Rozprawa doktorska

Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

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Wpływ wielopierścieniowych węglowodorów aromatycznych na aktywność biologiczną gleb leśnych w relacji do ilości i jakości glebowej materii organicznej

Effects of polycyclic aromatic hydrocarbons on the biological activity of forest soils in relation to the quantity and quality of soil organic matter

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Streszczenie

Dynamiczny rozwój technologiczny i cywilizacyjny wiąże się z eksploatacją zasobów naturalnych i rosnącą emisją szkodliwych związków, w tym wielopierścieniowych węglowodorów aromatycznych (WWA). Zanieczyszczenia WWA stanowią poważne zagrożenie dla środowiska glebowego. Obecnie podejmowane są działania, których celem jest zminimalizowanie negatywnych skutków akumulacji WWA w środowisku glebowym. Głównym celem przeprowadzonych badań było poznanie roli wielopierścieniowych węglowodorów aromatycznych w procesach kształtowania aktywności biologicznej gleb, w zależności od ilości i jakości glebowej materii organicznej oraz uziarnienia. W podjętych badaniach starano się ustalić jak skład gatunkowy drzewostanu wpływa na akumulację WWA w glebach leśnych. Przeprowadzone badania są próbą uzupełnienia wiedzy na temat wielkości akumulacji WWA w glebach leśnych w relacji do chemicznych i biochemicznych właściwości gleb. Zaplanowane cele badań zrealizowano przeprowadzając cztery doświadczenia na powierzchniach badawczych zlokalizowanych w Krakowie, na terenie Nadleśnictwa Chrzanów oraz na terenie Nadleśnictwa Rybnik. Uzyskane wyniki wskazują, że wielkość akumulacji WWA w glebach leśnych jest determinowana właściwościami gleb, zwłaszcza ilością glebowej materii organicznej, oraz uziarnieniem. Gleby o większym udziale drobnych frakcji zwłaszcza pyłu i iłu charakteryzują się wyższą zawartością WWA w porównaniu do gleb piaszczystych. Potwierdzono znaczenie wpływu sposobu zagospodarowania gleb (leśne oraz rolnicze) na ilość i jakość glebowej materii organicznej, od której zależy aktywność biochemiczna gleb, a w konsekwencji wielkość akumulacji WWA. Gleby leśny cechują się wyższą zawartością węgla organicznego przy jednoczesnej kilkukrotnie wyższej akumulacji WWA. Dodatkowo, aktywność enzymatyczna gleb leśnych jest efektem oddziaływania roślinności drzewiastej, która wpływa na glebę poprzez dostarczoną biomasę nadziemną oraz podziemną. Przeprowadzone badania wskazują na istotną rolę składu gatunkowego drzewostanu w kształtowaniu poziomów próchnicznych oraz zakwaszenia gleb wpływając w ten sposób na aktywność mikrobiologiczną, a w konsekwencji na akumulację WWA. Drzewostany liściaste korzystniej wpływają na biodegradację WWA poprzez stymulowanie aktywności biologicznej gleb. Skład frakcyjny glebowej materii organicznej decyduje o wielkości akumulacji WWA w glebach leśnych. Istnieje bezpośrednia zależność pomiędzy akumulacją WWA, a zawartością lekkiej niezwiązanej frakcji glebowej materii organicznej.

Słowa kluczowe: glebowa materia organiczna, wielopierścieniowe węglowodory aromatyczne, aktywność enzymatyczna, gleby leśne, właściwości gleb

Summary

Dynamic technological and civilization development is connected with exploitation of natural resources and increasing emission of harmful compounds, including polycyclic aromatic hydrocarbons (PAHs). Contamination with PAHs is a serious threat to the soil environment. Currently, efforts are being made to minimize the negative effects of PAH accumulation in the soil environment. The main objective of this study was to recognize the role of polycyclic aromatic hydrocarbons in the processes of shaping the biological activity of soils, depending on the amount and quality of soil organic matter and soil texture. The aim of the study was to determine how the species composition of forest stands affects the accumulation of PAHs in forest soils. The present research is an attempt to extend the knowledge on the accumulation of PAHs in forest soils in relation to the chemical and biochemical soil properties. The planned objectives of the study were carried out by conducting four experiments on research plots located in Cracow, in the Chrzanów Forest District and in the Rybnik Forest District. The results obtained indicate that the accumulation of PAHs in forest soils is determined by the soil properties, especially the amount of soil organic matter and the soil texture. The soils with a higher share of fine fractions, especially of silt and clay, are characterised by a higher PAH content as compared to sandy soils. The importance of soil management (forest and agricultural) on the quantity and quality of soil organic matter was confirmed. Forest soils are characterized by a higher content of organic carbon with a several times higher accumulation of PAHs. In addition, the enzymatic activity of forest soils is a result of the influence of the trees vegetation, which affects the soil through the aboveground and underground biomass supplied. The conducted studies indicate that the species composition of forest stands has a significant role in the formation of humus levels and soil acidification, thus influencing microbial activity and, consequently, PAH accumulation. Deciduous tree stands have more beneficial effect on PAHs biodegradation by stimulating biological activity of soils. The fractional composition of soil organic matter determines the magnitude of PAH accumulation in forest soils. There is a direct relationship between PAH accumulation and the content of free light fraction of soil organic matter.

Keywords: soil organic matter, polycyclic aromatic hydrocarbons, enzymatic activity, soil degradation, forest soils

Spis treści

1. Struktura pracy

Przygotowana rozprawa doktorska stanowi spójny tematycznie cykl czterech publikacji w czasopismach naukowych:

Publikacja nr 1

Łyszczarz S., Lasota J., Staszel K., Błońska E., 2021a. Effect of forest and agricultural land use on the accumulation of polycyclic aromatic hydrocarbons in relation to soil properties and possible pollution sources. Forest Ecology and Management, 490, 119105. https://doi.org/10.1016/j.foreco.2021.119105
(Pkt. MNiSW: 200; IF: 3,558)

Publikacja nr 2

Łyszczarz S., Lasota J., Szuszkiewicz M. M., Błońska E., 2021b. Soil texture as a key driver of polycyclic aromatic hydrocarbons (PAHs) distribution in forest topsoils. Scientific Reports, 11(1), 1-11. https://doi.org/10.1038/s41598-021-94299-x
(Pkt. MNiSW: 140; IF: 4,379)

Publikacja nr 3

Łyszczarz S., Lasota J., Błońska E., 2022. Polycyclic aromatic hydrocarbons accumulation in soil horizons of different temperate forest stands. Land Degradation & Development, 33(6), 945-959. https://doi.org/10.1002/ldr.4172
(Pkt. MNiSW: 200; IF: 4,977)

Publikacja nr 4

Lasota J., Łyszczarz S., Kempf P., Kempf M., Błońska E., 2021. Effect of Species Composition on Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Urban Forest Soils of Krakow. Water, Air, & Soil Pollution, 232(2), 1-12. https://doi.org/10.1007/s11270-021-05043-0
(Pkt. MNiSW: 70; IF: 2,574)

2. Wprowadzenie

Wielopierścieniowe węglowodory aromatyczne (WWA) są związkami organicznymi zbudowanymi z dwóch lub więcej połączonych ze sobą pierścieni benzenowych (Liu i in., 2008; Haritash i Kaushik, 2009). W środowisku naturalnym WWA powstają głównie w wyniku niecałkowitego spalania lub pirolizy materii organicznej (Vane i in., 2014). Można wyróżnić dwie drogi powstawania WWA. Pierwszą z nich jest naturalny proces emisji w wyniku pożarów lasów, łąk oraz erupcji wulkanów (Wang i in., 2007). Drugim, obecnie przeważającym źródłem wydzielania związków WWA do środowiska są czynniki antropogeniczne (Hu i in., 2017), obejmujące głównie procesy uzyskania energii z przemysłowego spalania węgla, emisji przemysłu koksowniczego i naftowego, obejmujące pracę silników spalinowych czy też ogrzewanie budynków mieszkalnych (Wang i in., 2013; Ruby i in., 2016). Większość związków WWA cechuje się zdolnością do bioakumulacji, wysokimi właściwościami mutagennymi, genotoksycznymi oraz teratogennymi negatywnie oddziaływującymi na zdrowie organizmów żywych oraz ich prawidłowy rozwój (Joner i in., 2001; Ma i in., 2010; Zhao i in., 2017; Jiao i in., 2019). Hydrofobowy charakter, słaba rozpuszczalność w wodzie oraz litofilność związków WWA sprawia, że środowisko glebowe jest głównym miejscem akumulacji ponad 90% całkowitej emisji tych związków (Eom i in., 2007; Li i in., 2009). WWA cechuje także niska mobilność w środowisku glebowym za sprawą silnego ich wiązania przez kwasy fulwowe, huminowe oraz huminy (Yang i in., 2011). Właściwości WWA czynią je związkami zaliczanymi do grupy Trwałych Związków Organicznych (TZO) (Nash, 2011; Ren i in., 2017). Ze względu na ilość pierścieni budujących WWA, możemy wyodrębnić związki o niskiej masie cząsteczkowej oraz liczbie pierścieni mniejszej od czterech (LMW) oraz związki o wysokiej masie cząsteczkowej z większą liczbą pierścieni (HMW) (Glaser i in., 2005). Związki o wysokiej masie cząsteczkowej charakteryzują się wyższą toksycznością oraz twałością w porównaniu z WWA o niskiej masie cząsteczkowej (Li i in., 2016; Nas i in., 2020). Zrozumienie mechanizmów biodegradacji tych zanieczyszczeń zagrażających środowisku glebowemu jest obiektem globalnego zainteresowania (Zhang i in., 2004; Chen i in., 2008). Według raportu Krajowego Ośrodka Bilansowania i Zarządzania Emisjami (2019) źródłem 83,7% emisji w Polsce jest spalanie nie związane z przemysłem. Pozostałe 16,3% emisji to efekt procesów produkcyjnych, gospodarki odpadami, rolnictwa oraz transportu drogowego. Zarówno gospodarstwa domowe jaki i przemysł wykorzystują spalanie węgla kamiennego i brunatnego jako główne źródło energii (Roszko i in., 2020).

Związki WWA w glebie ulegają procesom fotoutleniania, utleniania chemicznego, adsorpcji w cząstkach gleby, wymywania i degradacji mikrobiologicznej (Yuan i in., 2001; Haritash i Kaushik, 2009; Eker i Hatipoglu, 2019). Mikroorganizmy glebowe są kluczowym elementem optymalizującym obieg materii organicznej, zapewniającym właściwy rozwój roślin oraz kształtującym proces degradacji zanieczyszczeń w środowisku glebowym (Johnsen i in., 2005; Wang i in., 2020). Aktywność enzymatyczna mikroorganizmów jest skutecznym wskaźnikiem informującym o stanie jakości gleby i oceny zmian w środowisku glebowym (Gil-Sotres i in., 2005; Riffaldi i in., 2006). Biodegradacja zanieczyszczeń odbywa się głównie poprzez aktywność biochemiczną mikroorganizmów, która jest najskuteczniejszą i najwydajniejszą metodą naturalnej redukcji toksycznych związków WWA (Ghosal i in., 2016; Li i in., 2019). Uwalniane przez drobnoustroje enzymy przyspieszają rozkład materii organicznej odgrywając kluczową rolę w cyklach obiegu węgla (β-glukozydaza, celulaza, dehydrogenaza), azotu (amidaza, chitynaza, proteaza) czy też fosforu (fosfataza) w środowisku glebowym (Gil-Sotres i in., 2005; Berg i McClaugherty, 2008), które przyczyniają się do zmniejszenia akumulacji zanieczyszczeń w glebie. Można wyróżnić wiele czynników wpływających na aktywność mikroorganizmów a w konsekwencji na procesy biodegradacji WWA w glebach. Aktywność mikroorganizmów zależy od temperatury, dostępności tlenu, ilości składników odżywczych, struktury populacji mikroorganizmów oraz odczynu (Oleszczuk i in., 2007; Haritash i Kaushik, 2009). W procesie biodegradacji związków WWA pH gleby odgrywa kluczową rolę, determinując dostępność składników pokarmowych dla mikroorganizmów. Niskie pH gleby zmniejsza pojemność sorpcyjną w rezultacie redukując aktywność biologiczną i zakłócając optymalny obieg niezbędnych składników pokarmowych w środowisku (Mueller i in., 2012).

Akumuklacja związków WWA w środowisku glebowym powiązana jest ściśle z glebową materią organiczną i jej zdolnościami sorpcyjnymi w stosunku do zanieczyszczeń organicznych (Six i in., 2002; Ehlers i Loibner, 2006; Ukalska-Jaruga i in., 2019). Wiązanie związków WWA przez glebową materię organiczną opiera się na działaniu sił van der Waalsa wiązań hydrofobowych i międzycząsteczkowych sił wodorowych (Pignatello i in., 2012), ograniczając w ten sposób dyfuzję oraz uwalnianie organicznych zanieczyszczeń do roztworów glebowych (Wang i in., 2012). Ze względu na niejednorodny charakter materię organiczną gleby możemy podzielić na trzy zasadnicze frakcje: frakcję o gęstości mniejszej niż <1,7 g cm^{-3} niezwiązaną z koloidami glebowymi określaną labilną frakcją glebowej materii organicznej (fLF); frakcję związaną w okluzjach aregatów glebowych określaną jako lekką frakcję związaną glebowej materii organicznej (oLF); frakcję silnie związaną z cząstkami mineralnymi iłu i pyłu określaną jako frakcję ciężką glebowej materii organicznej (MAF) (Wambsganss i in., 2017). Frakcja ciężka glebowej materii organicznej jest odporna na procesy biodegradacji, ze względu na fizyko-chemiczne wiązania między cząstkami pyłu lub iłu (Luo i in., 2008; Grüneberg i in. 2013). Udział poszczególnych frakcji glebowej materii organicznej zależy od wielkości agregatów glebowych oraz udziału poszczególnych frakcji granulometrycznych (Jastrow i in., 2007). Frakcje glebowej materii organicznej wiązać toksyczne związki orgaczniczne powodują ich unieruchomienie w środowisku glebowym (von Lutzov i in., 2006; Duan i in., 2015). Znajomość udziału poszczególnych frakcji glebowej materii organicznej może służyć jako wskaźnik kondycji środowiska glebowego (Błońska i in., 2017).

Zawartość zakumulowanych związków WWA w poszczególnych warstwach gleb determinowana jest sposobem użytkowania (Maliszewska-Kordybach, 1999). Intensywne użytkowanie rolnicze redukuje aktywność biochemiczną oraz zawartość glebowej materii organicznej (Drosos i in., 2018). Wyższy odczyn, temperatura gleby, właściwości fizyczne wywołane orką oraz intensywne nawożenie mineralne gleb rolniczych prowadzi do zmniejszenia zawartości materii organicznej a w konsekwencji do niższej akumulacji WWA (Rong i in., 2007). Gleby ekosystemów leśnych charakteryzują się wyższym potencjałem akumulacji WWA (Jensen i in., 2007; Zhang i in., 2013; Ammer, 2019). Efektywność akumulowania związków WWA bezpośrednio skorelowana jest z ilością oraz jakością glebowej materii organicznej (Matzner, 1984). Odczyn oraz ilość makroelementów kształtują aktywność biologiczną gleb i jednocześnie wpływają na procesy biodegradacji WWA (Reich i in., 2005; Mareschal i in., 2010). W glebach leśnych ilość i jakość materii organicznej zależy w głównej mierze od składu gatunkowego drzewostanu (De Deyn i in., 2008; Błońska i in., 2017). Dostarczanie ścioły do wierzchnich warstw gleby wpływa na jej pH i zawartość makroelementów, które decydują o aktywności biologicznej i tempie procesów rozkładu materii organicznej oraz związanych z nią związków WWA (Hobbie i in., 2007). Gleby drzewostanów iglastych mają niższy odczyn w porównaniu z glebami drzewostanów mieszanych lub liściastych w efekcie dostarczanej ścioły (Jandl i in., 2007; Vesterdal i in., 2008; Magh i in., 2018). Zwiększona akumulacja WWA w glebach leśnych związana jest także z wyższą wilgotnością od której zależą procesy dekompozycji materii organicznej (Wania i McLachlan 2001; Chen, 2015). Dynamika rozkładu glebowej materii organicznej od której zależy zdolność akumulacji oraz biodegradacji WWA, wynika z typu próchnicy gleb leśnych (Błońska i in., 2020). Igły i liście absorbują związki WWA z powietrza, a te przenoszone są do gleb leśnych poprzez opad ściółki (Guggenberger i in., 1996). Wielosezonowa obecność aparatu asymilacyjnego gatunków drzew iglastych oraz obecność wosku i lipidów na powierzchni igieł sprzyja absorbowaniu lipofilnych związków WWA obecnych w atmosferze (Peng i in., 2012; Li i in., 2017; Lasota i Błońska, 2018).

3. Uzasadnienie wyboru tematu badawczego

Badania naukowe dotyczące wpływu WWA na środowisko glebowe dotyczyły do tej pory głównie gleb użytkowanych rolniczo. W dotychczasowych badaniach poświęcono mniej uwagi na wyjaśnienie procesów akumulacji WWA w glebach leśnych oraz poznanie czynników je kształtujących. Brak jest wiedzy na temat wielkości akumulacji WWA w glebach leśnych pozostających pod wpływem oddziaływania drzewostanów o różnym składzie gatunkowym. Dodatkowo brak informacji na temat wpływu właściwości gleb leśnych na procesy akumulacji i biodegradacji WWA. Dotychczasowe badania wskazują na rolę glebowej materii organicznej jako głównego czynnika w akumulacji WWA (Johnsen i in., 2005; Liu i in., 2008; Wang i in., 2011; Ukalska-Jaruga i in., 2019). Gleby leśne charakteryzują się odmiennymi właściwościami glebowej materii organicznej w porównaniu do gleb rolniczych. W glebach leśnych dominują typy próchnic z obecności organicznych poziomów nadkładowych. Przeprowadzone badanie są próbą uzupełnienia braku wiedzy na temat roli poziomów organicznych w akumulacji WWA. Gleby leśne charakteryzują się większym zróżnicowaniem uziarnienia, od piasków luźnych po pyły ilaste oraz iły. Ilość WWA determinowana jest uziarnieniem gleby (Duan i in., 2015; Yu i in., 2018). Udział drobnych frakcji (pyłu i iłu) decyduje o składzie frakcyjnym glebowej materii organicznej co może przełożyć się na ilość i trwałość WWA zakumulowanych w glebach. Obszary leśne znajdują się w zasięgu silnej antropopresji, dlatego ważne jest poznanie poziomu zanieczyszczeń WWA w środowisku glebowym. Skład gatunkowy drzewostanu jest istotnym czynnikiem decydującym o ilości i jakości glebowej materii organicznej od których zależy akumulacja WWA. Do tej pory nie prowadzono badań zmierzających do wyjaśnienia roli poszczególnych gatunków drzew leśnych w kształtowaniu akumulacji WWA.

4. Cel pracy

Głównym celem przeprowadzonych badań było poznanie roli wielopierścieniowych węglowodorów aromatycznych w procesach kształtowania aktywności biologicznej gleb, w zależności od ilości oraz jakości glebowej materii organicznej. W badaniach testowano następujące hipotezy badawcze: 1) sposób użytkowania gleb (leśny/rolniczy) wpływa na zawartość WWA poprzez właściwości gleby zwłaszcza poprzez jakość i ilość materii organicznej dostarczanej do gleby; 2) biologiczna aktywność gleb różnie użytkowanych wyrażona aktywnością enzymatyczną jest w większym stopniu kształtowana przez właściwości gleb niż zawartość PAH; 3) zawartość drobnych frakcji granulometrycznych zwłaszcza pyłu pełni kluczową rolę w akumulacji związków WWA w glebach leśnych; 4) skład gatunkowy drzewostanu wpływa na akumulację WWA poprzez ilość i jakość glebowej materii organicznej oraz zakwaszenie gleby; 5) akumulacja WWA w glebach leśnych jest związana ze składem frakcyjnym glebowej materii organicznej od której zależy aktywność biologiczna gleb; 6) gatunki liściaste w większym stopniu stymulują aktywność biologiczną gleby, wpływając na niższą zawartość związków WWA w porównaniu do gleb drzewostanów iglastych.

Do przeprowadzenia określonych celów badawczych i sprawdzenia poprawności postawionych hipotez wykonano cztery doświadczenia, których rezultaty opublikowano w publikacjach naukowych. Szczegółowe cele przeprowadzonych badań zostały przedstawione poniżej.

Publikacja nr 1. Głównym celem doświadczenia było określenie wpływu sposobu użytkowania gruntów na zawartość WWA w odniesieniu do właściwości gleb. W doświadczeniu skupiono się szczególnie na wyjaśnieniu wpływu jakości i ilości materii organicznej dostarczanej do gleby na poziom zanieczyszczenia WWA a w konsekwencji na aktywność biologiczną gleby.

Publikacja nr 2. Przeprowadzenie doświadczenia miało na celu określenie roli uziarnienia na akumulację WWA w glebach leśnych. W badaniu określono także aktywność enzymatyczną gleb w odniesieniu do typu próchnic i poziomu zanieczyszczeń WWA.

Publikacja nr 3. Celem doświadczenia była ocena wpływu składu gatunkowego drzewostanu na akumulację WWA w drzewostanach gospodarczych. Badaniami objęto gleby drzewostanów iglastych, liściastych oraz mieszanych wzrastających w jednakowych warunkach siedliskowych. Podjęto próbę powiązania składu gatunkowego z jakością akumulowanej próchnicy, aktywnością enzymatyczną oraz akumulacją WWA.

Publikacja nr 4. Celem badań było poznanie wpływu składu gatunkowego drzewostanów na poziom zanieczyszczenia gleb przez WWA na terenie lasów miejskich. Doświadczenie obejmowało porównanie akumulacji WWA w glebach pod ośmioma gatunkami drzew (cztery gatunki liściaste oraz cztery gatunki iglaste). Aktywność enzymatyczna stanowiła narzędzie do oceny wpływu poszczególnych gatunków oraz akumulacji WWA na kondycję biochemiczną badanych gleb lasów miejskich Krakowa.

5. Charakterystyka terenu badań

Doświadczenia, których wyniki przedstawiono w publikacji nr 1 (Łyszczarz i in., 2021a) oraz publikacji nr 3 (Łyszczarz i in., 2022) przeprowadzono na terenie Nadleśnictwa Rybnik (50° 05′ 55″ N; 18° 32′ 42″ E) (Ryc. 1). Średnia roczna temperatura regionu wynosi 8,4°C, a średnia roczna suma opadów 705 mm. Obszar badań charakteryzuje się występowaniem gleb rdzawych właściwych oraz brunatnych. Teren Nadleśnictwa Rybnik znajduje się pod wpływem oddziaływania jednych z największych emisji przemysłowych w Europie (EEA, 2020). Według prognozy oddziaływania na środowisko (2016) na badanym obszarze w latach 2007-2016 stwierdzono przekroczenie (5-12 ng·m^{-3}) dopuszczalnych norm średniorocznego stężenia benzo(a)pirenu (BaP). Dodatkowo dopuszczalne normy stężenia pyłu PM10 przekroczyły średnioroczną normę wynoszącą 20 µg·m^{-3}, osiągając wynik 53 µg·m^{-3}, a stężenie PM2.5 przekroczyło dopuszczalną normę 10 µg.m^{-3} i wynosiło 26 µg·m^{-3} (WHO, 2005).

Ryc. 1. Lokalizacja poszczególnych obszarów badań

Badania, których wyniki przedstawiono w publikacji nr 2 (Łyszczarz i in., 2021b) przeprowadzono na terenie Nadleśnictwa Chrzanów (50°7′18N; 19°31′29E) (Ryc. 1). Do analizy wybrano powierzchnie badawcze o zróżnicowanym uziarnieniu gleby (od piasku luźnego przez glinę piaszczystą do gliny pylastej). Średnia roczna temperatura dla tego obszaru wynosiła 7.8°C, a średnia roczna suma opadów 658 mm. Na badanym terenie dominowały gleby opadowoglejowe wytworzone z utworów wodno-lodowcowych. Na powierzchni badawczej dominował drzewostan sosnowo-dębowy w wieku od 60 do 80 lat znajdujący się pod wpływem depozycji zanieczyszczeń pochodzących głównie z Górnośląskiego Okręgu Przemysłowego oraz Rafinerii Trzebinia. Zgodnie z raportem o stanie środowiska w województwie małopolskim (2020) w latach 2012-2017, na terenie całego Nadleśnictwa Chrzanów średnioroczne stężenia benzo(a)pirenu (BaP) przekraczały dopuszczalne normy i wynosiło 5,5 ng·m^3. Roczne średnie stężenia pyłu zawieszonego PM10 w całym zasięgu Nadleśnictwa Chrzanów wynosiły 34 µg·m^3, a pyłu zawieszonego PM2.5 w atmosferze przekraczały dopuszczalną normę osiągając 27 µg·m^3.

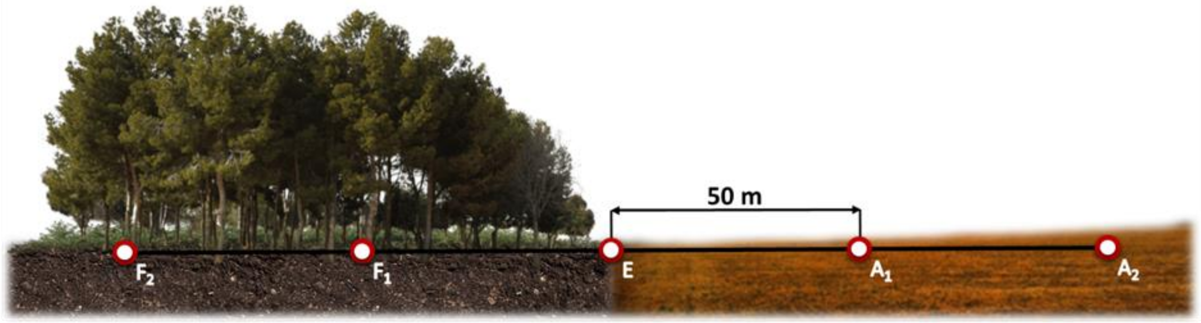
Doświadczenie, którego wyniki przedstawiono w publikacji nr 4 (Lasota i in., 2021) przeprowadzono w lasach miejskich Krakowa (50° 03′ 41″ N; 19° 56′ 18″ E) (Ryc. 1). Badaniami objęto kompleksy leśne miasta Krakowa takie jak: Las Reduta, Las Zesławice, Las Wolski i Las Tyniecki. Teren badań charakteryzował się występowaniem gleb płowych (Skiba i Drewnik, 2013). Średnia temperatura na badanym obszarze wynosiła 8.5°C, a średnia roczna suma opadów atmosferycznych wynosiła ok. 715 mm. W ostatnich latach Kraków stał się jednym z najbardziej zanieczyszczonych miast w Europie, w efekcie nadmiernych emisji SO_2, NOx, CO i benzo(a)pirenu (Wilczyńska-Michalik i Michalik, 2017). Duży transport publiczny, ruch samochodowy, bliskość górniczego regionu Górnego Śląska, port lotniczy w Balicach uważane są za główne przyczyny zanieczyszczenia gleb w Krakowie (Ciarkowska i in., 2019).

6. Metodyka badań i wyniki

6.1. Wpływ użytkowania leśnego i rolniczego na akumulację wielopierścieniowych węglowodorów aromatycznych w relacji do właściwości gleb i możliwych źródeł zanieczyszczeń

Wpływ sposobu użytkowania na zawartość WWA w odniesieniu do właściwości gleb został zaprezentowany w pracy: *Łyszczarz S., Lasota J., Staszel K., Błońska E. 2021. Effect of forest and agricultural land use on the accumulation of polycyclic aromatic hydrocarbons in relation to soil properties and possible pollution sources.* Badania przeprowadzono na terenie

Nadleśnictwa Rybnik. Do przeprowadzenia doświadczenia wytyczono sześć transektów o długości 200 m, z których co 50 m pobrano próbki gleby. Każdy transekt obejmował obszar leśny, obszar rolniczy oraz strefę ekotonową pomiędzy nimi (Ryc. 2).



Ryc. 2. Rozmieszczenie punktów poboru próbek w transekcie rolno-leśnym

Próbki gleby zostały pobrane z poziomu próchnicznego (0-15 cm), po usunięciu poziomu organicznego. Z każdego transektu pobrano 5 próbek gleby (2 próbki gleb leśnych, 2 próbki gleb rolniczych oraz 1 próbkę ze strefy przejściowej). Próbki gleb o naturalnym uwilgotnieniu przesiano przez sito o średnicy 2 mm i przechowywano w ciemności w temperaturze 4°C. W próbkach oznaczono zawartość WWA oraz aktywność biochemiczną. Uziarnienie określono metodą dyfrakcji laserowej (Analysette 22, Fritsch, Idar-Oberstein, Niemcy). pH gleby w H_2O i 1M KCl oznaczono stosując metodą potencjometryczną. Zawartość C i N oznaczono przy użyciu analizatora LECO CNS (TrueMac Analyzer Leco, St. Joseph, MI, USA). Zawartość kationów (Ca^{2+}, Mg^{2+}, K^+ i Na^+) oznaczono po ekstrakcji w 1M octanie amonu przy użyciu ICP (ICP-OES, Thermo iCAP 6500 DUO, Thermo Fisher Scientific, Cambridge, UK). Zawartość Cd, Cr, Cu, Ni, Pb i Zn oznaczono po mineralizacji w mieszaninie stężonego kwasu azotowego i nadchlorowego w stosunku 2:1 z wykorzystaniem ICP-OES. Zawartość WWA oznaczono wykorzystując wysokociśnieniową chromatografię cieczową (HPLC Dionex UltiMate 3000, wyposażonego w detektor fluorescencyjny i kolumnę Dionex UltiMate 3000 Column Compartment C18 5 µm oraz kolumnę HPLC 4,6·100-mm). Fazami ruchomymi były woda (A) i acetonitryl (B) przy szybkości przepływu 1 $ml \cdot min^{-1}$. W próbkach gleb oznaczono zawartość następujących WWA: naftalen (Nft), acenaften (Ace), fluoren (Flu), fenantren (Phe), antracen (Ant), fluoranten (Flt), piren (Pyr), benzo(a)antracen (BaA), chryzen (Chr), benzo(k)fluoranten (BkF), benzo(b)fluoranten (BbF), benzo(a)piren (BaP), dibenzo(ah)antracen (DahA), indeno(1,2,3-c,d)piren (IcdP) i benzo(g,h,i)perylen (BghiP). Do identyfikacji źródeł emisji WWA wykorzystano współczynniki diagnostyczne: BaP/BghiP (Katsoyiannis i in., 2007), Flu/(Flu+Pyr) (Ravindra i in., 2008), Flt/Flt+Pyr (Roberto i in., 2009) oraz IcdP/(IcdP+BghiP) (Yunker i in., 2012). Przy zastosowaniu substratów znakowanych fluorogenicznie oznaczono aktywność enzymów zewnątrzkomórkowych β-D-celobiozydazy (CB), β-ksylozydazy (XYL), N-acetylo-β-D-glukozaminidazy (NAG), fosfatazy (PH) i arylosulfatazy (SP) (Pritsch i in., 2004; Turner, 2010; Sannaullah i in., 2016). Do określenia biomasy mikrobiologicznej C, N i P wykorzystano metodę fumigacji i ekstrakcji (Jenkinson i Powlson, 1976; Vance i in., 1987). Analizę wariancji zastosowano do oceny różnic między średnimi wartościami badanych właściwości gleby. Obliczono współczynniki korelacji Pearsona pomiędzy badanymi właściwościami gleb. Dodatkowo do oceny zależności między właściwościami gleby a zawartością WWA zastosowano analizę składowych głównych (PCA). Różnice na poziomie istotności $P<0,05$ uznano za statystycznie istotne.

