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Wojciech Rykała

Oddziaływanie pożarów nielegalnych składowisk odpadów stałych na środowisko gleb i wód

Rozprawa doktorska

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Spis treści

Komentarz wprowadzający w tematykę rozprawy doktorskiej

Składam serdeczne podziękowania:

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Komentarz wprowadzający w tematykę rozprawy doktorskiej

1. Wprowadzenie

Wzrost wytwarzania odpadów stałych to istotny problem na całym świecie. Ilość i rodzaj powstających odpadów zwiększa się wraz ze wzrostem populacji. Jedną z najczęstszych, a zarazem najtańszą metodą gromadzenia i unieszkodliwiania niepotrzebnych odpadów stałych jest ich składowanie (Dąbrowska et al., 2018). Jednocześnie, wraz z legalnymi, powstają nielegalne składowiska odpadów, które stanowią potencjalne zagrożenie dla środowiska oraz zdrowia mieszkańców danego terenu. Powstają one najczęściej w lasach, obrzeżach terenów zamieszkałych, czy prywatnych działkach i pustostanach. Powodem ich tworzenia się są między innymi brak odpowiednich obiektów do przetwarzania odpadów (Ichinose et al., 2011) lub chęć taniego pozbycia się niewygodnego odpadu.

Jednym z najpoważniejszych zagrożeń na nielegalnych składowiskach odpadów jest pożar (Dąbrowska et al., 2023). Zjawisko to może powstać poprzez samoistny zapłon, związany miedzy innymi z warunkami atmosferycznymi (Øygard et al., 2014), lub reakcją chemiczną odpadu stałego z tlenem, przeskok iskry z maszyny pracującej na składowisku oraz umyślne podpalenie przez osoby trzecie. Ostatnia z nich jest jedną z najczęstszych przyczyn tego typu zdarzeń. Podpalenie ma zwykle na celu pozbycie się kosztownych do utylizacji odpadów stałych. Dodatkowym czynnikiem podsycającym pożar na dużych składowiskach odpadów jest łatwopalny metan, który może tworzyć się podczas rozkładu niektórych odpadów (Aderemi et al., 2012). Dane Państwowej Straży Pożarnej wskazują na to, iż od 2012 roku wzrasta liczba pożarów miejsc gromadzenia odpadów w Polsce z 75 przypadków do 243 w 2018 roku.

Odpady stałe, które uległy procesom niepełnego spalania podczas pożaru stają się nowym źródłem zanieczyszczeń środowiskowych, często znacznie bardziej niebezpiecznych niż substancje pierwotnie zdeponowane na składowisku. Podczas opadów dochodzi do wymywania zanieczyszczeń z nielegalnego składowiska oraz infiltracji powstałych odcieków w głąb terenu (Theepharaksapan et al., 2011). W zależności od budowy geologicznej podłoża i warunków hydrogeologicznych może dojść do migracji chmury zanieczyszczeń do warstwy wodonośnej. Jednym z przykładów takiej migracji jest przemieszczenie się zanieczyszczeń w kierunku przepływu wód gruntowych do pobliskiej rzeki. Duży wpływ na zakres rozprzestrzeniania się zanieczyszczeń ma ilość i jakość powstających odcieków, szybkość deponowania odpadów stałych na określonym terenie oraz warunki hydrogeologiczne. Konsekwencjami takich zdarzeń może być długoletnie i kosztowne zanieczyszczenie środowiska gruntowo-wodnego oraz konieczność przeprowadzenia dodatkowych prac związanych z monitoringiem wód podziemnych na danym terenie (Rykała et al., 2020). Wiąże się to z faktem, iż nielegalne składowiska odpadów najczęściej nie mają zabezpieczonego podłoża przed przedostawaniem się zanieczyszczeń do gleby. Dodatkowo, technologie rekultywacji wód gruntowych nie dają 100% szansy oczyszczenia warstwy wodonośnej do standardów wody pitnej (Dąbrowska et al., 2021).

Rodzaj i ilość produktów niepełnego spalania odpadów stałych, będących konsekwencją pożaru na składowisku, zależy od typu zdeponowanych materiałów. Do najbardziej powszechnych należą takie substancje jak węglowodory alifatyczne, wielopierścieniowe węglowodory aromatyczne (WWA) i ich pochodne podstawione grupami funkcyjnymi, np. fenole i chlorowane WWA (Raudonyte-Svirbutaviciene et al., 2022; Chrysikou et al., 2008;

Escobar-Arnanz et al., 2017). Typ gromadzonego i spalanego odpadu stałego ma również znaczenie w przypadku substancji nieorganicznych (Øygard et al. 2014; Tałałaj et al., 2016).

Wielopierścieniowe węglowodory aromatyczne (WWA, ang. *polycyclic aromatic hydrocarbons* - PAHs) są uważane za substancje niebezpieczne dla środowiska i zdrowia człowieka. Powszechne zainteresowanie nimi jest wynikiem ich właściwości mutagennych i rakotwórcze. Szesnaście z nich zostało uznanych przez Amerykańską Agencję Ochrony Środowiska (EPA) za substancje priorytetowe. Jako produkty niepełnego spalania różnych materiałów organicznych, takich jak biomasa, czy paliwa kopalne występują powszechnie w wielu środowiskach (Hisamuddin et al., 2022). Do głównych emitorów WWA można zaliczyć: transport, spalanie paliw w piecach domów jednorodzinnych (emisja niska) lub przemysł. Monitorowanie migracji WWA jest ważne ze względu na ich negatywny wpływ na środowisko przyrodnicze (Kuppusamy et al., 2016).

Innymi organicznymi związkami chemicznymi, które należy brać pod uwagę podczas monitorowania zanieczyszczeń środowiska gruntowo-wodnego są związki fosforoorganiczne. Należą one do substancji powszechnie spotykanych w smarach, budownictwie (pianki) lub niektórych plastikach w celu zmniejszenia ich palności (retardanty ognia) (van der Veen and de Boer, 2012). Są one łatwo uwalniane do środowiska poprzez wymywanie, ścieranie lub utlenianie (Marklund et al., 2003). Związki te uważa się za toksyczne, rakotwórcze i mogące powodować podrażnienia skóry.

