples of PCA use in environmental chemistry and pollution sources identification could be found in numerous studies (Golobočanin et al. 2004; Škrbić and Đurišić-Mladenović 2007a, b, 2010; Škrbić et al. 2010; Stafilov et al. 2011).

All statistical data analyses were done with open source R software (http://www.cran.r-project.org/).

Results and discussion

Descriptive statistics for variables measured in 21 composite soil samples are summarized in Tables 3 and 4. The statistic parameters were calculated for the whole set of the obtained results (Table 3), as well as for the heavy metal contents of the sample subgroups (Table 4) taking into account the sampling zone (urban or rural) and the land use type (grassland or market garden). The range of the heavy element concentrations was from 0.16 mg/kg found for Hg to 18,994 mg/kg for Fe (Table 3). Considering the calculated values of relative standard deviation, RSD, of the element levels (Table 3), Zn and Pb showed pronounced concentration gradient in the investigated samples, having RSDs approximately 67% and 40%, respectively. The variability of the rest of the obtained element contents was from about 23% (for Ni) to 38% (for Cu). The range of RSD values in the subgroups of the samples in accordance to the zone of sampling (urban or rural) and land usage type (grassland, garden) (Table 4) was very similar to the one observed for the overall data set (Table 3). As high relative standard deviation are reliable indicators of anthropogenic activity (Manta et al. 2002), wide variations seen for the Zn and Pb quantities could be directly related to the anthropogenic emission sources.

Table 3 Descriptive statistics of the total heavy metal contents (in milligram per kilogram) and the characteristics of 21 composite soil samples analyzed in this study

	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	pH	EC, mS/m	OM,%
Mean	1.63	14.7	3.53	22.3	10581	0.34	450	25.1	27.4	110	8.40	147	8.25
Median	1.07	14.9	3.48	19.7	10296	0.32	442	25.2	25.1	85.6	8.42	134	7.52
Standard deviation	0.41	4.3	0.92	8.6	2596	0.12	129	5.8	11.0	73.7	0.32	67	3.88
RSD,%	25.32	29.29	26.20	38.44	24.53	35.89	28.76	23.06	40.01	67.24	3.77	47.38	47.04
Minimum	0.75	6.07	2.08	8.36	6637	0.16	286	16.6	12.7	61.3	7.99	67	3.65
Maximum	2.32	22.4	5.44	45.7	18994	0.55	836	41.1	55.9	401	8.85	413	14.31
Kurtosis	−0.16	−0.36	−0.43	1.35	4.79	−0.97	2.68	3.14	1.42	12.97	5.26	9.71	8.21
Skewness	−0.62	−0.21	0.36	0.83	1.62	0.44	1.26	1.58	1.30	3.37	−1.74	2.66	2.47
P (S–W test)[a]	0.423	0.954	0.867	0.311	0.014*	0.165	0.052	0.002*	0.015*	0.000*	0.964	0.000*	0.311
Number of samples exceeding the national limits[b]	0	–	0	0	–	0	–	0	0	1			
Number of samples exceeding the Dutch target [c]/intervation values [d]	21/0	18/0	0/0	1/0	–	11/0	–	2/0	0/0	3/0			

[a] Values given for *P* (S–W test) are the probabilities calculated by the Shapiro–Wilk's test for detection of departure from the normal distribution of the heavy metal contents. If *P* values were higher than 0.05, the distribution was normal, while if *P* values were lower than 0.05 (indicated by asterisk) the distribution was found to be non-normal

[b] The national limits for soil are established to be 3 mg/kg for Cd, 100 mg/kg for Cr, Cu, and Pb, 2 mg/kg for Hg, 50 mg/kg for Ni, and 300 mg/kg for Zn (Official Bulletin of the Republic of Serbia 1994)

[c] Dutch standard target values for soil are 0.8 mg/kg for Cd, 9 mg/kg for Co, 100 mg/kg for Cr, 36 mg/kg for Cu, 0.3 for Hg, 35 mg/kg for Ni, 85 mg/kg for Pb and 140 mg/kg for Zn (The Netherlands Government Gazette 2000)

[d] Dutch standard intervention values for soil are 12 mg/kg for Cd, 240 mg/kg for Co, 380 mg/kg for Cr, 190 mg/kg for Cu, 10 mg/kg for Hg, 210 mg/kg for Ni, 530 mg/kg for Pb and 720 mg/kg for Zn (The Netherlands Government Gazette 2000)

Table 4 Descriptive statistics on the total heavy metal contents (in milligram per kilogram) of the soils grouped in accordance to the zone of sampling (urban or rural subgroup) and land usage (grassland or market garden subgroup)

	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Zone of sampling										
Urban										
Mean	1.59	14.3	3.33	21.9	10,685	0.30	424	23.2	28.8	111
Median	1.69	14.9	3.26	19.7	10,296	0.27	387	23.3	25.8	85.6
SD	0.40	4.3	0.88	9.0	3,031	0.12	142	3.3	11.5	83
RSD,%	25.13	29.59	26.52	41.05	28.37	38.28	33.38	14.18	40.01	74.68
Minimum	0.75	6.07	2.08	8.36	6,638	0.16	286	16.6	17.5	63.3
Maximum	2.09	22.4	5.04	45.7	18,994	0.55	836	27.4	55.9	400
n	15	15	15	15	15	15	15	15	15	15
Rural										
Mean	1.73	15.7	4.03	23.3	10,322	0.44	513	29.8	23.9	106
Median	1.78	16.0	3.87	23.2	10,384	0.45	515	26.7	23.1	88.9
SD	0.47	4.7	0.85	8.1	1,052	0.08	63	8.1	9.5	49
RSD,%	26.93	30.12	21.17	34.84	10.18	17.94	12.28	27.32	39.54	46.46
Minimum	0.96	9.53	2.87	13.6	8,626	0.33	419	22.5	12.3	61.3
Maximum	2.32	21.7	5.43	32.9	11,446	0.54	610	41.1	40.7	187
n	6	6	6	6	6	6	6	6	6	6
P (M-W test)[a]	0.392	0.586	0.139	0.697	0.876	0.016*	0.024*	0.073	0.436	0.156
Land usage										
Grasslands										
Mean	1.62	14.8	3.41	20.5	10,547	0.31	431	24.6	29.4	112
Median	1.69	14.9	3.27	19.7	9,881	0.27	397	25.2	25.9	85.6
SD	0.41	4.1	0.88	6.6	2,884	0.11	135	5.4	11.1	79
RSD,%	25.32	27.51	25.78	32.22	27.34	35.13	31.41	21.88	37.78	70.37
Minimum	0.75	7.66	2.08	8.36	6,638	0.16	286	16.6	17.8	63.3
Maximum	2.32	22.4	5.04	31.3	18,994	0.54	836	41.1	55.9	401
n	17	17	17	17	17	17	17	17	17	17
Market garden										
Mean	1.68	14.4	4.06	30.3	10,724	0.47	531	27.4	19.0	102
Median	1.86	16.0	3.84	29.9	10,755	0.49	514	24.0	20.0	80.1
SD	0.49	6.0	0.99	12.4	720	0.09	56	7.8	5.2	58
RSD,%	29.01	41.31	24.31	40.99	6.71	18.30	10.52	28.44	27.35	56.52
Minimum	0.96	6.07	3.14	15.9	9,941	0.37	486	22.5	12.3	61.3
Maximum	2.04	19.6	5.43	45.7	11,446	0.55	610	38.9	23.7	187.4
n	4	4	4	4	4	4	4	4	4	4
P (M-W test)[a]	0.474	0.929	0.282	0.128	0.474	0.016*	0.049*	0.788	0.039*	0.654

[a] Values given for *P* (M–W test) are the probabilities calculated by the Mann–Whitney non-parametric test for differences between the heavy metal contents in two subgroups of samples (urban/rural or grassland/market garden). Significant differences were found if *P* (M–W test) values were lower than 0.05, when they are indicated by asterisk

Analysis of chemical parameters of soil is important for an appropriate prediction of ecological consequences of the soil pollution with trace metals. The solubility of trace metals is often shown as a function of pH affected by the amount and kind of organic matter. Organic matter and some decomposition products can act as reducing agents and assist in mobilizing the heavy elements (Kabata-Pendias and Pendias 2001). With respect to the chemical characteristics of soil, the studied topsoils were typically alkaline in nature, with pH values from 7.99 to 8.85, organic matter (OM) contents from 3.65% to 14.31% and electrical conductivity (EC) as indicator of soluble salts (ions) in soil from 67 to 413 mS/m.[2] In such alkaline soils, heavy elements are likely to be in a less mobile form (Škrbić and Miljević 2002).

In accordance to the Shapiro–Wilk's test (*P* values given in Table 3), the Cd, Co, Cr, Cu, Hg, and Mn concentrations in the soil samples were found normally distributed, while the non-normality was observed for Fe, Ni, Pb, and Zn (Table 3). In the case of soil physicochemical characteristics, distribution of measured pH values and organic matter content were found to be normal, with the exception of electrical conductivity, which distribution was found to be non-normal ($P<0.05$).

According to the mean concentrations of elements in all samples (Table 3), the heavy element abundance could be ordered as follows: Fe>Mn>Zn>Pb>Ni>Cu>Co>Cr>Cd>Hg. The same order of the heavy element abundance was characteristic for the subgroup with urban samples, while slightly different average element pattern was observed in the rural subgroup of samples due to higher level of Ni than Pb: Fe>Mn>Zn>Ni>Pb>Cu>Co>Cr>Cd>Hg (Table 4). As the majority of the grassland soil samples originated from the urban zones, their heavy element patterns reflected the order of element abundances found for the "urban" subgroup. However, mean and median values of elements in the subgroup of the market garden soil samples showed distinctive pattern due to higher levels of Cu than Ni and Pb (Cu>Ni>Pb) in comparison to the subgroup with grassland samples.

In order to determine if there were significant differences among the analyzed heavy element contents in different subgroups of samples (urban vs. rural, grassland vs. market garden), the Mann–Whitney's test was applied (Table 4). Comparing the heavy element contents between the "urban" and "rural" subgroups, significant differences (*P* (M–W test)<0.05) were observed for Hg and Mn. Concentrations of both elements were significantly higher in the subgroup with rural soil samples. Comparing the concentrations of heavy elements in the subgroup with grassland samples and the one with market garden samples, content of Hg, Mn, and Pb showed significant differences (*P* (M–W test)<0.05). The contents of Hg and Mn were significantly higher in the "market garden" than in the "grassland" subgroup, while the opposite was found for the Pb contents.

Taking into account the differences obtained by the Mann–Whitney's test, the higher presence of Hg in the subgroups with rural and with market garden samples in comparison to the subgroups with urban and with grassland samples, respectively, can be attributed most probably to the agricultural activities, i.e., earlier use of fungicides containing Hg (although these have not been used in most countries for the last 20 years (Kabata-Pendias and Pendias 2001). It is also known that generally organic soils have a higher Hg content than mineral soils (those with less organic matter content). This is mainly due to a great capacity of humus, especially raw humus, for binding Hg (Kabata-Pendias and Pendias 2001). Increased concentrations of Mn in the "rural" and the "market garden soil" subgroups compared with the "urban" and the "grassland" subgroups, respectively, can be explained by fertilization of allotment soils because this element is essential in plant nutrition and controls the behavior of several other micronutrients (Kabata-Pendias and Pendias 2001). Lead is the element of most concern in environmental heavy metals pollution. The fate of anthropogenic Pb in soils has received much attention because this metal is non-essential for living systems and it is hazardous in small concentration. It is a well-known fact that road transport has been a major source for lead emissions compared to other anthropogenic sectors (Kummer et al. 2009). In the present study, higher mean levels of Pb were detected in the subgroup of urban soil samples in comparison to the one with rural soil samples what was obviously the consequence of the higher intensity of traffic in the urban zones than in the rural ones.

According to the national limits for heavy elements in soils (Official Bulletin of the Republic of Serbia 1994), only one sample of urban soil (no. 5) exceeded the maximum permissible value for Zn (Table 3). However, according to the latest Dutch soil quality standard (The Netherlands Government Gazette 2000) based on extensive studies of both the human and ecotoxicological effects of soil contaminants, in most analyzed samples, values for the Cd and Co concentrations were higher than the target values that indicate a sustainable soil quality (Table 3), but not sufficiently high to exceed the soil intervention values above which a serious case of soil contamination

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[2] mS/m (milli Siemens per meter)

exists, requiring remediation or an intervention procedure. The Hg content was above the target value in 11 samples: all the samples from the market gardens exceeded the Hg target values; also, all the samples from the "rural" subgroup exceeded it; only one samples from the recreational zone of the Novi Sad city area (no. 2) had the Hg content above the Dutch target value. In few instances the Dutch target values for Cu, Ni, and Zn were also exceeded (sample no. 13 in case of Cu, nos. 16 and 17 in case of Ni, and nos. 3, 5 and 16 in case of Zn). It is interesting to note that none of the samples exceeded the Pb limit set by the relevant national regulation or the Dutch soil quality standard despite the fact that leaded gasoline is still in use in Serbia.