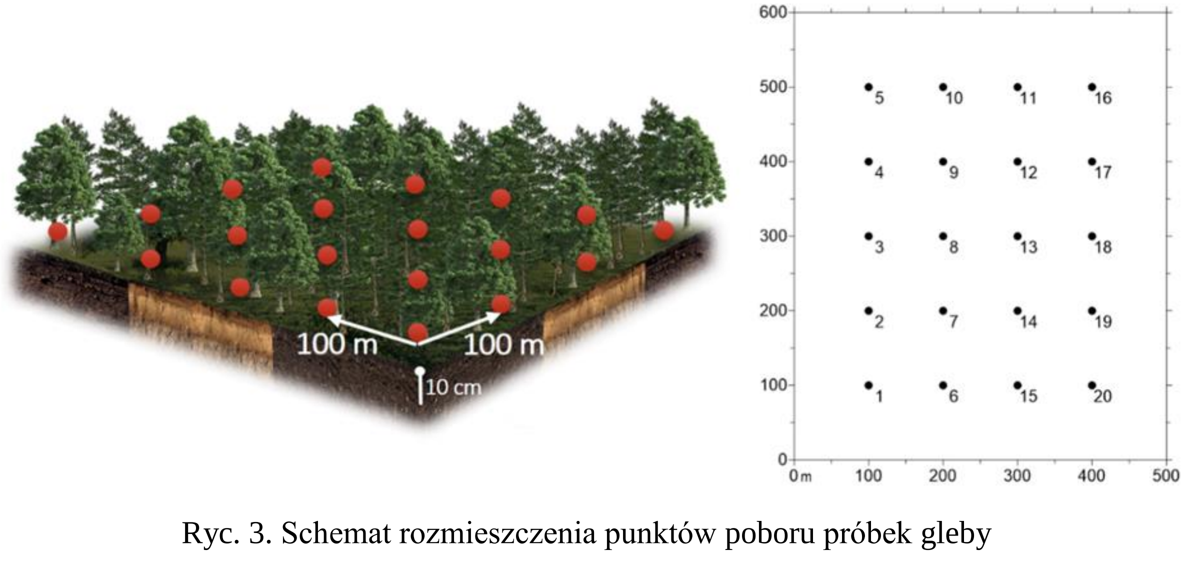
Niższą średnią wartością pH w H_2O cechowały się gleby leśne oraz gleby strefy ekotonowej (odpowiednio 4.15 i 4.40), natomiast średnie pH gleb rolniczych wynosiło 6.09. Istotne różnice stwierdzono odnośnie pH w KCl. Średnie pH KCl gleb leśnych wynosiło 3.44 a dla gleb rolniczych 5.32. Gleby leśne oraz gleby strefy ekotonowej charakteryzowały się statystycznie istotnie wyższą średnią zawartością C i N oraz wyższym stosunkiem C/N. Najwyższą średnią zawartością węgla organicznego odznaczały się gleby leśne (10.69%), a najniższą gleby rolnicze (1.46%). Najwyższą średnią zawartość azotu odnotowano w glebach leśnych (0.53%), a najniższą w glebach rolniczych (0.10%). Średnia wartość stosunku C/N dla gleb leśnych wynosiła 19.6, dla gleb strefy ekotonowej wynosiła 18.7, a dla gleb rolniczych 15.1. Statystycznie istotnie wyższą zawartość Ca stwierdzono w glebach rolniczych, a statystycznie istotnie wyższą zawartość Na stwierdzono w glebach leśnych., Nie odnotowano istotnych różnic w zawartości K i Mg w transekcie rolno-leśnym. Średnie wartości aktywności enzymatycznej oraz biomasy mikrobiologicznej były statystycznie istotnie zróżnicowane w zależności od typu użytkowania gleb. Wyższą aktywnością NAG, XYL i PH charakteryzowały się gleby leśne, w przypadku CB i SP różnice nie były statystycznie istotne. Gleby leśne charakteryzowały się także wyższymi średnimi wartościami mikrobiologicznej biomasy C, N i P. Metale ciężkie w poszczególnych glebach cechowały się zróżnicowaną zawartością, z wyjątkiem Mn i Zn. Najwyższą zawartość metali ciężkich odnotowano w glebach rolniczych, gdzie zawartość Cr, Cu, Ni i Pb była statystycznie istotnie wyższa niż w glebach leśnych i glebach strefy ekotonowej. Przeprowadzone analizy wykazały statystycznie wyższą zawartość WWA w glebach leśnych w porówaniu do gleb rolniczych. Średnia zawartość zakumulowanych WWA w glebach leśnych wynosiła 565.18 $\mu g \cdot kg^{-1}$, natomiast w glebach użytkowanych rolniczo była niższa i wynosiła 91.42 $\mu g \cdot kg^{-1}$. Zarówno w glebach rolniczych jak i leśnych dominowały czteropierścieniowe WWA. Gleby leśne charateryzowały się wyższą zawartością trzy-, cztero-, pięcio- i sześciopierścieniowych WWA w porównaniu z pozostałymi badanymi glebami. Najwyższą zawartość odnotowano w przypadku trójpierścieniowego fluorenu, którego zawartość w glebach leśnych wynosiła 1023 $\mu g \cdot kg^{-1}$. Poza fluorenem w glebach leśnych odnotowano wysokie zawartości fluorantenu, pirenu, benzo(a)antracenu, chryzenu, benzo(b)fluorantenu i indeno(1,2,3-c,d)pirenu. Współczynniki określające źródła emisji zwiazków WWA wskazały, że głównym źródłem zanieczyszczenia gleb w transekcie rolno-leśnym jest spalanie węgla. Pozostałe źródła emisji WWA to spalanie drewna i trawy oraz spalanie benzyny w pojazdach mechanicznych. Większość badanych enzymów (NAG, XYL i PH) oraz mikrobiologiczna biomasa były ujemnie skorelowane z pH. Aktywność enzymów i mikrobiologiczna biomasa istotnie korelowały z zawartością C, N i Na. Aktywność NAG, XYL i PH oraz mikrobiologiczna biomasa odznaczały się statystycznie istotną, dodatnią korelacją względem zawartości WWA. Szczególnie silną dodatnią korelację z WWA wykazała zawartość C, N i Na oraz w mniejszym stopniu, zawartość K. Zawartość WWA ujemnie korelowała z pH badanych gleb. W przypadku zawartości Cr, Cu, Pb i Zn stwierdzono ujemną korelację z zawartością C i N, a dodatnią z pH gleby. Czynniki 1 i 2, wyodrębnione w analizie PCA wyjaśniały łącznie 85,71% wariancji analizowanych właściwości gleb. Analiza PCA potwierdziła zależność między zawartością C i N, a zawartością WWA oraz potwierdziły odrębność gleb leśnych w stosunku do gleb rolniczych.

Przeprowadzone doświadczenie potwierdziło, że sposób użytkowania gleb kształtuje ich właściwości, poprzez dostarczaną do niej materię organiczną. Rodzaj dostarczanej materii organicznej warunkuje akumulację WWW oraz aktywność biochemiczną badanych gleb. Gleby leśne charakteryzowały się wyższym poziomem akumulacji WWA, w porównaniu z glebami użytkowanymi rolniczo. Dowiedziono także, że aktywność biologiczna gleby, wyrażona aktywnością enzymatyczną, zależy od ilości i jakości materii organicznej gleby, a w mniejszym stopniu od zakumulowanych w glebie WWA oraz metali ciężkich. Wysoka zawartość WWA nie powodowała ograniczenia aktywności biochemicznej gleb leśnych. Wskaźniki charakteryzujące źródła emisji WWA wskazały, że głównym źródłem emisji jest spalanie węgla. Doświadczenie potwierdza kluczową rolę ilości glebowej materii organicznej jako składnika biorącego udział w sorpcji i starzeniu się WWA. Badania wskazują, że większy dopływ detrytusu do gleb leśnych może przeciwdziałać hamowaniu aktywności enzymów glebowych przez WWA.

6.2. Uziarnienie gleby jako główny czynnik wpływający na zawartość wielopierścieniowych węglowodorów aromatycznych (WWA) w powierzchniowych poziomach gleb leśnych

Wyniki wpływu uziarnienia na akumulację WWA oraz aktywność enzymatyczną gleb leśnych przedstawia praca: *Łyszczarz S., Lasota J., Szuszkiewicz M. M., Błońska E., 2021. Soil texture as a key driver of polycyclic aromatic hydrocarbons (PAHs) distribution in forest topsoils.*

Powierzchnie badawcze zostały zlokalizowane na terenie Nadleśnictwa Chrzanów. Do przeprowadzenia doświadczenia pobrano próbki gleby z 20 punktów rozmieszczonych w regularnej siatce 100×100 m (Ryc. 3). Próbki gleb do analiz laboratoryjnych pobrano z poziomu próchniczno-mineralnego, z głębokości 0-10 cm po wcześniejszym usunięciu poziomu organicznego. W każdym punkcie poboru pobrano próbkę zbiorczą z czterech podróbek. W świeżych próbkach o naturalnym uwilgotnieniu oznaczono aktywność enzymów, mikrobiologiczną biomasę C i N oraz zawartość WWA. Przed przeprowadzeniem analizy próbki przechowywano w ciemności w temperaturze 4°C. Powierzchnie badawcze pogrupowano uwzględniając uziarnienie badanych gleb: I grupa obejmowała gleby o uziarnieniu piasku luźnego, II grupa obejmowała gleby o uziarnieniu gliny piaszczystej, III grupa obejmowała gleby o uziarnieniu gliny pylastej.



Ryc. 3. Schemat rozmieszczenia punktów poboru próbek gleby

Do określenia uziarnienia wykorzystano metodę dyfrakcji laserowej (Analysette 22, Fritsch, Idar-Oberstein, Niemcy). Metodą potencjometryczną określono pH gleby w H_2O i KCl. Do oznaczania węgla (C) i azotu (N) zastosowano analizator LECO CNS (TrueMac Analyzer Leco, St. Joseph, MI, USA). Metodą z wykorzystaniem ICP (ICP-OES Thermo iCAP 6500

DUO, Thermo Fisher Scientific, Cambridge, U.K.) oznaczono zawartość kationów zasadowych oraz zawartość Cd, Cr, Cu, Ni, Pb, Zn. Zawartość badanych metali ciężkich oznaczono po mineralizacji w roztworze stężonego kwasu azotowego i nadchlorowego w stosunku 2:1. Podobnie jak w poprzednim doświadczeniu, w celu określenia zawartości WWA wykorzystano metodę wysokociśnieniowej chromatografii cieczowej (HPLC). W próbkach gleby analizowano trzynaście wielopierścieniowych węglowodorów aromatycznych: naftalen (Nft), fluoren (Flu), fenantren (Phe), antracen (Ant), fluoranten (Flt), piren (Pyr), benzo(a)antracen (BaA) i chryzen (Chr), benzo(k)fluoranten (BkF), benzo(b)fluoranten (BbF), benzo(a)piren (BaP), indeno(1,2,3-c,d)piren (IcdP) i bezo(g,h,i)perylen (BghiP). Przy zastosowaniu substratów znakowanych fluorogenicznie oznaczono aktywność enzymów zewnątrzkomórkowych β-glukozydazy (BG), β-D-celobiozydazy (CB), β-ksylozydazy (XYL), N-acetylo-β-D-glukozaminidazy (NAG), fosfatazy (PH) i arylosulfatazy (SP) (Pritsch i in., 2004; Turner, 2010; Sannaullah i in., 2016). Do określenia biomasy mikrobiologicznej C i N wykorzystano metodę fumigacji i ekstrakcji (Jenkinson i Powlson, 1976; Vance i in., 1987). Podatność magnetyczną badanych gleb oznaczono za pomocą miernika podatności magnetycznej Bartington MS2 wyposażonego w czujnik MS2B (Bartington Instruments Ltd.). Do ukazania statystycznie istostnych różnic między średnimi wartościami badanych właściwości gleb zastosowano analizę wariancji. Współczynnik korelacji Pearsona wykorzystano do oceny zależności pomiędzy badanymi właściwościami. Wpływ właściwości gleby na zawartość WWA określono wykorzystując metodę drzew klasyfikacji i regresji (C&RT). Dodatkowo do oceny zależności między właściwościami gleby a zawartością WWA zastosowano analizę składowych głównych (PCA). Różnice na poziomie istotności $P < 0,05$ uznano za statystycznie istotne.

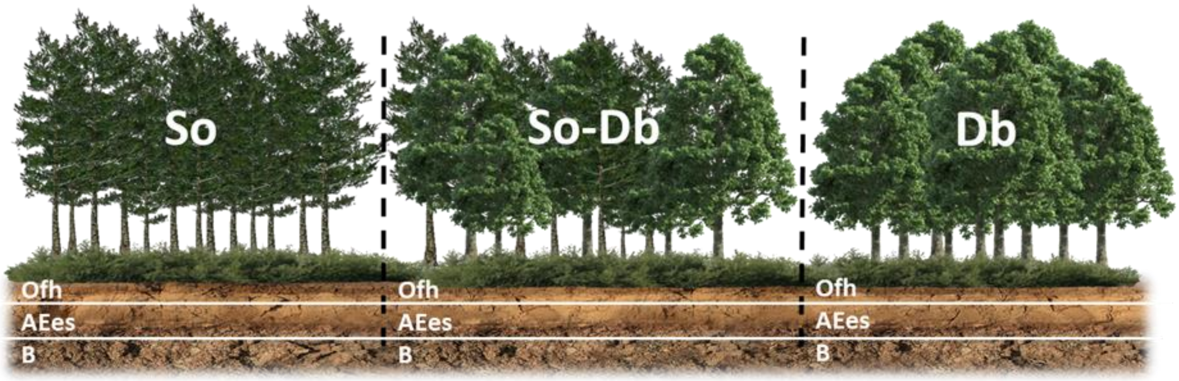
Średnie pH w H_2O gleb o uziarnieniu piasku luźnego wyniosło 4,01, gleb o uziarnieniu gliny piaszczystej wynosiło 4,21, a w glebach o uziarnieniu gliny pylastej pH wynosiło 4,06. Statystycznie istotnie wyższą zawartość węgla i azotu odnotowano w glebach o uziarnieniu gliny piaszczystej i gliny pylastej w porównaniu do gleb o uziarnieniu piasku luźnego. W glebach o uziarnieniu gliny piaszczystej odnotowano najwyższą zawartość węgla (6,43%), natomiast najniższą w glebach o uziarnieniu piasku luźnego (2,95%). Najwyższą aktywność wszystkich badanych enzymów odnotowano w glebach o uziarnieniu gliny pylastej. Odnotowane różnice aktywności enzymatycznej nie były statystycznie istotne. Gleby o drobniejszym uziarnieniu charakteryzowały się wyższymi wartościami mikrobiologicznej biomasy C oraz N w porównaniu do gleb o uziarnieniu piaszczystym. Statystycznie istotnie wyższą mikrobiologiczną biomasę azotu odnotowano w glebach o uziarnieniu gliny pylastej.

Aktywność enzymatyczna oraz biomasa mikrobiologiczna C i N korelowały istotnie dodatnio z zawartością kationów zasadowych. Badania nie potwierdziły istotnych korelacji pomiędzy właściwościami biochemicznymi a zawartością metali ciężkich, magnetometrii oraz zawartością WWA. Najwyższą statystycznie istotną zawartość metali ciężkich stwierdzono w glebach o uziarnieniu gliny piaszczystej i gliny pylastej. Podatność magnetyczna korelowała dodatnio z procentową zawartością iłu, natomiast ujemnie z zawartością piasku. Najwyższe średnie wartości podatności magnetycznej odnotowano w glebach o uziarnieniu gliny pylastej, gdzie wyniosła $59{,}82 \cdot 10^{-8}$ $m^3 \cdot kg^{-1}$, niższe w glebach o uziarnieniu gliny piaszczystej ($53{,}14 \cdot 10^{-8}$ $m^3 \cdot kg^{-1}$), natomiast najniższe w glebach o uziarnieniu piasku luźnego osiągając wartość $16{,}44 \cdot 10^{-8}$ $m^3 \cdot kg^{-1}$. Statystycznie istotnie wyższą zawartość WWA odnotowano w glebach o uziarnieniu piaszczystych gliny pylastej (1369,41 $\mu g \cdot kg^{-1}$) oraz w glebach o uziarnieniu gliny piaszczystej (178,35 $\mu g \cdot kg^{-1}$). Zawartość WWA w glebach o uziarnieniu gliny pylastej oraz gliny piaszczystej była istotnie wyższa w porównaniu do zawartości WWA w glebach o uziarnieniu piasku luźnego, gdzie zawartość WWA wyniosła 3,62 $\mu g \cdot kg^{-1}$. Gleby o o wyższej zawartości frakcji pyłu i iłu charakteryzowały się wyższym stężeniem węglowodorów 4, 5 i 6 pierścieniowych. Odnotowano istotną, dodatnią korelację pomiędzy zawartością iłu a zawartością metali ciężkich, podatnością magnetyczną oraz zwartością WWA. W przypadku zawartości Cr, Cu, Pb i Zn stwierdzono dodatnią korelację z zawartością pyłu. Zawartość metali ciężkich i podatność magnetyczna były silnie dodatnio skorelowane z zawartością C, N i zawartością kationów zasadowych (K, Mg oraz Na). Analiza z wykorzystaniem drzew regresyjnych potwierdziła znaczenie uziarnienia w kształtowaniu akumulacji WWA w glebach leśnych. Dodatkowo istotnym czynnikiem decydującym o ilość WWA w glebach jest zawartość węgla organicznego. Analiza PCA potwierdziła różnice we właściwościach gleb w odniesieniu do ich uziarnienia. Gleby piaszczyste utworzyły odrębną grupę, która charakteryzowała się mniejszą zawartością C, N, kationów zasadowych oraz WWA. Wyższa zawartość WWA cechowała gleby o cięższym uziarnieniu. Analiza PCA wyjaśniła 76,68% zmienności badanych cech. Czynnik 1 związany był z zawartością frakcji piasku, pyłu i iłu oraz zawartością kationów zasadowych, natomiast czynnik 2 związany był z zawartością WWA w badanych glebach.

Przeprowadzone badania potwierdziły znaczenie uziarnienia, a w mniejszym stopniu zawartości węgla organicznego w kształtowaniu akumulacji WWA w glebach leśnych. Wyższa zawartość pyłu pozytywnie wpłynęła na zawartość WWA i doprowadziła do wzrostu akumulacji WWA w glebach leśnych poprzez zwiększenie zdolności sorpcyjnych gleb. Zawartość węgla organicznego i zawartość azotu stymuluje aktywność enzymatyczną oraz mikrobiologiczną biomasę C i N w glebach leśnych o zróżnicowanym uziarnieniu. W trakcie przeprowadzonych badaniach nie potwierdzono wpływu zawartości WWA na ograniczenie aktywności biochemicznej badanych gleb leśnych. Uzyskane wyniki potwierdziły, że geochemiczne i magnetyczne metody okazały się użytecznym i skutecznym narzędziem w ocenie zanieczyszczeń (w szczególności metalami ciężkimi) gleb leśnych. Uzyskane wyniki sugerują, że przy ocenie zanieczyszczenia gleb przez WWA należy uwzględnić uziarnienie gleb oraz zawartość węgla organicznego.

6.3. Akumulacja wielopierścieniowych węglowodorów aromatycznych (WWA) w poziomach gleb różnych drzewostanów strefy umiarkowanej

Wyniki oceny wpływu składu gatunkowego drzewostanu na akumulację WWA w drzewostanach gospodarczych zostały przedstawone w pracy: *Łyszczarz S., Lasota J., Błońska E. 2021. Polycyclic aromatic hydrocarbons (PAHs) accumulation in soil horizons of different temperate forest stands.* Badaniami objęto gleby drzewostanów iglastych, liściastych oraz mieszanych wzrastających w jednakowych warunkach siedliskowych. Badania przeprowadzono na terenie Nadleśnictwa Rybnik. Do badań wytypowano drzewostany w wieku 80 lat oraz o podobnym zagęszczeniu koron drzew. Doświadczeniem objęto trzy drzewostany: jednogatunkowy z sosną zwyczajną (*Pinus sylvestris*), jednogatunkowy z dębem szypułkowym (*Quercus robur*) oraz drzewostany mieszane sosnowo-dębowe. Powierzchnie badawcze reprezentujące różne typy drzewostanów miały wielkość 2000 m^2, a odległość pomiędzy nimi wynosiła około 300 m (Ryc. 4). Drzewostany objęte badaniami rosły na glebach o podobnym uziarnieniu, gdzie zawartość piasku, pyłu i iłu wynosiła odpowiednio 81%, 16% i 3%. Próbki do analiz pobrano z poziomu organicznego (Ofh), próchnicznego mineralnego (AEes) i mineralnego (B). Łącznie do badań zebrano 27 próbek gleby (3 typy stanowisk × 3 powtórzenia każdego stanowiska × 3 horyzonty). Z każdego poziomu gleby pobrano zbiorcze próbki, składające się z 3 podpróbek. Pobrane próbki gleb wysuszono w temperaturze pokojowej a następnie określono ich właściwości fizykochemiczne. Uziarnienie gleb określono metodą dyfrakcji laserowej (Analysette 22, Fritsch, Idar-Oberstein, Niemcy). pH gleby w H_2O oznaczono metodą potencjometryczną. Zawartość C i N mierzono za pomocą analizatora pierwiastków LECO CNS (TruMac Analyzer Leco, St. Joseph, MI, USA). Zawartość Ca, K, Mg i Na oznaczono za pomocą ICP (ICP-OES Thermo iCAP 6500 DUO, ThermoFisher Scientific, Cambridge, U.K.). Zawartość fosforu określono metodą Braya-Kurtza.



Ryc. 4. Schemat pobierania próbek gleb w drzewostanach o różnym składzie gatunkowym

Do analizy aktywności enzymatycznej, mikrobiologicznej biomasy oraz zawartości WWA pobierano świeże próbki o naturalnym uwilgotnieniu, przesiewano je przez sito o średnicy 2 mm i przechowywano w ciemności w temperaturze 4°C. Aktywność enzymów zewnątrzkomórkowych β-D-celobiozydazy (CB), β-glukozydazy (BG), ksylanazy (XYL), N-acetylo-β-D-glukozaminidazy (NAG), fosfatazy (PH) oznaczano przy użyciu substratów znakowanych fluorogenicznie. Fluorescencję mierzono na czytniku płytek (SpectroMax), przy długości fali wzbudzenia 355 nm i długości fali emisji 460 nm. Aktywność dehydrogenaz (DH) oznaczono metodą Lenharda zgodnie z procedurą Casidy. Metodę fumigacji i ekstrakcji zastosowano do oznaczenia mikrobiologicznej biomasy C i N. Analizę ilości frakcji glebowej materii organicznej przeprowadzono metodą fizycznego frakcjonowanie z wykorzystaniem roztworu NaI (1,7 g-cm^{-3}). W efekcie przeprowadzonego frakcjonowania wydzielono labilną frakcję glebowej materii organicznej (fLF), lekką frakcję glebowej materii organicznej związanej w okluzjach agregatów (oLF) oraz ciężką związaną frakcję glebowej materii organicznej (MAF). W każdej z wydzielonych frakcji oznaczono zawartość C i N za pomocą analizatora LECO CNS TruMac (Leco, St. Joseph, MI, USA). Zawartość WWA oznaczono wykorzystując metodę opisaną we wcześniejszych podrozdziałach niniejszej pracy. Do określenia zależności pomiędzy właściwościami badanych gleb wykorzystano współczynnik korelacji Pearsona. Analiza składowych głównych (PCA) została wykorzystana w ocenie relacji pomiędzy właściwościami gleb a typem drzewostanu. W ocenie różnic między średnimi wartościami badanych właściwości gleb wykorzystano test Kruskala-Wallisa i dwukierunkową analizę wariancji. Metoda regresji wielorakiej posłużyła do opracowania modeli opisujących zależność między zawartością WWA, a właściwościami badanych gleb.

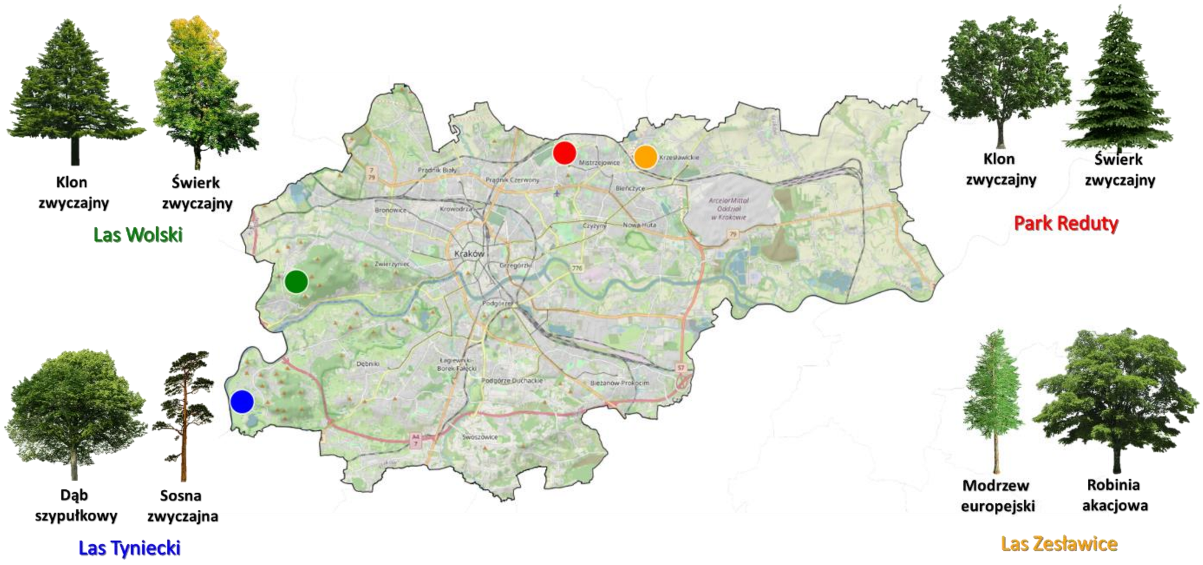
pH gleb badanych drzewostanów wahało się od 3,61 do 3,98 i wzrastało wraz z głębokością poszczególnych poziomów. Najniższymi wartościami pH odznaczały się gleby zlokalizowane pod drzewostanem sosnowym. Wyższymi wartościami pH charakteryzowały się gleby drzewostanów sosnowo-dębowych oraz dębowych. Poziomy organiczne badanych gleb charakteryzowały się istotnie wyższą zawartością C, N i P. Przeprowadzone analizy potwierdziły istotniejszy wpływ głębokości gleby w porównaniu do wpływu drzewostanu na zawartość C i N. Poziomy mineralne badanych gleb cechował znaczny spadek zawartości węgla organicznego oraz azotu. Węgiel organiczny osiągnął najwyższą zawartość w poziomie organicznym gleb drzewostanów sosnowych(291,0 $g \cdot kg^{-1}$), natomiast w glebie drzewostanów dębowych odnotowano najniższą zawartość (201,8 $g \cdot kg^{-1}$). W poziomie AEes drzewostanów sosnowo-dębowych i dębowych odnotowano istotnie wyższą akumulację C w porównaniu z glebą drzewostanów sosnowych. Gleby wszystkich badanych drzewostanów charakteryzowały się podobną zawartością C w poziomie B. W poziomach organicznych gleb drzewostanów sosnowych oznaczono najwyższą zawartość azotu wynoszącą 12,4 $g \cdot kg^{-1}$, niższą zawartość azotu odnotowano w poziomach organicznych gleb drzewostanów sosnowo-dębowych (10,4 $g \cdot kg^{-1}$), natomiast najniższą w glebach drzewostanów dębowych z średnią zawartością 10,0 $g \cdot kg^{-1}$. Typ drzewostanu i głębokość gleby ma jednoczesny wpływ na zawartość N ($p \leq 0{,}001$). Stosunek C/N był najwyższy w glebach drzewostanów sosnowych, a najniższy w glebach drzewostanów dębowych. Przeprowadzone analizy potwierdziły znaczenie typu drzewostanu w kształtowaniu stosunku C/N ($p \leq 0{,}01$). Suma kationów zasadowych osiągnęła statystycznie istotnie wyższe wartości w warstwach organicznych badanych gleb. Gleby drzewostanów sosnowo-dębowych i dębowych charakteryzowały się wyższą zawartością kationów zasadowych. Gleby wszystkich badanych wariantów drzewostanów charakteryzowały się istotnie wyższą aktywnością enzymatyczną w poziomach organicznych. Wraz z głębokością gleby malała atywność enzymów. Najwyższe wartości aktwyności DH i NAG odnotowano w poziomach organicznych gleb drzewostanów dębowych. W poziomach mineralno-próchnicznych gleb drzewostanów dębowych odnotowano najwyższą aktywność DH i PH. Poziomy organiczne gleb drzewostanów dębowych odznaczały się najwyższymi średnimi wartościami MBC wynoszącymi 2296,70 $\mu g \cdot kg^{-1}$, natomiast gleby drzewostanów sosnowych i sosnowo-dębowych osiągnęły niższe wartości kolejno 2086,33 i 2097,23 $\mu g \cdot kg^{-1}$. Typ drzewostanu wywierał istotny wpływ na mikrobiologiczną biomasę azotu w badanych glebach. Poziomy organiczne gleb drzewostanów dębowych charakteryzowały się najwyższymi wartościami MBN (461,25 $\mu g \cdot kg^{-1}$), a najniższą mikrobiologiczną biomasę azotu odnotowano w glebach drzewostanów sosnowych (266,57 $\mu g \cdot kg^{-1}$). Poziomy organiczne badanych gleb cechowały się istotnie wyższymi średnimi zawartościami C i N lekkiej frakcji glebowej materii organicznej. Najwyższe zawartości C i N lekkiej frakcji odnotowano w poziomach organicznych gleb drzewostanów sosnowych

(266,30 g·kg^{-1} i 6,65 g·kg^{-1} odpowiednio). Z kolei wierzchnie poziomy drzewostanów sosnowo-dębowych charakteryzowały się niższymi zawartościami C i N lekkiej frakcji (134,19 g·kg^{-1} i 5,10 g·kg^{-1} odpowiednio) a w przypadku drzewostanów dębowych oznaczono najniższe zawartości C i N lekkiej frakcji (105,22 g·kg^{-1} i 5,05 g·kg^{-1} odpowiednio). Istotnie wyższe średnie zawartości C i N lekkiej frakcji związanej glebowej materii organicznej odnotowano w poziomach próchniczno-mineralnych drzewostanów sosnowo-dębowych (11,16 g·kg^{-1} i 0,36 g·kg^{-1} kolejno) oraz dębowych (11,87 g·kg^{-1} i 0,48 g·kg^{-1} kolejno). Analizy potwierdziły istotną rolę typu drzewostanu na zawartość N i stosunku C/N ciężkiej frakcji MAF. Głębokość gleb istotnie wpływa na zawartości C i N frakcji glebowej materii organicznej. W przypadku C i N ciężkiej frakcji glebowej materii organicznej najwyższe wartości oznaczono w warstwie próchnicznej gleb drzewostanów sosnowo-dębowych (odpowiednio 12,42 g·kg^{-1} i 0,74 g·kg^{-1}) i drzewostanów dębowych (odpowiednio 14,04 g·kg^{-1} i 1,16 g·kg^{-1}). Najwyższą zawartością WWA charakteryzowały się poziomy organiczne wszystkich typów drzewostanów. W glebach wszystkich typów drzewostanów odnotowano spadek zawartości WWA wraz z głębokością gleby. Odnotowano istotny statystycznie związek głębokości gleby z akumulację WWA. Poziomy organiczne gleb drzewostanów sosnowych osiągnęły najwyższe zawartości WWA(3805,00 μg·kg^{-1}). W glebach drzewostanów sosnowo-dębowych zawartość WWA wynosiła 3087,09 μg·kg^{-1}, z kolei w glebach znajdujących się pod wpływem drzewostanów dębowych odnotowano najniższą zawartość WWA (2936,20 μg·kg^{-1}). W poziomach powierzchniowych gleb drzewostanów sosnowych i sosnowo-dębowych dominowały 3- i 4-pierścieniowe WWA. W glebach drzewostanów dębowych dominowały 4-pierścieniowe WWA, a następnie 3 i 5-pierścieniowe WWA. Najwyższą średnią zawartość trójpierścieniowych WWA stwierdzono w poziomach gleb drzewostanów sosnowych i dębowych. Z kolei poziomy glebowe drzewostanów dębowych wykazywały najwyższe zawartości 4-pierścieniowych WWA. Dla 5-pierścieniowych WWA najwyższe zawartości odnotowano w warstwach gleb z dębem, a dla 6-pierścieniowych WWA w warstwach gleb z sosną. Rodzaj drzewostanu nie miał statystycznie istotnego wpływu na zawartość WWA w zależności od liczby pierścieni WWA. Większość badanych enzymów istotnie korelowała z zawartością węgla organicznego i azotu. Potwierdzono także, że badane enzymy, oprócz DH i CB, istotnie korelowały z zawartością WWA. Stwierdzono także dodatnią zależność między zwartością WWA a C_{fLF}, N_{fLF} i C_{MAF}. Zawartość WWA wzrastała wykładniczo wraz ze wzrostem węgla organicznego, w szczególności dotyczyło to gleb drzewostanów sosonowych. Analiza regresji potwierdziła zależność pomiędzy zawartością WWA, a zawartością C labilnych i ciężkich frakcji glebowej materii organicznej. Analiza składowych głównych wyjaśnia 84% wariancji badanych właściwości gleb. PCA potwierdz ujemną korelację pomiędzy zawartością WWA, a pH badanych gleb. Potwierdzono także wyższą zawartość WWA w horyzontach organicznych badanych gleb, które charakteryzowało niższe pH oraz wyższe zawartości węgla organicznego.

Przeprowadzone badania potwierdzają znaczenie składu gatunkowego drzewostanu w kształtowaniu akumulacji WWA w glebach leśnych. Skład gatunkowy drzewostanu wpływa na ilość i jakość glebowej materii organicznej oraz zakwaszenie, co znajduje odzwierciedlenie w aktywności biochemicznej i degradacji WWA. Gatunki iglaste i liściaste drzew odmiennie wpływają na właściwości powierzchniowych poziomów glebowych, a tym samym na zawartość WWA. Gleby drzewostanów dębowych charakteryzowały się najniższą akumulacją WWA przy jednocześnie wysokiej aktywności biochemicznej wyrażonej aktywnością enzymatyczną i mikrobiologiczną biomasą. Drzewostany sosnowe poprzez obniżanie pH spowalniają rozkład glebowej materii organicznej w efekcie przyczyniając się do wyższej akumulacji WWA. Uzyskane wyniki potwierdziły także znaczenie składu frakcyjnego glebowej materii organicznej w kształtowaniu akumulacji WWA, a w szczególności rolę zawartości labilnej oraz ciężkiej frakcji glebowej materii organicznej. Poprzez skład gatunkowy drzewostanu, oddziałujemy na właściwości gleb takie jak pH oraz zawartość glebowej materii organizcznej, w efekcie wpływając na akumulację WWA i możliwość potencjalnej naturalnej biodegradacji organicznych zanieczyszczeń. Wprowadzanie domieszki gatunków liściastych oraz odejście od monokultur iglastych skutecznie wpływa na niższą akumulację WWA w glebach leśnych.