Wybrane obszary badań nielegalnych składowisk odpadów po pożarze przedstawiają sytuacje, w których ogień najprawdopodobniej został rozniecony umyślnie. Są to następujące lokalizacje: (i) w południowej części Polski (Trzebinia) oraz (ii) w południowo-zachodniej części Polski (wieś w okolicach Wrocławia). W obu przypadkach zostało pobranych kilkadziesiąt próbek glebowych oraz spalonych odpadów stałych nadal zalegających na składowisku. Dodatkowo, wykorzystując spalone odpady stałe ze składowiska w Trzebini, przeprowadzono symulację ich wymywania, dzięki której otrzymano odcieki imitujące infiltrację wody w głąb ziemi.

Głównymi celami badań były:

- określenie potencjalnego zagrożenia pożarów nielegalnych składowisk odpadów na środowisko przyrodnicze (gleba, wody podziemne);
- wykrycie i określenie rodzajów zanieczyszczeń, jakie występują podczas pożaru odpadów stałych na nielegalnych składowiskach;
- zaproponowanie działań minimalizujących skutki oddziaływania pożarów na nielegalnych składowiskach odpadów na środowisko przyrodnicze;
- określenie przyszłych badań, które można przeprowadzić na terenach nielegalnych składowisk odpadów po pożarze.

Prezentowane badania stanowią integralny wkład w wiedzę dotyczącą skutków i zagrożeń, jakie mogą prowadzić pożary na nielegalnych składowiskach odpadów. Jest to istotna kwestia ze względu na stale pojawiające się informacje dotyczące nowych ognisk zapalnych na tego typu obiektach. Badania te są unikalne w Polsce. O ile na świecie pojawiły się podobne badania, to w kraju wciąż tematyka stanowi marginalne zainteresowanie. Dodatkowym plusem tych badań jest ich interdyscyplinarność. Powiązane są one z tematyką chemii środowiskowej, geochemii oraz hydrogeologii, co daje możliwość szerszego zobrazowania przedstawianego problemu, jak również przedstawienie nowej wiedzy i możliwości przeciwdziałania negatywnym skutkom dla środowiska gruntowo-wodnego.

2. Obszar badań

2.1 Miejsca poboru próbek

Badania, na których oparto niniejszą pracę, zostały przeprowadzone w dwóch lokalizacjach nielegalnych składowisk odpadów stałych po pożarze. Oba miejsca powstały nielegalnie, bez odpowiednich zezwoleń, umożliwiających gromadzenia na nich odpadów stałych.

1. Nielegalne składowisko odpadów po pożarze w **Trzebini** jest zlokalizowane w południowej części Polski, przy ul. Słowackiego (Figura 1). Teren wokół składowiska porośnięty jest drzewami, a w sąsiedztwie znajduje się zakład karny i stacja elektroenergetyczna (odpowiednio na zachodzie i południu) oraz zakłady przemysłowe na północy. Badany obszar zajmuje ok. 28 000 m^2, a w jego obrębie znajduje się kilka zdewastowanych budynków użytkowych oraz różnego typu odpady stałe tj.: opony, tekstylia, czarne gumy i plastik. Pożar miał miejsce między 26-27 maja 2018 roku w godzinach nocnych. Konsekwencją zdarzenia była ogromna smuga czarnego dymu, która mogła stanowić zagrożenie dla zdrowia mieszkańców dalszej okolicy. Spaleniu uległo ok. 65% terenu nielegalnego składowiska odpadów.