In order to further evaluate the whole heavy metal soil burdens of the investigated sites, a soil metal index, SMI, was calculated in the following way (Škrbić and Đurišić-Mladenović 2010): for each composite soil sample, the percentage of the metal contents relative to the respective Dutch target values (presented below Table 3) were calculated first. These values were then summed up and divided with number of metals included in the calculation (i.e., the sum was divided with 8, since the relative percentages were calculated for eight heavy metals for which the Dutch reference values are available: Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn). The minimum and maximum SMI were calculated for the sample no. 6 and sample no. 17 (62% and 114%, respectively); there were two samples with SMEs below 70% (no. 6<no. 10), two with SMEs between 70% and 80% (no. 9<no. 1), three with SMEs between 80% and 90% (no. 11<no. 19<no. 12), nine with SMEs between 90% and 100% (no. 21<no. 7<no. 14<no. 15<no. 4<no.18<no.13<no.2<no.9), while SMIs above 100% were found for five samples (no. 5< no. 20<no. 8<no. 16<no. 17). These highest SMIs (>100%) were the result of the excessively high contents of few metals in relation to the references: Co, Zn, and Hg in sample no. 5; Co, Cd and Hg in sample no. 20; Co and Cd in sample no. 8; Co, Cd, Ni, Zn and Hg in sample no. 16; and Co, Cd, Ni and Hg in sample no. 17. Thus, only two samples from the Novi Sad city area (nos. 5 and 8), representing 13.3% of the total "urban" samples, were grouped in the samples with the highest total heavy metal burdens (with SMI>100%) together with three of five "rural" samples. Although it is well known that the mobility of heavy elements is low in alkaline soils (Škrbić and Miljević 2002), the elevated levels in market garden soils pose a risk because of a possible passage into the food chain. Moreover, contaminated urban soils may pose a risk to children in case of direct soil ingestion during the outdoor activities, while wind erosion and contaminated dust can affect people's lungs and skin (Bretzel and Calderisi 2006).

In order to assess the degree of the anthropogenic influence to the investigated soils, comparison of the obtained results with the average heavy element contents reported for 1,600 samples of regional surface soils from the Vojvodina Province (Ubavić et al. 1993) is presented in Fig. 1 in form of contamination ratios. The contamination ratio for each metal in each sample was calculated as ratio of the measured heavy element content and the mean content found in the soil of the Vojvodina region (Ubavić et al. 1993). Although all soils in the region probably bear some imprint of human activities and no longer reflect purely natural conditions, regional soils provide a baseline against which potentially more intense human activity in urban areas can be judged (Cannon and Horton 2009). According to the calculated contamination ratios (Fig. 1), most of the elements occurred in elevated levels in the analyzed soils compared to the average regional soil composition. The most prominent enrichment was found for Hg with contamination ratio in the range 13.1–45.1 and the median 26. In Fig. 1, it could be seen that the Hg contamination ratios above this median value were observed for ten samples (nos. 2, 12, 13, 15–21). For all these samples, except for samples no. 2 and 12, previous use of Hg-based fungicides could be the explanation for the high contents of Hg, since these samples were collected from the market gardens (nos. 13, 16, 19, 20), rural zones (nos. 17, 18, 21), and also in the vicinity of the closed fertilizers factory (no. 15). Concerning the Zn contamination ratios, Fig. 1 depicts sample no. 5 (residential area with low traffic in Novi Sad), as the most contaminated sample having 38 times higher Zn content than the Zn average of the Vojvodina soil. Not having any records about the origin and use of the analyzed soils, including the soil at the location no. 5, this enhancement could be explained only by some local accidental source. Contrary, the contamination ratios of Cd, Cr, Ni, Pb, and Cu for all sites were lower (Fig. 1).

Table 5 shows comparison between the results obtained for the "urban" samples ($n=15$; Table 4) with the heavy element surface soil concentrations found in the Novi Sad city area earlier (Škrbić and Čupić,

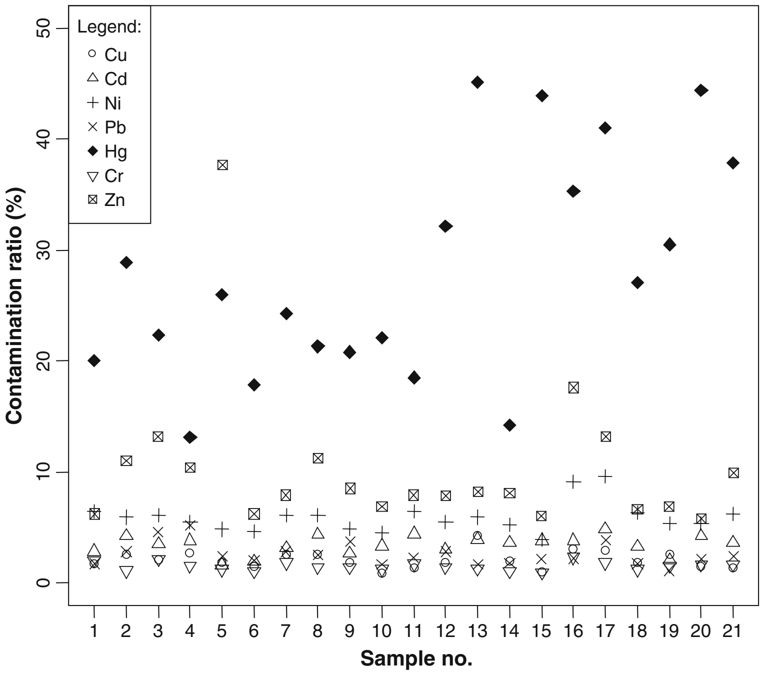


Fig. 1 Contamination ratios of the metal contents for individual samples and for all investigated samples calculated to the mean contents in the Vojvodina region (Ubavić et al. 1993)

Table 5 Average heavy metal concentrations (milligram per kilogram) in the surface soils within the Novi Sad city area and other urban soils elsewhere compared to the upper continental crust (Wedepohl 1995), the European topsoil average (Salminen et al. 2005) and median metal contents of the soils worldwide (Reimann and de Caritat 1998) (the data from cited studies are given in the original form, without an attempt to uniform the number of significant digits)

City	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Novi Sad city area, Serbia (this study)	1.59	14.3	3.33	21.9	10,685	0.30	424	23.2	28.8	111
Novi Sad, Serbia (Škrbić and Čupić 2004)	0.15	–[a]	–	30.86	8,009	–	251	–	10.75	85.45
Belgrade, Serbia (Marjanović et al. 2009)	1.8	16.5	–	46.3	–	–	417.6	–	298.6	174.2
Belgrade, Serbia (Crnković et al. 2006)	–	–	32.1	28.3	–	–	–	68.0	55.5	118
Zagreb, Croatia (Sollito et al. 2010)	0.40	10.9	54.6	56.1	–	–	597	35.2	23.2	77.9
Veles, Republic of Macedonia (Stafilov et al. 2010)	12	16	180	52	35,000	0.36	950	78	340	460
Kavala, Greece (Christoforidis and Stamatis 2009)	0.2	–	240.3	48.1	–	0.1	–	77.4	571.3	175.0
Sevilla, Spain (Madrid et al. 2004)	–	–	42.8	64.6	21,000	–	480	23.5	161	107
Coruna, Spain (Cal-Prieto et al. 2001)	0.3	11	39	60	–	–	–	28	309	206
Naples Italy (Imperato et al. 2003)	–	–	11	74	–	–	–	–	262	251
Palermo, Italy (Manta et al. 2002)	0.84	6.53	38.54	76.66	–	1.86	565.72	19.06	252.78	150.90
Glasgow, United Kingdom (Davidson et al. 2006)	–	–	43.2	111	30,600	–	442	48.8	389	177
Chicago, USA (Cannon and Horton 2009)	–	11.1	71.2	150.5	33,000	0.6	583.4	36.4	395	396.6
Annaba and the surroundings, Algeria (Maas et al. 2010)	0.44	–	30.9	39.0	24,270	–	355.0	–	53.1	67.5
Hong Kong China (Lee et al. 2006)	0.36	3.55	–	16.2	–	–	–	–	88.1	103
Upper continental crust (Wedepohl 1995)	0.1	11.6	35	14.3	30,890	0.06	530	18.6	17	52
European topsoil average (Salminen et al. 2005)	0.28	10	95	17	27,000	0.061	630	37	33	68
Soils worldwide (Reimann and de Caritat 1998)	0.3	–	–	25	–	–	545	20	17	70

[a] Data not analyzed in the original study

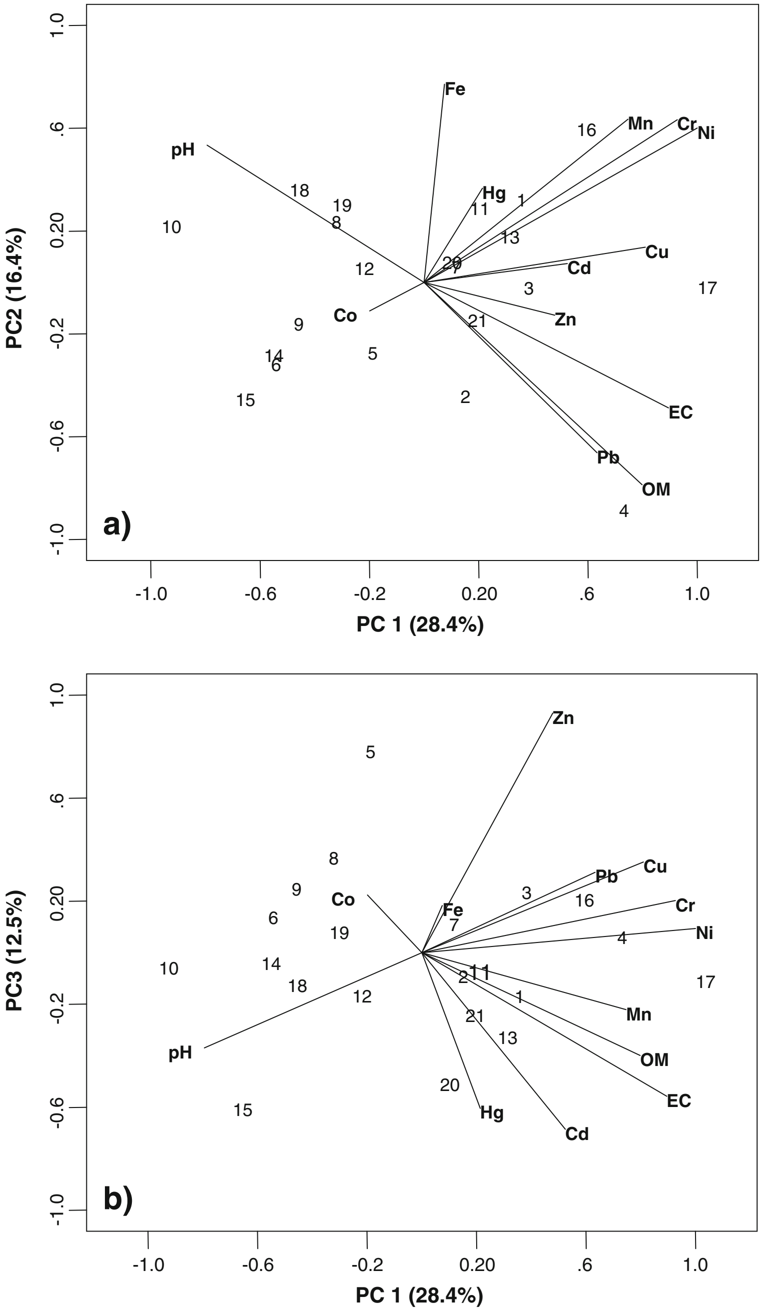
2004), in urban areas from the same region of Western Balkan Countries-WBCs: Belgrade, Serbia (Marjanović et al. 2009; Crnković et al. 2006), Zagreb, Croatia (Sollito et al. 2010), and Veles, Republic of Macedonia (Stafilov et al. 2010)), and also from other cities in the world (Cal-Prieto et al. 2001; Manta et al. 2002; Imperato et al. 2003; Madrid et al. 2004; Davidson et al. 2006; Lee et al. 2006; Cannon and Horton 2009; Christoforidis and Stamatis 2009; Maas et al. 2010).

Comparison of the data (Table 5) revealed that concentrations of Cr, Cu, Fe, Hg, and Pb in analyzed topsoil samples were lower than in the majority of other studies, while the content of Co was among the highest. When WBCs cities were taken into consideration, the highest soil metal contents could be seen for the Veles urban area, being the most polluted city in the Republic of Macedonia, since in the center of the town, a lead and zinc smelter plant is located (Stafilov et al. 2010). With respect to the heavy metal burdens reported for the Serbian capitol Belgrade (Marjanović et al. 2009; Crnković et al. 2006), it could be seen that this largest regional metropolis with almost two millions of inhabitants, had higher contents of Cr, Cu, Ni, Pb, and Zn than the Novi Sad city area, while both had similar contents of Cd, Co, and Mn. According to the content of Pb, the Novi Sad city soils were similar to those from the Croatian capital Zagreb (Sollito et al. 2010), having population of around one million and also allowed use of leaded gasoline. On the other hand, when the results from this study were compared to previous study on trace elements distribution in surface soils of Novi Sad sampled in 2001 (Škrbić and Čupić 2004), the increased concentrations of Cd, Fe, Mn, Pb, and Zn were observed. Since these elements are mainly traffic-related metals (Wilcke et al. 1998, Davis et al. 2001) emitted either through exhausts, tyre/brake abrasion, lubricants, etc. (Škrbić and Đurišić-Mladenović 2010), their increased concentrations could probably be related to the rising urban population that relies on the automobile as the means of transportation. Moreover, considering non-biodegradable nature of heavy elements, their increased content could be ascribed also to the accumulation in soil over the years. Similar increase of the Pb and Zn levels over the years could be also seen for the Belgrade soils (Marjanović et al. 2009; Crnković et al. 2006) (Table 5). Additionally, Table 5 compares the results with available reference values, showing that the former were generally higher than the upper continental crust (Wedepohl 1995) (except for Cr, Fe, and Mn) and the worldwide median values (Reimann and de Caritat 1998) (except for Cu and Mn). Concerning the European top soil averages (Salminen et al. 2005), the soil of Novi Sad city area was more polluted with Cd, Co, Cu, Hg, and Zn.

PCA was applied to help the data interpretation in order to identify the underlying pattern in the data set and distributional structure of soil samples regarding the heavy metals pollution. The results of the PCA of the data obtained in this study (set of 13 variables and 21 samples) after the log-transformation of the data are presented in Table S1 (see the electronic supplementary material).