6.4. Wpływ składu gatunkowego drzewostanu na akumulację wielopierścieniowych węglowodorów aromatycznych (WWA) w glebach lasów miejskich Krakowa

Wpływ składu gatunkowego drzew na akumulację wielopierścieniowych węglowodorów aromatycznych (WWA) w glebach lasów miejskich Krakowa przedstawiono w pracy: *Lasota J., Łyszczarz S., Kempf P., Kempf M., Błońska E., 2021. Effect of species composition on polycyclic aromatic hydrocarbon (PAH) accumulation in urban forest soils of Krakow*. Do zrealizowania doświadczenia wybrano drzewostany liściaste i iglaste zlokalizowane w lasach miejskich Krakowa. Badaniami objęto następujące gatunki drzew: świerk pospolity (*Picea abies*) i klon zwyczajny (*Acer platanoides*) w Lesie Reduta, sosnę zwyczajną (*Pinus sylvestris*) i dąb szypułkowy (*Quercus ro*bur) w Lesie Tynieckim, modrzew europejski (*Larix deciduas*) i robinię akacjową (*Robinia pseudoacacia*) w Lesie Zesławice oraz daglezję zieloną (*Pseudotsuga menziesii*) i buka zwyczajnego (*Fagus sylvatica*) w Lesie Wolskim. Każdy wariant powierzchni miał trzy powtórzenia, w sumie badaniami objęto 24 powierzchnie badawcze (4 lasy miejskie × 2 gatunki × 3 powtórzenia). W drzewostanach gatunków liściastych pobrano próbki z poziomu próchniczno-mineralnego (A) po wcześniejszym usinięciu poziomu ściółki. W glebach drzewostanów z gatunkami iglastymi próbki pobrano z poziomu organicznego (Ofh) oraz poziomu mineralnego próchnicy (A).



Ryc. 5. Lokalizacja powierzchni badawczych w lasach miejskich Krakowa.

Uziarnienie gleb określono metodą dyfrakcji laserowej (Analysette 22, Fritsch, Idar-Oberstein, Niemcy). pH gleb oznaczono metodą potencjometryczną w H_2O i KCl. Zawartość C i N oznaczono przy użyciu analizatora LECO CNS (TrueMac Analyzer Leco, St. Joseph, MI, USA). Zawartość Cd, Cr, Cu, Ni, Pb i Zn oznaczono wykorzystując ICP. . Do oznaczenia kwasowości hydrolitycznej zastosowano metodę Kappena, a do kwasowości wymiennej metodę Sokołowa (Ostrowska i in., 1991). Ilość poszczególnych związków WWA oznaczano metodą wysokociśnieniowej chromatografii cieczowej (HPLC). Określono zawartość trzynastu związków WWA: acenaftenu (Ace), fluorenu (Flu), fenantrenu (Phe), antracenu (Ant), fluoranteun (Flt), pirenu (Pyr), benzo(a)antracenu (BaA), chryzenu (Chr), benzo(k)fluorantenu (BkF), benzo(b)fluorantenu (BbF), benzo(a)pirenu (BaP), dibenzo(ah)antracenu (DBahA), indeno(1,2,3-c,d)pirenu (IcdP) i bezo(g,h,i)perylenu (BghiP). Wykorzystując substraty znakowane fluorogenicznie określono aktywność enzymów zewnątrzkomórkowych: β-D-cellobiozydazy (CB), β-ksylozydazy (XYL), N-acetylo-β-D-glukozaminidazy (NAG), fosfatazy (PH) i arylosulfatazy (SP) (Pritsch i in., 2004; Turner 2010; Sanaullah i in., 2016). Korelację Spearmana wykorzystano do określenia zależności pomiędzy badanymi cechami gleb. Do oceny różnic między średnimi wartościami właściwości zastosowano test U Manna-Whitneya. Analiza składowych głównych (PCA) została użyta do określenia związku pomiędzy badanymi właściwościami gleb, zwłaszcza zawartością WWA, a składem gatunkowym drzewostanów. Ogólny model liniowy (GLM) wykorzystano do określenia wpływu gatunku drzew i właściwości gleb na zawartość WWA. Metoda drzew klasyfikacyjnych i regresyjnych (C&RT) została wykorzystana do oszacowania wpływu gatunków drzew i parametrów fizyko-chemicznych gleb na zawartość WWA.

pH badanych gleb istotnie różniło się pomiędzy drzewostanami gatunków liściastych i iglastych. Gleby drzewostanów iglastych charakteryzowały się istotnie niższym pH w wodzie w porównaniu do gleb drzewostanów liściastych. Najniższe średnie wartości pH w poziomie próchnicznym odnotowano w glebach z daglezją zieloną (4,11), a najwyższe w glebach z klonem zwyczajnym (6,19). Gleby drzewostanów iglastych odznaczały się także istotnie wyższą kwasowością hydrolityczną i wymienną, zwłaszcza w poziomach organicznych gleb z sosną i świerkiem. Gleby drzewostanów liściastych i iglastych różniły się istotnie pod względem zawartości C i N, a najwyższą zawartość C odnotowano w poziomach organicznych gleb drzewostanów iglastych. Odnotowano istotną różnicę stosunku C/N pomiędzy glebami gatunków liściastych i iglastych w poziomach próchniczno-mineralnych (A). Badane gleby odznaczały się przewagą frakcji pylastej, z niewielkim udziałem piasku oraz frakcji ilastej. Nie odnotowano istotnych różnic w skłądzie frakcyjnym w poziomach mineralnych pomiędzy drzewostanami iglastymi a liściastymi. Istotnie wyższą zawartością kationów zasadowych charakteryzowały się poziomy mineralno-próchniczne gleb drzewostanów liściastych. Parametry biochemiczne gleb drzewostanów liściastych i iglastych różniły się istonie, w szczególności aktywność enzymów BG, NAG, SP i PH w poziomach próchniczno-mineralnych gleb drzewostanów liściastych. Poziomy organiczne drzewostanów iglastych, a w szczególności sosnowych, charakteryzowały się najwyższą średnią zawartością WWA (1,91 $\mu g \cdot g^{-1}$). Badane gleby drzewostanów iglastych zawierały statystycznie istotnie więcej WWA w poziomach próchniczno-mineralnych w porównaniu z glebami gatunków liściastych. We wsyzstkich przypadkach badanych gleb dominowały węglowodory 4- i 5-pierścieniowe, a udział węglowodorów 3-pierścieniowych był znikomy. W poziomach próchnicznych ilość zakumulowanych WWA była statystycznie istotnie i ujemnie skorelowana z pH gleb oraz zawartością kationów zasadowych. Zawartość WWA korelowało istotnie dodatnio z kwasowością i stosunkiem C/N. Aktywność BG, NAG, SP i PH w poziomie próchnicznym ujemnie korelowały z ilością WWA oraz pH gleb, a dodatnio z zawartością kationów zasadowych. Analiza GLM potwierdziła znaczenie aktywności biochemicznej wyrażonej aktywnością β-glukozydazy w kształtowaniu akumulacji WWA Analiza PCA potwiedziła znaczenie gatunku i zawartości węgla organicznego w kształtowaniu zawartości WWA oraz przedstawia zależność pomiędzy pH badanych gleb, ilością węgla organicznego i stopniem rozkładu glebowej materii organicznej. Analiza składowych głównych wyjaśniła 77,7% wariancji badanych właściwości. PCA przedstawia związek poziomów organicznych gatunków iglastych z zakwaszeniem, akumulacją słabo rozłożonej materii organicznej wyrażonej wysokim stosunkiem C/N oraz wysoką akumulację WWA. Ponadto analiza PCA wyodrębniła grupy poziomów próchniczno-mineralnych gleb gatunków liściastych i iglastych pod względem zakwaszenia, ilości i jakości glebowej materii materii organicznej, aktywności biochemicznej, a w szczególności zawartości WWA. Do identyfikacji cech determinujących zawartość WWA wykorzystano analizę drzew klasyfikacyjnych i regresyjnych. Cechy decydujące o akumulacji WWA w glebach lasów miejskich to rodzaj poziomu genetyczneg, gatunek drzew, aktywności β-glukozydazy i stosunek C/N. Największą akumulację WWA stwierdzono w poziomie organicznym przy aktywności BG < 114,04 nmol MUB g^{-1} s·m·h^{-1} i C/N >21,7.

Przeprowadzone badania potwierdziły znaczenie składu gatunkowego drzewostanów w kształtowaniu właściwości gleb, a w konsekwencji akumulacji WWA w glebach lasów miejskich Krakowa. Dobierając odpowiednie gatunki drzew możemy kształtować podstawowe właściwości gleb, takie jak pH czy ilość i jakość glebowej materii organicznej. Gatunki liściaste korzystnie wpływają na pH gleb oraz jakość materii organicznej co skutkuje zróżnicowaniem aktywności mikroorganizmów glebowych uczestniczących w procesach naturalnej biodegradacji WWA. Przeprowadzone doświadczenie potwierdziło pozytywny wpływ gatunków liściastych, a w szczególności klonu zwyczajnego na właściwości gleb ograniczając jednocześnie akumulację WWA w glebach lasów miejskich. Podczas planowania zagospodarowania lasów miejskich należy unikać wprowadzania monokultur gatunków iglastych, a w szczególności sosny i świerka. Potwierdzono, że gatunki iglaste zakwaszają glebę, ograniczając tym samym procesy biodegradacji zanieczyszczeń organicznych, w których uczestniczą mikroorganizmy glebowe.

7. Podsumowanie i wnioski

1. Sposób użytkowania gleb (leśny/rolniczy) wpływa na zawartość WWA poprzez kształtowanie właściwości gleb zwłaszcza jakości i ilości glebowej materii organicznej. Gleby użytkowane rolniczo charakteryzują się niższą zawartością węgla organicznego co skutkuje niższą zawartością WWA.
2. Rodzaj dostarczanej materii organicznej warunkuje akumulację WWW oraz aktywność biochemiczną badanych gleb wyrażoną aktywnością enzymatyczną oraz mikrobiologiczną biomasą. Większy dopływ detrytusu do gleb leśnych przeciwdziała hamowaniu aktywności enzymów glebowych przez WWA.
3. Uziarnienie gleb jest jednym z kluczowych parametrów decydującym o akumulacji WWA w glebach leśnych. Zawartość drobnych frakcji granulometrycznych zwłaszcza pyłu prowadzi do zwiększenia zawartości WWA w glebach leśnych. Wyższa zawartość pyłu pozytywnie wpłynęła na zawartość WWA poprzez zwiększenie zdolności sorpcyjnych gleb.
4. Zawartość węgla organicznego i zawartość azotu stymuluje aktywność enzymatyczną oraz mikrobiologiczną biomasę C i N w glebach leśnych o zróżnicowanym uziarnieniu. W trakcie przeprowadzonych badań nie potwierdzono wpływu zawartości WWA na ograniczenie aktywności biochemicznej badanych gleb leśnych.
5. Skład gatunkowy drzewostanów gospodarczych wpływa na akumulację WWA poprzez ilość i jakość dostarczanych do gleby szczątków organicznych oraz kształtowanie pH gleb. Gatunki iglaste i liściaste drzew odmiennie wpływają na właściwości powierzchniowych poziomów glebowych, a tym samym na zawartość WWA. Gleby drzewostanów dębowych charakteryzowały się najniższą akumulacją WWA przy jednocześnie wysokiej aktywności biochemicznej wyrażonej aktywnością enzymatyczną i mikrobiologiczną biomasą. Drzewostany sosnowe poprzez obniżanie pH spowalniają rozkład glebowej materii organicznej w efekcie przyczyniając się do wyższej akumulacji WWA.
6. Akumulacja WWA w glebach leśnych jest związana ze składem frakcyjnym glebowej materii organicznej od której bezpośrednio zależy aktywność biologiczna gleb. Zawartość WWA w glebach pozostających pod wpływem oddziaływania drzewostanów o różnym składzie gatunkowym dodatnio korelowała z zawartością labilnej oraz ciężkiej frakcji glebowej materii organicznej.

7. W lasach miejskich Krakowa gatunki liściaste silniej stymulują aktywność biologiczną gleb, wpływając na niższą zawartość związków WWA w porównaniu do gleb drzewostanów iglastych. Gatunkami szczególnie korzystnie wpływającymi na stymulowanie aktywności biochemicznej gleb lasów miejskich oraz zmniejszenie zawartości WWA jest klon zwyczajny oraz robinia akacjowa. W lasach miejskich należy unikać wprowadzania gatunków iglastych, zwłaszcza sosny i świerka, ponieważ działają zakwaszająco na glebę, ograniczając tym samym procesy rozkładu, w które zaangażowane są mikroorganizmy glebowe co przyczynia się do obniżenia biodegradacji WWA.
8. Wartość pH okazała się ważnym parametrem decydującym o biodegradacji WWA w glebach lasów miejskich Krakowa, ponieważ wpływa na dostępność składników pokarmowych, a tym samym na rozwój mikroorganizmów biorących udział w rozkładzie WWA.
9. W glebach lasów miejskich Krakowa silnie zanieczyszczonych przez WWA stwierdzono negatywny wpływ WWA na aktywność biochemiczną gleb wyrażoną aktywnością enzymów zewnątrzkomórkowych (BG, NAG, PH).

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Effect of forest and agricultural land use on the accumulation of polycyclic aromatic hydrocarbons in relation to soil properties and possible pollution sources

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ABSTRACT

This study investigated the effects of forest and agricultural land use on the accumulation of polycyclic aromatic hydrocarbons (PAHs) in relation to the chemical and biochemical properties of soil. The heavy metal content in soil samples was also determined; PAH diagnostic ratios were used to identify pollution emission sources. Soils from the Rybnik Forest District of Poland, which has suffered some of the most intense impacts from industrial PAH emissions in Europe, were investigated. Six 200-m-long transects were designated for the experiment, with samples taken every 50 m. These transects were located across forest, agricultural land, and ecotone zones. The organic C and total N contents, pH, hydrolytic acidity and base cation content of the soil samples were determined, as well as the microbial biomass of C, N and P, the enzymatic activity, and the PAH and heavy metal content. A significant impact of land management on the PAH content of the soil due to the supply of organic matter was confirmed. The forest soils were more contaminated with PAHs than the agricultural soils, with an average PAH content in the forest soils of 565.18 $\mu g \cdot kg^{-1}$, almost six times higher than in agricultural soils (91.42 $\mu g \cdot kg^{-1}$). In addition, soil biological activity, expressed by enzymatic activity, depended on the amount and quality of the soil organic matter and, to a lesser extent, on the PAHs and heavy metals accumulated in the soils. This study confirmed that organic matter has a significant impact on PAH accumulation and is the main soil component involved in the sorption and ageing of PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are pollutant organic compounds formed by two or more joined benzene rings. Some PAHs also have toxic and mutagenic properties (Jiao et al., 2017). PAHs have long-lasting bioaccumulation and biotransformative properties (Sun et al., 2018; Rajput et al., 2020) and exist in the natural environment due to pyrolysis or incomplete combustion (Chen and Chen, 2011). Although natural PAH emissions occur, for example, from volcanic eruptions and forest and meadow fires (Campos et al., 2019), most are currently anthropogenic emissions formed from the combustion of fossil and biomass fuels, and exhaust products (Liu et al., 2008). PAHs have low and high molecular weights, which can be deposited in soil (Gereslassie et al., 2018). The low water solubility and hydrophobicity of PAHs determine the amount accumulated in soils (Posada-Baquero et al., 2019). The global distribution of PAHs has increased over the last century because of their particular affinity to soil organic matter (SOM); more than 90% of the total mass of PAHs in the environment is stored in soils (Wild and Jones, 1995). According to Wick et al. (2011), the accumulation and toxicity levels of PAHs in soils stem from several factors, such as microbial degradation, atmospheric photolysis, sorption processes, and water and lipid solubility. The accumulation of PAHs is closely related to the presence of SOM and meso- and macrophore clay colloids (Cho et al., 2015; Duan et al., 2015; Tavakkoli et al., 2015). Organic matter is the binding agent for PAHs in the soil environment. It is responsible for the 'ageing' of PAHs, limiting their diffusion or release into the soil in solution (Luo et al., 2012; Wang et al., 2012). This control is mainly due to the effects of van der Waals forces, hydrophobic bonds and hydrogen intermolecular forces (Pignatello, 2012).

The enzymatic activity of microorganisms is an indicator of soil quality and has been used to evaluate changes taking place in the soil environment (Riffaldi et al., 2006; Błońska et al., 2018; Lasota et al., 2020). This activity depends primarily on pH, temperature, the availability of oxygen and nutrients, and the amount and type of

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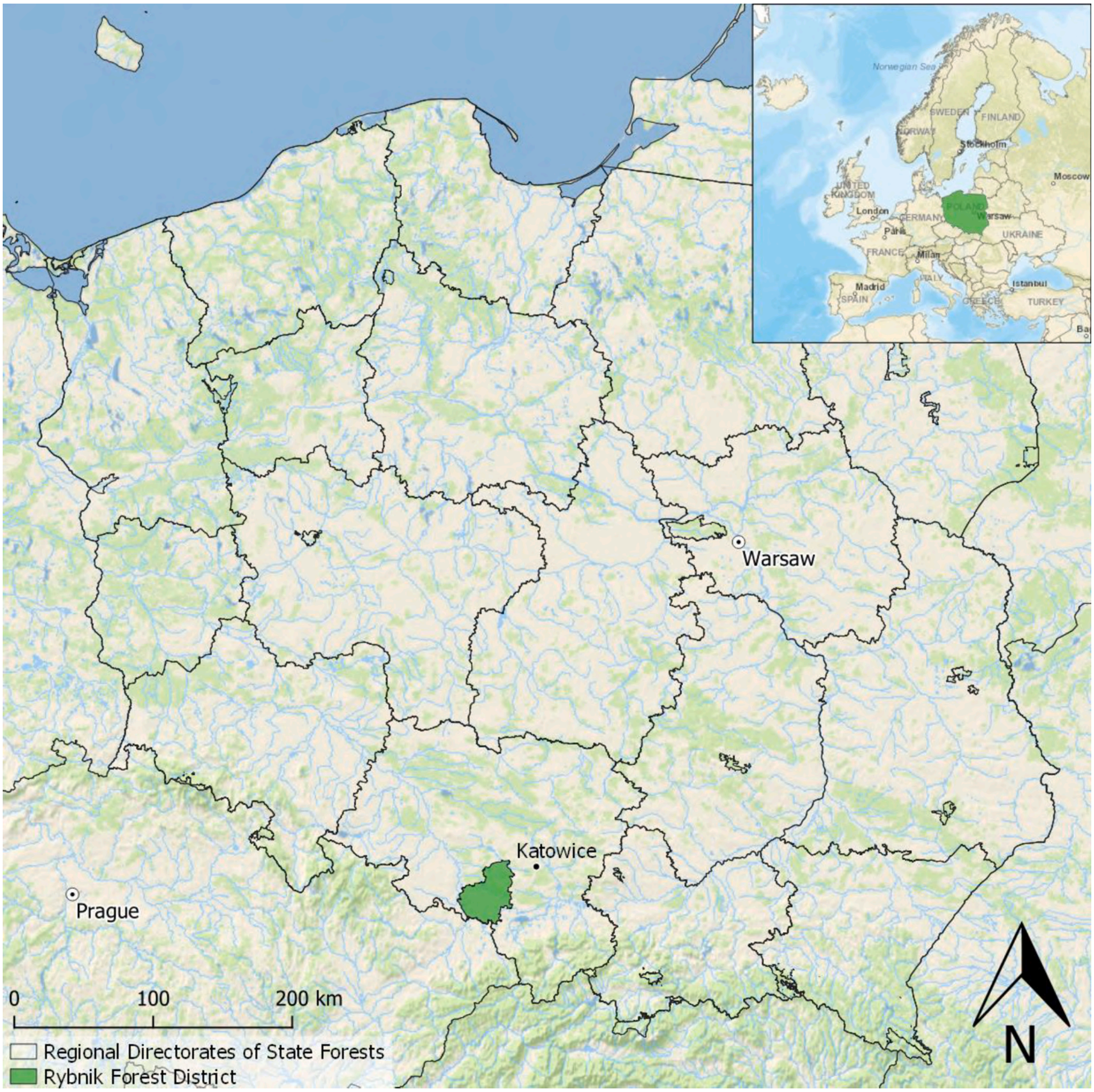

Fig. 1. Localization of study area - Rybnik Forest District.

microorganisms present. Moreover, it plays a key role in removing toxic PAHs from the soil environment (Haritash and Kaushik, 2009). The biological activity of microorganisms is the driving force behind the degradation of toxic PAH compounds in the soil environment (Yuan et al., 2001). The ageing of pollutants determines the bioavailability of PAHs and the microbial decomposition processes necessary to remove these toxic compounds from soils (Ortega-Calvo et al., 2015). The sorption of PAHs onto organic and inorganic soil colloids may reduce the bioavailability of these organic compounds as substrates for microorganisms. The accumulation of PAHs in the soil environment deteriorates its biological parameters, such as the associated enzymatic activity and microbial counts (Zhan et al., 2010). According to Tejada et al. (2007), the amount and type of organic matter affect the biological and biochemical properties of the soil environment. The organic matter involved in the sorption processes of organic pollutants minimises negative impacts relating to the number of soil microorganisms and their enzymatic activity (Gunasekara and Xing, 2003). Hydrolytic enzymes in the soil environment have been shown to play a key role in the C (β-d-cellobiose, β-glucosidase, β-xylosidase) and N (N-acetyl-β-D-glucosamine) cycles (Stock et al., 2019). They specifically contribute to the degradation of cellulose, hemicellulose and chitin (Parvin et al., 2018). The efficiency of the degeneration of the above-mentioned compounds into plant-absorbable nutrients is determined by the availability of substrates and reduction in nutrients. These processes significantly affect the C, N and P cycles in the environment (Adamczyk et al., 2014).

The PAH content in the arable layers of agricultural soils can affect habitat quality (Jensen and Mesman, 2007), with their accumulation depending on land utilisation and the addition of organic fertilisers (Maliszewska-Kordybach, 1999). The amount of accumulated PAHs in arable land soils also appears to be important to human health (Kobayashi et al., 2008). Forest ecosystems have been shown to play an important role in treating anthropogenic PAHs (Zhang et al., 2013), especially in forest soils (Jensen et al., 2007). Previous research has provided evidence that different humus types accumulate different amounts of PAHs due to differing SOM decomposition rates (Błońska et al., 2018). Needles and leaves absorb PAH compounds from the air, and these are transferred to forest soils via litterfall (Guggenberger et al.,

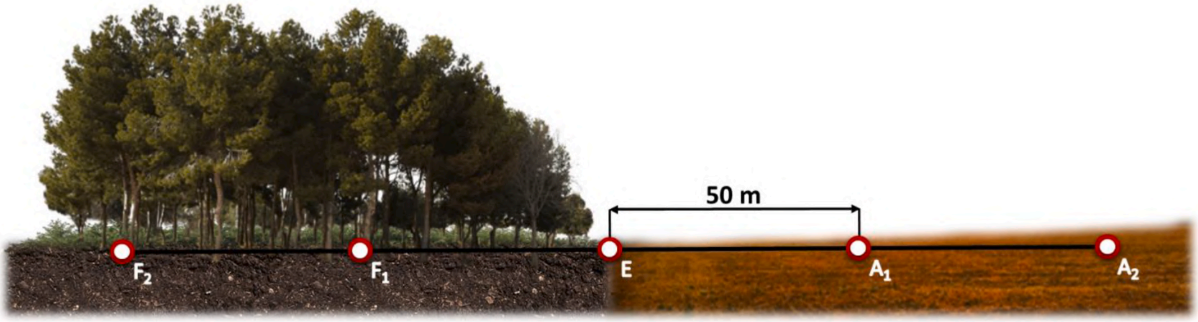

Fig. 2. Scheme of the sampling points location in the transect.

1996). The PAH content in soil is directly related to the SOM content, with the SOM layers in forest soils playing the role of PAH sinks (Matzner, 1984). Studies on the impacts of PAHs on the soil environment have been focussed on agricultural areas. This study aimed to look beyond this by investigating the effects of forest and agricultural land use on the accumulation of PAHs in relation to the chemical and biochemical properties of the soils. The heavy metal content in the soil samples was also determined, and PAH diagnostic ratios were used to identify pollution emission sources. The following hypotheses were tested: 1) land use influences the PAH content due to soil properties, which are especially affected by the quality and quantity of organic matter supplied to the soil; 2) the biological activity of the soils, expressed in terms of enzymatic activity, is determined by the soil properties and, to a lesser extent, by the PAHs and heavy metals accumulated in the soil; and 3) the PAH diagnostic ratio is a useful tool for identifying PAH sources in soils independent of land use.

2. Materials and methods

2.1. Study area and soil sampling

The study was conducted in the Rybnik Forest District of southern Poland (50° 05′ 55″ N, 18° 32′ 42″ E) (Fig. 1). The average annual temperature for this area is 8.4 °C, and the average annual rainfall is 705 mm. The field sites were located in an area where the soils derived from glacial moraines; they are dominated by Brunic Arenosols and Cambisols (World Reference Base, 2015). The research area is strongly influenced by industrial pollution from Poland. According to the Environmental Impact Assessment Report prepared for the Rybnik Forest District for the period 2017–2026, the average annual benzo(a)pyrene (BaP) concentrations exceed acceptable standards (1 ng·m^{3}) across the whole district. In the conurbation of Rybnik and Jastrzębie Zdrój, the average concentration of BaP is 5–12 ng·m^{3}, whilst in the Silesian zone, this is 5–10 ng·m^{3}. The average annual concentrations of particulate matter $<$ 10 μm in diameter (PM10) exceed the standard permitted concentration according to health protection criteria (40 μg·m^{3}) over the entire range of the Forest District (Environmental Impact Assessment Report for the Rybnik Forest District, 2016), with an average annual concentration of 53 μg·m^{3} recorded in Rybnik. The mean annual concentrations of PM2.5 in the atmosphere also exceed the admissible standard (according to health protection criteria) of 26 μg·m^{3} across the whole of the Rybnik Forest District (Environmental Impact Assessment Report for the Rybnik Forest District, 2016).

Table 1
Diagnostic ratios of PAHs to distinguish the emission sources.

PAH ratio	Range of values	Emission source	References
Flu/(Flu + Pyr)	<0.5	Petrol emission	Ravindra et al., 2008
	>0.5	Diesel emission	
Flt/(Flt + Pyr)	<0.4	Petrogenic	Roberto et al., 2009
	0.4–0.5	Fuel combustion	
	>0.5	Grass, wood, coal combustion	
IcdP/(IcdP + BghiP)	<0.2	Petrogenic	Yunker et al., 2002
	0.2–0.5	Petroleum combustion	
	>0.5	Grass, wood, coal combustion	
BaP/BghiP	<0.6	Non-traffic	Katsoyiannis et al., 2007
	>0.6	Traffic	

fluorene [Flu], fluoranthene [Flt], pyrene [Pyr], benzo(a)pyrene [BaP], benzo(g,h,i)perylene [BghiP], indeno(1,2,3-c,d)pyrene [IcdP].

The study areas were selected during field observations. Study plots with a uniform soil texture (sandy loam) were selected for analysis. Soil samples for laboratory testing were taken in May 2019. Six 200-m-long transects, located in forest, agricultural land and ecotone zones, were delineated, from which samples were taken every 50 m (Fig. 2). The central point of each transect was located at a border between forest and agricultural land. The samples were taken from the humus horizon (0–15 cm), after removing the organic horizon, in the forest and ecotone zone soils. The arable soils did not have organic horizons due to agricultural practices. To determine the enzyme activity, microbial biomass and PAH content, fresh samples containing natural moisture were taken, and these were sifted through a sieve (ø 2 mm) and stored at 4 °C in the dark prior to analysis.

2.2. Laboratory analysis

The particle size distribution was determined using laser diffraction (Analysette 22, Fritsch, Idar–Oberstein, Germany). The soil pH was determined in H_2O and 1 M KCl using the potentiometric method. The C and N contents were measured using an elemental analyser (LECO CNS TrueMac Analyzer Leco, St. Joseph, MI, USA). The cation concentrations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) were extracted using ammonium acetate and determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo iCAP 6500 DUO, Thermo Fisher Scientific, Cambridge, UK). The Cd, Cr, Cu, Ni, Pb and Zn contents were determined after mineralisation in a 2:1 mixture of concentrated nitric and perchloric acids by ICP-OES. The PAH contents were determined by extracting10 g of each soil sample using 70 ml of propan-2-ol. The samples were then centrifuged (4500 rpm, 5 min) and the supernatant collected. The supernatant was extracted to the solid phase (5 ml·min^{-1}) using a solid-phase extraction method (Chromabond® CN/SiOH). The residue was dissolved in acetonitrile and analysed using high-pressure liquid chromatography (HPLC) with a Dionex UltiMate 3000 HPLC system, equipped with a fluorescence detector and a Dionex UltiMate 3000 Column Compartment C18 5 μm and a 4.6x100-mm HPLC column. The mobile phases were water (A) and acetonitrile (B) at a flow rate of 1 ml·min^{-1}. Based on the standard PAH calibration mix (CRM 47940) at a concentration of 10 μg·ml^{-1}, calibration solutions were prepared at different concentrations (0.1, 0.2, 0.5, 1 and 2 μg·ml^{-1}). Each solution

Table 2
Basic chemical properties of the analysed soils of agroforestry transect.

	pH H_2O	pH KCl	C	N	P	C/N	Ca	K	Mg	Na
Forest	4.15 ± 0.13^{b}	3.44 ± 0.15^{b}	10.69 ± 5.69^{a}	0.53 ± 0.25^{a}	542.06 ± 150.57^{a}	19.59 ± 1.88^{b}	1.50 ± 0.67^{b}	0.46 ± 0.20^{a}	0.37 ± 0.12^{a}	0.06 ± 0.03^{b}
Edge point	4.40 ± 0.47^{b}	3.65 ± 0.41^{b}	6.97 ± 2.57^{a}	0.38 ± 0.15^{a}	373.39 ± 137.60^{a}	18.75 ± 2.59^{b}	2.11 ± 2.39^{ab}	0.46 ± 0.46^{a}	0.38 ± 0.27^{a}	0.05 ± 0.03^{ab}
Arable land	6.09 ± 0.74^{a}	5.32 ± 0.87^{a}	1.46 ± 0.40^{b}	0.10 ± 0.03^{b}	$400,65\pm135,29^{a}$	15.06 ± 1.52^{a}	3.47 ± 1.97^{a}	0.22 ± 0.15^{a}	0.34 ± 0.14^{a}	0.03 ± 0.01^{a}

mean ± SD; small letters in the upper index of the mean values mean significant differences between different land management; carbon and nitrogen content (%); Ca, K, Mg and Na (cmol(+)·kg^{-1}).

Table 3
Basic biochemical properties of the analysed soils of agroforestry transect.

	CB	NAG	XYL	SP	PH	MBC	MBN	MBP
Forest	113.40 ± 134.95^{a}	495.81 ± 428.56^{a}	131.09 ± 72.43^{a}	7.29 ± 13.38^{a}	1048.04 ± 650.45^{a}	876.20 ± 731.04^{a}	122.62 ± 52.22^{a}	6.68 ± 5.63^{a}
Edge point	65.95 ± 43.06^{a}	304.58 ± 258.00^{ab}	76.15 ± 59.00^{ab}	6.78 ± 13.82^{a}	616.58 ± 645.91^{ab}	627.76 ± 289.63^{ab}	95.54 ± 29.22^{ab}	3.64 ± 3.53^{ab}
Arable land	22.02 ± 33.73^{a}	35.26 ± 31.03^{b}	9.74 ± 15.84^{b}	2.67 ± 5.27^{a}	216.20 ± 185.24^{b}	292.39 ± 208.44^{b}	49.08 ± 34.36^{b}	1.57 ± 1.38^{b}

mean ± SD; small letters in the upper index of the mean values mean significant differences between different land management; β-D-cellobiosidase [CB], N-acetyl-β-D-glucosaminidase [NAG], β-xylosidase [XYL], arylsulphatase [SP] and phosphatase [PH] (mol MUB g^{-1} dry soil h^{-1}); MBC [microbial biomass carbon], MBN [microbial biomass nitrogen] and MBP [microbial biomass phosphorus] (μg·kg^{-1}).

was placed into the chromatography column, and the chromatograms obtained were used to produce a calibration curve. The soil samples were then analysed in triplicate. After every ninth analysis, a control sample (a calibration solution with a concentration of 0.1 μg·ml^{-1}) was injected. Naphthalene (Nft, two rings), acenaphthene (Ace, three rings), fluorene (Flu, three rings), phenanthrene (Phe, three rings), anthracene (Ant, three rings), fluoranthene (Flt, four rings), pyrene (Pyr, four rings), benzo(a)anthracene (BaA, four rings), chrysene (Chr, four rings), benzo(k)fluoranthene (BkF, five rings), benzo(b)fluoranthene (BbF, five rings), benzo(a)pyrene (BaP, five rings), dibenzo(ah)anthracene (DahA, five rings), indeno(1,2,3-c,d)pyrene (IcdP, six rings) and benzo(g,h,i)perylene (BghiP, six rings) were determined. Diagnostic ratios have been used to distinguish the emission sources of PAHs, specifically BaP/BghiP (Katsoyiannis et al., 2007), Flu/(Flu + Pyr) (Ravindra et al., 2008), Flt/Flt + Pyr (Roberto et al., 2009) and IcdP/(IcdP + BghiP) (Yunker et al., 2002) (Table 1).

The activity of extracellular enzymes (β-D-cellobiosidase [CB], β-xylosidase [XYL], N-acetyl-β-D-glucosaminidase [NAG], phosphatase [PH] and arylsulphatase [SP]) was determined using fluorogenically labelled substrates (Pritsch et al., 2004; Turner, 2010; Sanaullah et al., 2016). The fluorescence was measured on a multi-detection plate reader (SpectroMax), with an excitation wavelength of 355 nm and an emission wavelength of 460 nm. For the determination of microbial biomass C, N and P, the fumigation and extraction method was used (Jenkinson and Powlson, 1976; Vance et al., 1987).

2.3. Statistical analysis

The Pearson correlation coefficients for the soil characteristics were calculated. Principal component analysis (PCA) was used to evaluate the relationships between the soil properties and the PAH content. Analysis of variance was employed to assess the differences between the average values of the soil properties and the PAH content. Differences with $P < 0.05$ were considered to be statistically significant. All the analyses were performed using Statistica 13 software (StatSoft Inc., 2012).