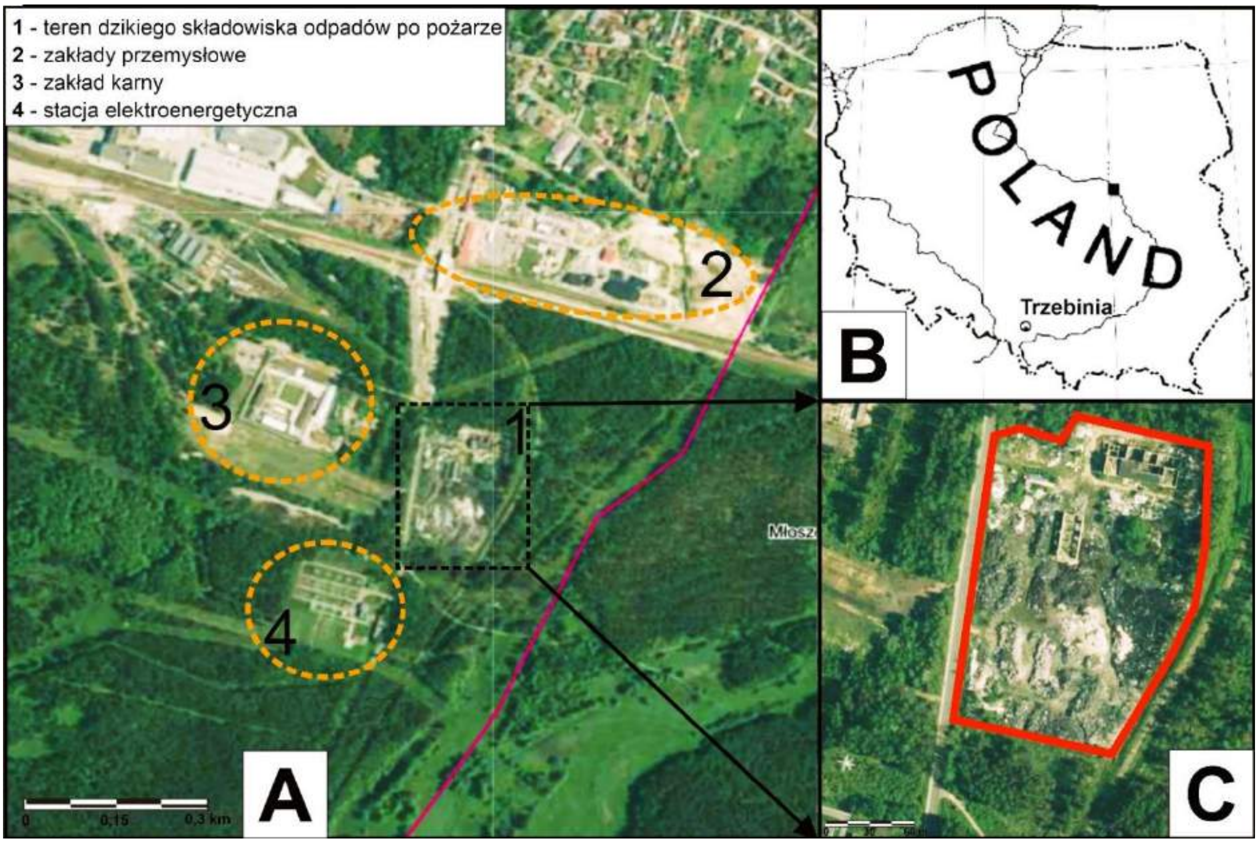

Fig. 1. (A-C) Lokalizacja nielegalnego składowiska odpadów stałych po pożarze w Trzebini wraz z pobliską infrastrukturą.

2. Nielegalne składowisko odpadów po pożarze we **wsi w okolicach Wrocławia** znajduje się w południowo-zachodniej części Polski. Obszar wokół składowiska otoczony jest polami uprawnymi, a pierwsze najbliższe gospodarstwa domowe znajdują się ok. 240m od centrum wysypiska. Na jego terenie znajduje się wiele deponowanych odpadów stałych, tj.: tekstylia, opakowania plastikowe, plastikowe części samochodowe oraz gąbki z tworzyw sztucznych. Pożar miał tam miejsce wielokrotne w 2021 roku, m. in. we wrześniu oraz listopadzie. Spaleniu uległo ok. 50% nielegalnego terenu składowiska odpadów.

Ze względu na brak zgody na ujawnienie dokładnej lokalizacji nielegalnego składowiska odpadów we wsi koło Wrocławia, nie została zaprezentowana oraz opublikowana mapa z omawianego terenu składowiska po pożarze.

2.2 Metodyka

Podczas kilku wyjazdów terenowych pobrano kilkadziesiąt próbek glebowych oraz spalonych odpadów stałych z obszaru dotkniętego pożarem i terenów sąsiadujących (Figura 2) (Tabela 1).

Fig. 2. Miejsca poboru próbek na nielegalnych składowiskach odpadów: A – Trzebinia, B – wieś w okolicach Wrocławia.

Próbki te zostały przetransportowane do laboratorium Instytutu Nauk o Ziemi w Sosnowcu, Uniwersytetu Śląskiego w Katowicach, gdzie zostały wysuszone w temperaturze otoczenia do stanu powietrznosuchego. Następnie próbki glebowe i spalonych odpadów stałych zważono, skatalogowano, rozdrobniono i ujednorodniono. Próbki wyekstrahowano dichlorometanem (DCM, cz.d.a.) w łaźni ultradźwiękowej w temperaturze 30°C przez 15 min (3x). Ekstrakty przesączono przez filtry bibułowe; klasa 3 m/N; średnicy 110 mm. Rozpuszczalnik odparowano i obliczono wydajność ekstraktu.

Do przygotowania odcieków ze spalonych odpadów stałych, próbki uprzednio wysuszone zostały zalane wodą demineralizowaną, a następnie przemyte zgodnie z normą PN-EN 12457-

2. Tak otrzymane odcieki poddano ekstrakcji do fazy stałej (SPE) na kolumnach Bakerbond Octadecyl (C18) Polar Plus (6 ml, 500 mg masy na kolumnę), celem wyodrębnienia związków organicznych. Ekstrakt przepuszczano przez kolumnę kondycjonowaną wstępnie metanolem (45 min.). Frakcję eluowano 10 ml octanu etylu. Następnie frakcję wysuszono przy użyciu helu, ponownie rozpuszczono w 1 ml DCM i przeniesiono do fiolki.

Ostatnim etapem badań było poddanie analizie otrzymanych ekstraktów próbek odpadów stałych oraz ekstraktów SPE z wyciągów wodnych metodą chromatografii gazowej ze spektrometrią mas (GC-MS). Analizy wykonano na chromatografie gazowym firmy Agilent Techn. 5890 II wyposażonym w kolumnę kapilarną. Jako gaz nośny zastosowano hel. Program temperaturowy ustawiono na 50°C (izotermicznie przez 2 min.), narastając do 175°C z szybkością 10°C/min, do 225°C - 6°C/min, do 300°C - 4°C/min, końcowa temperatura 300°C - izotermicznie przez 20 min. Chromatograf gazowy był bezpośrednio sprzężony z detektorem masowym HP 5971A pracującym w trybie EI (Electron Impact), 70 eV. Wyniki, czyli widma masowe, całkowite chromatogramy jonowe (TIC) oraz chromatogramy jonowe (fragmentogramy), rejestrowano w trybie pełnego skanu i opracowywano komputerowo posługując się programem MS Data Analysis firmy Hewlett-Packard. Zakres przemiatania widma od 50 do 650 a.j.m. w trybie pełnego skanu. Uzyskane wyniki porównywano z danymi literaturowymi oraz typowymi dystrybucjami analizowanych grup związków opublikowanymi w literaturze. Wszystkie obliczenia wskaźników geochemicznych prowadzone były na polach powierzchni pików integrowanych ręcznie.

Związki nieorganiczne w odciekach ze spalonych odpadów stałych takie jak: chlorki, siarczki oraz metale ciężkie: bor, arsen, kadm, miedź, ołów, rtęć i cynk były badane w akredytowanym laboratorium i2 Analytical Limited Sp. z o.o. w Rudzie Śląskiej, Polska. Chlorki analizowano metodą kolorymetryczną z wykorzystaniem analizatora dyskretnego, natomiast pozostałe analizowano za pomocą plazmy sprzężonej indukcyjnie (ICP-OES). Wszystkie analizy przeprowadzono przy użyciu akredytacji ISO 17025 oraz procedury L039-PL.