According to the Kaiser rule (Kaiser and Rice 1974), six principal components with eigenvalues larger than 1 were retained accounting for 83.6% of the total variance. Since PCA enabled the reduction from 13 original variables to 6 newly extracted components, it could be noted that the data were not compressed well by PCA, implying complex data structure due to simultaneous influence of several latent factors (sources) on the heavy element patterns in the soil samples. The first three components, PC1, PC2, and PC3 explained the largest parts of data variance (57.2% of the total variance), while the fourth (PC4), fifth (PC5), and sixth (PC6) components explained rather similar share of the data variance (10.9%, 9.5%, and 8.6%, respectively). Thus, first three, the most informative components, PC1, PC2, and PC3 are further discussed. The PC1 was significantly loaded with five heavy elements (Ni, Cr, Cu, Mn, Pb in descending order of loading values) and three soil characteristic variables (EC, OM, pH). The pH was the only variable negatively correlated with PC1, implying that lower values of pH in the range observed for the analyzed samples (7.99–8.85) favored the accumulation of Ni, Cr, Cu, Mn, and Pb. In addition, the observed negative correlation between soil pH and organic matter content indicated that the source of soil acidity was from organic matter decomposition coinciding with literature data (Škrbić and Đurišić-Mladenović 2007a; Jiries et al. 2002). The second largest PC, PC2, correlated with similar variables as PC1, but in slightly different manner; namely, it was negatively correlated with Pb, OM, and EC, while positively with Fe, Mn, Cr, Ni, and pH. Different correlations obtained for first two principal components with almost the same metals and the soil characteristics reflected two origins (sources) of the metals in the soils or their mixed sources that could not be clearly resolved. In other words, split loadings of the variables on both PC1 and PC2 suggested simultaneous influence of these latent factors on the soil metal patterns. The third component, PC3, was correlated with the metals that failed to load first two PCs: it was negatively correlated with Cd and Hg, and positively with Zn, meaning that high levels of Cd and Hg were correlated with low levels of Zn and vice versa. Obviously, PC3 implied the third source of the metal occurrence in the examined soils and taking into account previous discussion regarding the Hg presence, it could be assumed that PC3 most probably reflected the agrotechnical measures (the use of fertilizers). Metal that failed to load significantly the first three principal components was Co. The biplots of PC1 vs. PC2 and PC1 vs. PC3, showing simultaneously the component loadings and scores, are presented in Fig. 2. During the biplots construction, each

Fig. 2 The PCA biplots showing the results of principal component analysis of data obtained in this study: **a** PC1 vs. PC2, **b** PC1 vs. PC3



loading and score values were divided with the respective maximum values obtained for particular PC; thus, the biplots presented the relative positions of the element loadings and the sample scores within the range from −1 to +1. As it can be seen, Pb was the only heavy element correlated with soil characteristics, particularly with organic matter (OM, Fig. 2a). This was in accordance to the data of Bojinova et al. (1996) showing that Pb of the anthropogenic origin in the polluted soils is connected mostly with soil organic matter. The Ni, Cr, and Mn contents correlated closely among each other carrying the similar information. These later metals and also Pb, had split loadings on PC1 and PC2, influencing the dispersion of the samples along both PCs. The biplot PC1 vs. PC2 (Fig. 2a) also gave insight into the outlying samples: nos. 10 and 17 were the outliers along PC1, while samples no. 4 and 16 were the outliers along PC2. Each of these outliers had unique heavy element pattern; for instance, sample no. 4 (open area within the residential zone in Novi Sad, 20 m from the high traffic road) had the highest Pb level and organic matter content, indicating high influence of the traffic exhausts; samples no. 16 (market garden in the Šajkaš village) and no. 17 (low traffic zone in the Šajkaš village) had the highest content of Ni, and at the same time the former had the highest Cr level, whilst the later had the maximum Cd level; sample no. 10 (grassland in the park under the bridge in Novi Sad) had the lowest level of organic matter. The biplot PC1 vs. PC3 (Fig. 2b) revealed three more outlying samples (along PC3): sample no. 5 (residential area with low traffic in the Novi Sad) with the highest level of Zn, and samples no. 15 (high traffic zone near fertilizers factory in Novi Sad) and no. 20 (market garden in the Ravno Selo village) had the lowest level of Zn. Besides the outlying samples, biplots did not reveal sample discrimination based on the site locations (urban and rural) and/nor land-usage types, probably as a consequence of the mixed anthropogenic emissions.

Conclusion

The elements with the highest variability in the soil samples from the Novi Sad city area and its surrounding settlements were Zn and Pb, having the highest relative standard deviations that indicated strong anthropogenic influence on their contents. However, only one sample of urban soil was found to be above the maximum permissible value for Zn according to the Serbian soil regulation. Considering the Dutch soil quality standard, the target values of Cd, Co, and Hg were exceeded in majority of the analyzed soil samples, indicating soils polluted above the background levels, but not above the intervention values for which a serious case of soil contamination exists. The significantly higher contents of the Hg and Mn concentrations were observed in the subgroups of the rural and the market garden samples in comparison to the “urban” and the “grassland” subgroups of samples, respectively, which might be the consequence of the agriculture practice. The Pb contents were higher in the “grassland” sample subgroup compared to the “market garden” subgroup as a consequence of the vehicular exhausts, since majority of the grassland samples were collected in the urban zones. Additionally, the comparison of the data with those previously published for other cities, including those from the Western Balkan Countries, pointed out the similar or lower heavy element burdens, except in the case of Co. Principal component analysis revealed seven outlying samples and rather similar heavy element pattern among the rest (majority) of the samples, suggesting mixed emission sources.

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Levels of PAHs in soil samples from the vicinity of oil refinery Novi Sad-Serbia

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ABSTRACT

The levels of 16 polycyclic aromatic hydrocarbons (PAHs) from the priority list of the U.S. Environmental Protection Agency were determined in soil samples collected in Novi Sad (the capital of Vojvodina Province, Serbia), a region with chemical industry and oil refinery. Samples were also collected in an urban/residential zone and in a presumably unpolluted site (control sample). The sampling sites were chosen in order to study the influence of the oil refinery on PAH levels. The contents of PAHs were determined by GC/FID. Benzo(a) pyrene known to be carcinogenic formed 2-13% of the sum concentration of the identified PAHs for all investigated samples. Basic physical-chemical properties like organic matter content, pH and water content were determined for each composite soil sample. No significant correlation was observed between these variables and the PAH-load of soils. Data obtained were compared with ones previously found for soils in Novi Sad, as well as with soils collected throughout the world and compared to target values set by the Dutch authorities for unpolluted soil. The total carcinogenic potency for each sampling site was calculated and compared with the reference value obtained on the base of the target concentrations.

Keywords: carcinogenic potency; oil refinery; polycyclic aromatic hydrocarbons; soil; urban zone.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs) produced by the incomplete combustion of organic material, either natural, as with forest fires, or anthropogenic, such as by industrial activities, heating from fossil fuels or in motor vehicle. PAHs have been detected around the world even at sites which are located far from industrial activity such as in the polar regions (Wania & Mackay 1996). As the Artic is far from all industrial sources, anthropogenic PAHs could only reach it by long-range atmospheric transport (Wilcke 2007).

Atmospheric deposition is the most common source of pollution in soil (Li *et al.* 2001). Previous studies implied that POPs measured in soils correlate with those in the atmosphere, and therefore, soil PAH concentrations are usually considered good indicators of the surrounding pollution and environmental risks (Wild & Jones 1995).

Because of their persistence, low vapor pressures and high octanol/air partition coefficients, PAHs can strongly adsorb to soil organic matter and are likely to be retained for a long time (Wilcke 2007). Consequently, soil is one of the main reservoirs for PAHs in the environment. A number of law-abiding guidelines on soil quality are set to protect human and ecological health in developed countries, but the significance of soil protection is often neglected in developing countries and ones in transition, like Serbia.

To date, there is only limited data on PAH concentrations in the Serbian urban soil (Škrbić *et al.* 2005, Crnković *et al.* 2007). The extent of PAH-burden in Novi Sad soil was previously studied in 2001, covering the whole city area (Škrbić *et al.* 2005). However, there is no systematic long-term study on this subject and, consequently, there is no information available about the extent of soil pollution in the city over the years.

The major objective of this paper is to characterize the spatial distribution of soil PAHs and to compare these data with the previous findings, as well as to study the influence of oil refinery on their levels. The data are compared with those available in the literature for other urban areas worldwide. In addition, the total carcinogenic potency of soil samples was calculated in order to estimate the environmental and health risks.

MATERIALS AND METHODS

Soil collection

Novi Sad is the capital of the northern Serbian province of Vojvodina. It is located in the southern part of Europe, between the 19th and 20th degree of the east longitude and 45th and 46th degree of the north latitude, at the altitude of 72 to 80 m. Novi Sad lies on the left bank of the river Danube, namely on the 1255th km of its flow and on the mouth of one of the magisterial Danube-Tisa-Danube canals into the river Danube. With 15 suburban settlements, the territory of the City of Novi Sad encompasses a surface area of 702,7 km^2. It is the second largest city in Serbia, after Belgrade, and its large industrial and financial centre represents the most fertile agricultural and economical region in Serbia. One of the biggest industrial combines in the city is the oil refinery, located 3 km to the north of the city centre along with the thermal power plant, near the suburban settlement of Šangaj. The refinery complex consists of production facilities and storage tanks for crude oil and oil products (mainly gasoline and diesel fuel). During the 1999 NATO bombing of Yugoslavia, the Novi Sad oil refinery was bombarded daily and was severely damaged. Due to the uncontrolled combustion during refinery fires following the bombardments, many highly toxic substances were released, such as some PAHs, which are found to be highly carcinogenic (Škrbić 2008).

The samples of surface soils (0-5 cm) from representative areas were collected during one day with stable weather conditions in June 2007 by using a stainless steel corer. Five sampling sites were chosen in Šangaj near the Oil Refinery Novi Sad. Samples were collected in the local school backyard (three composite samples, nos. 1-3) and along the local road next to the refinery (two composite samples, nos. 4 and 5). In addition, samples were taken in an urban/residential zone (park-school backyard in the downtown of the city of Novi Sad, sample no. 7) and in a presumably unpolluted site, an arable zone far from direct anthropogenic PAH sources (control sample no. 6). Each sampling point was represented by a rectangular area of 20×50 m with four individual samples (about 250 g).

The collected samples were stored in prewashed glass bottles and immediately transported to the laboratory. The individual samples from each sampling site were mixed together and sieved through a steel mesh (˜2 mm) to remove large particles and organic debris, creating seven composite samples. The obtained composite samples were stored frozen until analysis and then dried in a desiccator for 24 hours prior to analysis.

Soil characterization

Basic physical-chemical properties were determined for each composite soil sample. pH measurements were carried out in deionized water (50 ml), after stirring the dried sample portion of 20 g for an hour. The organic matter content was determined as a weight loss by weighing the sample before and after heating at 500°C for 2 hours (Škrbić *et al.* 2005). Water content in the homogenized soil sample was obtained by oven drying at 105°C to the constant mass.

Chemicals

Organic solvents (for residue analysis), anhydrous sodium sulphate and silica gel 60 (70-230 mesh) were purchased from Promochem (Wesel, Germany).

Anhydrous sodium sulphate and silica gel were used after heating at 130°C for 4 h. Distilled water used in the extraction procedure was extracted with cyclohexane. Whatman No. 40 filter paper of 110 mm in diameter from Whatman (Springfield Mill, Maidstone, Kent, UK) was cyclohexane washed prior to use. Sixteen PAHs standard mixture (EPA Method 610) was purchased from Supelco (Bellefonte, PA, USA).

Analytical procedure

Laboratory glassware used in the procedure was washed with detergent, rinsed properly with distilled water and acetone and heated at 110°C for 24 hours. During the procedure, the glassware was wrapped with aluminium foil to prevent PAHs degradation by light.

PAHs determination from soil samples was based on US EPA Standard Methods 3550B, 3630C and 8100 (EPA, 1986). The samples (10 g) were mixed with anhydrous sodium sulphate (30 g), extracted twice with 50 ml dichloromethane (DCM) (each extraction step lasted for 20 minutes) in the ultrasonic apparatus and then filtered throughout filter paper. The obtained extract was concentrated to 1 ml by a rotary evaporator (Laborota 4000, Heidolph Instruments, Germany) and transferred to a column packed with 8 g activated silica gel pre-soaked in cyclohexane and pre-eluted with cyclohexane. The complete transfer of the extract was accomplished by washing the vessel with 2 ml cyclohexane. The first fraction eluted with 15 ml cyclohexane was discarded, whereas the second fraction containing PAHs was eluted with 55 ml of cyclohexane/DCM mixture (7:3, v/v). The eluate was concentrated to about 1 ml in a rotary evaporator, then evaporated in the gentle stream of nitrogen to near dryness. Prior to analysis the internal standard solution of 1,3,5-triphenylbenzene was added and the extract was redissolved in a mixture of DHM and methanol (1:1, v/v). The final volume of the extract was set to be 0.1 ml.

Analysis of the eluted fraction was carried out using DANI 1000 gas chromatograph (GC) equipped with a flame ionization detector (FID). GC/FID analysis was performed on RTX 5 capillary column coated with 5% diphenyl - 95% dimethylpolysiloxane (30 m x 0.25 mm I. D. x 0.25 μm film thickness). The temperature programme was as follows: initial temperature 50°C held for 4 minutes, increased at a rate of 25°C/min to 200°C, then increased at a rate of 4°C/min to 310°C and held for 4 minutes. The injection port and FID temperatures were kept at 280°C and 300°C, respectively. Helium was used as the carrier gas at a flow of 2 ml/min. Aliquot of 1 μl of the prepared sample was injected into the GC system in a splitless mode with a purge time of 4 minutes.

The PAHs identification was performed by a comparison of their retention time with those of standard mixture. The quantitative analysis was done by the internal standard method. Five calibration standards with concentration evenly distributed through the working range were prepared.