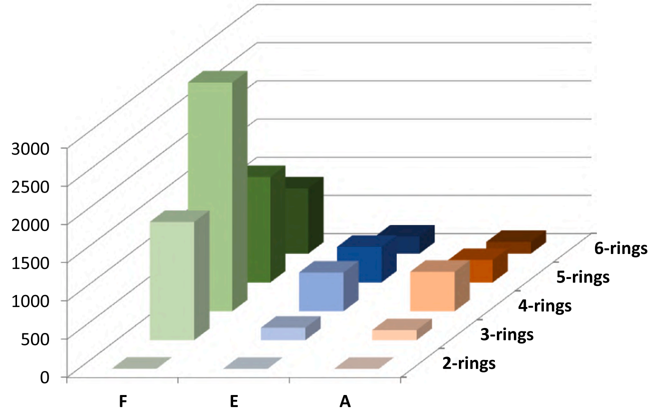

Fig. 3. PAH content (μg·kg^{-1}) in the soil depending on the benzene rings in transect points (F – forest site, E – edge point, A – arable land).

3. Results

The differences between the pH values of the forest and agricultural soils were statistically significant (Table 2), with lower pH values in H_2O recorded in the forest and border soils (4.15 and 4.40, respectively), while in the arable soils, the pH in H_2O was 6.09. Similar statistical differences were measured in the mean values of pH in KCl, which were 3.44 for the forest soils, 3.65 for the border soils and 5.32 for the arable soils (Table 2). The forest and border soils were characterised by statistically significant higher average C and N contents and C/N ratios. The highest mean C content was found in the forest soils (10.69%) and the lowest in arable soils (1.46%). The average N content was highest in the forest soils (0.53%) and lowest in the arable soils (0.10%). The mean C/N value for the forest soils was 19.6, whilst for the border soils, this was 18.7, and for the arable soils, 15.1. No statistically significant differences were found in the K or Mg content. Statistically significant higher Ca

Table 4
Heavy metals and PAHs content in soils of agroforestry transect.

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	ΣPAH
Forest	0.55 ± 0.22^{a}	2.93 ± 1.16^{a}	12.09 ± 1.82^{b}	5.12 ± 1.18^{b}	255.13 ± 159.73^{a}	3.77 ± 1.47^{b}	32.96 ± 3.92^{b}	42.57 ± 14.94^{a}	565.18 ± 513.21^{a}
Edge point	0.75 ± 0.37^{a}	3.30 ± 1.21^{a}	20.58 ± 5.82^{a}	11.28 ± 4.90^{a}	110.22 ± 46.35^{a}	10.42 ± 3.68^{a}	83.04 ± 44.31^{a}	50.56 ± 24.72^{a}	227.17 ± 184.58^{ab}
Arable land	0.69 ± 0.27^{a}	3.06 ± 0.82^{a}	23.17 ± 8.50^{a}	12.90 ± 4.59^{a}	94.96 ± 75.97^{b}	11.80 ± 4.10^{a}	92.92 ± 37.59^{a}	39.40 ± 8.75^{a}	91.42 ± 106.51^{b}

mean ± SD; small letters in the upper index of the mean values mean significant differences between different land management; Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (mg·kg^{-1}); ΣPAH (μg·kg^{-1}).

Table 5
The content of individual PAHs (μg·kg^{-1}) in soils depending on land management.

Molecular weight	Nunber of rings	Name of PAH	Forest	Edge point	Arable land
LMW	**2-rings**	**Nft**	2,40	0,43	1,13
	3-rings	**Ace**	26,42	2,60	13,28
		Flu	1023,00	107,79	85,50
		Phe	295,04	50,87	26,12
		Ant	203,20	0,84	5,94
		∑	1547,66	162,1	130,84
	4-rings	**Flt**	957,45	157,06	130,99
		Pyr	741,50	129,46	111,20
		BaA	561,90	82,63	134,26
		Chr	734,62	138,59	138,55
		∑	2995,47	507,74	515,00
HMW	**5-rings**	**BbF**	620,45	164,63	100,07
		BkF	281,05	104,75	59,99
		BaP	342,24	113,14	85,61
		DahA	137,20	83,64	50,69
		∑	1380,94	466,16	296,36
	6-rings	**BghiP**	247,45	103,34	79,21
		IcdP	608,21	123,27	74,52
		∑	855,66	226,61	153,73

LMW – low molecular weight, HMW – high molecular weight; naphthalane [Nft], acenapthene [Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], fluoranthene [Flt], pyrene [Pyr], benzo(a)anthracene [BaA], chrysene [Chr], benzo(k)fluoranthene [BkF], benzo(b)fluoranthene [BbF], benzo(a)pyrene [BaP], dibenzo(ah)anthracene [DahA], bezo(g,h,i)perylene [BghiP], indeno (1,2,3-c,d)pyrene [IcdP].

content was noted in the arable soils, and statistically significant higher Na content was found in the forest soils (Table 2).

In most cases, the enzyme activity and microbial biomass were statistically significantly different relative to the type of land management (Table 3). The forest soils were characterised by higher NAG, XYL and PH activity. However, in terms of CB and SP, the differences were not statistically significant. Higher microbial biomasses of C, N and P were found in the forest soils (Table 3). The heavy metal content varied in the different soils (Table 4): except for Mn and Zn, the highest heavy metal content was recorded in the agricultural soils (Table 4). The Cr, Cu, Ni and Pb contents were statistically significantly higher in the agricultural soils (Table 4). A statistically significantly higher PAH content was recorded in the forest than the arable soils (Table 4). The sum of the PAHs in the forest soils was 565.18 μg·kg^{-1}, whilst the total was 91.42 μg·kg^{-1} in the arable soils. Both the forest and agricultural soils were dominated by four-ring PAHs (Fig. 3 and Table 5). In the forest soils, a higher content of three-, four-, five- and six-ringed PAHs was observed, compared to the rest of the studied area. The highest percentage was recorded for three-ringed fluorene, which reached 1023 μg·kg^{-1} in the forest soils (Table 5). High contents of fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(b)fluoranthene and indeno(1,2,3-c,d) pyrene were also noted in the forest soils (Table 5). A comparison of the ratios used to determine the sources of the PAHs showed that the cause of soil contamination in all land uses is predominantly coal combustion (Fig. 4). Figs. 5 and 6 show that the pollutants in the soils are also from the combustion of wood and grass, and emissions from petrol in vehicles and other petroleum uses.

The enzyme activity and microbial biomass significantly correlated with C, N and Na content (Table 6). Most of the tested enzymes (NAG, XYL and PH) and the microbial biomass were negatively correlated with the pH. A statistically significant positive relationship was found between NAG, XYL and PH activity, the microbial biomass and the PAH content (Table 6). The PAH content correlated strongly and positively with the C, N and Na contents and, to a lesser extent, with the K content (Table 7). A negative, statistically significant relationship was found between the PAH content and the pH of the soils. For the Cr, Cu, Pb and Zn contents, a negative correlation with C and N content was noted, and a positive correlation with pH (Table 7). Factors 1 and 2, distinguished by the PCA for the organic horizons, explained a total of 85.71% of the variance in the soil properties (Fig. 7). The PCA confirmed the relationship between the C and N content and PAHs, and a group of forest soils was determined to be separate from the agricultural soils (Fig. 7).

4. Discussion

The results confirmed that land management has a significant impact on the PAH content due to the soil properties, especially the supply of organic matter to the soil. Moreover, it was proven that the biological activity of the soil, expressed in terms of enzymatic activity, depends on the amount and quality of the SOM and, to a lesser extent, on the PAHs and heavy metals that have accumulated in the soils. The forest soils were characterised by higher levels of PAH contamination than the agricultural soils. According to the scale of Maliszewska-Kordybach (1996), the forest soils studied were weakly contaminated or

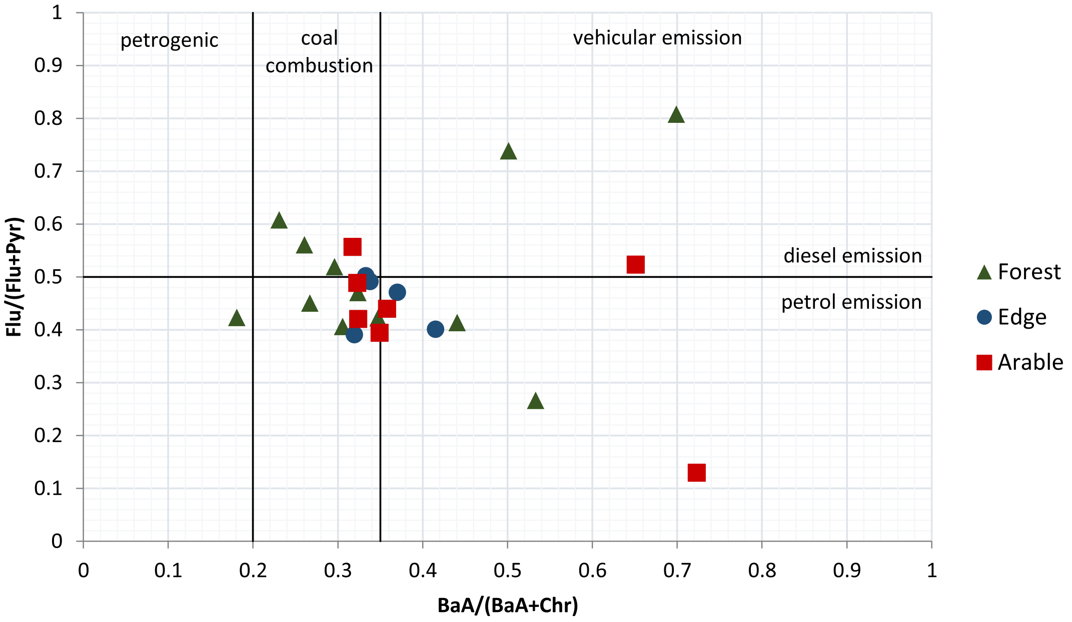

Fig. 4. Biplot of PAH diagnostic ratios Flu/(Flu + Pyr) and BaA/(BaA + Chr) for the identification of pollution emission sources.

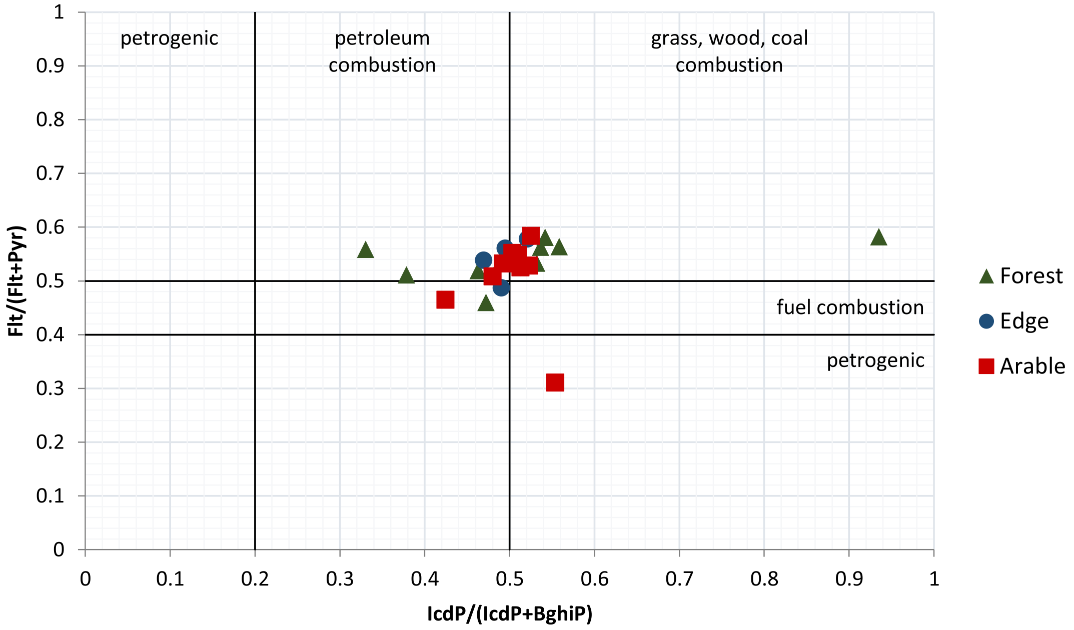

Fig. 5. Biplot of PAH diagnostic ratios Flt/(Flt + Pyr) and IcdP/(IcdP + BghiP) for the identification of pollution emission sources.

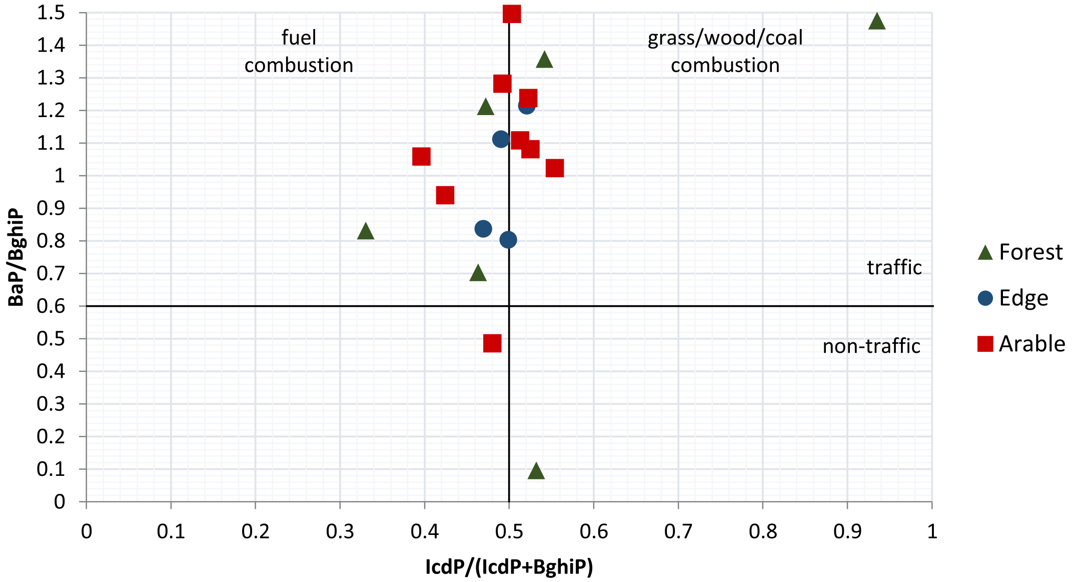

Fig. 6. Biplot of PAH diagnostic ratios BaP/BghiP and IcdP/(IcdP + BghiP) for the identification of pollution emission sources.

Table 6
Pearson correlation coefficients between biochemical properties and physicochemical properties, PAHs content in the soils of agroforestry transect.

	CB	NAG	XYL	SP	PH	MBC	MBN	MBP
C	0,393*	0,580*	0,736*	0,036	0,700*	0,685*	0,779*	0,621*
N	0,416*	0,585*	0,753*	0,074	0,740*	0,687*	0,803*	0,613*
P	0,434*	0,332	0,581*	0,236	0,624*	0,223	0,373*	0,418*
pH in H_2O	−0,322	−0,497*	−0,642*	−0,142	−0,460*	−0,465*	−0,605*	−0,471*
pH in KCl	−0,285	−0,466*	−0,611*	−0,142	−0,441*	−0,476*	−0,581*	−0,467*
Ca	0,010	−0,161	−0,255	0,067	−0,009	−0,200	−0,278	−0,250
K	0,297	0,397*	0,501*	0,421	0,721*	0,319	0,346	0,252
Mg	0,247	0,232	0,292	0,146	0,515*	0,286	0,192	0,233
Na	0,421*	0,540*	0,645*	−0,058	0,607*	0,633*	0,621*	0,577*
ΣPAH	0,224	0,436*	0,505*	0,032	0,501*	0,528*	0,583*	0,426*

*$p < 0.05$; carbon and nitrogen content (%); β-D-cellobiosidase [CB], N-acetyl-β-D-glucosaminidase [NAG], β-xylosidase [XYL], arylsulphatase [SP] and phosphatase [PH] (mol MUB g^{-1} dry soil h^{-1}); MBC [microbial biomass carbon], MBN [microbial biomass nitrogen] and MBP [microbial biomass phosphorus] (μg·kg^{-1}); Ca, K, Mg and Na (cmol(+)·kg^{-1}); ΣPAH (μg·kg^{-1})

Table 7
Pearson correlation coefficients between PAHs, heavy metals content and physicochemical properties of the soils of agroforestry transect.

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	ΣPAH
C	−0,222	−0,090	−0,460*	−0,401*	−0,331	0,318	−0,473*	−0,409*	0,853*
N	−0,139	−0,002	−0,440*	−0,376*	−0,266	0,374*	−0,440*	−0,386*	0,844*
P	0,371*	0,382*	0,015	0,057	0,436*	0,0128	0,076	0,513*	0,300
pH in H_2O	0,301	0,135	0,475*	0,444*	0,317	−0,336	0,554*	0,470*	−0,459*
pH in KCl	0,320	0,160	0,481*	0,452*	0,328	−0,319	0,541*	0,485*	−0,435*
Ca	0,424*	0,259	0,279	0,261	0,276	−0,133	0,390*	0,262	−0,222
K	0,225	0,265	−0,259	−0,318	−0,005	0,415*	−0,165	−0,364*	0,426*
Mg	0,318	0,224	−0,045	−0,082	0,092	0,136	0,110	−0,090	0,232
Na	−0,149	−0,108	−0,399*	−0,273	−0,307	0,196	−0,337	−0,316	0,797*

*$p < 0.05$; carbon and nitrogen content (%); Ca, K, Mg and Na (cmol(+)$\cdot$kg^{-1}); Ca, K, Mg and Na (cmol(+)$\cdot$kg^{-1}); ΣPAH (μg·kg^{-1}).

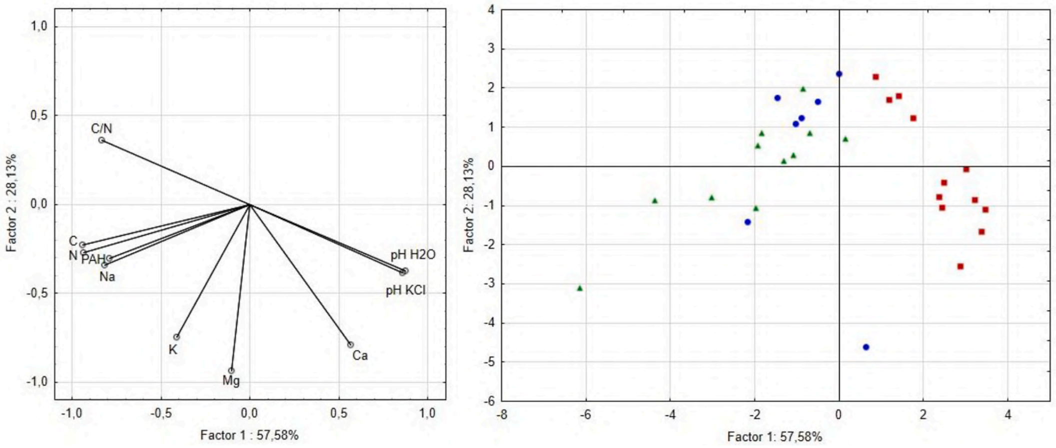

Fig. 7. The projection of variables on a plane of the first and second PCA factor (green symbols – forest; blue symbols – edge point; red symbols – arable land).

contaminated, while the agricultural soils were not contaminated. The average PAH content in the forest soils was 565.18 μg·kg^{-1}, almost six times higher than the average PAH content in the agricultural soils (91.42 μg·kg^{-1}). In this study, it was found that the higher PAH content in the forest soils is related to the SOM content. SOM consists of diverse components with various molecular weights, functional groups and polarities. These control the dynamics of any contaminants in the soil through hydrophobic and electrostatic interactions or the formation of chemical bonds (Petruzzelli et al., 2002; Ukalska-Jaruga et al., 2018). According to Chen et al. (2015), a higher accumulation of PAHs in forest soils is also associated with a higher humidity level, which results from the retention of rainwater by the plant cover. Forest layering favours the process of PAH accumulation by making their escape via water vapour more difficult. Wania and McLachlan (2001) argued that forests effectively 'pump' PAHs from the atmosphere into the forest soil, which acts as a large-capacity storage reservoir for these substances. Photodegradation is a process that regulates the residence time and fate of deposited PAHs in soils (Eker and Hatipoglu, 2019). It is assumed that, in a forest environment, this process is reduced because of the relatively low amount of light that reaches the soil, although more research is needed to precisely determine this relationship. The conditions in agricultural soils, especially the pH and amount of SOM, result in a relatively low PAH content due to the relatively high pH, the increased temperature, the availability of O_2, and the nutrients regularly supplied via agricultural treatments (Hao et al., 2007). Previous studies have shown that three-ringed PAHs are readily absorbed by maize roots, but that three- and four- to six-ringed PAHs are less likely to be absorbed into such plants (Zhang et al., 2017). Our results confirmed the presence of a large accumulation of four- to six-ringed PAHs, and the low amount of two- and three-ringed PAHs may be the result of their bioaccumulation in plants. The ratios calculated to determine the sources of the PAHs indicated that the PAHs which have accumulated in the soils are from carbon-burning processes. These processes include emissions from internal combustion engines. The study areas were located in a rural area within the influence of combustion and mining industry sites. Local households are predominantly heated by burning lignite; electricity in Poland is also largely generated by burning hard coal and lignite (Roszko et al., 2020). Our study confirmed that PAH diagnostic ratios are a useful tool for identifying PAH sources in soils of different land use. Values delimiting acceptable concentrations of heavy metals in soil are determined by the Regulations of the Minister of the Environment (2016), with the limiting values for the heavy metals tested in forest soils being: Cd – 10 mg·kg^{-1}; Co – 100 mg·kg^{-1}; Cr – 500 mg·kg^{-1}; Cu – 300 mg·kg^{-1}; Ni – 300 mg·kg^{-1}; Pb – 500 mg·kg^{-1}; and Zn – 1000 mg·kg^{-1}. The limiting values for the heavy metals in agricultural soils being: Cd – 3 mg·kg^{-1}; Co – 30 mg·kg^{-1}; Cr – 300 mg·kg^{-1}; Cu – 150 mg·kg^{-1}; Ni – 150 mg·kg^{-1}; Pb – 250 mg·kg^{-1}; and Zn – 500 mg·kg^{-1}. Our forest and agricultural soil samples did not exhibit any heavy metal values that exceeded these concentrations.

The forest soils were characterised by higher and significantly different microbial activity compared to the agricultural soils. This difference is due to the greater thermal and humidity stability of forests (Wallenstein and Hall, 2012) and the greater influence of trees on the quantity and quality of organic matter released to the soil environment (Vesterdal et al., 2008). This ultimately increases the pool of microorganisms and, thus, the soil enzymatic activity (Mukhopadhyay et al., 2017). The soils used for agricultural purposes had low enzyme activity, an effect of agricultural practices, which result in lower SOM (Drosos and Piccolo, 2018). Forest soils differ from agricultural soils in the amount of biomass hosted above and belowground, which results in differences in detrital input to the soil. The abundance and composition of the microorganisms depend on the litter and the influence of tree roots (Lladó et al., 2017). Organic matter content is influenced by plant biomass production and the contribution of dead organic matter, which provides energy and nutrients for soil microorganisms (Hairiah et al., 2006). The increased input of plant residues into forest soils relative to farmland leads to a high organic matter content, as well as high soil organic carbon in the unprotected fractions of soil organic matter, whereas a mineral clay soil may have the capacity to accumulate more stable C (Błońska et al., 2020).

5. Conclusions

Our findings confirm the importance of the type of land management to the PAH content of the soil. The coefficients calculated to determine the sources of the PAHs indicated that the main accumulations in the soils came from carbon-burning processes. Significant differences were found in the forest and agricultural soils concerning the PAHs, the soil organic carbon content, the enzymatic activity and the microbial biomass. The results indicate that land use is linked to the organic matter, a key element influencing PAH and heavy metal contents, and enzymatic activity. The results confirm that the amount of organic matter is the predominant soil component involved in the sorption and ageing of PAHs. It is implied that a higher detrital input into forest soils may counteract the inhibition of PAHs in soil enzyme activities. By introducing trees, we shape the quality and quantity of SOM, consequently affecting the microbiological properties of the soil, which translates into the possibility of biodegrading organic pollutants such as PAHs.

Declaration of Competing Interest

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

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Soil texture as a key driver of polycyclic aromatic hydrocarbons (PAHs) distribution in forest topsoils

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Due to the dynamic development of civilization and the increasing demand for energy, pollution by harmful chemicals, including polycyclic aromatic hydrocarbons (PAHs) compounds, is a serious threat to forest soils. The aim of the study was to determine the role of texture in the distribution of polycyclic aromatic hydrocarbons (PAHs) and trace elements in forest soils. The areas with different texture ranging from sand through sandy loam to silt loam were selected for the study. The study was carried out in the Chrzanów Forest District in southern Poland (50° 7′ 18 N; 19° 31′ 29 E), which in one of the most intensive industrial emission zones in Europe. The soil samples for properties determination were collected from locations distributed on a regular grid 100 × 100 m (20 points). The samples were collected from the humus horizon (0–10 cm) after removing organic horizon. Basic chemical properties, heavy metal content, polycyclic aromatic hydrocarbons (PAHs) content and magnetic susceptibility values were determined in soil samples. Additionally, enzymatic activity and microbiological biomass was determined in the samples. Our study confirmed the importance of texture in PAHs distribution. A strong correlation between PAHs content and silt content in the soils studied was noted. The regression tree analysis confirmed the importance of the silt content, followed by soil organic carbon in PAHs distribution. Organic carbon content and nitrogen content played a predominant role in controlling the microbial activity. In our study, we did not note a relationship between enzymatic activity, microbiological soil biomass and the amount of PAHs. This may be due to the effective sorption and immobilization of PAHs by particles of fine fractions, especially silt. Obtained results confirmed the usefulness of magnetic susceptibility in the assessment of heavy metals contamination of forest soils. We noted high correlation between magnetic susceptibility value and heavy metals content. Moreover, the relationship between magnetic susceptibility and soil texture of the topsoil was also observed.

Polycyclic aromatic hydrocarbons (PAHs) are characterized by high toxicity and mutagenicity[1]. As the number of benzene rings and molecular weight increase, their water solubility and biodegradability decrease, making them more toxic[2]. Polycyclic aromatic hydrocarbons in the soil environment are characterized by high durability, low mobility and high bioaccumulation capacity[3]. PAH compounds are classified as persistent organic pollutants[4] and the US Environmental Protection Agency has identified PAHs as one of the main ecosystem pollution problems, recommending monitoring of their content in plants, soil and aquatic environments[5]. Currently, as a result of increased human activity, anthropogenic PAHs emissions have increased significantly[6,7]. PAHs are formed mainly as a result of technological use of fossil fuels in high temperature conditions. The factors determining the accumulation of PAHs in soils are: distance from the emission source, climatic conditions, soil organic matter[8–10]. According to Terytze et al.[11], PAHs are characterized by a strong sorption affinity to soil organic matter. Extensive studies have been done with regard to the relationship of PAHs with total organic carbon (TOC) and elemental carbon (EC) in different environmental matrices[12]. According to Duan et al.[13], an important role in PAHs accumulation in the soil environment is played by meso- and macrophores and clay colloids responsible for sorption of pollutants. Clay can have a significant impact on PAHs sequestration in soil[14]. The addition of exogenous-rich carbon material such as biochar to the soil significantly changes the behavior and sorption potential of PAHs in

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the soil[15]. The type of stand significantly affects the content of polycyclic aromatic hydrocarbons in forest soils[16]. Lasota and Błońska[17] experiment provided evidence that the quantity and quality of soil organic matter plays an important role in controlling PAH amounts.

Monitoring by means of the characteristics of microbiological and biochemical properties of soils is successfully used in assessing the degree of soil contamination[18,19]. Enzyme activity could be a good indicator of soil quality because it is sensitive and reflects biological situation in the soil and is strongly correlated with important soil characteristics, such as organic matter and soil texture[20]. Weaker degradation of hydrocarbons is associated with lower biological activity of soils. Lasota and Błońska[17] noted in the mull humus type lower content of PAHs and at the same time the highest biological activity confirmed by high dehydrogenase activity. PAH degradation may not be directly correlated by the soil enzyme activity but related to soil indigenous population of PAH-degrading microorganism[21].

Soil magnetic susceptibility (MS) is an important parameter in pollution studies owing to its relationship with atmospheric deposition[22]. This works well due to the concomitance of technogenic magnetic particles (TMPs) with heavy metals[23]. It is well-known that the main sources of TMPs and heavy metals are high-temperature technological and combustion processes[24]. The deposition and accumulation of TMPs into topsoil leads to enhancement of magnetic signal and elevation of heavy metal contents[25–27]. The presence of TMPs in soil can be easily detected via magnetic susceptibility measurements (especially in the highly urbanized and industrialized areas). Moreover, magnetic parameters can be used to study various processes, which take place in soils and where magnetic minerals maybe used as indicators of changes and transformation[28–32]. Few of the studies show the state of contamination with heavy metals and PAHs in forest soils in connection with the magnetic susceptibility parameters[33].

The aim of the study is to determine the role of texture in the distribution of polycyclic aromatic hydrocarbons (PAHs) in forest soils. The areas with different texture ranging from sand through sandy loam to silt loam were selected for the study. The following research hypotheses were tested: (1) the content of silt strongly determined the distribution of polycyclic aromatic hydrocarbons in forest soils; (2) organic carbon plays an important role in the accumulation of PAHs and formation of the enzymatic activity of forest soils; (3) magnetic susceptibility is a useful tool in the assessment of contamination of forest topsoil with different texture.

Material and methods

Study area and soil sampling. The research was carried out in the Chrzanów Forest District in southern Poland (50° 7′ 18 N; 19° 31′ 29 E) (Fig. 1). The study plots with different texture were selected for the analysis (from sand by sandy loam to silt loam). The research area was dominated by a pine-oak stand of a similar age, i.e. 60–80 years. The average annual temperature for this area was 7.8 °C, and the average annual rainfall is 658 mm. The study area was located in an industrial emission zone, which comes mainly from Upper Silesian Industrial District. The elevated content of polycyclic aromatic hydrocarbons (PAH) in the studied soils was confirmed by earlier research[16]. The selection of the study plots was made during field observation. Before selecting the research plot, the authors, using a soil auger, checked the variability of the soil cover and assessed the accompanying vegetation. The study area was dominated by Stagnosols[34], created on water and glacial formations.

According to the Report on the state of the environment in the Małopolska Voivodeship in the period 2012–2017, the average annual benzo(a)pyrene (BaP) concentrations exceeded acceptable standards (1 ng m^3) across the whole Chrzanów Forest District. The average annual concentration of BaP near air pollution station in the neighborhood of the research area was 5.5 ng m^3. The average annual concentrations of particulate matter < 10 µm in diameter (PM10) over the entire range of the Chrzanów Forest District was 34 µg m^3. The mean annual concentrations of particulate matter < 2.5 µm in diameter (PM2.5) in the atmosphere exceeded the admissible standard (according to health protection criteria) of 27 µg m^3 across the whole of the Chrzanów Forest District.

Soil samples for laboratory analysis were collected in August 2018. The soil samples for properties determination were collected from locations distributed on a regular grid 100 × 100 m (20 points) (Fig. 2). The samples were collected from the humus mineral horizon (10 cm deep) after removing organic horizon. In all the cases, the samples for the study were collected from 4 sub-stands of soil. For determination of enzymes activity, microbial biomass and PAHs content, fresh samples of natural moisture were sieved through a sieve (ø 2 mm) and stored at 4 °C in the dark before analysis. The results were analyzed in three groups of surfaces separated on the basis of texture (I group with sand texture, II group with sandy loam texture and III group with silt loam).

Laboratory analysis. Freshly collected soil samples were dried and then sieved through a 2 mm mesh sieve. The particle size distribution was analyzed using a laser diffraction method (Analysette 22, Fritsch, Idar-Oberstein, Germany). The pH of soil samples in H_2O and KCl was determined by potentiometric method. An elemental analyzer (LECO CNS TrueMac Analyzer (Leco, St. Joseph, MI, USA)) was used to determine carbon (C) and nitrogen (N). By ICP method (ICP-OES Thermo iCAP 6500 DUO, Thermo Fisher Scientific, Cambridge, U.K.), the concentration of basic cations and the contents of Cd, Cr, Cu, Ni, Pb, Zn were determined. The contents of the studied heavy metals were determined after digestion in a 2:1 solution of concentrated nitric acid and perchloric acid.

From each soil sample collected, 10 g of soil was taken after mixing. Polycyclic aromatic hydrocarbons were extracted from the tested amount of soil in 70 ml of 2-propanol. The samples were centrifuged (4500, 5 min) and the supernatant was collected and later subjected to solid phase extraction (5 ml/min)—Solid Phase Extraction (Chromabond Cn/SiOH). The resulting extraction residue was dissolved in acetonitrile and analyzed by HPLC, equipped with a Dionex UltiMate 3000 Column Compartment—C18 5 µm, 4.6 × 100 mm HPLC column and a fluorescence detector (FLD). Water (A) and acetonitrile (B) was the mobile phase with a flow rate of 1 ml/min. A PAH mixture standard (CRM 47940) with a concentration of 10 µg/ml was used to calibrate the analyses.

Figure 1. Map of the study location. QGIS 3.16 software (https://www.esri.com/en-us/about/about-esri/overview) was used to create the map. The layer of the location map was the World Topographic Map basemap within QGIS 3.16 software. The map is credited to: Esri, HERE, DeLorme, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, OpenStreetMap contributors, and the GIS User Community.