Tabela 1. Lokalizacje oraz charakterystyka próbek.

Lokalizacja / Data	**Rodzaj próbek otrzymanych do badań laboratoryjnych**
Trzebinia / 24.04.2021r. oraz 24.11.2021r.	Próbki glebowe – próbki pobrane punktowo z miejsc na terenie składowiska oraz jego obrzeża (13 próbek); Próbki spalonych odpadów stałych – próbki pobrane punktowo z miejsc terenu składowiska, na którym zaobserwowano zapożarowanie odpadów stałych oraz ich różny typ (19 próbek); Próbki odcieków ze spalonych odpadów stałych – próbki otrzymane w wyniku przemywania zebranych wcześniej spalonych odpadów stałych (12 próbek).
wieś w okolicach Wrocławia / 20.05.2022r.	Próbki glebowe – próbki pobrane punktowo z miejsc na terenie składowiska oraz jego obrzeża (12 próbek); Próbki spalonych odpadów stałych – próbki pobrane punktowo z miejsc terenu składowiska, na którym zaobserwowano zapożarowanie odpadów stałych oraz ich różny typ (6 próbek).

3. Zagrożenia środowiska wynikające z pożarów na nielegalnych składowiskach odpadów

3.1 *Przyczyny pożarów na nielegalnych składowiskach odpadów*

Pożar na składowiskach odpadów stałych to jedno z najniebezpieczniejszych zdarzeń jakie może mieć miejsce na tego typu obszarach. Stanowi ono potencjalne zagrożenie dla pobliskiej infrastruktury, zdrowia mieszkańców oraz środowiska przyrodniczego. Przyczynami powstawania pożarów są między innymi: iskry pochodzące z maszyn pracujących na składowisku, niekontrolowane wyładowania atmosferyczne lub samozapłon (Øygard et al. 2014). Pożar może się rozprzestrzeniać w wyniku reakcji chemicznych wytwarzających ciepło, które oddziałuje na inne zalegające wokół odpady stałe. Innym czynnikiem jest gromadzący się metan. Na jego emisje ze składowiska mają wpływ takie czynniki jak: specyfikacja obszaru, rodzaj zalegającego odpadu stałego lub wilgotność. Do możliwych sytuacji, które mogą doprowadzić do pożaru nielegalnych składowisk należy zaliczyć także celowe podpalenie. Najczęstszym powodem tego typu działań jest chęć pozbycia się niechcianych odpadów stałych bez ich ewidencji, praktycznie bezkosztowo. Jest to coraz częściej spotykany na świecie nielegalny precedens.

3.2 *Konsekwencje pożarów na nielegalnych składowiskach odpadów*

Wyróżnia się trzy podstawowe kategorie środowiskowe dla konsekwencji pożarów na nielegalnych składowiskach (Morales et al., 2018; Powell et al., 2016). Pierwszą z nich jest sytuacja, w której podczas spalania odpadów część zanieczyszczeń przedostaje się do atmosfery poprzez powstanie gęstego, ciemnego dymu przenoszonego na setki metrów poza obszar epicentrum pożaru. Poziom substancji toksycznych uwalnianych do atmosfery jest zależny od wielkości pożaru, rodzaju odpadów stałych i warunków atmosferycznych podczas zdarzenia (Dąbrowska et al., 2023). Z badań przeprowadzonych przez Agencję Ochrony Środowiska (EPA) głównie emitowane są związki takie jak: tlenek węgla oraz dwutlenek (CO i CO_2), tlenki azotu (NOx), kwas solny (HCl), cyjanowodór (HCN), lotne związki organiczne (LZO), trwałe zanieczyszczenia organiczne (POPs), ketony, aldehydy oraz pyły zawieszone (https://www.epa.gov/clean-air-act-overview/air-pollution-current-and-future-challenges).

Następną konsekwencją pożaru jest zagrożenie dla wód podziemnych w rejonie nielegalnego składowiska odpadów. Przyczyną może być wymywanie zanieczyszczeń ze spalonych odpadów stałych poprzez opad atmosferyczny, a następnie infiltracja tak powstałych odcieków w głąb warstwy wodonośnej. Ostatnią kwestią jest zanieczyszczenie gleby wokół terenu objętego pożarem, co może prowadzić do kosztownych oraz długotrwałych negatywnych konsekwencji. Do najczęstszych zalicza się konieczność remediacji skażonej gleby (Cristaldi et al., 2017) oraz wyłączenia z użytku danego terenu na wiele miesięcy. Innym bardzo poważnym skutkiem pożarów na nielegalnych składowiskach odpadów jest zagrożenie dla zdrowia oraz życia człowieka. Wiele z zanieczyszczeń powstających podczas pożarów jest toksycznych, kancerogennych oraz mutagenicznych. Dodatkowo, mogą one prowadzić do podrażnień skóry, astmy, zawałów serca oraz niewydolności dróg oddechowych (Ifemeje et al., 2014).