The detection limits of the applied method for individual PAH compounds were about 0.01 μg/g. Quality control consisted of an analysis of blank, spiked and duplicate samples. Blank samples were treated and analyzed with the same method as the actual samples. Blank analysis showed no interference peaks with the individual PAH compounds analysis.

The samples fortified at two levels (1 μg/g and 20 μg/g) were prepared by adding a known volume of 16 EPA PAH standard solution and then analysed as previously described. The recoveries for PAHs were in the range of 69-90% (relative standard deviation (RSD) less than 12%). The obtained data were not adjusted on the basis of these recoveries.

RESULTS AND DISCUSSION

The basic physical and chemical properties of the composite soil samples through the investigated sites are listed in Table 1. The concentrations of PAHs in soil samples are presented in Table 2. Results are given as a mean value of duplicate analysis for each composite sample and each sampling site.

Table 1. Analysis of organic matter, water content and pH of investigated soil samples from Novi Sad (June 2007)

Soil characteristic	Sample no.						
	1	2	3	4	5	6	7
Loss of ignition, %	12.3	24.7	25.5	21.0	6.30	16.2	9.87
Water content, %	14.1	20.6	13.6	6.65	5.72	13.1	10.5
pH	6.6	6.7	6.7	7.2	7.2	7.8	7.7

Table 2. Content of polycyclic aromatic hydrocarbons (μg/g dw) in soil samples from Novi Sad (June 2007)

Dutch target values (μg/g) for unpolluted soil (VROM, 1994), benzo(a)pyrene equivalent factors (BPEF) and total carcinogenic potency (TCP) of each analyzed sample (μg BaPeq/g)

Compound	Sample no.							Dutch target value	BPEF	
	1	2	3	4	5	6	7		*	**
Naphthalene	1.13	0.97	12.5	1.26	1.36	nd	nd			
Acenaphthylene	2.18	3.01	8.83	2.13	1.11	nd	nd			
Acenaphthene	0.54	1.20	2.36	1.09	0.42	nd	nd			
Phenanthrene	0.85	1.20	3.62	1.26	0.78	0.05	0.06	0.045	0.00064	
Anthracene	0.30	0.29	1.54	0.44	0.08	0.10	0.07	0.050		
Fluorene	0.07	nd	0.57	0.18	0.57	nd	nd			
Fluoranthene	0.12	0.21	4.03	0.85	0.10	nd	0.10	0.020		
Pyrene	0.05	0.07	0.31	0.12	0.10	nd	0.11			
Chryzene	0.09	0.13	0.58	0.10	0.08	nd	0.12	0.020	0.026	
Benz(a)anthracene	0.05	0.06	0.37	0.10	0.03	0.05	0.11	0.020	0.014	0.006
Benzo(b)fluoranthene	0.70	0.69	1.72	0.51	0.27	0.06	0.08	0.11	0.076	
Benzo(k)fluoranthene	0.85	0.22	0.99	0.19	0.52	0.08	0.07	0.025	0.037	0.076
Benzo(a)pyrene	0.63	0.41	0.81	0.24	0.39	0.09	0.09	0.025	1	1

Compound	Sample no.							Dutch target value	BPEF	
	1	2	3	4	5	6	7		*	**
Dibenzo(ah)anthracene	1.34	1.93	5.27	1.48	0.33	0.14	0.06		0.89	
Benzo(ghi)perylene	0.13	0.06	2.47	0.24	0.05	nd	0.05	0.020	0.012	
Indeno(1,2,3-cd)pyrene	0.14	0.21	1.00	0.35	0.05	0.10	0.06	0.025	0.067	0.080
$\sum$PAHs	9.17	10.7	46.9	10.5	6.25	0.67	0.98			
TCP1***	1.94	2.24	5.78	1.63	0.73	0.22	0.16	0.029****		
TCP2***	0.76	0.50	1.10	0.32	0.46	0.11	0.11	0.029****		

nd-not detected;

* according MOE 1997;

** according Zapponi et al. 1993;

*** TCP1 and TCP2 are calculated by applying BPEFs reported by MOE (1997) and Zaponni et al. (1993), respectively;

**** reference values of TCP calculated according the Dutch target values and BPEFs reported by MOE (1997) and Zaponni et al. (1993), respectively

The $\sum$PAHs value refers to the sum of identified PAH components in the investigated samples, which ranged from 0.67 μg/g in the control sample to 46.93 μg/g in the schoolyard near the oil refinery. Mean $\sum$PAH value and standard deviation for all samples were 12.17 μg/g and 15.89 μg/g, respectively, with a median value of 9.17 μg/g. PAH profiles of analyzed samples are shown in Fig. 1. Of the PAHs detected, low-molecular weight PAHs, including 2- and 3-ring PAHs, contributed significantly to the $\sum$PAH concentration in samples near the oil refinery (nos. 1 - 5), while their contributions were much less in the control sample (no. 6) and in the one from the urban zone (no. 7), in which higher-molecular weight PAHs (from 4- to 6-ring compounds) dominated. Wilcke (2007) hypothesized that there are two distinct PAH soil patterns: a background and a human-made one. A large part of the composition of PAH mixtures in soils can be explained as simple mixing of these two major source groups. The background signal is dominated by natural PAHs produced biologically or released by vegetation fires or volcanic exhalations, including also ubiquitous atmospherically distributed anthropogenic emissions. The other source pattern originates from the combustion of fossil fuels dominated by the presence of a number of high-molecular weight PAHs (Wilcke 2007) irrespective of the different fuels and combustion conditions. Furthermore, soils which are contaminated by spills of unburnt petroleum might also be characterized by high concentrations of low-molecular weight PAHs, particularly naphthalene and phenanthrene (Aislabie *et al.* 1999). Thus, it could be concluded that the main source of PAHs detected in soils 6 and 7 were fossil fuel combustion processes. As the lower molecular weight PAHs are more volatile than the higher molecular weight PAHs, higher loadings of low-molecular PAHs in the vicinity of the oil refinery could be explained by the volatilization from the accidental spillage or leaks of oil from storage tanks and transportation lines, which contributed to the localized soil loadings of PAHs.

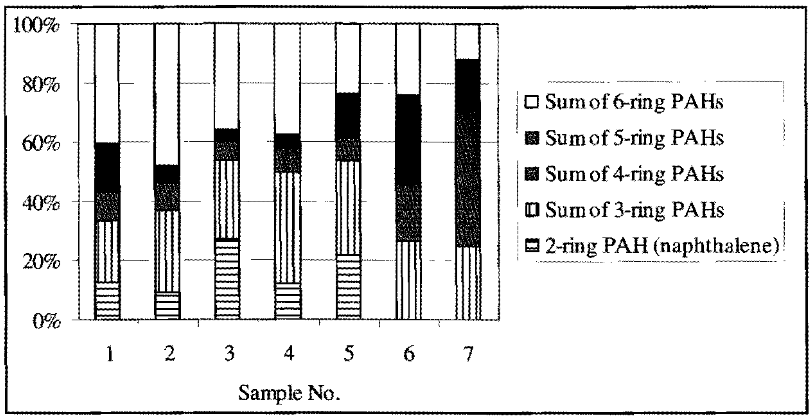

Fig. 1 PAHs profile of analyzed soil samples

In only one sample in the vicinity of the refinery, the determined concentrations was higher than the intervention value for soil sanitation set by the Dutch government of 40 μg PAH/g (VROM 1994, van Brummelen *et al.* 1996). Nevertheless, all identified compounds were detected in the quantities higher than the target values (0.020-0.050 μg/g) regulated by the Dutch goverment for unpolluted soil (see Table 2).

The total carcinogenic potency (TCP) of each sampling site and the reference one obtained using the Dutch target values for unpolluted soil are also presented in Table 2. Comparison of the estimated values revealed that all sites had the carcinogenic potency above the reference one. Benzo(a)pyrene, known to be carcinogenic, was identified in all samples and was above the Dutch target level of 0.025 μg/g. It formed 2-13% of $\sum$PAH in investigated samples.

Previously determined PAH contents in surface soils of Novi Sad (Škrbić *et al.* 2005, see Table 3) coincided with the levels found in the urban zone and the control sample. The loads in the samples near the refinery were much higher. Considering the reported background PAH concentration in Bulgaria of 2-22 μg/kg (Atanassov 2001) and the suggested level of endogenous total PAHs concentrations in soils of 1-10 μg/kg (Edwards 1983), it could be concluded that the soils of Novi Sad were contaminated above the natural and background level. On the other hand, a comparison of the present data with those reported in other parts of the world (Table 3) revealed that our values were within the range of the published ones.

Table 3. PAHs concentrations in soil throughout the world

Location, soil origin	Number of PAHs included in the total content	Soil depth, cm	Range of $\sum$PAHs or mean value*, μg/g	Reference
Welsh, UK, urban soil	14	0-5	0.119-54.50	Jones *et al.*, 1989
Brno, Czech Republic, urban soil	16		0.175-45.75	Strnad *et al.*,1994
Basel, Switzerland, urban soil	16	0-20	11.10-11.90	Niederer, 1995
Estonia, urban soil	12	0-10	0.011-153.00	Trapido *et al.*, 1999
Tokushima, Japan, urban soil	13	0-5	0.08-1.64	Yang, 2002

Location, soil origin	Number of PAHs included in the total content	Soil depth, cm	Range of $\sum$PAHs or mean value*, μg/g	Reference
New Orleans, USA,	16	0-2.5		Mielke *et al.*, 2004
urban area			0.906-7.285	
suburban			0.527-3.753	
Tarragona County, Spain	16	0-3		Nadal *et al.*, 2004
industrial area			0.166; 1.002	
residental area			0.736	
Novi Sad, Serbia, urban soil	16	0-5	0.307-1.452	Škrbić *et al.*, 2005
Hong Kong, urban soil	16	0-10	0.169	Zhang *et al.*, 2006
Nepal, urban soil	16	0-5	0.136-6.273	Aichner *et al.*, 2007

*Values are given as in the original paper

In order to get a rough estimate of PAH-soil characteristic correlation in the Novi Sad region, Pearson's correlation between analyzed geochemical factors and soil $\sum$PAH concentrations was applied. No statistically significant correlation was observed between the used variables applying the criteria value of probability $p < 0.05$. However, the correlation coefficient between $\sum$PAH contents and LOI values (0.624), as well as between $\sum$PAH contents and pH (-0.586), could be considered as negligible. This is in accordance with the well known fact that organic matter of soil is responsible for the binding of PAHs, while lower values of pH favours the accumulation of semi-volatile organic pollutants (Carter and Suffet 1982).

CONCLUSION

Sixteen priority EPA polycyclic aromatic hydrocarbons (PAHs) were determined in composite soil samples from seven sites throughout the area of Novi Sad (Vojvodina Province, Serbia). The highest total contents of PAHs were determined for soil samples in the vicinity of the oil refinery, in which the PAH-loads were up to 47 times higher than in the sample from the urban zone; the maximum PAHs concentration found was higher than the intervention value for soil sanitation set by the Dutch authorities.

Low-molecular weight PAHs were predominant at the sites close to the refinery, while high-molecular weight compounds contributed mostly to the total PAH content in the urban soil and the control sample.

Carcinogenic potency of PAH mixtures found in the investigated soils were above the reference one estimated on the base of the Dutch target values for unpolluted soil.

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Organochlorine pesticides and polychlorinated biphenyls in surface soils of Novi Sad and bank sediment of the Danube River

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The contents of 16 organochlorine pesticides (OCPs) and six so-called indicator polychlorinated biphenyls (PCBs) were determined in the surface zone (0–5 cm) of soil and sediment samples, taken from different locations in the city of Novi Sad, capitol of Vojvodina Province (North of the Serbia) covering residential and commercial area, recreational and arable zone. The total organochlorine pesticides concentration in soil varied from 2.63 to 31.78 ng g^{-1} dry weight, while the level in sediment was 10.35 ng g^{-1} dry weight. Maximum content of identified individual organochlorine pesticide in soil samples was 10.40 ng g^{-1} dry weight for p,p-DDE in the market garden and 6.31 ng g^{-1} dry weight for p,p'-DDT in sediment of the Danube River, although their application is restricted in Serbia. Some of investigated PCBs were identified only in the soil samples from a park-school backyard in the city downtown (0.32 ng g^{-1} dry weight) and market garden (0.22 ng g^{-1} dry weight), and also in sediment sample from left bank of the Danube River (0.41 ng g^{-1} dry weight). Data of the OCPs and PCBs present in this study were compared with the ones found for soils and river sediments throughout the world, and with limit values set by soil and sediment quality guidelines. Also, correlation between the levels of certain pesticides and soil characteristics (organic matter, pH and clay content) was investigated.

Keywords: Organochlorine pesticides; Polychlorinated biphenyls; Soil; River sediment; Legislative.

Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) have become a major issue of research in order to investigate their environmental occurrence, biochemical and toxic effects and human exposure.[1−4] Despite their ban or restricted use[5] they are still present in various environment compartments and subjected to cycling processes[6] and long range transport.[7] Soils and sediments are an important reservoir[8] for organochlorine compounds (OCCs) and agricultural soil is likely the largest sink of OCPs and major source of emissions.

The contamination of soil and sediment with persistent organochlorine compounds (OCCs) may be related to point sources, e. g., industrial discharges and waste plant effluents, but more frequently, it is attributed to diffuse sources: precipitation, runoff, particle transport.[9]

Due to their similar physicochemical properties, the fate of organochlorine pesticides and polychlorinated biphenyls is expected to be largely similar in the sediment and soil, but the characteristics of the medium has to be considered. Compared with Western Europe and North America less information concerning the levels of OCCs in soil and sediment is available from Eastern Europe.[10−12]

In the present study, surface soil and sediment samples collected from the city of Novi Sad (Serbia) were analyzed for residual levels of OCCs in order to evaluate their concentrations and distribution. The investigation included the top surface layer of the Danube River sediment along the coastal area where the infiltration galleries for water supply of inhabitants of Novi Sad are located. Therefore, the investigation of OCCs concentration in aquatic environments is needed to provide important information on the environment that serves as an indicator of contaminant loading.