Calibration solutions had concentrations of 0.1 µg/ml, 0.2 µg/ml, 0.5 µg/ml, 1 µg/ml, and 2 µg/ml. Samples of the prepared solutions were dosed onto the chromatograph column. The generated chromatograms determined the standard curve. Later, soil samples were dosed in triplicate. At the end of each analysis, an "unknown" sample was applied, which was a 0.1 µg/ml calibration solution used as control material. Thirteen polycyclic aromatic hydrocarbons were analyzed in the soil samples: naphthalene (Nft), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), and chrysene (Chr), benzo(k) fluoranthene (BkF), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IcdP), and bezo(g,h,i)perylene (BghiP).

Enzymatic activity was determined using fluorogenic labeled substrates[35,36]. The fluorogenic enzyme substrates that were used for analysis were based on 4-methylumbelliferone (MUB). The following substrates were used: MUB-β-ᴅ-cellobioside for β-ᴅ-cellobiosidase (CB), MUB-β-ᴅ-xylopyranoside for xylanase (XYL), MUB-N-acetyl-β-ᴅ-glucosaminide for N-acetyl-β-ᴅ-glucosaminidase (NAG), MUB-β-ᴅ-glucopyranoside for β-glucosidase (BG)[37]. 2.75 g of soil from each sample was measured and mixed with 92 ml of universal buffer (pH 6.0). The resulting soil solution was pipetted into wells located on a microscope plate that contained the substrate and a modified universal buffer. Fluorescence was determined by incubating the soil suspension determined for 1.5 h at 35 °C in 96-well microplates (Puregrade, Germany). Fluorescence was then immediately determined on a multi-detector plate reader (SpetroMax), with excitation at 355 nm and emission at 460 nm. Carbon in microbial biomass (MBC) and nitrogen in microbial biomass (MBN) were determined by fumigation and extraction[38,39].

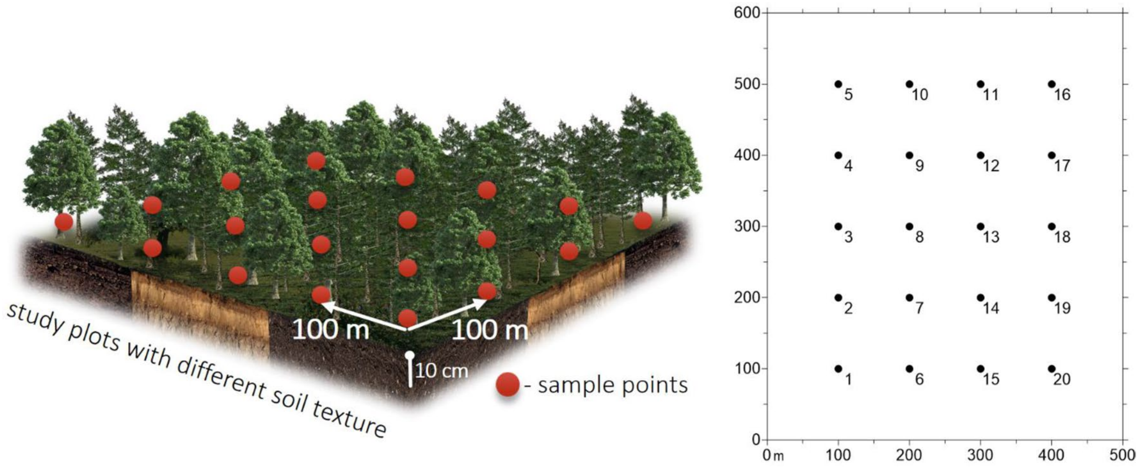

Figure 2. Scheme of the sampling points locations. GIMP 2.10.20 (https://www.gimp.org), Surfer 10 software and elements from the Freepik website (https://www.freepik.com) were used to create the structure of the figure.

Class	Sand	Silt	Clay	pH H_2O	pH KCl	C	N	C/N	Ca	K	Mg	Na
Sand	93 ± 2^b	6 ± 2^b	1 ± 1^b	4.01 ± 0.21^a	3.17 ± 0.25^a	2.95 ± 1.47^b	0.12 ± 0.05^b	25.8 ± 5.6^a	0.27 ± 0.22^b	0.05 ± 0.02^b	0.07 ± 0.04^b	0.01 ± 0.01^a
Sandy loam	57 ± 10^a	37 ± 9^a	5 ± 2^a	4.21 ± 0.50^a	3.50 ± 0.43^a	6.43 ± 2.35^a	0.34 ± 0.14^a	19.8 ± 5.9^a	1.75 ± 0.77^a	0.15 ± 0.07^a	0.35 ± 0.22^a	0.02 ± 0.01^a
Silt loam	41 ± 2^a	53 ± 2^a	4 ± 1^a	4.06 ± 0.23^a	3.43 ± 0.29^a	5.86 ± 0.39^a	0.34 ± 0.09^a	18.5 ± 5.9^a	0.89 ± 0.47^{ab}	0.12 ± 0.03^a	0.25 ± 0.11^{ab}	0.02 ± 0.01^a

Table 1. Basic properties of analysed soils. Mean ± standard deviation; sand, silt and clay content (%); carbon and nitrogen content (%); Ca, K, Mg and Na content (cmol(+)/kg). Small letters in the upper index of the mean values mean significant differences between texture class.

By measuring magnetic susceptibility in the studied soil samples, the proportion of magnetic particles was determined. In the laboratory, low-field magnetic susceptibility (volumetric—κ) was measured at two different frequencies: low (465 Hz) and high (4650 Hz) using a Bartington MS2 magnetic susceptibility meter equipped with an MS2B sensor (Bartington Instruments Ltd.) Based on the measurements of κ values, the bulk magnetic susceptibility (χ) and the percentage frequency-dependent magnetic susceptibility (χ_{fd}) were determined[40].

Statistical analysis.

ANOVA test was used to evaluate the differences between the mean values of the soil properties. Pearson correlation coefficients for the soil characteristics were calculated. The principal component analysis (PCA) method was used to evaluate the relationships between soil properties and PAH content. The classification and regression tree (C&RT) approach was applied to estimation of soil properties influence on PAH content. Differences with $P < 0.05$ were considered statistically significant. All analyses were performed using Statistica 12 software.

Results

Physicochemical properties.

The soils studied were divided into three groups, which differed significantly in sand, silt and clay content. The highest silt content was recorded in soils with sandy loam and silt loam texture (Table 1). No statistically significant differences in pH of the soils studied were noted. Average pH in H_2O of soils with sand, sandy loam and silt loam texture was 4.01, 4.21 and 4.06 (Table 1). Soils with the texture of sandy loam and silt loam were characterized by statistically significantly higher carbon and nitrogen content compared to soils with sand texture (Table 1). The highest carbon content was recorded in soils with sandy loam grain size (6.43%) and the lowest in soils with sand grain size (2.95%). The mean nitrogen content in soils with sandy loam and silt loam texture is 0.34% and in sandy soils it is significantly lower at a level of 0.12%. No statistically significant differences in C/N of the soils studied were recorded (Table 1). The content of alkaline cations was significantly lower in sandy soils (Table 1). In soils with different grain sizes, different enzymatic and microbial biomass of C and N was noted (Table 2).

Biochemical properties.

High activity of CB, BG, NAG and XYL was recorded in soils with sandy loam and silt loam texture (Table 2). The differences in enzymatic activity were not statistically significant. In the case of microbial biomass C and N, the results were similar to the enzymatic activity. High microbial biomass C and N was recorded in soils with a finer grain size. The microbial biomass N was statistically significantly higher in soils with silt loam texture (Table 2). Enzymatic activity and microbial biomass C and N correlated significantly with C, N and Na content (Table 3). In case of CB, BG, MBC and MBN a positive correlation with potassium

Class	CB	BG	NAG	XYL	MBC	MBN
Sand	9.95 ± 3.46^{a}	9.15 ± 8.15^{a}	9.56 ± 6.81^{a}	11.69 ± 8.76^{a}	348.71 ± 186.94^{a}	39.30 ± 30.71^{b}
Sandy loam	16.62 ± 14.36^{a}	21.95 ± 13.18^{a}	16.93 ± 8.62^{a}	15.29 ± 10.76^{a}	571.20 ± 285.82^{a}	63.49 ± 36.89^{ab}
Silt loam	14.74 ± 6.91^{a}	19.44 ± 11.30^{a}	20.37 ± 10.20^{a}	14.57 ± 10.54^{a}	446.50 ± 54.13^{a}	95.02 ± 28.29^{a}

Table 2. Enzyme activities of soil and microbial biomass carbon and nitrogen. Mean ± standard deviation. Small letters in the upper index of the mean values mean significant differences between texture class. *CB* β-D-cellobiosidase, *BG* β-glucosidase, *NAG* N-acetyl-β-D-glucosaminidase, *XYL* xylanase (nmol MUB/gd s/h), *MBC* microbial biomass carbon, *MBN* microbial biomass nitrogen (μg/g).

	CB	BG	NAG	XYL	MBC	MBN
N	0.6234*	0.5516*	0.5321*	0.4851*	0.6076*	0.6392
C	0.6083*	0.4818*	0.3877	0.4936*	0.6272*	0.5783
Sand	−0.3690	−0.4212	−0.3241	−0.2795	−0.4041	−0.3635
Silt	0.3903	0.4484*	0.3541	0.3002	0.4004	0.3678
Clay	0.1094	0.1015	−0.0183	0.0366	0.3451	0.2460
pH in H_2O	−0.2914	−0.1549	−0.2329	−0.4048	−0.0870	0.0161
pH in KCl	−0.0528	0.1370	0.0645	−0.1986	0.1879	0.2857
Ca	−0.1498	−0.1244	−0.1456	−0.3139	−0.0962	0.0173
K	0.5456*	0.5059*	0.4410	0.4351	0.5995*	0.6072*
Mg	0.0062	0.0142	−0.0020	−0.1739	0.0442	0.1610
Na	0.7006*	0.7628*	0.6017*	0.5191*	0.6510*	0.6109*
PAHs	0.0114	0.0465	−0.0883	−0.0678	0.1144	−0.0087
Cd	0.2406	0.1309	0.0607	0.0688	0.0729	0.1067
Co	0.4145	0.4498*	0.4387	0.2139	0.2599	0.2966
Cr	0.4060	0.3896	0.3929	0.2261	0.3049	0.3565
Cu	0.3650	0.3432	0.3605	0.2121	0.3154	0.3385
Mn	0.0820	0.1250	−0.0060	−0.1687	0.0608	−0.0236
Ni	0.1007	0.2463	0.2543	0.0656	−0.0418	−0.1686
Pb	0.5166*	0.4369	0.4099	0.3470	0.4459*	0.4393
Zn	0.3731	0.3884	0.3136	0.1219	0.2505	0.2820

Table 3. Correlation between biochemical properties and basic properties of soils. *$p < 0.05$.

Class	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	χ	χ_{fd}	ΣPAHs
Sand	0.67 ± 0.60^{b}	0.33 ± 0.15^{b}	4.86 ± 2.06^{b}	18.13 ± 7.45^{b}	18.25 ± 9.30^{b}	6.73 ± 2.96^{b}	53.16 ± 27.96^{b}	22.69 ± 14.44^{b}	16.44 ± 7.37^{b}	1,47 ± 0.12^{b}	3.62 ± 2.37^{b}
Sandy loam	1.55 ± 0.65^{a}	1.92 ± 1.22^{a}	22.81 ± 13.82^{a}	34.07 ± 14.83^{a}	97.89 ± 61.45^{a}	6.96 ± 2.25^{a}	197.83 ± 127.96^{a}	83.64 ± 40.14^{a}	53.14 ± 40.14^{a}	1,74 ± 1.10^{a}	178.35 ± 115.11^{a}
Silt loam	1.35 ± 0.25^{a}	2.93 ± 1.88^{a}	22.14 ± 11.68^{a}	35.91 ± 5.56^{a}	181.69 ± 119.86^{a}	7.81 ± 1.37^{a}	162.38 ± 37.71^{a}	84.06 ± 40.62^{a}	59.82 ± 32.50^{a}	1.19 ± 0.50^{a}	1369.41 ± 1003.39^{a}

Table 4. Heavy metals content, magnetic susceptibility and PAHs content in soils. Mean ± standard deviation; χ—mass magnetic susceptibility (10^{-8} m^3/kg); χ_{fd} (%)—frequency-dependent magnetic susceptibility; Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn (mg/kg); ΣPAHs sum of polycyclic aromatic hydrocarbons content (μg/kg).

content was noted. No significant correlations of biochemical parameters with heavy metals, magnetometry and PAHs content were found (Table 3).

Polycyclic aromatic hydrocarbons and heavy metals content. The highest content of heavy metals was recorded in the soils with sandy loam and silt loam texture (Table 4). The differences were statistically significant. The relationship between magnetic susceptibility and soil texture of the topsoil was also observed. Magnetic susceptibility was directly correlated with the percentage of silt and inversely correlated with the percentage of sand, suggesting that magnetic particles are associated with finer soil fraction. Magnetic susceptibility gradually decreases with sand fraction content (Table 4), i.e. the highest mean values of χ were recorded in soils with silt loam texture (59.82×10^{-8} m^3/kg), lower in soils with sandy loam texture (53.14×10^{-8} m^3/kg) and the lowest in sandy soils (16.44×10^{-8} m^3/kg). In contrast, the percentage values of frequency-dependent magnetic susceptibility (χ_{fd}) were comparable, regardless of soil texture and show similar patterns for study soil fraction (i.e. did not exceed 2%, Table 4). The highest sum of PAHs was recorded in soils with heavy texture (sandy loam

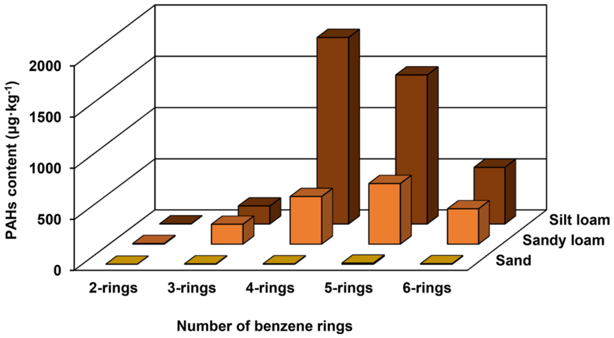

Figure 3. PAHs content (µg/kg) in soil depending on the benzene rings, was generated using Statistica 13 software.

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	χ	PAHs
N	0.5625*	0.7640*	0.8775*	0.7434*	0.4303	0.1207	0.8754*	0.7981*	0.7341*	0.0971
C	0.6605*	0.5139*	0.6531*	0.6445*	0.3019	0.1306	0.8110*	0.6271*	0.6042*	0.2561
C/N	− 0.1513	− 0.7007*	− 0.7085*	− 0.5109*	− 0.4170	− 0.0055	− 0.4440*	− 0.6330*	− 0.5307*	0.1319
Sand	− 0.5205*	− 0.7026*	− 0.6662*	− 0.6187*	− 0.5031*	− 0.1723	− 0.6365*	− 0.6801*	− 0.5083*	− 0.4640*
Silt	0.5209*	0.7186*	0.6672*	0.6079*	0.5026*	0.1840	0.6246*	0.6845*	0.5223*	0.4696*
Clay	0.4169	0.4042	0.5055*	0.5721*	0.3948	− 0.0002	0.5983*	0.4971*	0.2799	0.3184
pH in H_2O	0.0208	0.1931	0.1992	− 0.1385	0.2226	− 0.3404	− 0.0789	0.2724	0.0655	− 0.1653
pH in KCl	0.0616	0.4228	0.3952	0.0537	0.2933	− 0.2504	0.0813	0.4303	0.3204	− 0.1450
Ca	0.2674	0.3149	0.4196	0.0998	0.3368	− 0.2073	0.2541	0.4576*	0.1363	− 0.1177
K	0.5226*	0.6680*	0.8664*	0.7150*	0.3428	0.0961	0.8879*	0.7639*	0.6482*	0.0718
Mg	0.4736*	0.5591*	0.6784*	0.3713	0.4916*	− 0.1401	0.5051*	0.6991*	0.4159	− 0.1187
Na	0.5581*	0.7437*	0.7153*	0.6110*	0.4702*	0.1887	0.6809*	0.7783*	0.6976*	0.2519
χ	0.5508*	0.7539*	0.7450*	0.7262*	0.5296*	0.2148	0.6814*	0.7622*	1.000	− 0.0347

Table 5. Correlation between heavy metals content, PAHs content, magnetic susceptibility and soil properties. *$p < 0.05$.

and silt loam). The mean sum of PAHs was 3.62 µg/kg in soils with sand texture, 178.35 µg/kg in sandy loam and 1369.41 µg/kg in silt loam texture. These values were significantly higher compared to sandy soils (Table 4). In soils with a higher silt content, high contents of 4, 5 and 6 ring hydrocarbons were recorded (Fig. 3). In the case of most heavy metals, magnetic susceptibility and PAHs, a significant positive correlation with silt content and a negative correlation with sand content was observed (Table 5, Fig. 4). For Cr, Cu, Pb and Zn, a positive correlation with clay content was noted (Table 5). Heavy metals content and magnetic susceptibility were strongly positively correlated with N, C and selected alkaline cations (K, Mg and Na) (Table 5). Moreover, the high and significant correlation between χ and Cd, Co, Cr, Cu, Mn, Pb and Zn was stated (Table 5).

Correlations. The regression tree for PAHs content in soils confirmed the importance of texture in shaping the distribution of PAHs (Fig. 5). The regression tree indicates silt content as a variable explaining the concentration of PAHs in the studied soils. Carbon content in soils determines PAHs distribution in forest soils to a smaller extent (Fig. 5). The PCA analysis confirmed the differences in properties of soils with different texture. Sandy soils form a separate group which is characterized by lower contents of C, N, alkaline cations and PAHs. Soils with heavier texture were characterized by higher PAHs content and more favorable soil properties (Fig. 6). Factors 1 and 2 explain 76.68% of the variability of the examined features. Factor 1 is related to the content of sand, silt, clay and alkaline cations. Factor 2 is related to the content of PAHs in the tested soils (Fig. 6).

Discussion

The study carried out confirmed the validity of the first hypothesis. Soil texture, especially the silt content, was importance in PAHs distribution in forest soils. A significant correlation of PAHs content in soils with the content of silt fraction was recorded. The share of particular granulometric fractions to a large extent determines the soil sorption properties[20,41]. Previous studies have confirmed the importance of soil texture in PAHs accumulation[42,43]. In soils with heavier texture like sandy loam, silt loam, high content of 4, 5 and 6 ring aromatic hydrocarbons was recorded. The key factors determining the stability of PAHs in soil include their structure and properties[44]. Two and three-ringed hydrocarbons which have a lower molecular weight and higher water solubility are more susceptible to degradation than those with more rings. An increase in the number of rings in PAH molecules

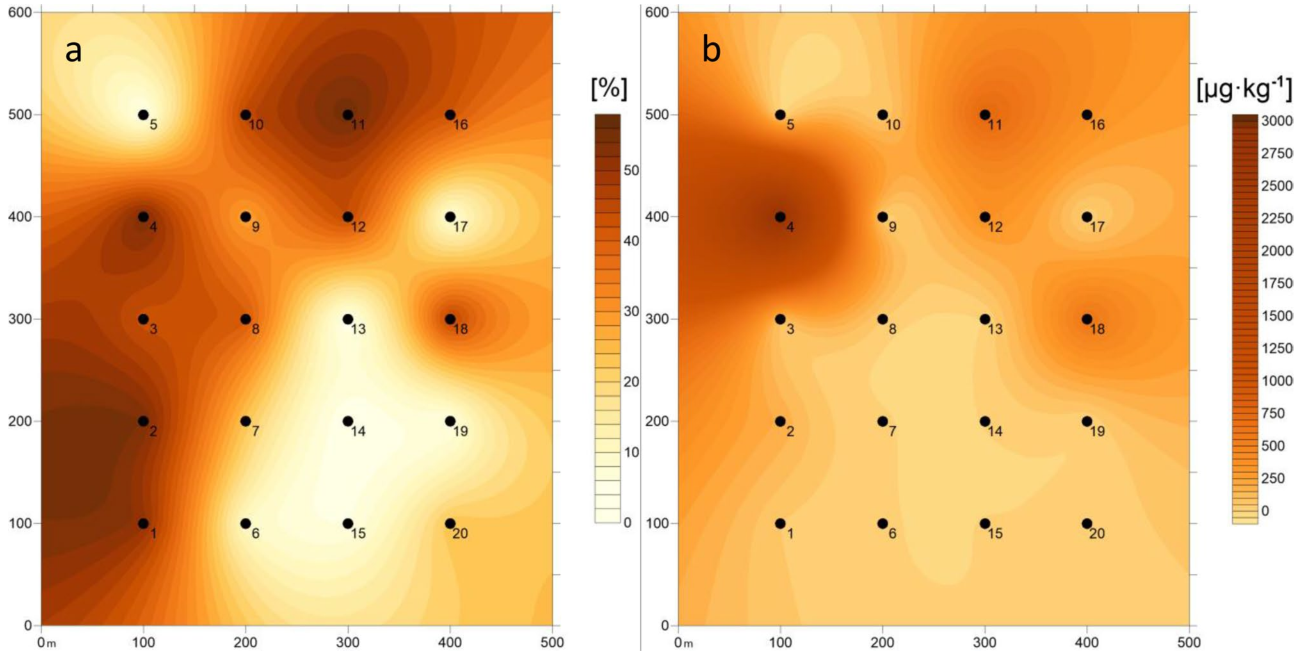

Figure 4. Spatial distribution of silt (**a**) and PAHs (**b**) content in soils, was plotted using Surfer 10 software.

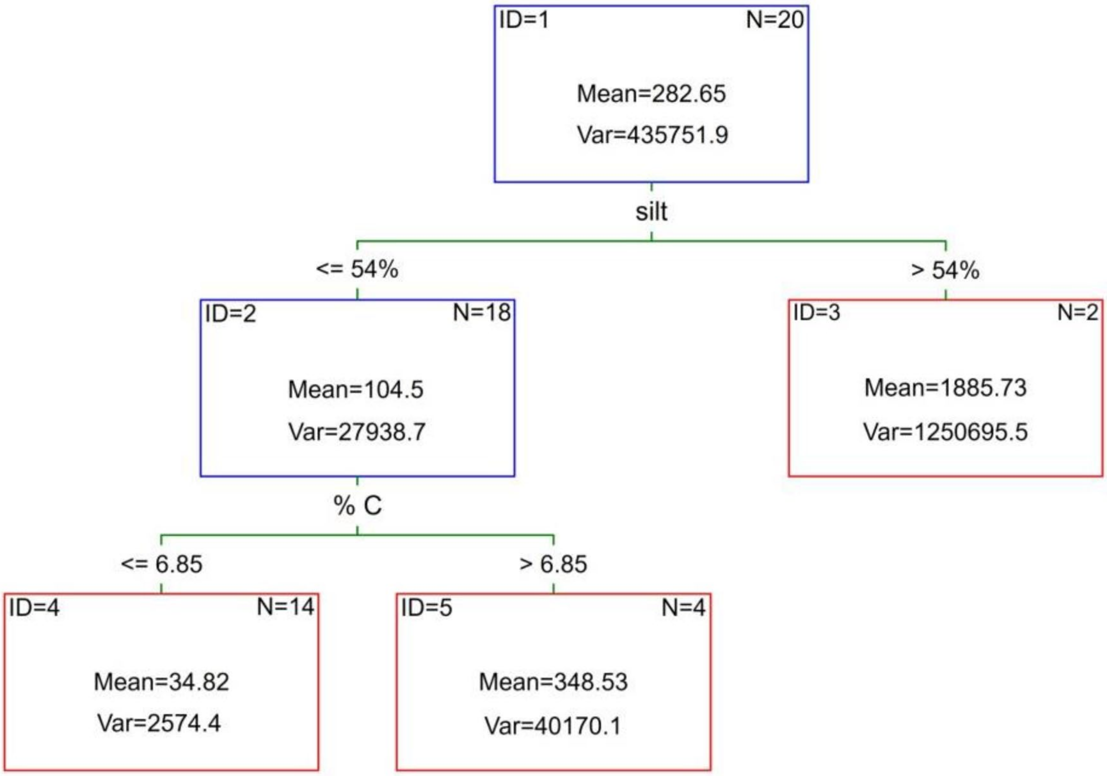

Figure 5. The regression tree (C&RT) for PAHs content in soils, was generated using Statistica 13 software.

increases their molecular weight and hydrophobic properties, thus reducing microbiological degradation[19]. Due to water solubility, 2-ring PAHs and to a lesser extent 3-ring PAHs are more available for biological degradation and uptake[45]. Sorption and degradation are key processes that affect the fate and transport of PAHs in the environment[46].

When listing the soil properties that determine PAHs accumulation in soils, soil organic matter is indicated first, followed by soil texture. Our study shows that texture is more important in shaping PAHs distribution in

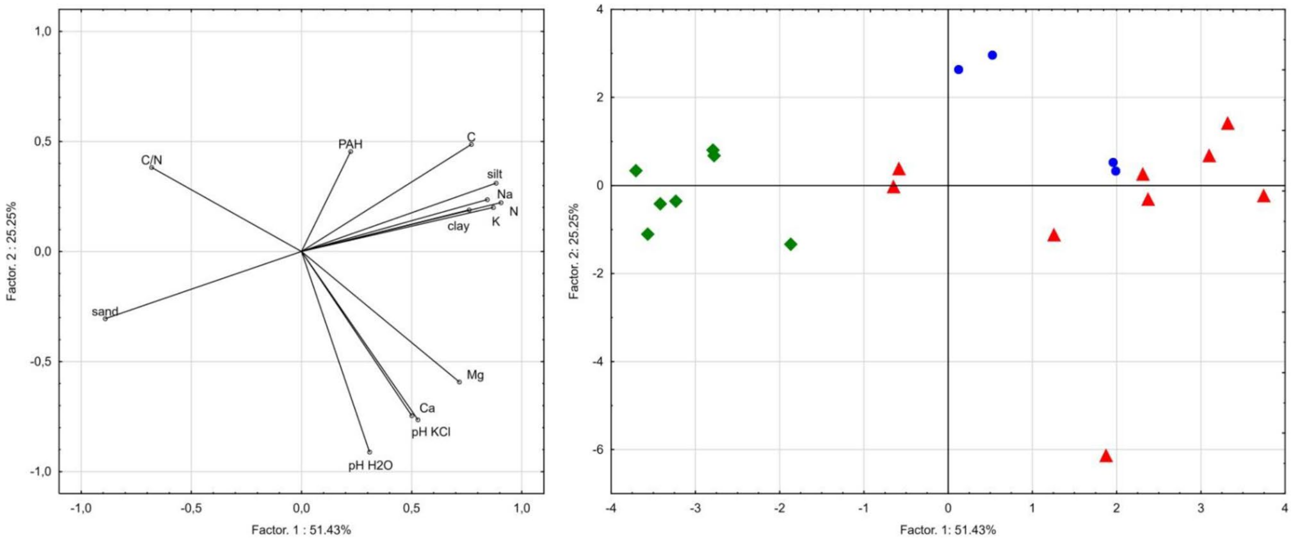

Figure 6. The projection of variables on a plane of the first and second PCA factor (green symbols—sand; red symbols—sandy loam; blue symbols—silt loam), was generated using Statistica 13 software.

forest soil. The regression tree analysis confirmed the importance of silt content, followed by soil organic carbon in PAHs distribution. Many studies demonstrated that PAHs adsorb strongly on the surface of soil particles and organic matter and are therefore not easily biodegradable[17,47]. In our study, we did not note a relationship between soil enzymatic activity and PAHs content in soils. This may be due to the strong binding of PAHs by fine fraction particles, especially silt. Maliszewska-Kordybach and Smreczak noted that high PAHs concentrations did not affect enzymatic activity[48]. This is related to the low solubility of these compounds and consequently low bioavailability to soil biota. Baran et al. noted a stimulating influence of PAHs on dehydrogenase activity and biochemical potential fertility indicator, which was attributed to an adaptation of the soil microflora and the use of pollutant as a C and energy source[49]. When there are significant differences in the amount of soil organic matter, it has a greater effect on enzyme activity than low-level exotic pollutants[50]. The enzymatic activity and microbial biomass of the soils studied correlated very strongly with the carbon and nitrogen content of the soils. There was a strong correlation between the organic carbon content and the enzymes involved in the C and N cycles. Changes in the dynamics of soil microorganisms are related to the availability of substrates[51]. Dou et al. noted a significant relationship between arylsulphatase, phosphatase and β-D-glucosidase activity and C, N and P concentration in soils[52]. Soil organic matter is a carrier of enzymes, affects the microbial biomass and community structure[53,54]. It is revealed that SOC was positively correlated with soil microbial community and organic carbon availability was reported to be major determine for preservation of soil microbial diversity[55]. Nitrogen affects many ecosystem functions, plant community diversity and microbial communities[56]. In our study, we noted the stimulating role of nitrogen on enzymatic activity and microbial biomass C and N. N addition indirectly affects soil enzyme activity through changes in the composition of microbial communities[57]. Summarizing the analyses carried out, the second hypothesis concerning the role of organic carbon in shaping PAHs content and enzymatic activity of forest soils is correct.

The permissible content of heavy metals was exceeded most in soil with sandy loam and silt loam texture. The clay and silt fractions are the main carrier of the soil's adsorption properties. According to Kabata-Pendias[58], the admissible level of Cd amounts to 1 mg/kg, Co to 10 mg/kg, Cr to 60 mg/kg, Cu to 30 mg/kg, Ni to 20 mg/kg, Pb to 50 mg/kg and Zn to 100 mg/kg. The metal contents found in uncontaminated soils were not exceeded for manganese, chromium, cobalt and nickel. In our study, we confirmed a strong relationship between heavy metals and soil texture, organic carbon content and the content of alkaline cations. Verla et al. showed that clay particle size had strong influence on heavy metals mobility[59]. Soil organic matter and clay minerals is the main component of soil that possess significant sorption capacity relative to metals through exchange sorption, complexing or chelation[19]. High level of PAHs were recorded in soil with sandy loam and silt loam texture. The sum of PAHs in that soils exceed 100 µg/kg, the threshold values of classification according to Maliszewska-Kordybach criteria[60]. The studied soils with highest PAHs content were dominated by the silt fraction which conducive to PAH accumulation. According to Lu et al. the highest PAH concentration was associated with clay and silt fraction[61].

Our data set indicate that the mean topsoil value of mass magnetic susceptibility (42×10^{-8} m^3/kg) was higher than the mean topsoil values found by Dearing et al. and Hanesch and Scholger for typical Stagnosol[62,63]. Observed differences might be an effect of particular parent material, soil properties (e.g. soil texture), environmental settings, or impact of industrial emission. Three times higher magnetic susceptibility was determined in topsoil with fine grains (Table 4). This phenomenon was proved by significant (both positive and negative) correlation between magnetic susceptibility and soil texture in topsoil (Table 5), as reported by many other[64–66]. On the other hand, the presence of ultra-fine superparamagnetic grains of pedogenic origin was not confirmed by percentage frequency-dependent magnetic susceptibility measurements[62]. The values of χ_{fd} in the study soil samples were low (i.e. below 2%, Table 4), suggesting the technogenic or geogenic origin of magnetic particles.

However, in the case of relatively low values of both χ and χ_{fd}, and due to the fact that the study area was located in the industrial emission zone, the presence of geogenic iron minerals ought to be excluded.

Conclusions

Our analysis confirmed the importance of the soil texture, followed by soil organic carbon in PAHs distribution. High silt content positively affected PAHs content and led to an increase in the PAHs accumulation in forest soil by increasing the sorption capacity of soils. Organic carbon content and nitrogen content stimulates enzyme activity and microbial biomass C and N. Obtained results confirmed that the integrated geochemical and magnetic methods proved to be a useful and effective tool in the assessment of contaminants (in particular heavy metals) of forest soil. Based on this study there is clear evidence that PAH pollution assessments need to consider grain size and soil organic carbon.

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Author contributions

S.Ł., J.L. M.M.S. and E.B. collected and analyzed the data and wrote the first draft. S.Ł., J.L. E.B provided the study idea. S.Ł., J.L and E.B reviewed the draft. All authors read and approved the final.

Competing interests

The authors declare no competing interests.

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SPECIAL ISSUE ARTICLE

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Polycyclic aromatic hydrocarbons accumulation in soil horizons of different temperate forest stands

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Abstract

Pollution due to polycyclic aromatic hydrocarbons (PAHs) is a serious environmental issue. The aim of this study was to determine the effect of stand species composition on PAH content. The research covered the stand soils of the Rybnik Forest District, which experiences some of the highest deposition of industrial emissions in Europe. Pine, pine–oak and oak stands growing in the same soil conditions were selected for the study. Samples for further analyses were collected from the organic, humus mineral and mineral soil horizons. The organic C and N concentrations, pH, alkaline cation content, microbiological biomass of C and N, soil enzyme activity, soil organic matter (SOM) fractions and PAH content were determined. The oak stand soils were characterised by the lowest accumulation of PAHs (2936.0 μg kg^{-1}) with high biochemical activity expressed by enzyme activity (dehydrogenases, *N*-acetyl-*β*-D-glucosaminidase, phosphatase) and high microbiological biomass. In contrast, pine stand soils are acidified; hence, SOM decomposition is slowed, resulting in a high accumulation of PAHs (3805.0 μg kg^{-1}). A strong correlation ($r = 0.825$) between PAH accumulation and SOM free light fraction (fLF) C concentration was noted. The stand species composition plays an important role in shaping the quality and quantity of SOM and soil acidification, which is reflected in the microbial activity and PAH accumulation in forest soils. Such accumulation in forest soils is related to the fractional composition of SOM, which is due to the influence of species composition through the supplied biomass.