3.3 *Przypadki pożarów nielegalnych składowiskach odpadów na świecie*

Sytuacje pożarów na nielegalnych składowiskach odpadów to nieustanny problem, z którym boryka się wiele krajów europejskich i światowych. Jednym z przykładów jest pożar w Grecji z 2006 roku, około 20 km od miasta Salonki. Na terenie składowiska znajdowały się głównie odpady komunalne oraz szpitalne. Pożar strawił większą część nielegalnego składowiska, a za jego zapłon uznaje się nagromadzenie metanu. Konsekwencją zdarzenia było zanieczyszczenie atmosferyczne oraz potencjalne skażenie gleby na pobliskim terenie (Øygard et al. 2014). Innym przykładem jest pożar nielegalnego składowiska opon w Hiszpanii. Zdarzenie wystąpiło 14 maja 2016 roku, a jego całkowite ugaszanie trwało trzy tygodnie. Spaleniu mogło ulec nawet kilkadziesiąt ton zużytych opon. W przeprowadzonych badaniach konsekwencji pożaru (Nadal et al., 2016) wykryto 3-5 pierścieniowe węglowodory aromatyczne. Przykład składowiska z Norwegii pokazuje, że ogień objął 10% całkowitej powierzchni nielegalnego składowiska. Zbadano tam powstające odcieki ze spalonych odpadów stałych (Lemieux et al., 2004). Stwierdzono podwyższone pH, przewodność oraz podwyższone stężenia metali ciężkich. Jednakże, ostatecznie stężenia te nie stanowiły długotrwałego zagrożenia dla środowiska przyrodniczego. Natomiast w Stanach Zjednoczonych po pożarze maty uszczelniającej składowisko, na którym znajdowały się rozdrobnione zużyte opony, dokonywano monitoringu ilości zanieczyszczenia dostającego się do atmosfery. Zaobserwowano bardzo wysokie stężenia WWA oraz pyłów zawieszonych $PM_{2.5}$ (Downard et al., 2015).

4. Wyniki i dyskusja

Przeprowadzone badania pozwoliły na zidentyfikowanie substancji organicznych wydzielających się podczas pożarów nielegalnych składowisk, gdzie zdeponowano odpady stałe o różnym pochodzeniu. W celu określenia potencjalnego zagrożenia pożarów nielegalnych składowisk odpadów na środowisko gruntowo-wodne oznaczono stężenia WWA, metylofenantrenów oraz ich wskaźniki diagnostyczne w glebach i próbkach spalonych odpadów stałych. Natomiast w otrzymanych odciekach z przemywania spalonych odpadów stałych wykryto stężenia antropogenicznych organicznych fosforanów oraz związków nieorganicznych. Dodatkowo w celu ocenienia zagrożenia dla zdrowia człowieka określono wskaźniki toksyczności WWA. Związkiem odniesienia do obliczeń stosuje się benzo(a)piren (BaP), jako odnośnik siły rakotwórczości równoważnika toksyczności (TEF) innych związków. Gdy wynosi on poziom 0 oznacza, że związek nie jest rakotwórczy. Równoważnik toksyczności RTBaP (TEQ) jest sumą stężeń wyznaczonych WWA i ich względnych współczynników toksyczności (i) (Nisbet et al., 1992):

$$\text{(i)}\quad RTBaP = 0{,}001 \times [Na] + 0{,}001 \times [Acy] + 0{,}001 \times [Ace] + 0{,}001 \times [Fl] + 0{,}001 \times [Fen] + 0{,}01 \times [An] + 0{,}001 \times [Flu] + 0{,}001 \times [Pir] + 0{,}1 \times [BaA] + 0{,}01 \times [Ch] + 0{,}1 \times [BbF] + 0{,}1 \times [BkF] + 1 \times [BaP] + 5 \times [DBA] + 0{,}1 \times [BghiP] + 0.1 \times [IP]$$

Obliczono również równoważnik mutagenności (MEQ) i kancerogenności (TCDD-TEQ). MEQ określono jako suma stężeń poszczególnych WWA i ich względnych współczynników mutagenności (ii) oraz TCDD-TEQ, jako względnych współczynników kancerogenności (iii) (Rogula-Kozłowska et al., 2013):

(ii) $\mathrm{MEQ} = 0{,}00056 \times [\mathrm{Acy}] + 0{,}082 \times [\mathrm{BaA}] + 0.017 \times [\mathrm{Ch}] + 0.25 \times [\mathrm{BbF}] + 0{,}11 \times [\mathrm{BkF}] + 1 \times [\mathrm{BaP}] + 0{,}31 \times [\mathrm{IP}] + 0{,}29 \times [\mathrm{DBA}] + 0{,}19 \times [\mathrm{BghiP}]$

(iii) $\mathrm{TCDD\text{-}TEQ} = 0{,}000025 \times \mathrm{BaA} + 0{,}00020 \times [\mathrm{Ch}] + 0{,}000354 \times [\mathrm{BaP}] + 0{,}00110 \times [\mathrm{IP}] + 0{,}00203 \times [\mathrm{DBA}] + 0{,}00253 \times [\mathrm{BbF}] + 0{,}00487 \times [\mathrm{BkF}]$

Negatywny wpływ WWA wyrażono za pomocą stosunków WWA uważanych za kancerogenne do sumy wszystkich oznaczanych WWA, gdzie im wartość jest bardziej zbliżona do 1, tym WWA stanowią większe zagrożenie dla populacji (iv):

(iv) $\Sigma \mathrm{WWA}_{\mathrm{carc}}/\Sigma \mathrm{WWA} = ([\mathrm{BaA}] + [\mathrm{BaP}] + [\mathrm{BbF}] + [\mathrm{BkF}] + [\mathrm{Ch}] + [\mathrm{DBA}] + [\mathrm{IP}]) / ([\mathrm{SWWA}])$

4.1 Stężenia WWA w glebie i próbkach spalonych odpadów stałych

W analizowanych próbkach wykryto szereg WWA (Figura 3) tj.: naftalen (N) ($m/z = 128$), acenaften (Ace) ($m/z = 154$), acenaftylen (Acy) ($m/z = 152$), fluoren (F) ($m/z = 166$), fenantren (P) ($m/z = 178$), antracen (A) ($m/z = 178$), fluoranten (Fl) ($m/z = 202$), piren (Py) ($m/z = 202$), benzo(ghi)fluoranten (BghiFl) ($m/z = 228$), benzo(a)antracen (BaA) ($m/z = 228$), chryzen (Ch) ($m/z = 228$), benzo(c)fenantren (BcPhe) ($m/z = 252$), benzo(b + k)fluoranten (Bb + kF) ($m/z = 252$), benzo(a)fluoranten (BaF) ($m/z = 252$), benzo(c)fluoranten (BcF) ($m/z = 252$), benzo(a)piren (BaP) ($m/z = 252$), benzo(e)piren (BeP) ($m/z = 252$), perylen (Pe) ($m/z = 252$), indeno[1,2,3-cd]piren (IP) ($m/z = 276$), benzo(ghi)perylen (BghiP) ($m/z = 276$) oraz dibenzo(a + h)antracen (DB) ($m/z = 278$).