This study was of a limited, local scale, but to date no survey exists for the Novi Sad area concerning the levels of organochlorine compounds in these types of samples. In addition, the data were compared with the ones found in other areas throughout the world and with limit values set by soil and sediment quality guidelines.

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Materials and methods

Description of the investigated sites

With 300,000 inhabitants, Novi Sad is the second largest city in Serbia. It is located on the Danube River, approximately 70 km northwest of Belgrade, in the Province of Vojvodina. It is a commercial and industrial center of the Province with intense traffic and a wide range of industrial activities, and a crossroads of major land and water ways.

The soil sampling sites were chosen in order to cover the whole city area: downtown, outskirt, the districts of the city where the E-75 motorway and Flour Milling industry (FMI) are located and left bank of the Danube River in the vicinity of the Oil Refinery (OR) and infiltration galleries (IG) used for water supply of inhabitants of Novi Sad.

The infiltration galleries are located some hundred meters downstream of the Novi Sad Oil Refinery and in the vicinity of PP Power Plant. In addition, within the Oil Refinery complex located on the left bank of the Danube River PCB-containing transformers are still in use. Danube-Tisa-Danube (DTD) Canal commonly used for waste plant effluents empties into the river nearby the Oil Refinery. The quality of abstracted groundwater is closely linked to that of the Danube River as well as to the quality of the groundwater located within the catchment area of the infiltration galleries. Thereby the quality of the abstracted groundwater is also closely linked to potential sources of contamination located upstream of the river and within the catchments of the infiltration galleries.

Soil and sediment sampling

The samples were collected during one day with stable weather conditions at the beginning of April 2002. Surface soils (0–5 cm) were taken from representative areas. Four soil samples (~250 g) from each sampling site were collected within a rectangular area of approximately 20 × 50 m. The sampling was designed to investigate organochlorine compounds concentrations in representative soils: residential and commercial area, park-school backyard (No. 1 in the downtown of the city and outskirts No. 2), market garden (No. 3), industrial area (No. 4) and roadside arable fields (No. 5). The locations of the sampling sites are shown in Figure 1.

Four sediment subsamples along the left bank of the Danube River were also collected to obtain the composite sediment sample (No. 6). The distance between sampling sites was approximately 30 m, that is distance between water wells located in the coastal area of the Danube River. The collected samples were stored in prewashed glass bottles and immediately transported to the laboratory. After being bulked, ground and sieved (~2 mm), six composite samples (~1 kg) were stored in a closed amber glass beaker at a temperature about 4°C for no more then ten days prior to analysis.

Chemicals

Organic solvents (Pesticide grade) were purchased from Promochem (Wesel, Germany); anhydrous sodium sulphate and sulfuric acid (95–98%) from Merck (Darmstadt, Germany); Florisil 60–100/PR and copper powder from Sigma Aldrich Chemie Gmbh (Steinheim, Germany). Environmental Protection Agency (EPA) 608 Pesticides Calibration Mix standard containing 20 μg mL^{-1} of each component (α-, β-, γ-, δ-HCH, p,p'-DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane), p,p'-DDE, p,p'-DDD, aldrin, dieldrin, endrin, endrin aldehyde, endosulfan I and II, endosulfan sulfate, heptachlor, heptachlor epoxide) in hexane/toluene mixture was purchased from Supelco (Bellefonte, PA, USA). A working PCB stock solution was prepared from the individual standard stock solutions of six indicator PCB congeners (International Union of Pure and Applied Chemistry (IUPAC) nos. 28, 52, 101, 138, 153, 180), 10 μg mL^{-1} isooctane, obtained from Sigma. Opportune dilutions of the working solution containing organochlorine compounds were made for instrumental calibration and for sample spiking. Distilled water used in the extraction procedure was previously extracted with n-hexane. Florisil was heated at 150°C during 12 h before use, while anhydrous sodium sulphate was heated at 600°C for 6 h in a furnace to remove impurities. Copper powder was activated with concentrated HCl and washed with water, methanol, methylene chloride and hexane, then was stored in hexane. The laboratory glassware was washed with detergent, rinsed with distilled water and acetone and then heated to 130°C overnight prior to use.

Soil and sediment characterization

The soil and sediment organic matter was determined by mass loss on ignition at 500°C for 2 h.[13] Particle size analysis of the samples was determined by the sedimentation method.[14] The pH measurements were carried out in deionized water at a soil (sediment)/water ratio of 1/2.5 with potentiometric glass electrode. Water content of the samples necessary for the expression of OCPs and PCBs contents per dry weight was measured gravimetrically by heating a known amount of the sample at 105°C to the constant mass. Results are presented as mean value of duplicate analysis.

Analysis

Sample extraction of OCPs and PCBs and cleanup were carried out according to the EPA methods 3540, 3660, 3665 and 3620.[15] Soil and sediment samples (about 20 g) were extracted in a Soxhlet apparatus with hexane/acetone (1:1) for 12 h. After the extract washing and acetone removal, and sulphur removal with copper powder, the extract was split into two portions. One of them was concentrated by rotary evaporator and cleaned up through a chromatographic column filled with activated Florisil. The column was eluted

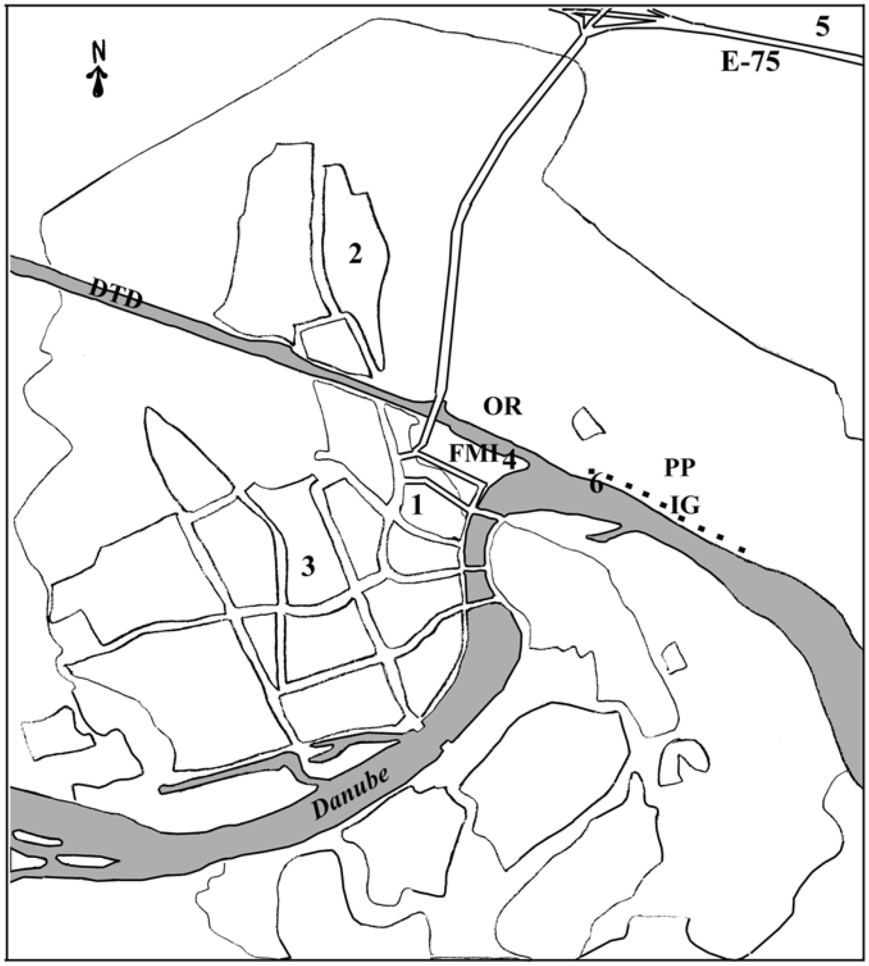

Fig. 1. The study area. Sampling locations: 1—park-school backyard, downtown; 2—park-school backyard, outskirts; 3—market garden; 4—industrial area; 5—roadside arable area; 6—left bank of the Danube River. DTD: Danube-Tisa-Danube Canal; E-75: motorway; FMI: Flour Milling Industry; IG: infiltration galleries, OR: Oil Refinery; PP Power Plant.

with 6%, 15% and 50% ethyl ether in hexane to obtain OCP fraction.

The second portion was cleaned up with concentrated sulphuric acid to obtain colorless extract. By the Florisil column filled with anhydrous sodium sulphate on the top, PCBs from hexane layer were recovered in petroleum ether. The final step in both cases involved the evaporation to near dryness by rotary evaporator and under gentle nitrogen stream. Prior to the analysis the extract was redissolved in 1 mL n-hexane and analyzed by gas chromatography (GC).

Sample analysis was carried out using HP 6890 gas chromatograph equipped with HP-5 fused silica column (60 m × 0.32 mm i.d., film thickness 0.25 μm) coupled to electron capture detector (ECD). The temperature program was as follows: initial temperature 120°C, held 2 min, with 10°C min^{-1} to 180°C, then with the run of 5°C min^{-1} to 290°C. Helium was used as the carrier gas with nominal initial flow through column of 2.2 mL min^{-1}. The injector and detector temperatures were maintained at 290 and 310°C, respectively. A 1 μL of extracts was injected into GC systems in splitless mode with purge time of 0.75 min. The OCPs and PCBs identification was performed by comparison of their retention time with those of standard mixtures. The quantitative analysis was done by the external standard method. Five calibration standards were prepared.

The detection limits of the applied methods for individual organochlorine compounds were between 0.04 and 0.1 ng g^{-1}. Quality control consisted of analysis of blank, spiked and duplicate samples. Blank samples were included in every batch of samples to check for possible contamination. They were treated and analyzed with the same method as the actual samples. Blank analysis showed no interference peaks with the individual organochlorine compounds analysis.

The spiked samples were prepared by adding known volume of standard solutions to the sample showing the lowest total OCPs and PCBs level (sample No. 5). The two fortification levels of 0.5 and 5 ng g^{-1}dry weight are used. The spiked samples were stored (for equilibrium) and then analyzed in five replicates as previously described. Since the sample used for fortification contained OCP residues, the recovery for these pesticides was calculated from the difference in the amount between the spiked and unspiked samples. The recoveries for OCPs were in the range of 69–90% (relative standard deviation (RSD), less than 12%), while for PCBs they were in the range of 66–85% (relative standard deviation, RSD, less than 15%), that is acceptable.[16] The residue data were not adjusted on the basis of these recoveries. Obtained results were presented as mean value of the duplicates.

Results and discussion

Soil and sediment characteristics

Organic content and physical parameters of the soil and sediment such as pH (H_2O), water content and particle size distribution are given in Table 1. The range of organic matter in the investigated soil samples was 4.23–8.09%, while the level for sediment was 0.55%. Soil samples of park-schoolyard in outskirts (sample 2), see in Figure 1, roadside arable area (sample 5) and market garden (sample 3) had similar organic content (5.82%, 6.01% and 6.19%, respectively) while minimum and maximum values for organic content were observed in soil samples from the industrial area (sample 4) and park-school backyard in the downtown of the city (sample 1), respectively. The clay content ranged from 4 to 9%. A small change in clay content can significantly affect soil characteristics like the cation exchange capacity, because of the much higher surface area to volume ratio for clay size particles as opposed to sand size particles. Sand was the predominant component of sample 4, while the sediment sample 6 consisted of sand. Variation in pH within sites was minor due to the calcareous nature of the soil.

Organochlorine pesticides in soil

The obtained levels of pesticides based on the standard mixture of 16 OCPs in the investigated soil samples are presented in Table 2. Non-detectable samples were assigned as zero in calculating the total organochlorine pesticides concentrations. This value in soil varied from 2.63 ng g^{-1} dry weight for roadside arable area (sample 5), see Figure 1, to 31.78 ng g^{-1} dry weight for sample from park-school backyard in the downtown of the city (sample 1). The OCP-load in the soils could be rated as follows: school backyard in the downtown of the city > grassland from industrial area > market garden > school backyard in outskirts > arable field.

The minimum total content of HCHs of 1.35 ng g^{-1} dry weight was obtained in sample 3 (market garden) followed by 3.61 ng g^{-1} in sample 1 (backyard in the downtown) and 11.36 ng g^{-1} in sample 4 (grassland from industrial area), while in samples from the outskirts (Nos. 2 and 5) none of the HCH isomers were detected. High content of HCHs in sample 4, preferentially because of pronounced level of γ-HCH, could be attributed to the usage of lindane due to the protection of wheat grains against diseases during the storage in the flour milling industry (Fig. 1).

In the samples 1 and 4 the following rank was observed: γ-HCH> δ-HCH> β-HCH; in the sample 3, δ-HCH was not detected while the content of γ-HCH was again higher than β-HCH. Of all analyzed HCH isomers α-HCH was not identified in any of the samples.

The highest total DDT content was observed in the market garden (sample 3) due to the high level of p,p'-DDE (10.40 ng g^{-1}), while in samples 2 and 5 DDT and its metabolites were not identified as in the case of HCHs. p,p'-DDD was not detected in any of the samples. DDT was identified in samples 1 and 4 (grasslands in the downtown of the city and industrial area) with a 3-fold concentration in the former compared to the later one. In these

Table 1. Analysis of organic matter,[3] particle size distribution,14 pH and water content of investigated soil and sediment samples from Novi Sad areas (April 2002).