KEYWORDS
degradation, enzyme activity, forest soils, polycyclic aromatic hydrocarbons, soil organic matter

1 | INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds comprising two or more interconnected benzene rings and are known to contaminate soil environments (Cao et al., 2020; Ghosal et al., 2016; Sun et al., 2012). The prevalence of PAHs in the soil is mostly of anthropogenic origin (Zhou et al., 2005) due to the increasing use of energy from the combustion of fossil fuels, oil and internal combustion engines (Lui et al., 2017; Tiwari et al., 2011). Atmospheric PAHs accumulate easily in the soil due to their sorption capacity (Eom et al., 2007; Kováts et al., 2021) and arrive at the land surface through both wet and dry deposition (Choi et al., 2009; Ding et al., 2007). Organic pollutants are stored, captured and delivered to the litter in forest soils by tree crowns (Matzner, 1984). The accumulation of PAHs in soils depends on the amount and quality of the organic matter and, in particular, the pH (Aichner et al., 2015; Chaineau et al., 2005; Lladó et al., 2009; Wu et al., 2008). As a result of the impact of woody vegetation, forest soils are characterised by a high concentration of organic carbon, which is reflected by an increased accumulation of PAHs compared to agricultural soils (Łyszczarz et al., 2021). Soil organic matter (SOM) consists of diverse components with varied molecular weights, functional groups and polarities, which control soil contaminant dynamics through hydrophobic and electrostatic interactions as well as chemical bond formation (Ukalska-Jaruga et al., 2018). In addition, soil mineral particles (silt and clay) are important for accumulating PAHs in the soil environment (Luo et al., 2008).

The pH is an important parameter in the PAH biodegradation process because it is a key factor for the availability of nutrients and, thus, for the development of microorganisms involved in PAH degradation. Strong soil acidification results in a reduction of sorption capacity, causing reduced biological activity and disruption of the C, N and P cycles in the forest ecosystem (Mueller et al., 2012). The amount and quality of organic matter in forest soils is determined by the species composition of the stand (Błońska et al., 2016; Błońska et al., 2017; De Deyn et al., 2008).Through litterfall and root systems, the stand shapes soil pH and soil chemical properties (Mareschal et al., 2010; Reich et al., 2005). Coniferous stand soils have a lower pH compared to mixed or deciduous stand soils (Jandl et al., 2004). The fall of litter in deciduous stands has a positive effect on soil pH and provides macroelements that improve the biological activity of the forest soil and promote organic matter decomposition (Błońska et al., 2016; Hobbie et al., 2007).The soil organic matter, due to its heterogeneous structure and composition, shows strong sorption properties for the most persistent organic pollutants, including PAHs (Ehlers & Loibner, 2006; Ukalska-Jaruga et al., 2015). SOM contains three distinct fractions: the free light fraction (fLF), aggregate-occluded light fraction (oLF) and mineral-associated fraction (MAF) (Wambsganss et al., 2017). The fractional composition of SOM determines its sorption capacity (Gruba et al., 2015; Six et al., 2002). Labile C can remain in the ground from weeks to years, and recalcitrant C can persist for decades or even centuries (von Lutzov et al., 2006). SOM associated with minerals can be stabilised due to its protection from mineralisation through chemical or physicochemical binding between SOM and clay or silt particles (Six et al., 2002). The light fraction is more susceptible to changes in soil use and altered litter inputs (Grüneberg et al., 2013; Li, Vogeler, & Schwendenmann, 2019). SOM fractions can serve as an indicator of carbon accumulation changes (Błońska et al., 2017).

The processes of SOM decomposition depend on the diversity and activity of the soil microorganisms. The primary decomposers (bacteria and fungi) release extracellular hydrolytic enzymes into their immediate environment, catalysing organic matter decomposition (Berg & McClaugherty, 2008). Thus, the enzymatic activity provides information about the condition of the soil environment and the soil microorganism activity (Gil-Sotres et al., 2005; Li, Luo, et al., 2019). Soil microorganisms and enzymes are responsible for the C (β-glucosidase, cellulases, dehydrogenase), N (amidase, chitinase, protease) and P (phosphatase) cycles (Makoi & Ndakidemi, 2008). Toxic organic compounds such as PAHs can be degraded by enzymes secreted by microorganisms (Haritash & Kaushik, 2009). Biodegradation of these pollutants depends primarily on the moisture, pH, soil temperature and bioavailability of the organic matter contained in the soil (Johnsen et al., 2005). The biological breakdown of persistent organic pollutants by microorganisms is one of the most important and effective methods of removing PAHs from the environment (Azadi & Shojaei, 2020; Ghosal et al., 2016). The rate of biodegradation changes is influenced by the composition and activity of the microorganisms and the contamination's properties and age (Lors et al., 2012).

The aim of this study was to determine the accumulation of PAHs in soils influenced by differing species composition of forest stands. Pine, pine–oak and oak stands growing on the same soil conditions (Brunic Arenosols) were selected for the research. We also aimed to determine the activity of extracellular (β-D-cellobiosidase, β-glucosidase, xylanase, *N*-acetyl-β-D-glucosaminidase, phosphatase) and intracellular (dehydrogenases) enzymes and fractional composition of SOM in relation to the species composition of forest stands and accumulation of PAHs. The following hypotheses were tested during the study: (1) stand species composition influences PAH accumulation through the amount and quality of SOM and soil acidification; (2) deciduous species positively influence the enzymatic activity of the soil, increasing PAH degradation; and (3) PAH accumulation in forest soils is related to the fractional composition of the SOM.

2 | METHODS

2.1 | Study area and soil sampling

Our study was conducted in the Rybnik Forest District of southeastern Poland (50°05′55″ N; 18°32′42″ E) (Figure 1). The average annual temperature in this area is 8.4°C, and the average annual rainfall is 705 mm. The field sites were located in an area where the soils derived from glacial sand; they are dominated by Brunic Arenosols (IUSS Working Group WRB, 2015). The Rybnik Forest District is located in one of the areas in Europe most exposed to industrial emissions (EEA, 2020). The average annual concentrations of benzo(a) pyrene (5–12 ng m^{-3}) for the Rybnik Forest District for the years 2007–2016 exceeded the admissible standards according to Directive 2004/107/EC (Directive, 2004; Environmental Impact Assessment Report, 2016). The average annual PM10 concentration recorded in Rybnik Forest District, 53 μg m^{-3}, also exceeded the permissible standard (20 μg m^{-3}). Similarly, the average annual concentrations of PM2.5, 26 μg m^{-3}, exceeded the permissible standard (10 μg m^{-3}) (WHO, 2005).

The research used stands of similar age with the same tree canopy density. The age of the stands was 80 years. We focused on three forest stands: monospecific Scots pine (*Pinus sylvestris*), pedunculate oak (*Quercus robur*) and mixed pine and oak. Each study plot had an area of 2,000 m^2, and the mean distance between plots was 300 m. The stands grew on soils with a similar grain size; the average contents of sand, silt and clay were 81%, 16% and 3%, respectively. The samples were taken from the organic (Ofh), humus mineral (AEes) and mineral horizons (B) (Figure 2). In total, 27 soil samples were investigated (3 types of stands × 3 repetitions of each stand × 3 horizons). Composite soil samples, consisting of 3 subsamples from different

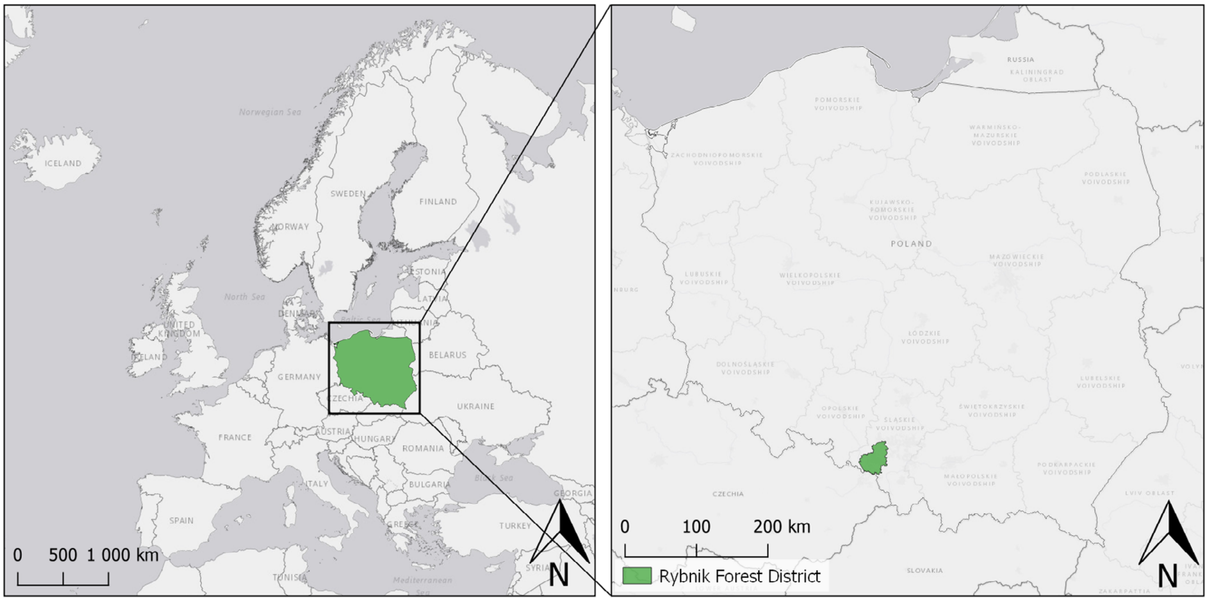

FIGURE 1 Location of the study area—Rybnik Forest District (Poland) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 2 Scheme of soil sampling in different forest stands [Color figure can be viewed at wileyonlinelibrary.com]

points, were collected from each horizon. Three repetitions were taken from each study plot. All soil samples for laboratory testing were collected in June 2020.

2.2 | Laboratory analysis

The soil samples were dried in air at room temperature to determine soil properties. Dry soil samples were sieved (2 mm). The soil properties were analysed using common pedological methods (Pansu & Gautheyrou, 2006; van Reeuwijk, 2002). The particle size distribution was determined using laser diffraction (Analysette 22, Fritsch, Idar-Oberstein, Germany). The soil pH was calculated in H_2O using the potentiometric method. The C and N concentrations were measured using an elemental analyser (LECO CNS TruMac Analyzer Leco, St. Joseph, MI). Ca, K, Mg and Na contents were determined by an ICP (ICP-OES Thermo iCAP 6500 DUO, ThermoFisher Scientific, Cambridge, UK). Available phosphorus was measured using the Bray–Kurtz method.

To analyse enzyme activity, microbial biomass and PAH content, naturally moist fresh samples were taken, sieved (2 mm) and stored at 4°C in the dark before analysis. The PAH contents were determined from 10 g of each soil sample, extracted using 70 mL of 2-propanol (Klamerus-Iwan et al., 2015; Łyszczarz et al., 2021). The samples were centrifuged (4500 rpm, 5 min), and the supernatants were collected. The supernatants were extracted to the solid phase (5 ml/min) using solid-phase extraction (CHROMABOND® CN/SiOH). The residue was dissolved in acetonitrile and analysed using high-pressure liquid chromatography (HPLC) with a DionexUltiMate 3000 HPLC system, equipped with a fluorescence detector and a DionexUltiMate 3000 Column Compartment C18 5 μm with a 4.6 × 100-mm HPLC column. The mobile phases were water (A) and acetonitrile (B) at a flow rate of 1 ml/min. Based on the standard PAH Calibration Mix (CRM 47940) at a concentration of 10 $\mu g\ ml^{-1}$, calibration solutions at different concentrations (0.1, 0.2, 0.5, 1 and 2 $\mu g\ ml^{-1}$) were prepared. Each prepared solution was placed into the chromatography column, and the chromatograms obtained were used to produce a calibration curve. The soil samples were then analysed in triplicate. After every ninth analysis, a control sample (a calibration solution with a concentration of 0.1 $\mu g\ ml^{-1}$) was injected. The concentrations of naphthalene [Nft], acenaphthene[Ace], fluorene [Flu], phenanthrene [Phe], anthracene [Ant], fluoranthene [Flt], pyrene [Pyr], benzo(a)anthracene

[BaA], chrysene [Chr], benzo(k)fluoranthene [BkF], benzo(b) fluoranthene [BbF], benzo(a)pyrene [BaP], dibenzo(ah)anthracene [DBahAnt] indeno(1,2,3-c, d)pyrene [IcdP] and benzo(g, h, i)perylene [BghiP] were determined.

The activity of the extracellular enzymes (β-D-cellobiosidase [CB], β-glucosidase [BG], xylanase [XYL], *N*-acetyl-β-D-glucosaminidase [NAG], phosphatase [PH]) was determined using fluorogenically labelled substrates (Pritsch et al., 2004; Sanaullah et al., 2016; Turner, 2010). The fluorescence was measured on a multidetector plate reader (SpectroMax), with an excitation wavelength of 355 nm and an emission wavelength of 460 nm. The dehydrogenase activity (DH) was determined using Lenhard's method according to the Casida procedure (Alef, 1995). The fumigation and extraction method was used to determine the microbial biomass of C, N and P (Jenkinson & Powlson, 1976; Vance et al., 1987).

The physical separation of SOM fractions was performed using the method described by Sohi et al. (2001). A sample of soil (15 g) was placed in a 200-ml centrifuge tube, and 90 ml of NaI (1.7 g cm^{-3}) was added. Each tube was gently shaken for 1 min and centrifuged for 30 min. The fLF was removed using a pipette and collected on a glass-fibre filter. The soil remaining at the bottom of the centrifuge tubes was mixed with another 90 ml of NaI and subjected to sonication (60 W for 200 s) to destroy aggregates. After centrifugation, the matter released from aggregates, the oLF, was collected on a glass-fibre filter. The remaining fraction was assumed to consist of the MAF of the SOM. After drying (40°C), the subsamples of the different fractions were weighed and analysed for C_{fLF}, C_{oLF} and C_{MAF}, respectively, using a LECO CNS TruMac Analyzer (Leco, St. Joseph, MI, USA).

2.3 | Statistical analysis

The Pearson correlation coefficients for the soil characteristics were calculated. Principal component analysis (PCA) was used to evaluate the relationships between the soil properties and PAH content. The Shapiro–Wilk test was used to assess normality, and Levene's test was used to check the homogeneity of variances. The Kruskal–Wallis test and two-way ANOVA were utilised to assess the differences between the average values of the soil properties and the PAH content. The multiple regression method was used to develop models describing the relationship between the PAH content and soil properties. All statistical analyses were performed using the statistical programs R (R Core Team, 2020) and R Studio (RStudio Team, 2020).

3 | RESULTS

3.1 | Physicochemical properties

The soil pH ranged from 3.61 to 3.98 and increased with soil depth (Table 1). The type of stand and soil depth has an effect on soil pH. The soils from pine stands were characterised by the lowest pH. The soils of pine–oak and oak stands were characterised by a similar pH. The concentrations of C, N and P were significantly higher in the organic horizons of the tested soils (Table 1). The conducted analyses confirmed the highest importance of the soil depth in comparison to the forest stand for the concentration of C and N in the studied soils ($p \le 0.001$) (Table 1). In the mineral horizons, there was a clear decrease in C and N concentration. The highest concentration of organic carbon, 291.0 g kg^{-1}, was recorded in the organic horizon of the pine stand soils. The lowest C concentration, 201.8 g kg^{-1}, was found in the soil of oak stands. In the AEes horizon of the pine–oak and oak stands, a significantly higher accumulation of C was noted compared to the pine stand soil. The soils of all examined stands were characterised by a similar C concentration in the B-horizon. The highest nitrogen concentration was recorded in the organic horizons of the pine stand soils (12.4 g kg^{-1}). A lower nitrogen concentration was observed in the pine–oak stand soils (10.4 g kg^{-1}in the Ofh horizon), and the lowest nitrogen concentration was recorded in the organic horizons of the oak stand soils (10.0 g kg^{-1}). The type of stand and soil depth have an interactive effect on N concentration ($p \le 0.001$). The C/N ratio was highest in the pine stand soils and the lowest in the oak stand soils. The conducted analyses confirmed the importance of the stand type in shaping C/N ratio ($p \le 0.01$) (Table 1). The sum of alkaline cations reached significantly statistically higher values in the organic-horizons of the tested soils (Table 1). Soils of pine–oak and oak stands were characterised by a higher content of basic cations.

3.2 | Microbial enzymatic activity and biomass

In all stands, the organic soil horizons were characterised by significantly higher enzymatic activity (Table 2). The activity of enzymes decreased significantly with the depth of the soil profile. Enzyme activities (BG, NAG, XYL, PH) were significantly influenced by the soil depth ($p \le 0.001$) (Table 2). In the case of DH and NAG activity, the highest values were recorded in the organic horizons of the oak stand soils. In the mineral humus horizons, the highest activities of DH and PH were recorded in the oak stand soils (Table 2). The highest MBC was noted in the organic horizon of the oak stands (2296.70 μg kg^{-1}) (Table 2). Soils of pine and pine–oak stands had similar MBC values in the organic horizons (2086.33 and 2097.23 μg kg^{-1}, respectively). The highest MBN was recorded in organic horizons of oak stands (461.25 μg kg^{-1}), decreasing in the pine–oak stand soils (421.62 μg kg^{-1}), and the lowest in the pine stand soils (266.57 μg kg^{-1}) (Table 2). A significant effect ($p \le 0.01$) of type of stand was apparent on MBN (Table 2).

3.3 | Soil organic matter fraction parameters

The significantly highest average C and N concentrations in the fLF were found in the organic horizons of the soils studied (Table 3). The highest C and N concentrations in the fLFs were observed in the organic horizon of the pine stand soils (266.30 and 6.65 g kg^{-1},

TABLE 1 The basic properties of soils under influence of different tree stands

Stand type	Horizon	pH	C	N	C/N	P	Ca	K	Mg	Na
Pine	Ofh	$3.61 \pm 0.06^{a,A}$	$29.10 \pm 5.11^{b,D}$	$1.24 \pm 0.21^{b,D}$	$23.56 \pm 1.44^{a,A}$	$772.34 \pm 51.61^{b,C}$	$3.19 \pm 2.36^{b,B}$	$0.77 \pm 0.34^{b,C}$	$1.28 \pm 0.53^{b,B}$	$0.11 \pm 0.03^{b,BC}$
	AEes	$3.61 \pm 0.26^{a,A}$	$1.91 \pm 0.04^{a,A}$	$0.07 \pm 0.01^{a,A}$	$29.53 \pm 3.56^{b,B}$	$164.33 \pm 55.63^{a,A}$	$0.30 \pm 0.16^{a,A}$	$0.03 \pm 0.01^{a,A}$	$0.16 \pm 0.01^{a,A}$	$0.02 \pm 0.01^{a,A}$
	B	$3.84 \pm 0.14^{a,BC}$	$1.41 \pm 0.33^{a,A}$	$0.05 \pm 0.02^{a,A}$	$31.13 \pm 5.07^{b,B}$	$262.97 \pm 179.47^{a,AB}$	$0.57 \pm 0.63^{ab,A}$	$0.14 \pm 0.19^{a,AB}$	$0.52 \pm 0.62^{ab,A}$	$0.04 \pm 0.05^{a,A}$
Pine-Oak	Ofh	$3.77 \pm 0.08^{a,ABC}$	$23.23 \pm 2.14^{c,C}$	$1.04 \pm 0.13^{c,CD}$	$22.33 \pm 1.15^{a,A}$	$648.93 \pm 51.69^{b,C}$	$4.93 \pm 1.00^{b,BC}$	$1.13 \pm 0.13^{b,D}$	$1.80 \pm 0.05^{b,B}$	$0.12 \pm 0.02^{b,C}$
	AEes	$3.80 \pm 0.10^{a,ABC}$	$11.14 \pm 0.97^{b,B}$	$0.50 \pm 0.04^{b,B}$	$22.57 \pm 2.37^{a,A}$	$347.60 \pm 54.74^{b,AB}$	$0.62 \pm 0.14^{a,A}$	$0.27 \pm 0.11^{a,AB}$	$0.51 \pm 0.12^{a,A}$	$0.07 \pm 0.02^{a,AB}$
	B	$3.95 \pm 0.03^{b,BC}$	$1.48 \pm 0.23^{a,A}$	$0.06 \pm 0.01^{a,A}$	$23.73 \pm 2.50^{a,A}$	$265.57 \pm 157.17^{b,AB}$	$0.77 \pm 0.47^{a,A}$	$0.13 \pm 0.07^{a,AB}$	$0.37 \pm 0.34^{a,A}$	$0.05 \pm 0.04^{a,A}$
Oak	Ofh	$3.97 \pm 0.20^{a,C}$	$20.18 \pm 2.90^{c,C}$	$1.00 \pm 0.17^{c,C}$	$20.27 \pm 0.81^{a,A}$	$683.20 \pm 61.60^{b,C}$	$5.67 \pm 1.22^{b,C}$	$1.21 \pm 0.12^{b,D}$	$1.89 \pm 0.03^{b,B}$	$0.12 \pm 0.03^{b,C}$
	AEes	$3.73 \pm 0.05^{a,AB}$	$10.84 \pm 0.99^{b,B}$	$0.47 \pm 0.06^{b,B}$	$23.30 \pm 2.95^{a,A}$	$380.30 \pm 67.72^{a,B}$	$0.90 \pm 0.36^{a,A}$	$0.39 \pm 0.12^{a,AB}$	$0.54 \pm 0.12^{a,A}$	$0.05 \pm 0.01^{a,A}$
	B	$3.98 \pm 0.05^{a,C}$	$1.41 \pm 0.33^{a,A}$	$0.05 \pm 0.02^{a,A}$	$31.13 \pm 5.07^{b,B}$	$262.97 \pm 179.47^{a,AB}$	$0.87 \pm 0.36^{a,A}$	$0.25 \pm 0.12^{a,AB}$	$0.65 \pm 0.52^{a,A}$	$0.04 \pm 0.05^{a,A}$
	S	**	ns	ns	**	ns	**	***	*	ns
	H	**	***	***	**	***	***	***	***	***
	SxH	ns	***	***	ns	ns	ns	ns	ns	ns

Note: Mean ± SD; C, N concentration (g kg^{-1}); P concentration (mg kg^{-1}); Ca, K, Mg and Na (cmol[+] kg^{-1}); small letters in the upper index of the mean values mean significant differences between soil horizons of the current tree stands (a, b, c) and between soil horizons of other stand type (A, B, C, D), result of Kruskal–Wallis test

Abbreviations: H, horizon effect; ns, not significant; S, type of stand effect; SxH, combined stand and horizon effect.

$^{*}p \le 0.05$, $^{**}p \le 0.01$, $^{***}p \le 0.001$

TABLE 2 The biochemical properties of soils under influence of different tree stands

Stand type	Horizon	DH	CB	BG	NAG	XYL	PH	MBC	MBN	MBC/N
Pine	Ofh	$0.30 \pm 0.16^{a,A}$	$1.13 \pm 0.85^{ab,A}$	$6.43 \pm 4.29^{b,C}$	$7.24 \pm 4.51^{b,ABC}$	$5.34 \pm 2.14^{ab,CD}$	$33.92 \pm 16.68^{b,CD}$	$2086.33 \pm 486.03^{b,C}$	$266.57 \pm 111.60^{b,B}$	$8.24 \pm 1.33^{b,A}$
	AEes	$1.38 \pm 0.77^{b,ABC}$	$1.60 \pm 0.14^{b,AB}$	$2.32 \pm 1.69^{a,ABC}$	$5.25 \pm 2.90^{ab,AB}$	$6.91 \pm 2.96^{b,CD}$	$9.39 \pm 5.44^{a,AB}$	$76.17 \pm 57.09^{a,A}$	$21.03 \pm 7.81^{a,A}$	$3.31 \pm 2.42^{a,A}$
	B	$1.03 \pm 0.98^{ab,ABC}$	$0.47 \pm 0.81^{a,A}$	$3.00 \pm 1.75^{a,ABC}$	$3.43 \pm 1.65^{a,AB}$	$1.85 \pm 1.19^{a,AB}$	$30.32 \pm 9.89^{ab,CD}$	$68.00 \pm 47.75^{a,A}$	$62.70 \pm 79.01^{a,A}$	$6.58 \pm 8.90^{ab,AB}$
Pine-Oak	Ofh	$1.19 \pm 0.37^{b,ABC}$	$1.63 \pm 0.86^{b,AB}$	$5.84 \pm 2.09^{b,BC}$	$8.93 \pm 2.57^{b,BC}$	$7.80 \pm 2.18^{b,A}$	$42.30 \pm 15.18^{c,D}$	$2097.23 \pm 584.86^{b,C}$	$421.63 \pm 76.75^{b,C}$	$4.94 \pm 0.97^{a,A}$
	AEes	$0.95 \pm 0.19^{ab,ABC}$	$0.15 \pm 0.19^{a,A}$	$0.38 \pm 0.19^{a,A}$	$1.18 \pm 0.38^{a,A}$	$0.62 \pm 0.16^{a,A}$	$3.32 \pm 1.19^{a,A}$	$489.90 \pm 76.40^{a,AB}$	$144.93 \pm 47.91^{a,AB}$	$3.73 \pm 1.64^{a,A}$
	B	$0.47 \pm 0.15^{a,AB}$	$0.32 \pm 0.55^{a,A}$	$1.12 \pm 0.67^{a,A}$	$4.44 \pm 2.19^{a,AB}$	$1.07 \pm 1.58^{a,A}$	$24.27 \pm 7.79^{b,BCD}$	$181.70 \pm 168.56^{a,A}$	$38.23 \pm 31.78^{a,A}$	$9.89 \pm 11.60^{b,AB}$
Oak	Ofh	$1.90 \pm 0.88^{ab,BC}$	$1.03 \pm 0.21^{b,A}$	$5.65 \pm 0.85^{b,BC}$	$12.86 \pm 5.91^{b,C}$	$4.39 \pm 0.74^{b,BC}$	$44.50 \pm 10.30^{c,D}$	$2296.70 \pm 652.78^{b,C}$	$461.23 \pm 82.77^{b,C}$	$4.91 \pm 0.70^{a,A}$
	AEes	$2.05 \pm 1.77^{b,C}$	$0.04 \pm 0.06^{a,A}$	$0.87 \pm 0.19^{a,A}$	$1.91 \pm 0.57^{a,A}$	$1.56 \pm 0.68^{a,AB}$	$18.48 \pm 16.53^{a,ABC}$	$897.30 \pm 187.08^{a,B}$	$154.90 \pm 66.72^{a,AB}$	$6.49 \pm 2.80^{a,AB}$
	B	$1.03 \pm 0.98^{a,ABC}$	$2.85 \pm 2.39^{c,B}$	$1.97 \pm 0.57^{a,AB}$	$1.85 \pm 1.67^{a,A}$	$1.49 \pm 1.52^{a,AB}$	$27.53 \pm 8.15^{b,BCD}$	$241.10 \pm 187.43^{a,A}$	$62.70 \pm 79.01^{a,A}$	$24.55 \pm 34.02^{b,B}$
	S	ns	ns	*	ns	*	ns	ns	**	ns
	H	ns	ns	***	***	***	***	***	***	ns
	SxH	ns	**	ns	*	**	ns	ns	ns	ns

Note: Mean ± SD; small letters in the upper index of the mean values mean significant differences between soil horizons of the current tree stands (a, b, c) and between soil-horizons of other stand type (A, B, C, D), result of Kruskal–Wallis test

Abbreviations: BG, β-glucosidase; CB, β-D-cellobiosidase; DH, dehydrogenase; H, horizon effect; MBC, microbial biomass carbon; MBN, microbial biomass nitrogen (µg kg^{-1}); NAG, *N*-acetyl-β-D-glucosaminidase; ns, not significant; PH, phosphatase (nmol MUB $g^{-1} \cdot C \cdot hr^{-1}$); S, type of stand effect; SxH, interactive stand and horizon effect; XYL, xylanase

$^{*}p \le 0.05$, $^{**}p \le 0.01$, $^{***}p \le 0.001$

TABLE 3 The soil organic matter fractions content in soils under influence of different tree stands

Stand type	Horizon	C_{fLF}	N_{fLF}	C/N_{fLF}	C_{oLF}	N_{oLF}	C/N_{oLF}	C_{MAF}	N_{MAF}	C/N_{MAF}	$\sum PAH$
	Ofh	$198.43 \pm 105.43^{b,C}$	$6.65 \pm 2.51^{b,D}$	$28.83 \pm 4.80^{b,B}$	$8.87 \pm 6.96^{b,AB}$	$0.36 \pm 0.30^{a,AB}$	$25.08 \pm 1.64^{a,AB}$	$11.54 \pm 2.08^{b,B}$	$0.50 \pm 0.11^{b,B}$	$23.40 \pm 2.16^{b,C}$	$3805.00 \pm 1193.27^{b,C}$
	AEes	$0.00 \pm 0.00^{a,A}$	$0.00 \pm 0.00^{a,A}$	$0.00 \pm 0.00^{a,A}$	$4.64 \pm 1.42^{a,A}$	$0.18 \pm 0.04^{a,A}$	$25.77 \pm 2.80^{a,ABC}$	$4.74 \pm 2.68^{a,A}$	$0.29 \pm 0.14^{a,A}$	$15.43 \pm 2.37^{a,AB}$	$650.67 \pm 496.48^{a,A}$
	B	$1.26 \pm 0.53^{a,A}$	$0.04 \pm 0.02^{a,A}$	$28.73 \pm 3.07^{a,B}$	$3.54 \pm 1.58^{ab,A}$	$0.13 \pm 0.07^{a,A}$	$29.07 \pm 3.10^{a,BC}$	$5.89 \pm 2.33^{a,A}$	$0.36 \pm 0.09^{ab,AB}$	$16.07 \pm 2.45^{a,AB}$	$90.67 \pm 35.57^{a,A}$
Pine-Oak	Ofh	$134.19 \pm 11.09^{c,BC}$	$5.10 \pm 0.31^{c,CD}$	$26.27 \pm 0.59^{b,B}$	$4.20 \pm 0.32^{a,A}$	$0.15 \pm 0.02^{a,A}$	$27.77 \pm 1.62^{ab,ABC}$	$7.58 \pm 0.49^{b,A}$	$0.44 \pm 0.04^{a,AB}$	$17.20 \pm 1.25^{a,B}$	$3087.00 \pm 1132.70^{b,BC}$
	AEes	$74.36 \pm 11.87^{b,AB}$	$2.89 \pm 0.36^{b,BC}$	$25.67 \pm 1.19^{b,B}$	$11.16 \pm 1.11^{b,B}$	$0.36 \pm 0.02^{b,AB}$	$30.67 \pm 1.70^{b,C}$	$12.42 \pm 0.67^{c,B}$	$0.74 \pm 0.05^{b,C}$	$16.90 \pm 2.16^{a,B}$	$713.67 \pm 398.57^{a,A}$
	B	$0.43 \pm 0.41^{a,A}$	$0.01 \pm 0.02^{a,A}$	$6.77 \pm 11.72^{a,A}$	$3.76 \pm 0.97^{a,A}$	$0.15 \pm 0.05^{a,A}$	$25.27 \pm 2.37^{a,AB}$	$5.49 \pm 0.91^{a,A}$	$0.37 \pm 0.10^{a,AB}$	$15.30 \pm 1.51^{a,AB}$	$91.67 \pm 36.50^{a,A}$
Oak	Ofh	$105.22 \pm 20.38^{c,B}$	$5.05 \pm 1.02^{c,CD}$	$20.90 \pm 0.61^{a,B}$	$3.74 \pm 0.74^{a,A}$	$0.16 \pm 0.03^{a,A}$	$23.27 \pm 5.69^{a,A}$	$6.77 \pm 1.26^{a,A}$	$0.47 \pm 0.03^{a,AB}$	$14.47 \pm 3.72^{a,AB}$	$2936.00 \pm 664.27^{b,BC}$
	AEes	$44.98 \pm 9.64^{ab,AB}$	$1.98 \pm 0.56^{ab,AB}$	$22.97 \pm 1.46^{a,B}$	$11.87 \pm 2.28^{b,B}$	$0.48 \pm 0.13^{b,B}$	$25.10 \pm 2.43^{a,AB}$	$14.01 \pm 1.82^{b,B}$	$1.16 \pm 0.18^{b,D}$	$12.20 \pm 1.37^{a,A}$	$2344.67 \pm 1842.73^{ab,B}$
	B	$1.04 \pm 0.30^{a,A}$	$0.05 \pm 0.01^{a,A}$	$21.10 \pm 0.79^{a,B}$	$3.54 \pm 1.58^{a,A}$	$0.13 \pm 0.07^{a,A}$	$29.07 \pm 3.10^{A,BC}$	$5.89 \pm 2.33^{a,A}$	$0.36 \pm 0.09^{a,AB}$	$16.07 \pm 2.45^{a,AB}$	$108.67 \pm 93.15^{a,A}$
	S	ns	ns	ns	ns	ns	ns	ns	***	**	ns
	H	***	***	***	***	***	ns	***	***	**	***
	SxH	***	***	***	***	***	ns	***	***	**	ns

Note: Mean ± SD; $\sum PAH$ ($\mu g\ kg^{-1}$); small letters in the upper index of the mean values mean significant differences between soil horizons of the current tree stands (a, b, c) and between soil horizons of other stand type (A, B, C, D), result of Kruskal–Wallis test

Abbreviations: C_{fLF}, carbon of free light fraction; C_{MAF}, carbon of mineral associated fraction; C_{oLF}, carbon of occluded light fraction; H, horizon effect; N_{fLF}, nitrogen of free light fraction; N_{MAF}, nitrogen of mineral associated fraction ($g\ kg^{-1}$); ns, not significant; N_{oLF}, nitrogen of occluded light fraction; S, type of stand effect; SxH, interactive stand and horizon effect

$^{**}p \le 0.01$; $^{***}p \le 0.001$

respectively). The surface horizons of the pine–oak stands were characterised by lower values of the C and N concentrations in the fLFs (134.19 and 5.10 g kg^{-1}, respectively), and the surface horizons of the oak stands by the lowest values (105.22 and 5.05 g kg^{-1}, respectively). Significantly higher mean C and N concentrations in the oLF were recorded in the humus mineral horizons of the pine–oak stand (11.16 and 0.36 g kg^{-1}, respectively) and oak stand soils (11.87 and 0.48 g kg^{-1}, respectively) (Table 3). In the case of the C and N of the MAF, the highest values were determined in the humus horizon of the pine–oak stand soils (12.42 and 0.74 g kg^{-1}, respectively) and oak soils (14.04 and 1.16 g kg^{-1}, respectively) (Table 3).The conducted analyses confirmed the importance of soil depth in shaping the C and N of the SOM fractions ($p \leq 0.001$). The type of stand influenced the concentration of MAF N and C/N ($p \leq 0.001$ and $p \leq 0.01$, respectively) (Table 3).