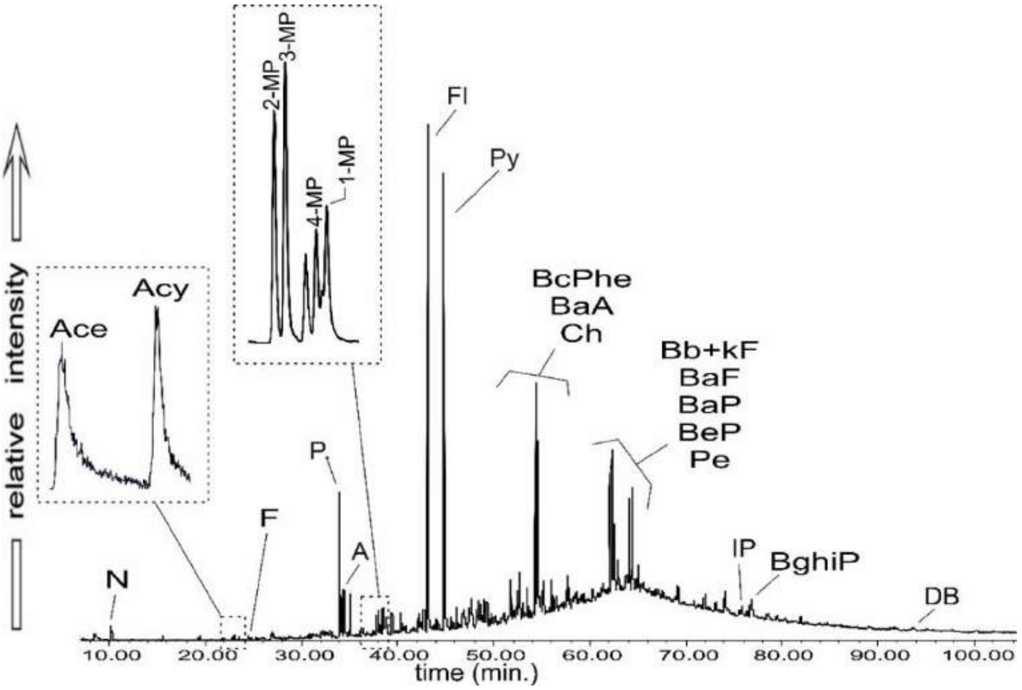

Fig. 3. Dystrybucja niepodstawionych WWA w ekstrakcie próbki glebowej S5S ($m/z = 128+152+154+166+178+202+228+276+278$) oraz chromatogram jonowy metylofenantrenów ($m/z = 192$).

Wyniki sumy stężeń WWA (ppm/g gleby) ze składowisk wykazują stosunkowo większą ich zawartość w próbkach glebowych niż w próbkach spalonych odpadów stałych najprawdopodobniej ze względu na silną akumulację w glebie zanieczyszczeń spowodowaną sorpcją WWA. Wysokie stężenia w próbkach glebowych, a zwłaszcza: WR2G, WR5G, WR12G (Trzebinia) oraz S1S, S5S, S8S, S9S i S10S (wieś w okolicach Wrocławia) mogą wskazywać na miejsca, w których pobliżu występowały największe epicentra pożarów na nielegalnych składowiskach odpadów, co doprowadziło do wysokiej emisji WWA do środowiska. Wyjątkowo wysokie zawartości WWA stwierdzono w próbkach spalonych odpadów z Trzebini WR4O (212.045 ppm) i WR6O (150.549 ppm), co może świadczyć o intensywnym pożarze w tych miejscach. Inną przyczyną występowania wysokich stężeń w tych próbkach spalonych odpadów może być ograniczone rozproszenie zanieczyszczeń z ich pierwotnego źródła (Wang et al., 2011). Niższe ∑ stężeń WWA w próbkach spalonych odpadów stałych mogą wskazywać na niższą temperaturę zapożarowania, a co za tym idzie mniej intensywny proces spalania.

Stwierdzono większą zawartość procentową (Figura 4) najlżejszych 2 i 3 pierścieniowych WWA (N, P, A, Ace, Acy i F) w próbkach spalonych odpadów stałych niż w próbkach glebowych. Antracen, który, jak się uważa powstaje podczas niepełnego spalania (Simoneit, 1998), został wykryty w podwyższonych stężeniach w większej liczbie próbek spalonych odpadów stałych. Natomiast w próbkach glebowych lepiej zachowały się 5-pierścieniowe WWA (BcPhe, Bb+kF, BaF, BcF, BaP, BeP, Pe oraz DB), co może być spowodowane mniejszą lotnością tych związków o wysokich masach cząsteczkowych podczas tego typu pożarów.