	Location (No. of sample)					
Soil and sediment characteristics	*Park-school backyard, downtown (1)*	*Park-school backyard, outskirts (2)*	*Market garden (3)*	*Industrial area (4)*	*Roadside arable fields (5)*	*River bank (6)*
	Organic matter, %					
Loss of ignition	8.09	5.82	6.19	4.23	6.01	0.55
	Particle size distribution, %					
Clay (<0.002 mm)	6	5	9	4	5	0
Dust (0.002–0.05 mm)	49	55	45	27	56	0
Sand (0.05–2 mm)	45	40	46	69	39	100
pH (H_2O)	7.80	8.02	7.90	7.95	8.10	8.12
Water content, %	18.6	20.4	16.6	15.4	17.3	30.2

Table 2. Mean content of organochlorine pesticides (OCPs) (ng g^{-1} dry weight), in surface soil and sediment samples from the urban area of Novi Sad (April 2002), and residue limit according to Dutch legislation[17] and MacDonald et al.[18]

	Location (No. of sample)						*Legislation*		
	Soil					*Sediment*	*Soil*	*Sediment*	
Compound	*Park-school backyard, downtown (1)*	*Park-school backyard, outskirts (2)*	*Market garden (3)*	*Industrial area (4)*	*Roadside arable fields (5)*	*River bank (6)*	*The Netherland, new proposal[17], MPC*[a]	*MacDonald et al.[18], TEL*[b]	*The Netherland, new proposal[17], MPC*
$\alpha-$HCH	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	310		310
$\beta-$HCH	0.21	<0.1	0.15	0.35	<0.1	<0.1	101		11
$\delta-$HCH	1.50	<0.1	<0.1	2.91	<0.1	<0.1			
γ-HCH	1.90	<0.1	1.20	8.10	<0.1	<0.1	1.0	0.94	44
p,p'-DDT	6.30	<0.1	<0.1	1.98	<0.1	6.31	10^+		9.8^+
p,p'-DDE	3.50	<0.1	10.40	1.10	<0.1	0.52	13^+	1.42^+	5.8^+
p,p'-DDD	<0.1	<0.1	<0.1	<0.1	<0.1	0.91	21^+	3.54^+	3.9^+
Aldrin	0.64	<0.05	<0.05	<0.05	<0.05	<0.05	38		9.2
Dieldrin	0.95	<0.05	<0.05	0.15	<0.05	0.43	43	2.85	10
Endrin	4.70	1.90	0.59	2.23	2.22	0.51	0.95	2.67	2.6
Endrin aldehyde	3.20	2.90	1.23	1.46	0.41	0.52			
Endosulfan I	0.59	<0.05	<0.05	1.00	<0.05	0.23			
Endosulfan II	0.36	<0.05	<0.05	0.87	<0.05	0.51			
Endosulfan sulfate	6.00	<0.05	<0.05	<0.05	<0.05	0.41			
Heptachlor	1.10	<0.05	0.50	4.30	<0.05	<0.05			
Heptachlor epoxide	0.83	<0.05	<0.05	0.53	<0.05	<0.05		0.6	
ΣHCH	3.61	<0.1	1.35	11.36	<0.1	<0.1			
ΣDDT	9.80	<0.1	10.40	3.08	<0.1	7.74		7	
ΣOCP	31.78	5.40	14.07	24.98	2.63	10.37			

[a] MPC-maximum permissible concentration.

[b] TEL-threshold-effect level represents the concentration below which adverse effects are expected to occur only rarely.

$^+$sum of o,p'- and p,p'-isomers.

samples the value of p,p'-DDT/p,p'-DDE ratio was 1.8. A small value of the p,p'-DDT/p,p'-DDE ratio (<1) is indicative of aged (microbially degraded) DDT. Thus obtained ratio value may suggest the latest use/deposition from the atmosphere.[10]

Total level of cyclodiene insecticides were in the range from 2.32 to 18.37 ng g^{-1} dry weight. Endrin and endrin aldehyde were presented in all the samples. Endosulfan (I and II) was detected in samples 1 and 4, while endosulfan sulfate was found only in sample 1 with a maximum level of cyclodiene insecticides (6.00 ng g^{-1}). It could be concluded that the decomposition of endosulfan was favored by the alkaline soil condition[19]. Heptachlor was observed in the samples 1, 3 and 4, while its breakdown product (heptachlor epoxide), more persistent than heptachlor was presented in the samples 1 and 4 indicating the present use of heptachlor in sample 3.

The level of HCHs (<0.1–1.35 ng g^{-1}) in agricultural surface soil (0–5 cm) of Novi Sad (samples 3 and 5) was almost close to the lower values investigated by Zhang et al.[20] (nd-8.96 ng g^{-1}), and Chen et al.[21] (<0.14–42.31 ng g^{-1}); while the content of DDTs (<0.1–10.40 ng g^{-1}) was similar to the lower results of Bidleman and Leone[22] (0.10–1490 ng g^{-1}), Zhang et al.[20] (nd-94.07 ng g^{-1}) and Chen et al.[21] (7.60–831.32 ng g^{-1}). Also, the maximum concentration of individual pesticide obtained for p,p'-DDE (10.40 ng g^{-1}) in sample 3 was similar with a lower limit of Chen et al.[21] (1.98–144.59 ng g^{-1}), Bidleman and Leone[22] (0.10–1300 ng g^{-1}), and Harner et al.[23] (<0.02–112 ng g^{-1}).

The concentrations of all the detectable OCPs in the soils of Novi Sad were preliminary compared with the corresponding target value according to Dutch value due to the absence of a national standard for identifying soil pollution. The contents of OCPs in the investigated soil samples were much lower than maximum acceptable concentration (MAC) set by the new proposal of the Dutch legislation[17] except of γ-HCH for samples 1, 3 and 4 (MAC is 1 ng g^{-1}) and endrin for samples 1, 2, 4 and 5 (MAC is 0.95 ng g^{-1}) (Table 2).

Different order of sentences in order to overcome the deletion of the heading it should be: "In order to get a rough estimate of OCP behavior in area of Novi Sad, Pearson correlation between several soil geochemical factors and soil OCP concentration was applied, for it is well known that the intensity of OCP degradation depends upon several environmental factors, temperature, soil type and pH, redox potential, moisture and organic carbon content.[24,25] Also, substance specific parameters, such as water solubility, vapor pressure and Henry's law often play a dominant role. For correlation significance, the criteria value of probability ($p < 0.05$) was used. Correlation of the soil pH with organic content matter resulted in a negative variation ($r = -0.54$), suggesting the source of soil acidity is from organic matter decomposition.[2] Significant correlations of the soil pH with total DDT and total OCP were found, $r = -0.89$ and $r = -0.88$, respectively, indicating the source of soil acidity is causing the reduction of total DDT and total OCP investigated. This is in accordance with the finding of Bollag and Loll[26] and Carter and Suffet[27] who showed that in alkaline solutions carboxylic and phenolic functional groups on the humic polymer are probably dissociated and pesticides may attach to it by cation exchange. Several researchers[28,29] note that the molecular configuration of humic acid changes with pH, shifting from a stretched formation at neutrality to a coiled one at lower pH. Khan[29] uses this phenomenon as an explanation for differences in the adsorption of paraquat and diquat by humus.

Of the investigated pesticides, the only positive and significant correlation was obtained for clay and p,p'-DDE ($r = 0.95$) indicating the adsorption of p,p'-DDE by ion exchange and by weaker physicochemical processes in soils having an organic matter content lower than 6%. In this case clay may compete with humic materials for binding p,p'-DDE.[26]

Also, positive and significant correlations were found for soil samples from site 1 and site 4 ($r = 0.84$), and site 2 and site 5 ($r = 0.95$), indicating similarity between them concerning OCP content. Former samples belonged to the urban area, while the later ones to the outskirts. Different level of pesticides could be attributed to the latest use.

Organochlorine pesticides in sediment

In sediment sample, total level of OCPs was 10.35 ng g^{-1} dry weight. Nine OCP compounds were determined with a dominant level of p,p'-DDT (6.31 ng g^{-1}); these can be arranged in descending order as follows: total DDT>total cyclediene insecticides, while HCHs were not found (Table 2). Similar order was obtained for the sediments samples (given as mean values) taken along the bank of the Ebro River (Spain)[30], which passes through agricultural areas like the Danube River: DDTs (3.076 ng g^{-1}) >cyclediene (0.421 ng g^{-1}) >HCHs (0.007 ng g^{-1}).

Comparison with literature data revealed that the levels of identified OCPs (p,p'-DDT, p,p'-DDD and endosulfan I) in the Danube River sediment were similar with the lower values of the ones determined for sediments from Buffalo River, South Africa (which passes through agricultural areas) (1.9–110.0 ng g^{-1}, 1.3–47.7 ng g^{-1} and 1.9–92.0 ng g^{-1}, respectively)[31] and for the sediment of Queme River (nd-70.0 ng g^{-1}, nd-4.33 ng g^{-1} and nd-15.0 ng g^{-1}, respectively)[5] which drains the largest part of Benin cotton belt. However, contents of these identified OCPs in the Danube River sediment were slightly higher than values given for the Tonghui River of Beijing (nd-0.011 ng g^{-1}, nd-0.008 ng g^{-1} and nd-0.07 ng g^{-1}).[32]

In addition, the results obtained for the Danube River sediment were compared with sediment quality guidelines (Table 2). It could be seen that the concentrations of the analyzed OCPs were much lower than the maximum acceptable

Table 3. Mean content of polychlorinated biphenyls (PCBs) (ng g^{-1} dry weight), in surface soil and sediment samples from the urban area of Novi Sad (April 2002).

	Location (No. of sample)					
	Soil					*Sediment*
Compound	*Park-school backyard, downtown (1)*	*Park-school backyard, outskirts (2)*	*Market garden (3)*	*Industrial area (4)*	*Roadside arable fields (5)*	*River bank (6)*
PCB 28	0.05	<0.04	0.05	<0.04	<0.04	0.07
PCB 52	0.06	<0.04	0.07	<0.04	<0.04	0.09
PCB 101	0.11	<0.04	0.10	<0.04	<0.04	0.14
PCB 138	0.10	<0.04	<0.04	<0.04	<0.04	0.11
PCB 153	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
PCB 180	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
ΣPCBs	0.32		0.22			0.41

concentration set by the Dutch legislation[17] for the protection of aquatic environments and below threshold-effect level (TEL), which represents the concentration below which adverse effects are expected to occur only rarely.[18]

Polychlorinated biphenyls in soil and sediment

The obtained levels of polychlorinated biphenyls based on the standard mixture of 6 PCBs in the investigated soil and sediment samples are presented in Table 3. Non-detectable samples were assigned as zero in calculating the total PCBs concentrations. The total PCB levels found in the soil samples from park-school backyard in the downtown in the city and market garden were 0.32 ng g^{-1} dry weight and 0.22 ng g^{-1} dry weight, respectively. In the samples from park-schoolyard in outskirts (sample 2), industrial area (sample 4) and roadside arable area (sample 5) concentrations of PCBs were below detection limit. The content of these compounds in sediment sample from left bank of the Danube River was 0.41 ng g^{-1} dry weight.

Lipophilic affinity of PCBs result in the accumulation of these substances in soil with higher organic content[33] like in the sample 1, but PCBs may be influenced by particle fractions such as clay[34] in sample 3.

PCB 101 had the highest concentration in the samples where PCBs were identified, followed by PCB 138, 52 and 28 (sample 1 and 6), and PCB 52 and 28 (sample 3), while congeners 153 and 180 were not detected. Area of Novi Sad with low concentrations of PCB 28 and PCB 52 in the soil has probably been subjected to long-range transport of PCBs rather than short-range transport from local sources. A long–range transport mechanism may result in a preference for lighter congeners due to the increased atmospheric residence time. But, it was possible that the low presence of heavy congeners (PCB 101 and PCB 138) originated from short-range transport due to leakage of dielectric fluid in transformers present in the Novi Sad area which had a PCB composition with penta- to hexa-chlorinated congeners.

Bank sediment contained PCBs in slightly higher concentrations than those in soil. The primary sources of these organochlorine compounds in the river could be the industrial activities along the basin, municipal effluents and tributaries. However, the very low levels of PCBs observed in the soil and sediment samples in Novi Sad area correspond with the lack of production and low usage of PCBs in Eastern European countries.[12]

Levels of 6 PCBs in the soil samples from Novi Sad area were similar with lower limit of the results taken from the literature: for the pasture, scrub, grassland, woodland in United Kingdom (0.33–8.7 ng g^{-1})[35], for agriculture land, Germany (0.95–3.84 ng g^{-1})[36], for remote area, worldwide (0.26–97 ng g^{-1})[37], for remote, suburban, urban and industrial area, France (0.86–8.4 ng g^{-1})[38], and for agricultural and grassland, Switzerland (0.86–8.4 ng g^{-1}).[39]

Opposite, in Slovakia twenty-five years of the manufacture of PCBs have undoubtedly resulted in the increased environmental contamination of the suroundiing area. The PCBs levels of soil samples taken close to the waste disposal sites of Chemko factory ranged from 170 to 5800 ng g^{-1}, while substantially increased soil contamination (3900–53000000 ng g^{-1}) was observed in the vicinity of sites where PCBs have been landfilled or stored or used, such as heat-exchanging fluids in facilities preparing asphalted gravel.[11] Also, PCBs concentrations in soil samples from former Chlorofen (Polish PCBs mixture) plant[40] were between 600 and 589500 ng g^{-1}, while increased levels were also observed in soil samples (up to 3400 ng g^{-1}) taken from a former Soviet Army base in Poland.[41]

The content of 6 PCBs in bank sediment of the Danube River was similar to the lower level of data for the Tonghui River of Beijing (0.78–8.47 ng g^{-1})[32], but much lower than the results for sediment of the rivers Rhine, Danube, and

Volga, (200 ng g^{-1}, <40 ng g^{-1} and <40 ng g^{-1}, respectively), three large rivers in Europe, with large catchment areas covering a substantial part of western and eastern Europe.[42] An important number of hydrological dams for electric energy and a nuclear power station that are spread along the Ebro River[30] could be responsible for the increased PCB pollution detected in sediments from the middle section, 1771.8 ng g^{-1}. In the study of Mai et al.[43], the PCB concentrations determined from samples of the Zhunjiang River (48.3–486 ng g^{-1}) suggest that those sediments were moderately to strongly contaminated by PCBs. The PCBs concentrations in the upper layers of sediment cores (183 and 232 ng g^{-1}) in Western Scheldt estuary show that PCB pollution[44] is probably due to the heavy industrialization of the river catchment area with continuous input of pollutants.