3.4 | Polycyclic aromatic hydrocarbon content

The highest PAH content was recorded in the organic soil horizons of all stand variants (Table 3 and Figure 3). The PAH content decreased with soil depth, regardless of the stand variant. A statistically significant effect of soil depth on PAH accumulation relative to the number of rings in the PAH was observed (Table 4). The largest concentration of PAHs was recorded in the organic horizons of the pine stand soils (3805.00 μg kg^{-1}). In the Ofh horizon of the pine–oak stand soils, the average PAH content was 3087.09 μg kg^{-1} and in the oak stand soils, it was 2936.20 μg kg^{-1} (Table 3 and Figure 3). In the surface horizons of the pine and pine–oak stand soils, 3- and 4-ring PAHs were dominant (Figure 3). In the oak stand soils, 4-ring PAHs dominated, followed by 3- and 5-ring PAHs. The highest mean content of 3-ring PAHs occurred in the soil horizons of the pine and oak stands (Figure 4). In turn, the soil horizons of the oak stand showed the highest values for 4-ring PAHs. For 5-ring PAHs, the highest values were reached in the oak soil horizons, and for 6-ring PAHs, the highest values were noted in the pine soil horizons. The stand type did not have a statistically significant impact on the PAH content in relation to the number of rings in the PAH (Table 4).

3.5 | Correlations

The activity of enzymes strongly correlated with the C and N concentrations: in the case of BG, XYL, NAG and PH, it was a positive relationship. For most of the enzymes studied, statistically significant positive correlations with the PAH content were noted, apart from

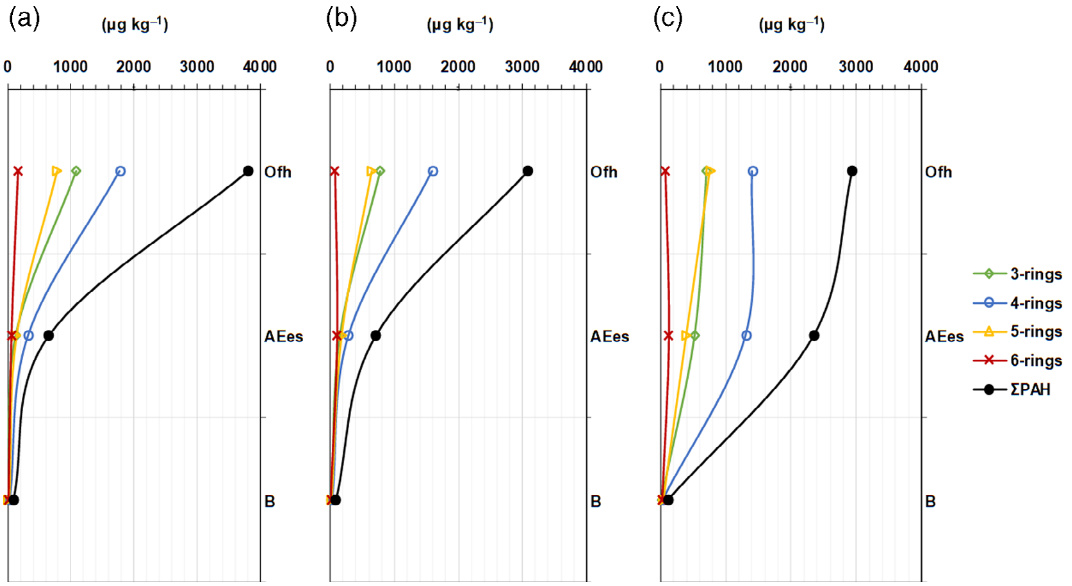

FIGURE 3 Average PAHs content in relation to the number of rings in different soil horizons of the pine (a), pine–oak (b) and oak stands (c) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Two-way ANOVA results for PAHs content in relation to the number of rings

Parameter	3-rings PAH	4-rings PAH	5-rings PAH	6-rings PAH
S	ns	ns	ns	ns
H	***	***	***	**
SxH	ns	ns	ns	ns

Abbreviations: H, horizon effect; ns, not significant; S, type of stand effect; SxH, interactive stand and horizon effect

**$p \leq 0.01$; ***$p \leq 0.001$

DH and CB activity (Table 5). Furthermore, a positive relationship between the concentration of PAHs and C_{fLF}, N_{fLF} and C_{MAF} was found in the soils studied (Table 5). A significant positive correlation between the PAH content and the amount of organic carbon was present, particularly in the pine stand soils, where PAHs increased exponentially with organic carbon (Figure 5). Multiple regression analysis confirmed relationships between the PAH content and the C of the light and heavy fractions of the SOM. Multiple regression models explained 84% of the variance in PAH content (Table 6). Factors 1 and 2, distinguished in the PCA analysis, explained a total of 67.39% of the variance of the properties of the tested soils (Figure 6). The PCA analysis confirmed the negative correlation between the PAH content and the pH of the tested soils. The PAH content was positively correlated with the C_{fLF} and N_{fLF} (Figure 6). The PCA analysis confirmed a higher PAH content in the organic horizons of the studied soils, where a lower pH and a higher C concentration were observed. Mineral horizons were associated with the higher concentrations of C and N of the oLF and MAF (Figure 6).

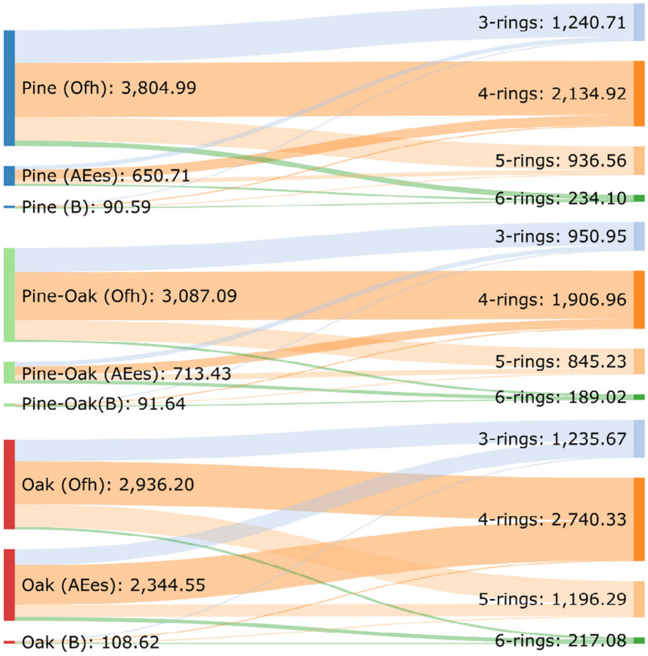

FIGURE 4 Sankey diagram presenting the average PAHs content in terms of number of rings (μg kg^{-1}) in each soil horizon according to stand type [Color figure can be viewed at wileyonlinelibrary.com]

4 | DISCUSSION

The results obtained in this study confirm that the stand species composition significantly affects the amount and quality of the SOM supplied to the soil and, consequently, the forest soil PAH accumulation. The conducted analyses confirmed the effect of soil depth on PAH accumulation, which decreased with depth due to fewer humic substances being present. The highest average accumulation of PAHs in organic horizons was recorded in the soils of the pine stands, lower in the soils of the mixed pine–oak stands and the lowest in the oak stand soils (Figures 3 and 4). In all investigated soils, the amount of PAHs accumulated in the organic horizons indicated the third, moderate degree of soil contamination (1000–5000 μg kg^{-1}), according to the classification proposed by Maliszewska-Kordybach (1996). At the

TABLE 5 Correlations between biochemical properties, soil organic matter fraction content and basic properties, PAHs content in relation to the number of rings in all horizons of the tested soils

	pH	C	N	C/N	P	3-rings	4-rings	5-rings	6-rings	PAHs
DH	0.342	−0.173	−0.123	−0.325	−0.002	−0.148	−0.018	−0.058	0.009	−0.069
CB	0.088	0.051	0.038	0.407*	−0.066	0.115	0.084	0.099	−0.083	0.098
BG	−0.165	0.711***	0.707***	−0.154	0.587**	0.649**	0.640**	0.625**	0.204	0.681**
NAG	0.054	0.554**	0.570***	−0.279	0.508**	0.494*	0.511*	0.446*	0.110	0.522*
XYL	−0.380*	0.509*	0.501*	−0.037	0.413*	0.506*	0.528*	0.394*	0.080	0.521*
PH	0.216	0.479*	0.482*	−0.087	0.410*	0.539**	0.520*	0.469*	0.046	0.543**
MBC	−0.250	0.919***	0.942***	−0.571**	0.887***	0.690***	0.778***	0.855***	0.456*	0.828***
MBN	−0.040	0.760***	0.805***	−0.563**	0.679***	0.566**	0.717***	0.786***	0.355	0.738***
C_{fLF}	−0.338	0.910***	0.891***	−0.443*	0.769***	0.819***	0.795***	0.643***	0.386*	0.825***
N_{fLF}	−0.311	0.955***	0.951***	−0.540*	0.850***	0.822***	0.817***	0.704***	0.415*	0.853***
C_{oLF}	−0.401*	0.204	0.176	−0.239	0.239	−0.041	0.091	0.064	0.511*	0.071
N_{oLF}	−0.381*	0.230	0.202	−0.252	0.291	0.012	0.164	0.100	0.545**	0.135
C_{MAF}	−0.275	0.465*	0.441*	−0.424*	0.344	0.350	0.407*	0.318	0.549**	0.414*
N_{MAF}	−0.078	0.127	0.118	−0.335	0.036	0.082	0.202	0.071	0.322	0.159

Note: n-rings PAHs and total average of PAHs

Abbreviations: BG, β-glucosidase; CB, β-D-cellobiosidase; C_{fLF}, carbon of free light fraction; C_{MAF}, carbon of mineral associated fraction; C_{oLF}, carbon of occluded light fraction; DH, dehydrogenase; MBC, microbial biomass carbon; MBN, microbial biomass nitrogen; NAG, *N*-acetyl-β-D-glucosaminidase; N_{fLF}, nitrogen of free light fraction; N_{MAF}, nitrogen of mineral associated fraction; N_{oLF}, nitrogen of occluded light fraction; PH, phosphatase; XYL, xylanase

$^{*}p \le 0.05$; $^{**}p \le 0.01$; $^{***}p \le 0.001$

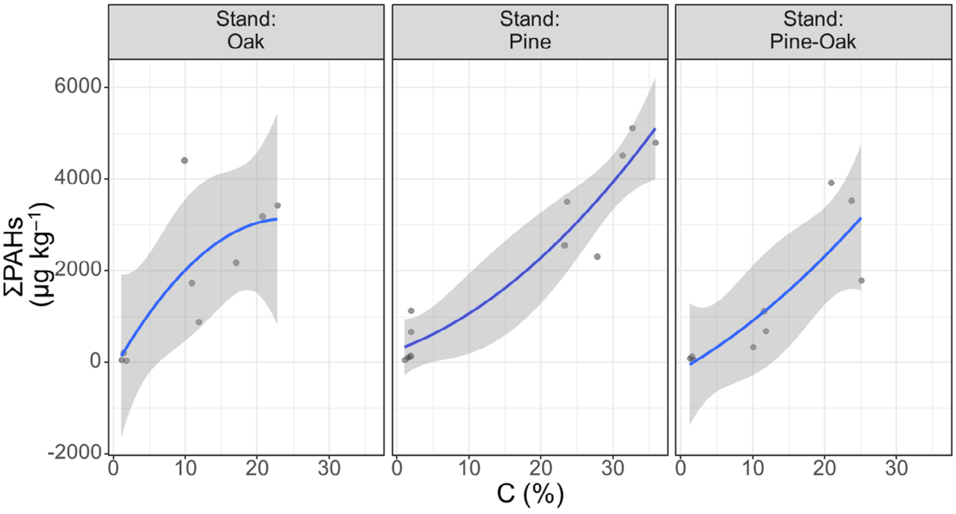

FIGURE 5 Dependence scatter plots of the content of C and the total content of PAHs in soils of the tested stands (regression line indicates a 95% confidence) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 6 Multiple regression analysis for content of PAHs in relation to the chemical properties of soil

R^2	Equation parameter	β	p
0.84	C_{fLF}	15.007	***
	C_{MAF}	70.423	*

Note: R^2 describes the percentage of explained variance, β is the regression coefficient for given equation parameter and p is the significance level for the equation parameter
$^{*}p \leq 0.05$; $^{***}p \leq 0.001$

same time, the soils with the highest PAH accumulations were characterised by acidification and less decomposed organic matter. The quality and quantity of SOM is an effect of the stand species composition, which has already been described by other authors (Błońska et al., 2021; Gruba et al., 2015; Jandl et al., 2007; Schulp et al., 2008; Vesterdal et al., 2008; Zhang et al., 2008). The deciduous species in the stand improve the biogeochemical cycles of the organic matter by providing nutrients (Ammer, 2019; Augusto et al., 2015). Coniferous species, particularly pine, provide litterfall to the soil, which acidifies the top soil horizons. Our statistical analyses confirm the importance of the stand type in shaping the pH of the studied soils (Table 1). As a result of the coniferous species' influence, the microbiological decomposition processes of the fallen organic matter on the soil surface are generally slower (Błońska et al., 2016; Eisalou et al., 2013; Magh et al., 2018; Schulp et al., 2008). The trees provide the soil with carbon substrates and the nutrients used by microorganisms in the decomposition processes through the litterfall and root systems (Błońska, 2015; Błońska et al., 2021). The beneficial effect of deciduous species on the topsoil was reflected in higher pH values and increased alkaline cation content. It was also observed that the proportion of deciduous species in the stand had a significant positive effect on the biochemical properties of soils expressed by enzymatic activity and microbial biomass, as reflected in organic matter decomposition processes and PAH biodegradation potential (Table 2). An increased share of deciduous tree species in the stand leads to the relocation of carbon to the ground biomass, resulting in a beneficial increase in nutrient utilisation efficiency compared to coniferous monocultures (Błońska et al., 2017; Epron et al., 2013). An increased PAH accumulation capacity in the organic horizons of coniferous stand soils is also due to the effect of the assimilation of pollutants from the atmosphere due to the presence of photosynthetic apparatus throughout the year (Hill et al., 2002; Lasota & Błońska, 2018; Peng et al., 2012). Increased PAH accumulation in coniferous forest soils can be explained by the presence of wax and lipids on the needle surface, which absorb and accumulate lipophilic PAHs present in the contaminated atmosphere (Li et al., 2017). Our study noted a strong positive relationship between enzymatic activity with organic carbon and PAH content in soils (Table 5). The lack of limitation of enzyme activity in soil samples with high PAH content can be explained by the masking effect of SOM. The strong affinity of SOM for PAHs and the simultaneous high enzymatic activity in samples with a high concentration of organic carbon explains the observed relationships. Similar results have been obtained previously for the case of the relationship between enzyme activity and heavy metal content with simultaneous high accumulation of organic carbon (Lasota et al., 2020).

Our research confirmed the validity of the third hypothesis regarding the importance of the SOM fractions in the accumulation of PAHs in forest soils. In our study, the PAH content was closely related to the amount of organic carbon and nitrogen contained in the SOM fLF (Tables 5 and 6). According to Cachada et al. (2018), the amount and quality of the SOM and its fractions control the accumulation of PAHs in soils. The soils of pine stands are characterised by a higher proportion of SOM light fractions due to the slowdown of decomposition processes. Additionally, a high C/N ratio of the light fraction of the soils of pine stands confirms the weaker decomposition of organic residues. In the case of the soils of oak stands, a significantly lower C/N ratio of the light fractions of SOM was recorded. The light fraction present in the soil is formed by partially decomposed plant residues and animal remains in the intermediate stage of decomposition between the stabilised carbon (Błońska, 2015). According to Li et al. (2014), the organic fraction has stronger sorption properties than the mineral fraction. The biodegradation efficiency of PAHs by microorganisms is related to the

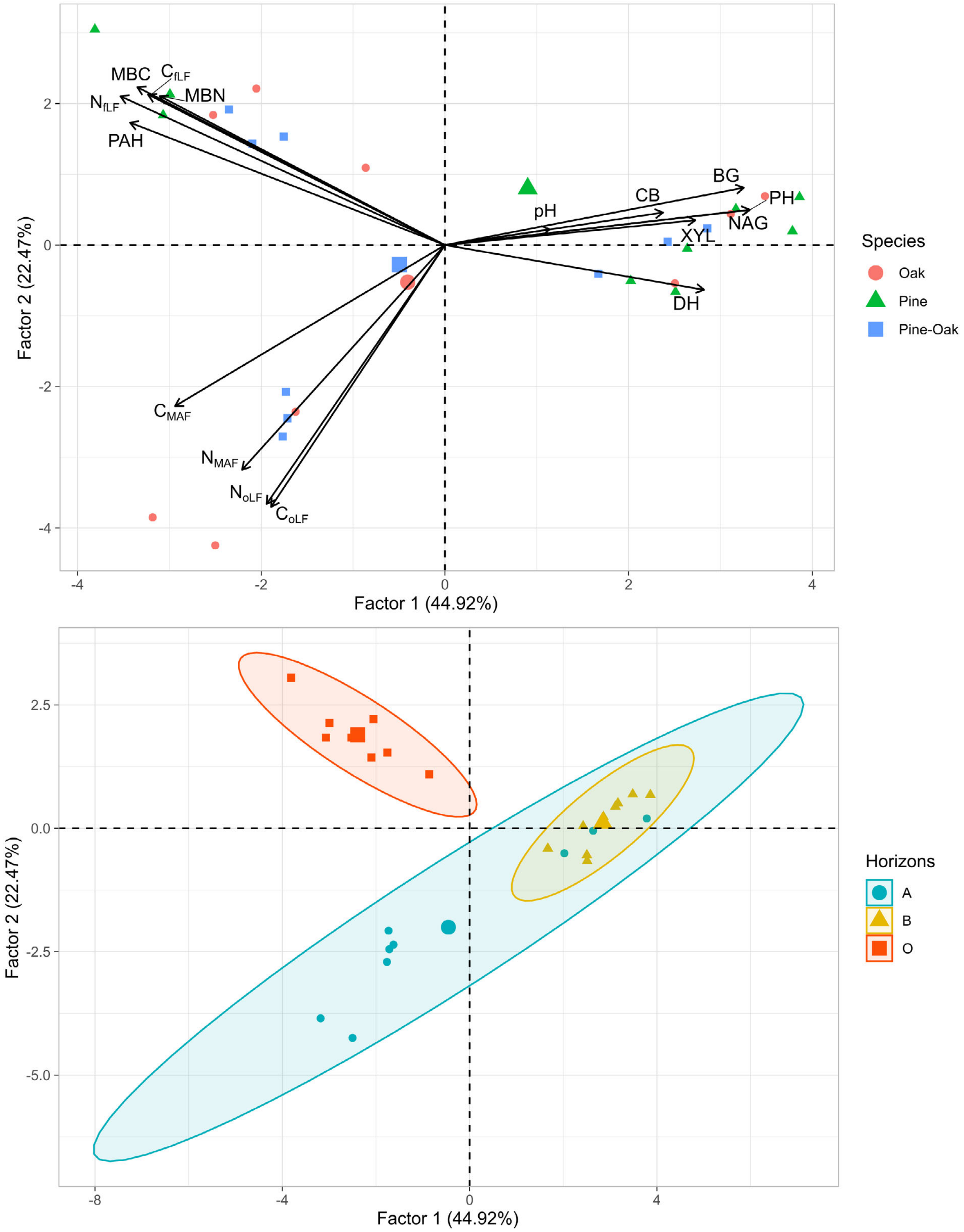

FIGURE 6 Projection of the variables on the factor plane [Color figure can be viewed at wileyonlinelibrary.com]

bioavailability of compounds dissolved in the soil solution (Ghosal et al., 2016; MacKay & Gschwend, 2001). According to Jastrow et al. (2007), the biological activity of soils is regulated by the structures of the organic matter present and is determined by the soil aggregate size. In our study, positive relationships were observed between the C and N contents of the organic matter fLF, the PAH content and most of the studied soil enzymes (Tables 5 and 6). Strong sorption of PAH compounds within organic matter structures reduces bioavailability, as well as the desorption and diffusion of pollutants by microorganisms (Ukalska-Jaruga et al., 2015, 2018).

According to Oleszczuk (2007), strong sorption of PAH compounds occurs under low pH conditions, which are characteristic for soils from coniferous stands in our study. The low soil pH may result from the presence of a significant amount of humic and fulvic acids (Maliszewska-Kordybach et al., 2010), which significantly reduce the bioavailability of organic matter and PAHs in soil solutions (Haynes, 2005; Lasota & Błońska, 2018). Strongly absorbed, soil-accumulated PAH compounds inaccessible to microorganisms are subject to an ageing process (Zhang et al., 2011). Ni et al. (2008) claim that an effective method of bioremediation of soils contaminated with PAHs is to reduce the fLF content of the organic matter. However, Wilson and Jones (1993) suggest that the bioremediation method of reducing the organic matter fLF is only effective for low molecular weight PAHs. The presence of oak in a stand could be an effective factor in the process of natural soil bioremediation and elimination of toxic soil contamination levels, particularly for stands exposed to intensive industrial emissions. However, more research is required on the impact of the other deciduous species forming the stands. Their role in reducing PAHs in the soil through beneficial effects on the amount and quality of SOM and the amount of nutrients they contribute is unknown.

5 | CONCLUSIONS

Our research confirms the importance of stand species composition in PAH accumulation in forest soils. The stand species composition influences the amount and quality of SOM and acidification, which is reflected in the biochemical activity and degradation of organic pollutants in the soil. Deciduous species significantly influence the properties of surface soil horizons and, consequently, the PAH content. The soils of oak stands were characterised by the lowest accumulation of PAHs with high biochemical activity indicated by enzyme activity and microbiological biomass. Pine stand soils are acidified, slowing the decomposition of SOM and resulting in a high accumulation of PAHs. Our results confirmed the importance of the fractional composition of SOM in PAH accumulation. The free light fractions (fLFs) of the SOM and the mineral-associated fraction (MAF) are of the highest importance in PAH accumulation. By selecting the species composition of the forest stand, we can influence the soil properties (i.e., pH, SOM) that determine PAH accumulation. Avoiding coniferous monocultures and introducing admixtures of deciduous species will lower the accumulation of PAHs in forest soils.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Effect of Species Composition on Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Urban Forest Soils of Krakow

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are among the most hazardous organic pollutants due to their toxic, carcinogenic, mutagenic properties, wide distribution, recalcitrance and stability in the environment. The study objective is to determine the impact of the species composition of tree stands on PAH accumulation in urban forest soils of Krakow. The study compared the impact of deciduous and coniferous species on similar soils on PAH biodegradation. Basic physicochemical properties, activity of enzymes involved in the nutrient cycle and PAH content were measured in soil samples. Our study shows lower accumulation of PAHs in soils with deciduous tree stands, which are characterized by higher pH and higher biochemical activity expressed by enzymatic activity. There is statistically significant difference in the enzymatic activity in the soils of deciduous tree stands, which results in differences in PAH accumulation. Among the studied deciduous species, soils with Norway maple and locust were characterized by highest enzymatic activity. At the same time, soils under these species were characterized by the lowest PAH accumulation. Among the coniferous species, highest PAH accumulation was observed under pine and spruce, where low enzymatic activity was observed at the same time.

Keywords Acidity · Biochemical activity · Deciduous species · Coniferous species · Krakow · Soil organic matter

1 Introduction

Increase in the soil environment pollution with persistent organic pollutants has been observed for many years. This group includes polycyclic aromatic hydrocarbons (PAHs). PAHs are generated during the processes of hydrolysis and incomplete combustion of organic matter; they can be created naturally or as a result of human activity (Srogi 2007). Polycyclic aromatic hydrocarbons are substances with carcinogenic and mutagenic potential (Błaszczyk et al. 2017). The effect of PAHs on soil results in changes of the physicochemical properties of the solution and toxicity towards cells and tissues of living organisms (Oleszczuk 2007; Zhan et al. 2010). PAHs have ring structure meaning that they are resistant to biodegradation, and carcinogenic index increases with the growth of the number of aromatic rings (Marston et al. 2001). The biological decomposition of organic pollutants such as PAHs by microorganisms is one of the most significant and efficient means of removing these compounds from the environment. PAHs in soils are subject to

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microbiological transformations with the participation of fungi, bacteria and actinomycetes, as well as sorption, leaching, reactions with other compounds and photodegradation (Wilcke and Amelung 2000). The biodegradation consists in the decomposition of exogenous substances present in the environment with the participation of metabolic pathways of living organisms, mainly bacteria, fungi and plants (Gan et al. 2009). The degradation process depends on the composition and activity of microorganisms, pH, access to oxygen or nutrient content (Mrozik et al. 2003). One of the most important parameters affecting the amount of PAHs in soil is the content of organic matter, which is characterized by high sorption capacities (Błońska et al. 2016a; Lasota and Błońska 2018). Organic matter is the binding factor for PAHs in soil environment and it is responsible for the ageing of PAHs, restricting their diffusion or release to soil in the solution (Luo et al. 2012; Wang et al. 2012). Soil microorganisms constitute the main motor for the biochemical cycle, affecting the decomposition of organic compounds (Deng et al. 2016). The quality of the litter directly affects microbial decomposer communities, which are related to the decomposition of litter by the secretion of extracellular enzymes (Graça and Poquet 2014). Soil properties can be affected by the species composition of vegetation, i.e. amount and quality of soil organic matter, acidification or the amount of nutrients (Błońska et al. 2016b; Błońska et al. 2017). Coniferous and deciduous species of trees affect soil properties differently via the plant litter fall and root systems (Błońska et al. 2021). Coniferous species lead to pH reduction, and as a consequence to reduce the enzymatic activity of soils (Błońska et al. 2016a). Deciduous species contain more easily decomposed components than coniferous species. It is known that changes in soil properties are associated with changes in its microbial structure. Communities of soil microorganisms impact on the function of soil, because they participate in the nutrient cycle and carbon storage (Xue et al. 2018). The belowground microbial communities are acting as regional drivers of the aboveground biotic communities such as plant species diversity and productivity (Van Der Heijden et al. 2008). Measurements of the extracellular enzymes activity involved in the nutrient cycles originating from organic compounds provide information about the biogeochemical circulation that occurs in soil (Yavitt et al. 2004). The availability of C and nutrients in the soil, especially in the rhizosphere, strongly affects the microbial biomass and catalytic efficiency of enzymes (Loeppmann et al. 2016).

The study objective is to determine the effect of tree stand species composition on PAH accumulation in urban forest soils of Krakow. In the study, influence of deciduous and coniferous species growing on similar soils was compared. We tested the following research hypotheses: (1) by providing more easily decomposable organic matter, deciduous species stimulate biochemical activity of soils, which results in lower PAH content; (2) coniferous species reduce soil pH and increase soil acidity, which results in lower enzymatic activity and reduces PAH biodegradation.

2 Materials and Methods

2.1 Study Area and Soil Sampling

The study was conducted in the urban forest in the Kraków (50° 03′ 41″ N; 19° 56′ 18″ E) (Fig. 1). The research covered Reduta Forest, Zesławice Forest, Wolski Forest and Tyniec Forest. The area covered by the study is occupied by Luvisols (Skiba and Drewnik 2013). The soils studied were characterized by a similar moisture. The average temperature in the study area was 8.5 °C and the average annual precipitation was about 715 mm. Kraków is the second largest town in Poland with an area 327 km^2. Kraków has become one of the most polluted cities in Europe, in recent years (Wilczyńska-Michalik and Michalik 2017). The main contaminations are SO_2, NO_x, CO and benzo(a)pyrene. The dense public transport, private car traffic, close proximity to the mining region of Upper Silesia, Balice airport and long-distance road traffic were reasons for soil pollution in Krakow (Ciarkowska et al. 2019).

The study was conducted in 2020. Deciduous and coniferous stands were selected for further analysis in each of the four Kakow urban forests covered by the study. The study covered Norway spruce (*Picea abies*) and Norway maple (*Acer platanoides*) in Reduta Forest, Scots pine (*Pinus sylvestris*) and English oak (*Quercus robur*) in the Tyniec Forest, European larch (*Larix deciduas*) and black locust (*Robinia pseudoacacia*) in the Zesławice Forest, and Douglas fir (*Pseudotsuga menziesii*) and European beech (*Fagus sylvatica*) in

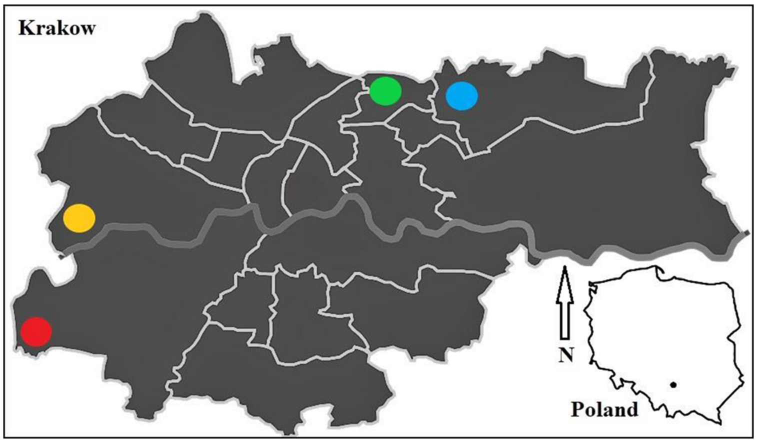

Fig. 1 Localization of study plots in urban forest of Krakow (green point—Reduta Forest; blue point—Zesławice Forest; yellow point—Wolski Forest; red point—Tyniec Forest)

the Wolski Forest. Each variant of study plots was in three repetitions. In total, 24 study plots were investigated (4 urban forest × 2 species × 3 repetitions). Soil samples were collected on each study plot for laboratory analysis. On plots with deciduous species, soil samples were taken from the humus mineral horizon (A). On the other hand, on the plots with coniferous species, soil samples were collected from the organic horizon (Ofh) and humus mineral horizon (A). In the soils of deciduous and coniferous stands, the samples for analysis were collected after removing the litter level.

2.2 Laboratory analysis

The texture was determined using laser diffraction (Analysette 22, Fritsch, Idar-Oberstein, Germany). The soil pH was determined in H_2O and KCl using the potentiometric method. C and N were measured using an elemental analyser (LECO CNS TrueMac Analyzer Leco, St. Joseph, MI, USA). The cation concentrations and contents of Cd, Cr, Cu, Ni, Pb and Zn were determined by inductively coupled plasma analysis (ICP-OES Thermo iCAP 6500 DUO, Thermo Fisher Scientific, Cambridge, UK). We used the Kappen method to determine the hydrolytic acidity and Sokolow method to determine the exchangeable acidity (Ostrowska et al. 1991). The PAHs were determined in 10 g of each soil sample, extracted using 70 ml of propan-2-ol. The samples were centrifuged (4500 rpm, 5 min) and the supernatant collected. The supernatants were extracted to the solid phase (5 ml/min) using solid-phase extraction (CHROMABOND® CN/SiOH). The residue was dissolved in acetonitrile and analysed using high-pressure liquid chromatography (HPLC) with a Dionex UltiMate 3000 HPLC system, equipped with a fluorescence detector and a Dionex UltiMate 3000 Column Compartment C18 5 μm with a 4.6 × 100-mm HPLC column. The mobile phases were water (A) and acetonitrile (B) at a flow rate of 1 ml/min. Based on the standard PAH Calibration Mix (CRM 47940) at a concentration of 10 μg/ml, calibration solutions at different concentrations (i.e. 0.1, 0.2, 0.5, 1 and 2 μg/ml) were prepared. Each prepared solution was placed into the chromatography column, the chromatograms obtained being used to produce a calibration curve. The soil samples were then analysed in triplicate. After every ninth analysis, a control sample (a calibration solution with a concentration of 0.1 μg/ml) was injected. Acenapthene (Ace), fluoren (Flu), phenanthrene (Phe), antracen (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene (BbF), benzo(a)pyrene (BaP), dibenzo(ah)anthracene (DBahA) indeno(1,2,3-c,d)pyren (IcdP), and bezo(g,h,i)perylene (BghiP) were determined. The activity of extracellular enzymes (β-D-cellobiosidase - CB, β-xylosidase - XYL, N-acetyl-β-D-glucosaminidase - NAG, phosphatase - PH and arylsulphatase - SP) was determined using fluorogenically labeled substrates (Pritsch et al. 2004; Turner 2010; Sanaullah et al. 2016). The fluorescence was measured on a multidetection plate reader (SpectroMax), with excitation at a wavelength of 355 nm and emission at 460 nm.

2.3 Statistical analysis

The Spearman correlation coefficients for the soil characteristics were calculated. The distribution was checked for normality. *U* Mann–Whitney test was used to evaluate the differences between the mean values of properties. Principal component analysis (PCA) was used to evaluate the relationships between the soil properties and PAH content. A general linear model (GLM) was used to investigate the effect of tree species and soil properties on PAH content. The classification and regression tree (C&RT) approach was applied to estimate the influence of tree species and soil properties on PAH content. Differences with $P<0.05$ were considered statistically significant. All the analyses were performed using Statistica 13 software (StatSoft 2012).