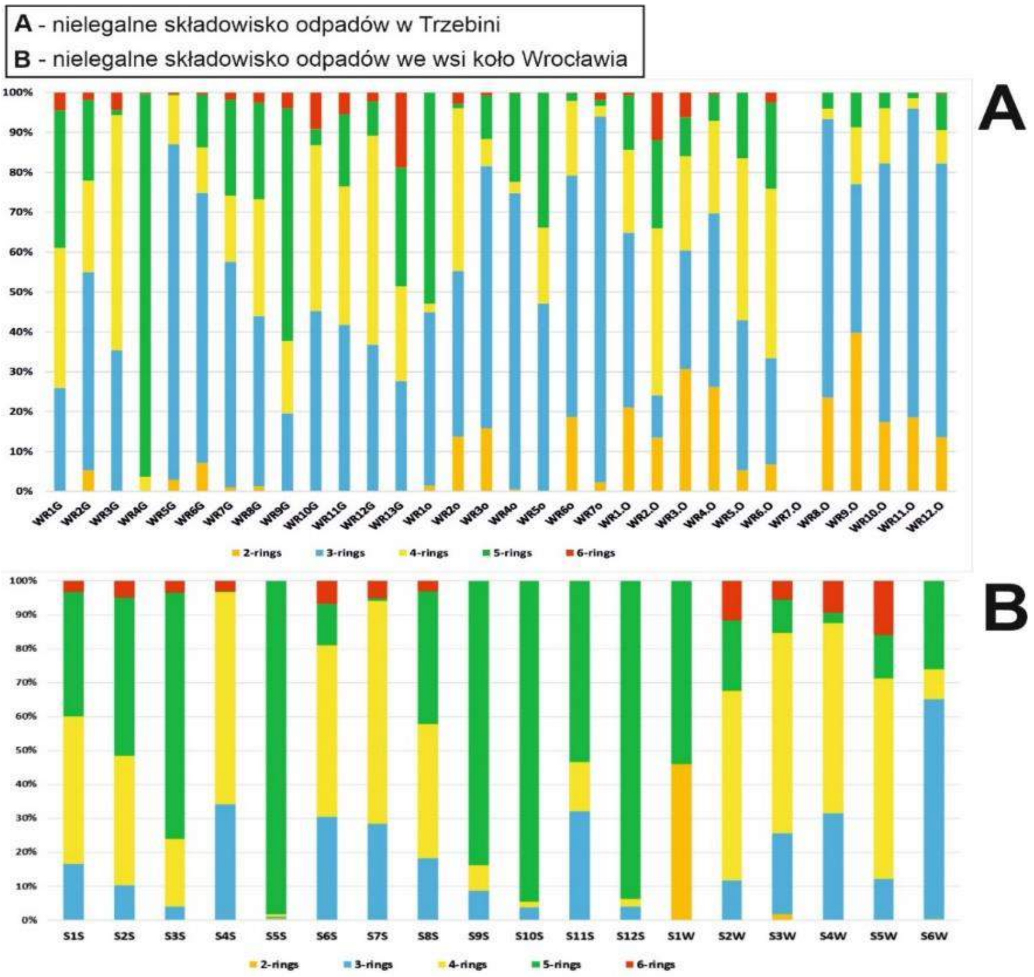

Fig. 4. Względna procentowa 2-6 pierścieniowych WWA w próbkach.

Jedną z najważniejszych kwestii, którą należało zbadać, było określenie źródła zanieczyszczeń na badanych terenach, które są obszarami o dużym nasyceniu przemysłem współczesnym lub dawnym (Trzebinia) lub rolniczym (wieś pod Wrocławiem). W obu przypadkach użytkowanie terenu wiąże się z emisją zanieczyszczeń organicznych. Jako potencjalne źródła WWA można wskazać ruch uliczny, spalanie paliw kopalnych w pobliskich zakładach/domach prywatnych, działalność rolniczą związana z użytkowaniem ciężkiego sprzętu lub opisywany pożar na nielegalnych składowiskach odpadów stałych. W celu identyfikacji typu źródła emisji wykorzystano współczynniki diagnostyczne WWA (Figura 5). Zestawiono ze sobą trzy rodzaje wskaźników diagnostycznych WWA: fluorantenu i pirenu do: (i) antracenu i fenantrenu, (ii) benzo(a)antracenu i chryzenu oraz (iii) indeno[1,2,3-cd]pirenu i benzo(g,h,i)perylenu. Zarówno w przypadku pożaru na nielegalnym składowisku w Trzebini oraz we wsi koło Wrocławia próbki glebowe wykazują wartości zbliżone i grupują się w polu diagramu odpowiadającemu spalaniu biomasy lub węgla kamiennego jako źródło WWA (Figura 5). Oznacza to, iż materiałem wyjściowym mogła być biomasa pochodzenia lądowego (tj. z roślin naczyniowych) lub odpady stałe pochodzące z tego surowca tj.: tekstylia, drewno, czy papier. Natomiast w przypadku próbek spalonych odpadów stałych zaobserwowano różne trendy. Próbki odpadów ze składowiska we wsi koło Wrocławia wykazują zbliżoną tendencję rozmieszczenia na diagramach, co ich glebowe odpowiedniki. Może to potwierdzać fakt występowania i spalania tam odpadów, m. in.: tekstylnych, czy tworzyw sztucznych, które były widoczne makroskopowo na terenie składowiska. Nie wykryto w tych próbkach najcięższych WWA (Rykała et al., 2023), co może wiązać się z lokalizacją tego składowiska z dala od ruchu ulicznego i otaczającymi go polami uprawnymi. Jedynym możliwym źródłem zanieczyszczeń organicznych w przypadku tego terenu mógłby być ciężki sprzęt rolniczy wykorzystujący silniki diesla, ale w takim przypadku punkty grupowałyby się w polu odpowiadającym spalaniu ropy naftowej.

Próbki spalonych odpadów stałych z nielegalnego składowiska odpadów w Trzebini wykazują odmienną tendencję. Charakterystyczną cechą dla tych próbek jest ogromny rozrzut oznaczeń. Może to świadczyć o dużej różnorodności spalanego odpadu stałego na tym terenie, co potwierdzają także wcześniejsze obserwacje tego składowiska. Część próbek widoczna jest w przedziale spalania biomasy i węgla kamiennego, co może potwierdzać spalanie tego typu odpadów stałych, które zaobserwowano makroskopowo i zebrano z ww. składowiska. Jednocześnie kilka próbek znajduje się w obszarze spalania ropy naftowej. Prawdopodobnie jest to potwierdzenie brania udziału w pożarze odpadów ropopochodnych, tj.: czarnych gum oraz zużytych opon, które również zostały zebrane podczas badań terenowych. Dodatkowym faktem jest wykrycie najcięższych WWA (IP, BghiP), które występują najczęściej w spalaniu i użytkowaniu odpadów ropopochodnych (Rogge et al., 1993).