Also, the concentrations of PCBs in the soils and sediment of Novi Sad were preliminary compared with the corresponding soil and sediment quality guidelines. The contents of PCBs in the investigated soil sample 1 was lower, while the level for sample 3 was slightly higher than maximum acceptable concentration (MAC) (0.3 ng g^{-1} dw) set by the Dutch legislation.[17]

In addition, the level obtained for the Danube River sediment was slightly higher than the maximum acceptable concentration (0.3 ng g^{-1}) set by the Dutch legislation[17] for the protection of aquatic environment and much lower than threshold-effect level (TEL), 34.1 ng g^{-1} dw, which represents the concentration below which adverse effects are expected to occur only rarely.[18] It is important to note that the sum of 6 indicator PCBs only represent a portion of total PCBs in samples. But, in the light of results presented in Bollag and Loll[26] review, concerning the xenobiotic binding into soil humus, it can be presumed that low organic content in the investigated sediment sample probably had influence on higher mobility of these pollutants. When this fact is taken into account, observed PCB level in sediment cannot be neglected, especially considering the vicinity of infiltration galleries.

Conclusion

On the basis of obtained data, grouping of all organochlorine compounds by chemical affinity could be arranged in descending order as follows: total cyclodiene>total DDT>total HCH>total PCB. Five species of Stockholm Convention pesticides (DDT, aldrin, dieldrin, endrin, heptachlor) were detectable in the soils and three (DDT, dieldrin, endrin) in the river sediment of Novi Sad. In addition, HCH isomers were determined in the samples from the park-school backyard in the downtown of the city, market garden, and industrial area, while PCBs in the samples from park-school backyard in the downtown of the city, market garden, and bank sediment. Significant correlation of the soil pH with total DDT and with total OCP, as well as of clay content with p,p'-DDE were found. Comparison of the obtained OCPs and PCBs contents with literature data and soil and sediment quality guidelines revealed that the presence of these compounds in soil and sediment samples from Novi Sad was not pronounced. On the other hand, taking into consideration the very low content of organic matter in the sediment sample it might lead to the enhanced mobility of analyzed contaminants, and because of the vicinity of groundwater table and infiltration galleries, the drinking water supply of Novi Sad seems to be at risk of being polluted.

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Polycyclic Aromatic Hydrocarbons in Surface Soils of Novi Sad and Bank Sediment of the Danube River

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Concentrations of 16 EPA polycyclic aromatic hydrocarbons (PAHs) in the surface soil samples of Novi Sad city urban area and in the Danube bank sediment sample were measured in 2001. The sampling sites were chosen in order to cover the whole city area and the results correspond to a network of six representative sampling sites. The total content of PAHs ranged from 307 to 1452 μg/kg with arithmetic mean value of 667 μg/kg and median of 382 μg/kg that represented typical PAH level of soils throughout Novi Sad urban area. Value of total PAHs content obtained in bank sediment sample along the Danube River was 975 μg/kg. Benzo(a)pyrene known to be carcinogenic formed 6–14% of the sum concentration of the identified PAHs for all investigated samples. Data were compared with the ones found for soils and river sediments throughout the world, and with target values set by Dutch authorities for unpolluted soil. The total carcinogenic potency for each sampling site was calculated and compared with the ones obtained on the base of the target concentrations. It was revealed only one sampling site with carcinogenic potency below the value calculated for unpolluted soil.

Key Words: Soil; Sediment; Polycyclic aromatic hydrocarbons.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) released into the environment arise mainly from anthropogenic sources. They are formed by combustion, either natural as with forest fires or anthropogenic, such as industrial activities, heating from fossil fuels, or in motor vehicle.

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PAHs belong to the semi-volatile organic contaminant class and occur in the atmosphere under gaseous and particulate phases. They reach the soil by dry or wet deposition processes causing its contamination. Gaseous and particle-bound PAHs can be transported over long distances before deposition.[1] They are accumulated mainly in the humus layer of soil. The further pathway of PAHs dissipation in contaminated soil may be volatilization, irreversible sorption, leaching, accumulation by plants, and biodegradation.[2] PAHs with three and more rings tend to be strongly adsorbed to the soil. Strong sorption coupled with very low water solubility and very low vapor pressures make leaching and volatilization insignificant pathway of PAHs dissipation. Also plants hardly take up any PAHs from soil.[3,4]

PAHs are quite resistant to degradation, but soil bacteria are the primary degraders of PAHs in soil.[5] The range of half-lifes for PAHs in soil estimated by different researchers is quite different. They vary, depending on the compound, from 2 months to 2 years[6] and from 8 to 28 years.[7]

When the release of PAHs into the environment exceeds their degradation capacity, a significant accumulation of PAHs is observed in soil, plants, and water bodies. Since environmental contamination by PAHs presents a risk to both human health and biosystems mainly due to their potentially toxic, carcinogenic, and/or mutagenic effects on animals and human beings, United States Environmental Protection Agency (USEPA) has identified 16 PAHs as "priority pollutants."

PAHs concentration in soil correlates significantly with the corresponding levels in air and house dust,[8] urban street dust,[9] and plants,[10] therefore PAHs determination in soil may provide important information on the environmental pollution state. However, the environmental legislation in Serbia does not quantitatively regulate their occurrence in soil. With some exception, this situation is encountered worldwide.

PAHs concentrations in the soil of Novi Sad have never been studied systematically, and the extent of soil pollution in the city remains unknown. The objectives of this study included the investigation of the concentration of PAHs in the surface soil throughout Novi Sad and the evaluation of soil environmental quality in terms of PAHs contamination. In addition, the data were compared with the ones found in other urban areas throughout the world.

The investigation also included the top surface layer of the Danube River sediment along the coastal area where the infiltration galleries for water supply of inhabitants of Novi Sad are located due to obtain the pollution with PAHs. Therefore, the investigation of PAHs concentration in aquatic environments is needed to provide important information on the environment that serves as an indicator of contaminant loading.

MATERIALS AND METHODS

Sites of Investigation

With 300,000 inhabitants, Novi Sad is the second largest city in Serbia. It is located on the Danube River, approximately 70 km northwest of Belgrade, in the Province of Vojvodina; between the 19 and 20° Eastern longitude and the 45 and 46° Northern latitude; 70–80 m above sea level. It is a commercial and industrial center of the Province with intense traffic and wide range of industrial activities, and a crossroad of major land and water ways. Potential sources of pollutants for soils in the city are related to industrial, commercial, agricultural activities, and automobile exhaust.

The soil sampling sites were chosen in order to cover the whole city area, and their selection was based on the expected contamination with PAHs. Therefore, the study was concentrated on the urban core area, including the districts of the city where the motorway and Flour Milling industry are located and on the sediment sample from the Danube bank in the vicinity of the Oil Refinery and infiltration galleries used for water supply of inhabitants of Novi Sad.

The quality of abstracted groundwater is closely linked that of the Danube River as well as to the quality of the groundwater located within the catchment area of infiltration galleries. Thereby the quality of the abstracted groundwater is also closely linked to potential sources of contamination located upstream of the river and within the catchments of the infiltration galleries.[11]

For each investigated locality, the total carcinogenic potency was calculated. The concentrations of PAHs which have a well-known carcinogenic activity were used[12,13] and expressed as toxicological benzo(a)pyrene equivalent (BPE) unit. A BPE unit is the amount of specific PAH which has the same carcinogenic potency of a weight unit of benzo(a)pyrene (B(a)P). The total carcinogenic potency (TCP) is expressed as a sum of B(a)P toxicity equivalents, which are calculated multiplying the concentrations of the different PAHs by appropriate factors of carcinogenic activity:

$$\mathrm{TCP} = \sum_{i=1}^{n} c_{\mathrm{PAH}_i} \cdot \mathrm{BPEF}_i$$

where n is the number of the identified carcinogenic PAHs in each collected sample with known factors of carcinogenic activity (BPEFs) (see Table 2); c_{PAH} is the concentration of identified individual PAH in the sample with known factors of carcinogenic activity (BPEFs), μg/kg; and BPEF is the relative carcinogenic potency of a given PAHs components to benzo(a)pyrene.

The reference total carcinogenic potency was calculated as a sum of multiplied Dutch target concentrations[14] for unpolluted soil with appropriate

BPEFs due to estimation of the toxicity and carcinogenity of the investigated sites.

Soil and Sediment Sampling

The samples were collected during one day with stable weather conditions at the beginning of January 2001. Surface soils (0–5 cm) were taken from representative areas by using a stainless steel corer. At each site four individual soil samples (~250 g) were collected from a rectangular area of approximately 20 × 50 m. The sampling was designed to investigate PAHs concentrations in representative soils of the residential and commercial area, park-school backyards (No. 1 in the downtown of the city and outskirts No. 2), market garden (No. 3), industrial area (No. 4) and roadside arable fields (No. 5). For details about the location of sampling sites see sketch map (Fig. 1).

Four surface sediment subsamples along the left bank of the Danube River (No. 6) were also taken. The distance between sampling sites was approximately 30 m that is distance between water wells located in the coastal area of the Danube River. The collected samples were stored in prewashed glass bottles and immediately transported to the laboratory. The four samples from each location were mixed together and sieved through a steel mesh (~2 mm) to remove large

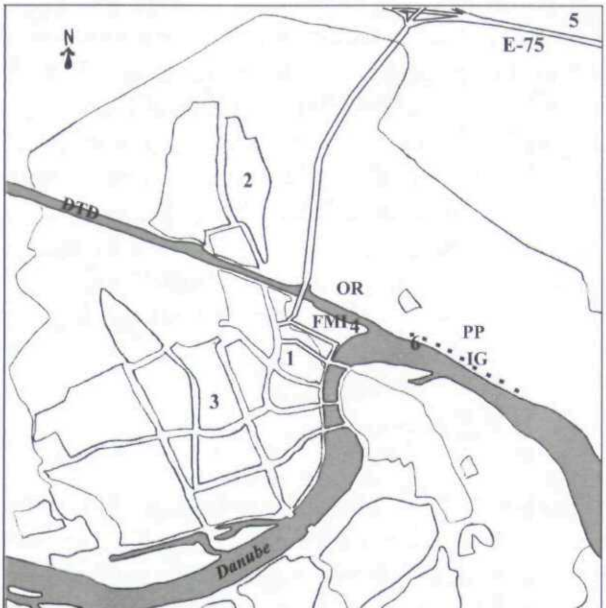

Figure 1: The study area. 1–6 sampling locations; DTD Danube-Tisa-Danube Canal; E-75 motorway; FMI Flour Milling Industry; IG infiltration galleries, OR Oil Refinery; PP Power Plant.

particles and organic debris, creating six composite samples (~1 kg) which were stored in closed amber glass beaker (previously rinsed with hexane) at the temperature about 4°C for not more than ten days prior to analysis.

Soil and Sediment Characterization

Basic chemical-physical properties like the organic matter content, particle size distribution, and water content necessary for the expression of pollutant amount per dry matter, were determined for each composite soil and sediment sample. The procedures used have been described elsewhere.[15,16]

Chemicals

Organic solvents (HPLC grade), sodium sulphate, and potassium hydrogen carbonate were purchased from Merck (Hohenbrunn, Germany), while silica gel 60, 70–230 mesh and aluminium oxide, neutral, 70–230 mesh from Fluka (Buchs, Switzerland); sodium sulphate, silica gel, and aluminium oxide were used after heating at 180°C for 24 h; distilled water was extracted with hexane; 16 PAHs standard mixture (EPA Method 610) was purchased from Supelco (Bellefonte, PA, USA).

Analytical Procedure

Applied procedure for PAHs extraction from samples previously described by Škrbić and Miljević[11] is based on Lee et al. method.[17] Scheme of the procedure is presented in Fig. 2.

All glassware used in the procedure was washed with liquid soap and rinsed properly with distilled water and pure acetone and baked in oven at 100°C for 24 h. During the procedure glassware was wrapped with aluminium foil to prevent PAHs degradation by light.

Sample analysis was carried out using HP 6890 gas chromatograph. HP-5 fused silica column (30 m × 0.32 mm i.d., film thickness 0.25 mm) coupled to FID was used. Temperature program was as follows: initial temperature 50°C, held for 3 min, then increased at a rate of 10°C/min to 300°C and held for 4 min. Helium was used as the carrier gas with nominal initial flow through column of 2.2 mL/min, and the injector and detector temperatures were maintained at 290 and 310°C, respectively. A 1 μL of samples was injected into GC systems in splitless mode with purge time of 0.75 min. The quantitative analysis was done by the external standard method and PAHs identification was performed by comparison of their retention time with those of authentic standards. A solution of the standard mixture of 16 PAHs recommended by the EPA method 610 was separated and analyzed in the same conditions as real samples. The detection limits of the applied method for each individual component were ranged from 5 to 10 μg/kg.