3 Results

Statistically significant differences in the pH of the studied soils were observed between deciduous and coniferous species. Independently of the urban forest location, soils of coniferous were characterized by significantly lower pH. The lowest mean pH in the humus mineral horizon was recorded for Douglas fir (pH H_2O 4.11), and highest for maple (pH H_2O 6.19) (Table 1). Soils of coniferous species were characterized by a significantly higher hydrolytic and exchange acidity. Highest acidity levels were recorded in organic horizons of coniferous species, in particular pine and spruce (Table 1). Soils of deciduous and coniferous species differed clearly in the content of carbon and nitrogen. The highest organic carbon content was recorded in organic horizons of coniferous species (spruce 23.52%, larch 20.40%, Douglas fir 10.93% and pine 27.66%). Significant difference in the C/N ratio between deciduous and coniferous species was found in humus mineral horizons (A). Deciduous species (with the exception for beech) were characterized by a better distribution of organic matter expressed by the C/N ratio (Table 1). The studied soils were characterized by high contribution of silt fraction, with lower sand contribution and clay constituted an admixture (Table 2). No significant differences in the content of individual fractions in humus mineral horizons could be found between deciduous and coniferous species (Table 2). Humus mineral horizons of deciduous species were characterized by a significantly higher content of basic cations, in particular of Ca and Mg.

Soils of the studied deciduous and coniferous species differed in the enzymatic activity, in particular BG, NAG, SP and PH activity. Humus mineral horizons of deciduous species differed statistically significantly by the higher activity of BG, NAG, SP and PH (Table 3). No significant differences in CB activity in humus mineral horizons could be found between deciduous and coniferous species. Highest

Table 1 Acidity, carbon and nitrogen content in soil under influence of different tree species

Forest	Species	Horizon	pH H_2O	pH KCl	Hh cmol(+) kg^{-1}	Hw	C %	N	C/N
R	M	A	6.19±0.09^{a}	5.27±0.13^{a}	5.98±0.29^{b}	0.28±0.04^{b}	2.28±0.24^{b}	0.24±0.02^{a}	9.67±0.23^{b}
	S	O	3.91±0.16	3.23±0.06	59.79±3.69	13.11±1.22	23.52±1.53	0.99±0.07	23.86±0.63
		A	4.27±0.09^{b}	3.72±0.10^{b}	18.69±0.91^{a}	7.61±0.55^{a}	3.95±0.08^{a}	0.22±0.01^{a}	17.60±0.54^{a}
Z	R	A	6.34±0.34^{a}	5.78±0.51^{a}	3.01±1.12^{b}	0.31±0.08^{b}	3.97±0.09^{a}	0.32±0.01^{a}	12.37±0.09^{b}
	L	O	4.20±0.04	3.62±0.06	44.42±5.57	7.34±0.24	20.40±0.92	1.03±0.04	19.72±0.68
		A	4.72±0.13^{b}	3.70±0.40^{b}	14.58±1.94^{a}	3.62±0.38^{a}	3.59±0.32^{a}	0.24±0.03^{b}	14.79±0.28^{a}
W	B	A	4.66±0.14^{a}	3.75±0.06^{a}	11.43±0.99^{a}	4.60±0.07^{b}	5.22±0.59^{a}	0.33±0.03^{a}	15.78±0.34^{a}
	D	O	4.04±0.08	3.35±0.04	22.45±2.16	7.79±0.39	10.93±0.75	0.51±0.04	21.34±0.40
		A	4.11±0.01^{b}	3.41±0.02^{b}	11.80±0.74^{a}	6.16±0.25^{a}	3.49±0.19^{b}	0.25±0.01^{b}	13.84±0.64^{b}
T	O	A	5.42±0.40^{a}	4.71±0.59^{a}	5.17±1.95^{b}	0.96±0.66^{b}	3.72±0.16^{a}	0.24±0.01^{a}	15.21±0.41^{b}
	P	O	3.90±0.13	3.36±0.16	46.15±1.29	8.42±0.48	27.66±0.48	1.26±0.09	22.04±1.35
		A	4.38±0.06^{b}	3.46±0.06^{b}	18.52±1.25^{a}	5.07±0.61^{a}	4.03±0.16^{a}	0.25±0.02^{a}	16.39±0.60^{a}

Urban forest: *R*, Reduta forest; *Z*, Zesławice forest; *W*, Wolski forest; *T*, Tyniec Forest. Species: *M*, maple; *S*, spruce, *R*, Robinia; *L*, larch, *B*, beech; *D*, Douglas fir; *O*, oak; *P*, pine. Horizon: *A*, mineral humus horizon; *O*, organic horizon; *Hh*, hydrolytic acidity; *Hw*, exchangeable acidity; *C*, organic carbon; *N*, total nitrogen. Small letters in the upper index of the mean values mean significant differences between species in humus mineral horizon (A)

PAH accumulation characterized organic horizons of coniferous tree stands (Fig. 2). The highest total PAH content was recorded in organic horizons of pine tree stands (mean content was 1.91 μg g^{-1}). In all investigated urban forest locations, the humus mineral horizons (A) of coniferous species exhibited statistically significantly higher PAH accumulation in comparison to deciduous species. Mean total PAH level in humus mineral horizons of coniferous species ranged from 0.196 μg g^{-1} to 0.385 μg g^{-1}, and for deciduous species from 0.061 μg g^{-1} to 0.146 μg g^{-1} (Fig. 2). 4- and 5-ring hydrocarbons were predominant in the investigated soils independently of the analysed horizon and species (Table 4). In the soils of the investigated tree stands, no 2-ring PAHs could be found and the contribution of 3-ring hydrocarbons was minor (Table 4). In the humus mineral horizon, the total PAH level was statistically significantly and negatively correlated with pH and content of base cations, and positively correlated with acidity and C/N ratio (Table 5). The activity of BG, NAG, SP, and PH in the A horizon negatively correlated with total PAH level (r=−0.887, r=−0.823, r=−0.804 and r=−0.777, respectively). In addition, the enzymatic activity correlated positively with pH, base cation content and P content and negatively with soil acidity (Table 5). GLM analysis confirmed the significance of biochemical activity expressed by β-glucosidase activity in the formation of PAH accumulation (Table 6). In addition, significance of species and organic carbon content in the formation of PAH amount was revealed. PCA analysis confirmed a clear relationship between acidification of the investigated soils, amount of organic carbon and the degree of soil organic matter decomposition expressed by the C/N ratio (Fig. 3). The two primary factors had a significant impact on the variance of properties (77.7%). PCA indicated strong relationship of organic horizons of coniferous species with acidification, accumulation of poorly decomposed organic matter and high PAH accumulation. PCA produced clear groups of humus mineral horizons of deciduous and coniferous species in terms of acidification, quantity and quality of soil organic matter, biochemical activity and above all PAH content (Fig. 3). Classification and regression tree charts were used to identify the characteristics that determine PAH accumulation in urban forest soils (Fig. 4). They are type of soil horizon, species,

Table 2 Base cations content and texture of soil under influence of different tree species

Forest	Species	Horizon	Ca cmol(+) kg^{-1}	Mg	K	Na	BC	P mg kg^{-1}	sand %	silt	clay
R	M	A	15.82±8.10^{a}	1.28±0.14^{a}	0.29±0.02^{b}	0.01±0.01^{b}	17.41±7.98	81.20±15.31^{a}	20.0±2.0^{a}	73.7±1.5^{a}	6.4±1.6^{a}
	S	O	23.84±3.38	6.91±0.56	3.18±0.28	0.52±0.05	34.40±3.94	45.96±8.05	-	-	-
		A	5.61±0.36^{b}	1.20±0.06^{a}	0.49±0.05^{a}	0.15±0.02^{a}	7.44±0.32	16.44±1.72^{b}	19.0±1.0^{a}	75.3±1.5^{a}	5.7±0.6^{a}
Z	R	A	23.02±2.69^{a}	3.35±0.15^{a}	0.47±0.07^{b}	0.06±0.00^{b}	26.89±2.81	52.50±2.62^{a}	16.1±5.9^{a}	76.7±5.8^{a}	7.2±1.1^{a}
	L	O	22.30±1.15	5.99±0.42	2.70±0.25	0.42±0.01	31.41±0.87	38.04±4.77	-	-	-
		A	6.78±0.32^{b}	1.37±0.11^{b}	0.66±0.06^{a}	0.19±0.02^{a}	8.99±0.42	22.50±2.51^{b}	22.1±1.8^{a}	72.7±2.0^{a}	5.4±0.0^{b}
W	B	A	6.90±0.26^{a}	0.48±0.07^{a}	0.29±0.04^{a}	0.01±0.00^{b}	4.35±2.95	75.65±1.36^{a}	24.4±2.7^{a}	71.5±2.3^{a}	4.3±0.4^{a}
	D	O	2.90±0.35	0.54±0.01	0.27±0.01	0.03±0.01	3.74±0.38	80.46±5.35	-	-	-
		A	0.59±0.01^{b}	0.13±0.00^{b}	0.06±0.00^{b}	0.03±0.00^{a}	0.82±0.00	26.12±1.22^{b}	22.7±1.6^{a}	71.9±1.0^{a}	5.6±0.4^{a}
T	O	A	6.03±4.20^{a}	0.48±0.29^{b}	0.17±0.03^{b}	0.00±0.00^{b}	6.69±4.52	52.69±1.13^{a}	23.7±2.1^{a}	72.0±1.7^{a}	4.3±0.6^{a}
	P	O	18.17±0.99	4.97±0.42	2.57±0.23	0.39±0.11	26.10±1.20	77.41±7.21	-	-	-
		A	3.26±0.26^{a}	1.18±0.09^{a}	0.47±0.05^{a}	0.12±0.01^{a}	5.02±0.14	46.24±10.39^{a}	21.3±1.2^{a}	74.7±1.5^{a}	4.1±1.1^{a}

Urban forest: *R*, Reduta forest; *Z*, Zesławice forest; *W*, Wolski forest; *T*, Tyniec Forest. Species: *M*, maple; *S*, spruce; *R*, Robinia; *L*, Larch; *B*, beech; *D*, Douglas fir; *O*, oak; *P*, pine. Horizon: *A*, mineral humus horizon; *O*, organic horizon. Small letters in the upper index of the mean values mean significant differences between species in humus mineral horizon (A)

Table 3 Enzyme activity (nmol MUB g^{-1}d.s. h^{-1}) of soils under influence of different species

Forest	Species	Horizon	CB nM MUB g^{-1} h^{-1}	BG	NAG	XYL	SP	PH
R	M	A	0.87 ± 0.98^{a}	90.65 ± 10.37^{a}	21.04 ± 1.78^{a}	7.33 ± 7.44^{a}	4.04 ± 1.62^{a}	330.02 ± 72.48^{a}
	S	O	5.46±1.52	101.79±10.35	26.19±2.63	39.36±12.01	0.07±0.06	264.33±9.60
		A	1.84 ± 0.77^{a}	25.50 ± 4.64^{b}	11.39 ± 2.03^{b}	9.66 ± 1.22^{a}	0.00 ± 0.00^{b}	91.23 ± 18.26^{b}
Z	R	A	13.00 ± 7.88^{a}	108.38 ± 29.89^{a}	27.64 ± 9.45^{a}	12.03 ± 4.54^{a}	5.69 ± 0.72^{a}	252.21 ± 56.92^{a}
	L	O	5.64±0.70	146.78±27.65	18.34±2.50	35.47±3.76	0.07±0.12	305.36±24.42
		A	3.28 ± 0.69^{a}	42.01 ± 15.04^{b}	14.50 ± 2.25^{b}	2.90 ± 2.27^{b}	0.03 ± 0.06^{b}	211.55 ± 28.17^{a}
W	B	A	2.84 ± 2.25^{a}	48.28 ± 18.36^{a}	14.19 ± 4.44^{a}	0.25 ± 0.30^{b}	0.51 ± 0.54^{a}	233.30 ± 35.92^{a}
	D	O	5.74±2.82	120.35±24.89	60.05±7.08	34.43±1.10	3.00±1.75	298.69±4.01
		A	2.67 ± 1.05^{a}	30.17 ± 5.37^{a}	18.05 ± 1.64^{a}	6.29 ± 3.05^{a}	0.14 ± 0.08^{a}	216.89 ± 7.62^{a}
T	O	A	2.15 ± 0.71^{a}	75.05 ± 13.50^{a}	34.45 ± 8.73^{a}	0.61 ± 0.88^{b}	1.36 ± 0.75^{a}	218.52 ± 39.34^{a}
	P	O	5.51±1.27	99.31±7.92	43.98±5.55	49.02±9.79	0.00±0.00	236.70±41.28
		A	2.34 ± 0.38^{a}	19.35 ± 2.84^{b}	9.35 ± 2.84^{b}	7.15 ± 0.80^{a}	0.00 ± 0.00^{b}	90.30 ± 36.57^{b}

Urban forest: *R*, Reduta forest; *Z*, Zesławice forest; *W*, Wolski forest; *T*, Tyniec Forest. Species: *M*, maple, *S*, spruce; *R*, Robinia; *L*, larch; *B*, beech; *D*, Douglas fir; *O*, oak; *P*, pine. Horizon: *A*, mineral humus horizon; *O*, organic horizon; *CB*, β-D-cellobiosidase; *BG*, β-glucosidase; *NAG*, N-acetyl-β-glucosaminidase; *XYL*, β-xylosidase; *SP*, sulphatase; *PH*, phosphatase. Small letters in the upper index of the mean values mean significant differences between species in humus mineral horizon (A)

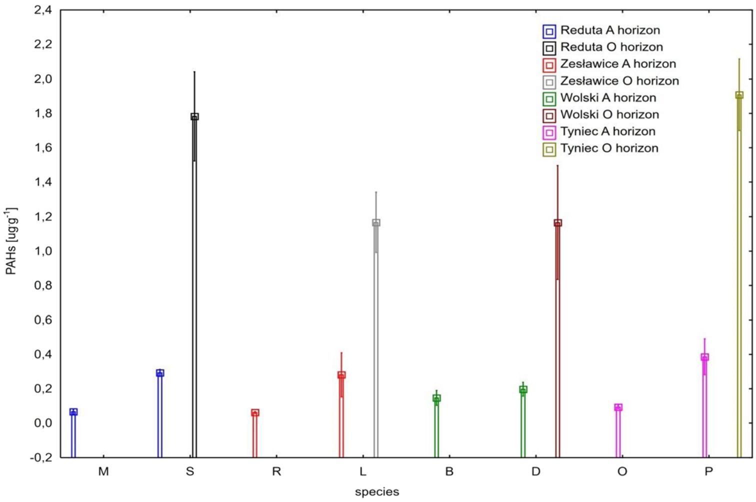

Fig. 2 Sum of PAH content in soil under influence of different species (M, maple; S, spruce; R, Robinia; L, larch; B, beech; D, Douglas fir; O, oak; P, pine)

β-glucosidase activity and C/N ratio. The highest PAH accumulation was fund in organic horizon at a BG activity < 114.04 nmol MUB g^{-1}d.s. h^{-1} and C/N >21.7 (Fig. 4).

4 Discussion

The conducted research has confirmed the validity of the advanced research hypotheses. Species composition is important in PAH accumulation in urban forests of Krakow. By means of the provided organic matter, tree species affect the chemical properties of soils, and as a consequence the biochemical activity and biodegradation of PAHs. Deciduous species provide soil with easily decomposable organic matter, and the components released during its decomposition raise soil pH. We recorded lower PAH accumulation under deciduous tree stands in urban forests of Krakow. Soils of such stands were characterized by higher pH and higher biochemical activity expressed by the activity of enzymes involved in the cycle of C, N, P and S. According to Maliszewska-Kordybach (2005), some soil properties (acidity, content of fine fractions and organic matter content) affect the course of PAH decomposition. Soil characteristics greatly influence the efficiency of microbial PAH degradation (Zhang et al. 2006; Lors et al. 2012). Better quality of soil organic matter was observed for deciduous stands, expressed as the C/N ratio. Lowered nitrogen availability may restrict the activity of soil microorganisms, and thus the processes of organic matter decomposition (Treseder 2008; Averill and Waring 2017). According to Zhou and Hua (2004), appropriate level of nutrients, particularly of nitrogen, is necessary for improved PAH bioremediation. Earlier study indicates marked differences in the release of nutrients, particularly of C, N and P during the decomposition of plant litter of deciduous and coniferous species (Błońska et al. 2021). More carbon and nitrogen are released to soil from deciduous litter than from coniferous litter, which results in increased activity and diversity of the microbial community. Apart from the fall of plant litter, tree stands affect soil properties via their root systems, which apart from organic matter provide nutrients via root secretions. Root secretions provide soil with sugars, amino acids, organic acids, hormones and vitamins as well as high-molecular compounds such as enzymes, which translates into higher metabolic activity of the microflora, which is abundant in the rhizosphere (Lu et al. 2012). Earlier research confirmed the increased biodegradation rate of organic contaminants in the rhizosphere zone as compared with non-rhizosphere zone (Zhuang et al. 2007). Wang et al. (2019) found that the influence of deciduous rhizosphere on the microorganism biomass, enzyme activity and N mineralization rate was 2-fold higher than for coniferous species. The tree stand species composition has a very pronounced effect on soil pH, which is of key significance for PAH biodegradation. According to Pawar (2015), biodegradation processes can be enhanced by considering the

Table 4 PAH content (μg g^{-1}) in soil under influence different species taking into account the number of rings

			Broadleaved species	Coniferous species	
			A - horizon	O - horizon	A - horizon
LMW	3rings	Flu	0.00000±0.00000^{a}	0.00066±0.00065	0.00000±0.00000^{a}
		Ant	0.00000±0.00000^{a}	0.00012±0.00022	0.00000±0.00000^{a}
		Ace	0.00044±0.00040^{b}	0.01363±0.00577	0.00218±0.00141^{a}
		Phe	0.02021±0.00974^{b}	0.09447±0.03375	0.03261±0.00808^{a}
		∑	0.02065±0.00990^{b}	0.10888±0.03920	0.03479±0.00925^{a}
	4rings	Flt	0.01337±0.00817^{b}	0.29030±0.10936	0.04715±0.02055^{a}
		Pyr	0.01209±0.00742^{b}	0.28454±0.07566	0.06026±0.06110^{a}
		BaA	0.00509±0.00301^{b}	0.14098±0.04033	0.03061±0.03692^{a}
		Chr	0.00965±0.00626^{b}	0.25943±0.07022	0.03970±0.01897^{a}
		∑	0.04020±0.02417^{b}	0.97526±0.28004	0.17772±0.07720^{a}
HMW	5rings	BbF	0.01436±0.00376^{b}	0.13371±0.03306	0.02935±0.00882^{a}
		BaP	0.00641±0.00324^{b}	0.12605±0.02902	0.02148±0.01099^{a}
		BkF	0.00256±0.00171^{a}	0.02834±0.01590	0.00348±0.00140^{a}
		DBahA	0.00013±0.00005^{b}	0.00211±0.00092	0.00071±0.00102^{a}
		∑	0.02346±0.00821^{b}	0.29021±0.07037	0.05502±0.02042^{a}
	6rings	BghiP	0.00319±0.00133^{b}	0.04070±0.00945	0.00763±0.00310^{a}
		IcdP	0.00443±0.00212^{b}	0.09033±0.02536	0.01390±0.00673^{a}
		∑	0.00762±0.00332^{b}	0.13103±0.03476	0.02153±0.00973^{a}
		∑PAHs	0.09192±0.04052^{b}	1.50537±0.41661	0.28905±0.10111^{a}

PAH: *Flu*, fluoranthene; *Ant*, anthracene; *Ace*, acenapthene; *Phe*, phenanthrene; *Flt*, fluoranthene; *Pyr*, pyrene; *BaA*, Benzo(a)anthracene; *Chr*, chrysene; *BbF*, benzo(b)fluoranthene; *BaP*, benzo(a)pyrene; *BkF*, benzo(k)fluoranthene; *DBahA*, dibenz(a,h)anthracene; *BghiP*, benzo(g,h,i)perylene; *IcdP*, indeno(1,2,3-cd)perylene; *LMW*, low molecular weight PAHs; *HMW*, high molecular weight. Small letters in the upper index of the mean values mean significant differences between broadleaved and coniferous species in humus mineral horizon (A)

enzymes present in soil and their active role varying pH values. The capacity of microorganisms to degrade PAHs in soil environment depends on the physical and chemical properties of soils, in particular on its pH. Higher soil pH results in higher activity of microorganisms, whereas the diversity and activity of microorganisms are limited in acidic environment (Uzarowicz et al. 2020). According to the aforementioned authors, the low enzymatic activity and low bacterial counts were associated with highly acidic soils (pH H_2O 3.0-3.9). It can be assumed that higher PAH accumulation in soils with coniferous stands is associated with their acidifying effect. The acidifying effect of tree species on sandy

Table 5 Correlations between enzyme activity, PAH content and soil properties in mineral humus horizon (A)

	pH H_2O	pH KCl	Hh	BC	C	N	C/N	P	PAHs
PAHs	− 0.830*	− 0.755*	0.891*	− 0.601*	0.382	− 0.126	0.697*	− 0.549*	1.000
CB	0.168	0.062	− 0.231	0.129	0.211	0.350	− 0.104	− 0.079	0.050
BG	0.854*	0.785*	− 0.914*	0.622*	− 0.240	0.244	− 0.713*	0.503*	− 0.887*
NAG	0.632*	0.611*	− 0.878*	0.283	− 0.417*	0.094	− 0.702*	0.357	− 0.823*
XYL	− 0.051	0.085	0.091	0.154	0.060	− 0.004	− 0.071	− 0.243	0.273
SP	0.760*	0.764*	− 0.915*	0.508*	− 0.250	0.263	− 0.776*	0.569*	− 0.804*
PH	0.643*	0.475*	− 0.785*	0.431*	− 0.405*	0.133	− 0.700*	0.516*	− 0.777*

*$p < 0.05$

Table 6 Summary of GLM analysis of the effect of the soil properties and tree species on the PAH content

	F	*p* value
Species	1.770	0.1907
pH	0.046	0.8343
C	0.094	0.7652
BG	**17.431**	**0.0015**
Species × pH	1.850	0.1737
Species × C	**6.356**	**0.0036**

bold values -$p < 0.05$

soil was in the order of spruce = pine > oak, while that on loess was pine > beech > hornbeam (Błońska et al. 2016b). Our study shows stronger degradation of PAHs in soils with deciduous tree stands, which are characterized by higher pH and higher biochemical activity expressed by enzymatic activity. Statistically significant difference in the activity of enzymes involved in C, N, P and S transformations in deciduous stand soils was observed in comparison with coniferous stands, which results in the differences of PAH accumulation. Among the studied deciduous species, highest enzymatic activity characterized soils were Norway maple and locust. At the same time, soils under these species were characterized by the lowest PAH accumulation. Among the coniferous species, highest PAH accumulation was observed under pine and spruce, where low enzymatic activity was observed at the same time. In our study, we have been able to record a strong relationship of the enzymatic activity with pH and with organic carbon content. The pH value has a significant effect on the activity of microorganisms in the soil, and many enzymes are very sensitive to the pH of soil. The soil pH influences the activity of soil enzymes by controlling ionization caused by conformational changes of enzymes, availability of substrates and enzymatic cofactors (Błońska et al. 2021). Soil organic matter is the main source of enzyme substrate, and the content of organic matter greatly affects the activity of soil enzyme (Zhang et al. 2020). It has been recognized that PAHs are degraded by the synthesis of lignin modifying enzymes like lignin peroxidases, manganese peroxidases laccases and other oxidases (Cao et al. 2020). Catabolic activity of microorganisms in PAH degradation depends largely on the environmental conditions (pH, temperature and nutrients), counts and type of microorganisms, character or properties of the degraded PAHs (Singh and Ward

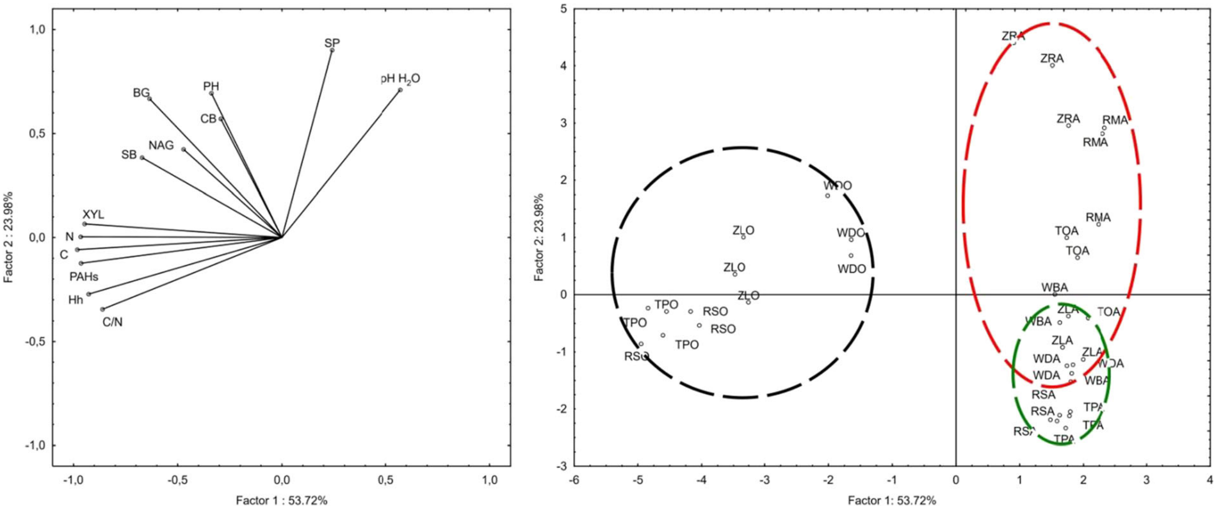

Fig. 3 The projection of variables on a plane of the first and second PCA factor (DH, dehydrogenase activity; CB, β-D-cellobiosidase; XYL, β xylosidase; NAG, N-acetyl-β-D-glucosaminidase; BG, β-glucosidase; PH, phosphatase; SP, arylosulphatase; C, organic carbon content; N, total nitrogen content; Hh, hydrolytic acidity; black circle, organic horizon of coniferous species; red circle, humus mineral horizon of broadleaved species; green circle, humus mineral horizon of coniferous species; R, Reduta forest; Z, Zesławice forest; W, Wolski forest; T, Tyniec Forest; species: M, maple; S, spruce; R, Robinia; L, larch; B, beech; D, Douglas fir; O, oak; P, pine)

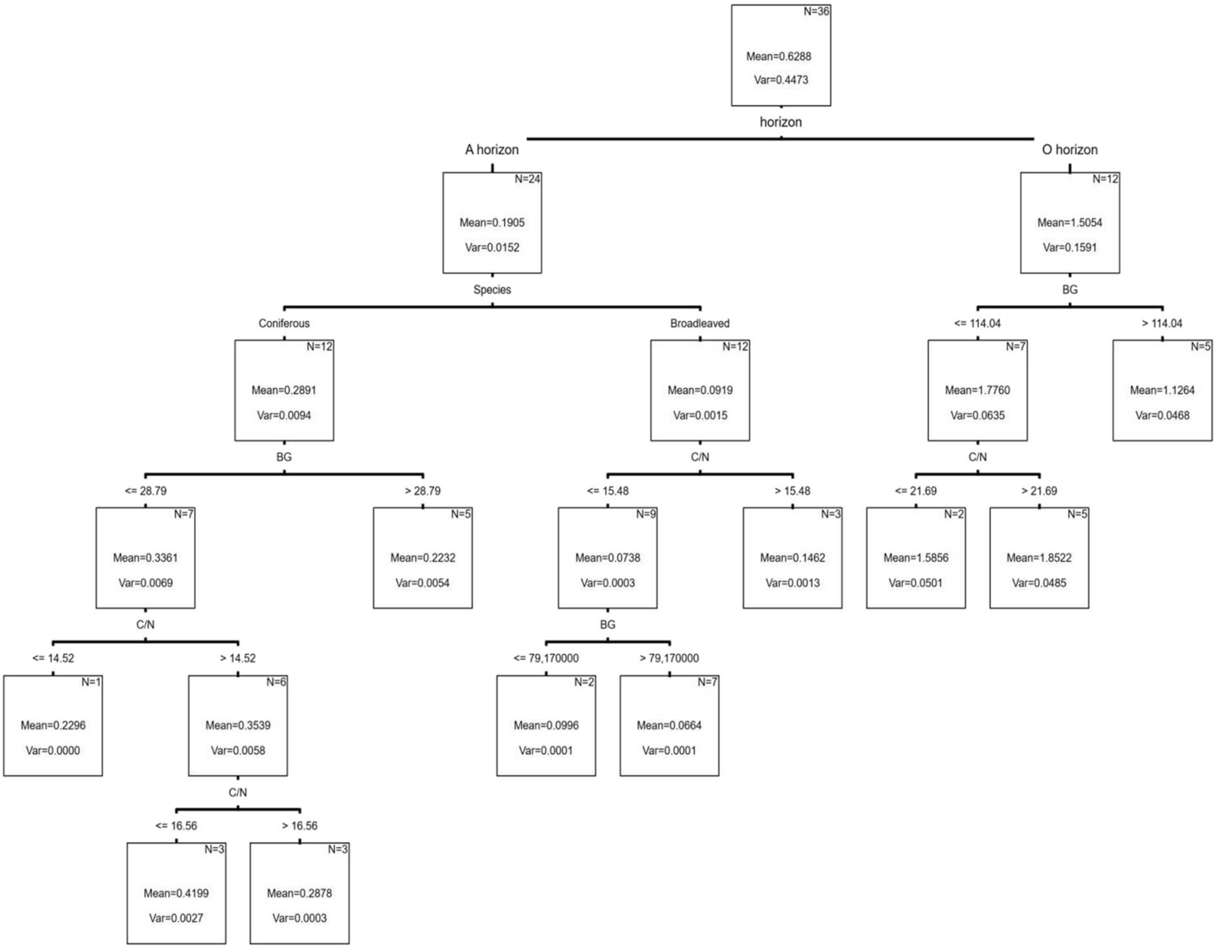

Fig. 4 The regression tree (C&RT) for PAH content in soil

2004). PAH biodegradation is activated by different catalytic enzymes secreted by microorganisms. According to Suszek-Łopatka et al. (2019), the increase of soil moisture enhanced PAH toxicity differently depending on the soil. Our study included soils with similar moisture; therefore, this factor did not influence the amount of PAH. Different microbe species such as *Pseudomonas*, *Sphingomonas*, *Micrococcus*, *Xanthomonas*, *Corynebacterium*, *Enterobacter*, *Paenibacillus*, *Bacillus*, *Aeromonas*, *Microbulbifer*, *Mycobacteria*, *Acinetobacter* and *Aspergillus* are characterized by PAH biodegradation capacity (Sakshi and Haritash 2020). At the same time with PAHs, significant amounts of heavy metals accumulate in the surface horizon of urban soils (Rodriguez-Seijo et al. 2015). According to Ciarkowska et al. (2019), the Krakow soils were characterized by the high levels of PAHs and heavy metals. It can be assumed that PAH and heavy metals inhibited enzymatic activity in the study soils of Krakow.

5 Conclusions

The conducted study has confirmed the importance of tree stand species composition in the formation of soil properties, and consequently PAH biodegradation in the urban forests of Krakow. Via the appropriate selection of species we can influence on the quantity and quality of soil organic matter and soil pH, which results in the diversification and activity of soil microorganisms participating in the distribution of organic pollutants. Our study shows that deciduous, and in particular Norway maple and locust have more favourable influence on soil properties, which translates into lower PAH accumulation in the urban forests of Krakow. Introduction of coniferous species, in particular of pine and spruce, should be avoided in urban forests, as they have acidifying effect on soil, thus restricting the processes of decomposition, in which soil microorganisms are involved. The value of pH has turned out to be an important parameter in PAH biodegradation in urban forest soils of Krakow, because it comprises the key factor for the availability of nutrients, and thus for the development of microorganisms involved in PAH decomposition.

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Declarations

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Oświadczam, że mój wkład polegał na sformułowaniu problemu badawczego, zaprojektowaniu eksperymentu, przeprowadzeniu doświadczenia w terenie oraz zebranie próbek, opracowaniu i interpretacji wyników, przygotowaniu wstępnej wersji manuskryptu i edycji ostatecznej wersji manuskryptu.

I declare that my contribution was following: determination of research problem, design of experiment, conduct field experiment and collect samples, statistical data analysis and interpretation of results, preparation the preliminary version of manuscript, preparation and edition of final version of manuscript.

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Udział / Contribution: 60%

mgr inż. Stanisław Łyszczarz Stanisław Łyszczarz

Oświadczam, że mój wkład polegał na sformułowaniu problemu badawczego, zaprojektowaniu eksperymentu, przeprowadzeniu doświadczenia w terenie oraz zebranie próbek, opracowaniu i interpretacji wyników, przygotowaniu wstępnej wersji manuskryptu i edycji ostatecznej wersji manuskryptu.

I declare that my contribution was following: determination of research problem, design of experiment, conduct field experiment and collect samples, statistical data analysis and interpretation of results, preparation the preliminary version of manuscript, preparation and edition of final version of manuscript.

Udział / Contribution: 20%

dr hab. inż. Jarosław Lasota prof. URK

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Udział / Contribution: 20%

prof. dr hab. inż. Ewa Błońska

Oświadczenia o udziale autorów w publikacji / Declaration of author contribution

Lasota, J., **Łyszczarz, S.**, Kempf, P., Kempf, M., Błońska, E. 2021. Effect of Species Composition on Polycyclic Aromatic Hydrocarbon (PAH) Accumulation in Urban Forest Soils of Krakow. Water, Air, & Soil Pollution, 232(2), 1-12. DOI: 10.1007/s11270-021-05043-0

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Udział / Contribution: 40%

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Udział / Contribution: 30%

mgr inż. Stanisław Łyszczarz Stanisław Łyszczarz

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Udział / Contribution: 20%

dr inż. Piotr Kempf ....

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Udział / Contribution: 5%

dr inż. Marta Kempf ....Kempf..........

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Udział / Contribution: 5%

prof. dr hab. inż. Ewa Błońska ....Błońska..........