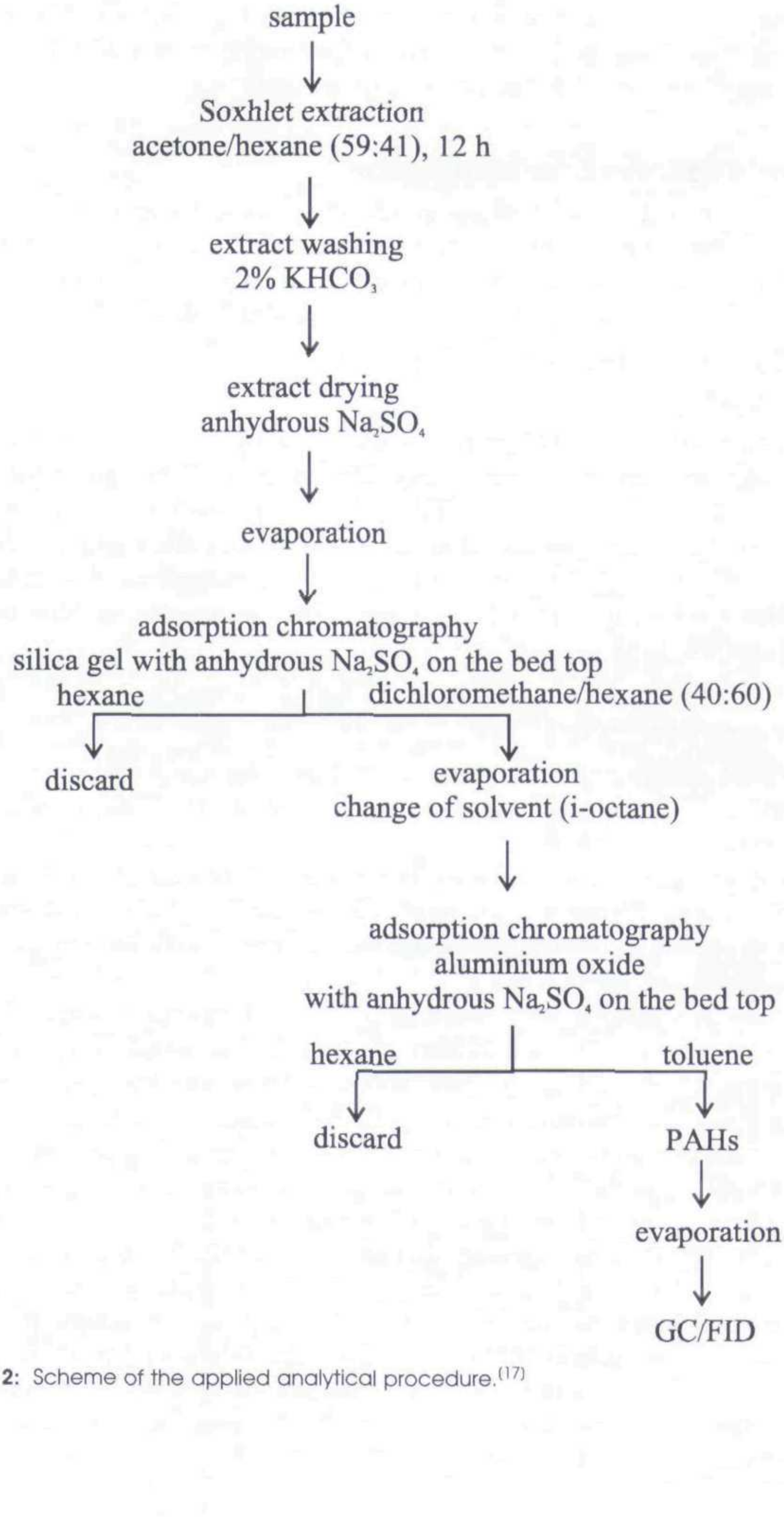

Figure 2: Scheme of the applied analytical procedure.(17)

Recovery efficiencies were determined by processing a solution containing known PAHs concentrations following the same experimental procedure used for the treatment of composite samples. This study showed that the recovery efficiencies for 16 PAHs species ranged from 65 to 90% depending on their molecular weight, which was in agreement with previously reported mean recovery value of 90% obtained for phenanthrene, anthracene, crysene, benzo(a)anthracene, and benzo(a)pyrene.[11] The blank tests for PAHs were accomplished using the same procedure as the recovery-efficiency tests except without adding the known standard solution before extraction. Obtained results were blank corrected and presented as mean value of the duplicates.

RESULTS AND DISCUSSION

The basic physical and chemical properties of the composite soil and sediment samples through the investigated sites are listed in Table 1. The range of organic matter in the investigated soil samples was 4.32–8.19%. In the sediment sample less than 1% of organic matter was determined. Soil samples signed 2, 3, and 5 had similar organic content while minimum and maximum values for organic content were obtained in soil samples 4 and 1, respectively.

Taking into consideration results of particle size analysis, it could be concluded that soil samples 1, 2, 3, and 5 were similar among themselves. Sand was predominant component of sample 4, while the sediment sample 6 was consisted of sand.

The concentrations of PAHs in soil and sediment samples are presented in Table 2. Results are given as mean value of duplicate analysis for each composite sample and each sampling site.

The ΣPAHs refers to the sum of identified PAHs components in the investigated samples. The ΣPAHs values ranged from 307 to 1452 μg/kg. Arithmetic mean and median value of total PAHs content obtained from the mean ΣPAHs values determined for every studied soil sample, were 667 and 382 μg/kg, respectively. Maximum PAHs level was determined for soil sample No. 4 showing

Table 1: Analysis of organic matter, particle size distribution, and water content of investigated soil and sediment samples from Novi Sad areas (January 2001).

	Sample					
Soil characteristic	**1**	**2**	**3**	**4**	**5**	**6**
Organic matter (%)						
Loss of ignition	8.19	5.89	6.39	4.32	6.10	0.54
Particle size distribution (%)						
Clay (<0.002 mm)	6	5	9	4	7	0
Dust (0.002–0.05 mm)	47	52	42	25	51	0
Sand (0.05–2 mm)	47	43	49	71	42	100
Water content (%)	20.3	22.9	14.8	14.5	18.1	28.1

Table 2: Content of polycyclic aromatic hydrocarbons (PAHs) in soil and sediment samples from Novi Sad areas (January 2001), Dutch target value for unpolluted soil,(14) carcinogenic activity factors (BPEFs),(12,13) and total carcinogenic potency (TCP).

	Sample						Dutch target value	BPEF	
Compound	**1**	**2**	**3**	**4**	**5**	**6**		[12]	[13]
	(μg/kg dry matter)								
Naphthalene	104	111	42	263	130	n.d.			
Acenaphthylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Acenaphthene	89	82	23	n.d.	171	102			
Phenanthrene	n.d.	n.d.	n.d.	n.d.	n.d.	294	45	0.00064	
Anthracene	n.d.	n.d.	n.d.	229	n.d.	n.d.	50		
Fluorene	n.d.	n.d.	n.d.	n.d.	54	n.d.			
Fluoranthene	n.d.	122	n.d.	n.d.	175	n.d.	20		
Pyrene	n.d.	n.d.	n.d.	171	63	n.d.			
Chryzene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	0.026	
Benzo(a)anthracene	n.d.	n.d.	n.d.	80	n.d.	n.d.	20	0.014	0.006
Benzo(b)fluoranthene	60	n.d.	59	n.d.	81	n.d.		0.11	0.076
Benzo(k)fluoranthene	41	n.d.	32	104	99	372	25	0.037	0.076
Benzo(a)pyrene	43	20	44	127	87	81	25	1	1
Dibenzo(ah)anthracene	n.d.	n.d.	66	n.d.	n.d.	n.d.		0.89	
Benzo(ghi)perylene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	0.012	
Indeno(1,2,3-cd)pyrene	45	n.d.	41	478	n.d.	126	25	0.067	0.080
ΣPAHs	382	335	307	1,452	860	975			
TCP_1[a]	54	20	113	164	100	103	29[b]		
TCP_2[a]	54	20	54	174	101	119	29[c]		

n.d.—not detected.
[a] TCP_1 and TCP_2—calculated by applying BPEFs developed by(12) and,(13) respectively.
[b,c] Reference values of TCP calculated according BPEFs developed by(12) and,(13) respectively.

the influence of the industrial enterprises (Oil Refinery, Power plant, Fertilizer plant, Flour Milling industry) on soil PAHs pollution. The mean ΣPAHs value in soil near the industrial area (No. 4) was fourfold that in the residential one (No. 1, 2, and 3), while in the soil sample No. 5 collected near motorway the higher PAHs concentration was also found, i.e., twice that in the residential area.

The determined concentrations were much lower than the intervention value for soil sanitation, as used by the Dutch government that is 40,000 μg PAHs/kg,[14,18] but taking into account the obtained values of identified PAHs components it could be concluded that they were above the target values set by Dutch goverment for unpolluted soil for almost all studied cases except for site No. 2 regarding the quantified level of benzo(a)pyrene.

Benzo(a)pyrene, known to be carcinogenic (has sufficient evidence of carcinogenicity in experimental animals) according to the estimation of the International Agency for Research on Cancer,[19] was identified in all investigated soil samples and was above the target level of 25 μg/kg set by Dutch goverment for soil samples No. 1, 3–5, and formed 6–14% of ΣPAHs in soil samples from Novi Sad investigated area.

Table 3: Polish standard limiting PAHs content (μg/kg) in the soil surface layer.(25)

Total PAHs content	Pollution class	Soil assessment
<200	0	Unpolluted (natural content)
200–600	I	Unpolluted (increased content)
600–1,000	II	Slightly polluted
1,000–5,000	III	Polluted
5,000–10,000	IV	Heavily polluted
>10,000	V	Very heavily polluted

Considering the reported background PAHs concentrations in Bulgaria of 2–22 μg/kg[20] and suggested level of endogenous total PAHs concentrations in soils of 1–10 μg/kg[21] it could be concluded that the soils of Novi Sad are contaminated above the natural and background level. But in accordance with the range of background PAHs levels of soil in Italy which were between 100–1000 μg/kg[22] and of up to 1000 μg/kg in Czech Republic[23] the urban area of Novi Sad has not been contaminated. The same conclusion could be drown out by comparing the median value of 382 μg/kg with median values as 300–400 μg/kg found for rural European soils PAHs level.[24]

A comparison of our data with a Polish standard soil PAHs contamination[25] given in Table 3 showed the following: soil samples (No. 1–3) were within the first pollution band (unpolluted soil with increased PAHs content). The arable soil near motorway E-75 (No. 5) was situated close to upper limit of the second pollution band (slightly polluted soil), while the level of soil pollution in the industrial area (No. 4) qualified it as polluted (the third pollution class).

Comparison with literature data (Table 4) also revealed that our data for urban area are within the values for almost all investigated sites and in some

Table 4: Total PAHs concentrations in soil throughout the world.

Location, soil origin	Number of PAHs included in the total content	Soil depth (cm)	Range of ΣPAHs (μg/kg)
This work,	16	0–5	
Urban area			307–1,452
Agricultural soil			860
Welsh, UK, urban soil(26)	14	0–5	666–54,500
Japan, urban soil(27)	8	0–3	800–1,300
Brno, Czech Republic, urban soil(28)	16	0–20	175–45,750
Basel, Switzerland, urban soil(29)	16	0–20	11,100–11,900
Zabrze, Poland, urban soil(25)	11	—	4,130
Krakow, Poland, urban soil(30)	8	0–20	370–770
Estonia, urban soil(31)	12	0–10	11.2–153,000
Tokushima, Japan, urban soil(32)	13	0–5	80–1,640
Czech Republic, agricultural soil(23)	16	0–30	693–1,067
Slovak Republic, agricultural soil(33)	12	0–30	204–1,093
Bulgaria, arable soil(34)	16	0–30	31–56

— = Not defined.

Table 5: Concentration ranges of polycyclic aromatic hydrocarbons (PAHs) in sediments collected from different locations.

Location	Number of PAHs included in the total content	Range of PAHs (μg/kg)
The Danube River, this work	16	975
The Tiber River, Italy(22)	13	4–625
The Jiulong River Estuary, China(36)	16	59–1,177
Ten rivers, Malaysia(37)	15	41–494
Pearl River Delta, China(38)	16	408–10,811
The Tonghui River, China(39)	16	127–928
The Gao-ping River, Taiwan(40)	16	8–356

instances are very close to the lower determined values for Krakow in Poland[25] and in Japan.[27,32] It is evident from ΣPAHs content in arable soil sample (No. 5) near motorway Belgrade-Novi Sad (E-75) that it is similar with the values of the ones determined for the agricultural soils of Czech Republic[23] and Slovakia,[33] while it is much higher than that obtained for Bulgaria.[34]

On the base of fluoranthene/pyrene ratio for sample No. 5 it was obviously related to pyrolytic origins as the value was greater than 1.[35] Therefore, the possible source of contamination was incomplete combustion.

PAHs level in the top surface layer of the sediment sample No. 6 consisted of sand are compared with the summary of total PAHs concentrations (μg/kg dry matter) in surface river sediments from various sites in the world (Table 5).

Our result is in agreement with the content of total PAHs found in surface sediment of some rivers throughout the world and is always close to the upper limits. According to[38] it could be considered moderately polluted. Taking into account that the determined value represented the present-day contamination and that the sediment consisted only of sand it is indicated the possible risk due to the vicinity of the infiltration galleries for water supply of inhabitants of Novi Sad.

The total carcinogenic potencies of each sampling site and the reference ones according to the carcinogenic activity factors developed by the Canadian Ministry of the Environment[12] and Zapponi and Valente,[13] are presented in Table 2. Regardless of the used carcinogenic activity factors, carcinogenic potency of site No. 2 was below, while of the others were 2–6 times higher than the reference ones indicating the increased carcinogenic burden of soils from the sites No. 1, 3–5, and of sediment No. 6.

CONCLUSION

Sixteen priority EPA polycyclic aromatic hydrocarbons (PAHs) were determined in composite soil samples from the representative sites throughout urban area of Novi Sad (Vojvodina Province, Serbia) and in the composite sample of the Danube bank sediment.

Maximum total content of PAHs was determined in the soil sample represented the industrial area (No. 4).

In accordance with background PAHs level of soil in some European countries (Italy, Czech Republic), the urban area of Novi Sad has not been contaminated. However, taking into account the values of identified PAHs components it could be concluded that they were above the target values set by Dutch government in almost all studied cases.

Value of ΣPAHs in analyzed surface sediment represented the present-day contamination is in agreement with those ones found in the sediment of some rivers throughout the world.

The total carcinogenic potency of each sampling site was compared with the reference ones and it was revealed only one site with the carcinogenic potency below the reference ones (site No. 2).

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