Powyższe wyniki wskazują, iż pożary na nielegalnych składowiskach odpadów miały istotny wpływ na zanieczyszczenie pobliskiego środowiska przyrodniczego. Jednakże, należy również zwrócić uwagę na aspekt wieloletniego zanieczyszczania terenów czynnikami zewnętrznymi. Na terenie Trzebini przez wiele lat były zlokalizowane silne emitory, w tym zakłady przemysłowe, m.in. Kopalnia Węgla Kamiennego Siersza, zakład tworzyw ogniotrwałych „Stella", rafineria Trzebinia (obecnie ORLEN Południe S.A.). Dodatkowo na północ od nielegalnego składowiska znajdują się tory kolejowe, przez które przejeżdżały dawne lokomotywy spalinowe oraz parowozy (linia kolejowa istnieje od drugiej połowy XIX w.). Kolejnym aspektem jest pobliska droga, przez którą dziennie przejeżdżają samochody zdzierając opony, emitując cząstki zanieczyszczeń i spalin do środowiska. Substancje emitowane z wszystkich tych źródeł mogą akumulować się na stałe w glebie, która stanowi swoiste „archiwum zanieczyszczeń”.

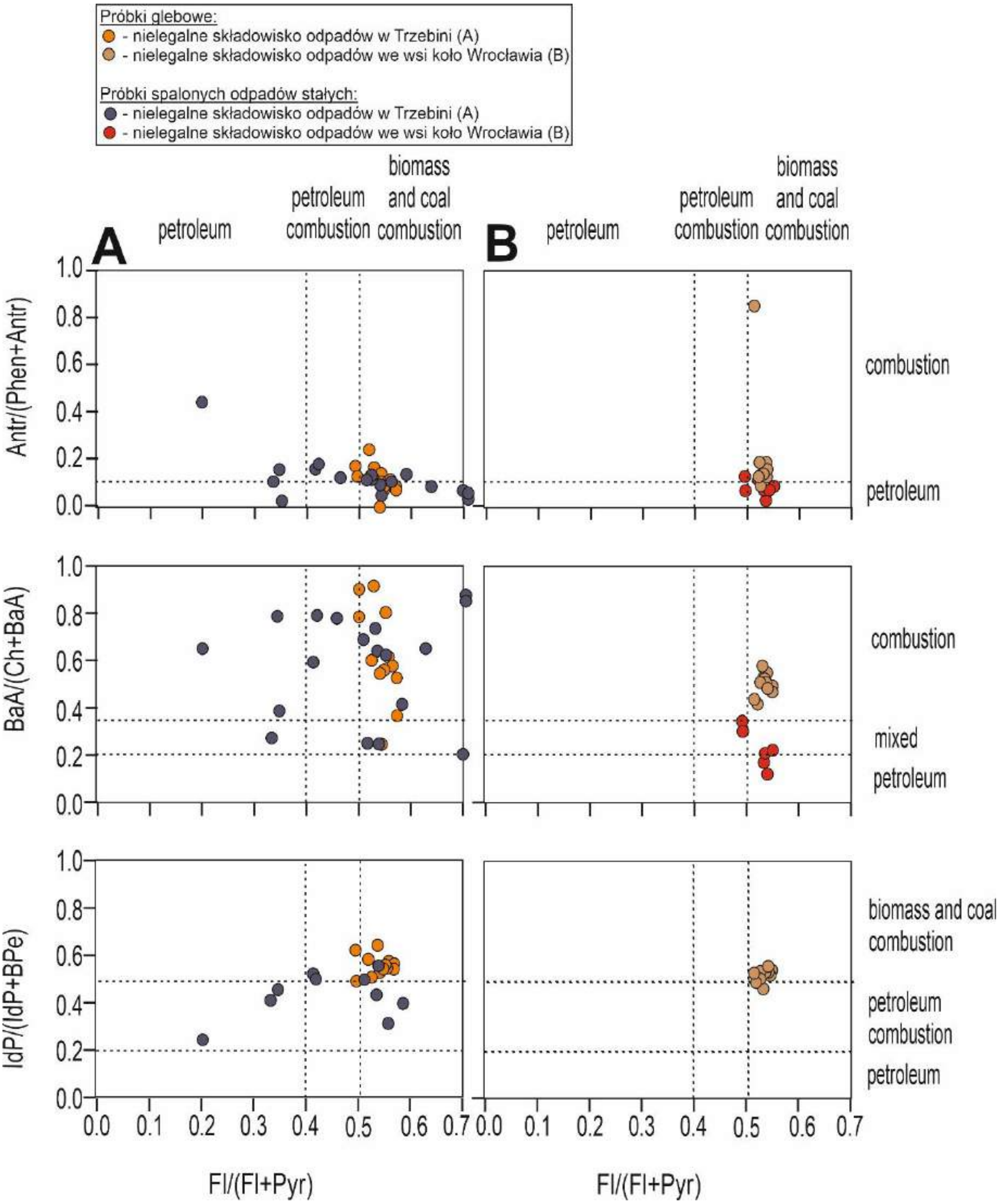

Fig. 5. Wykresy diagnostyczne WWA w glebach oraz spalonych odpadach stałych. A – antracen, P – fenantren, Fl – fluoranten, Py – piren, BaA – benzo(a)antracen, Ch – chryzen, IP – indeno(1,2,3-cd)piren, BghiP – benzo(ghi)perylene (Charriau et al., 2009).

Podwyższone poziomy zawartości WWA w niektórych badanych próbkach glebowych (WR5G - 149.558 ppm, WR12G - 184.611 ppm w Trzebini; S5S - 853.532 ppm, S9S - 167.742 ppm we wsi w okolicach Wrocławia) wskazują na potrzebę specjalistycznej rekultywacji na tego typu terenach, jak po pożarach nielegalnych składowisk odpadów (Gan et al., 2009). Konsekwencją pożarów nielegalnych składowisk może być wieloletni brak możliwości inwestycyjnych na danym terenie, który nie będzie nadawał się pod jakąkolwiek zabudowę. Tak silne zanieczyszczenie obszaru wymaga usunięcia i oczyszczenia dużej warstwy powierzchni gleby, zwykle metodami *ex-situ*, a co za tym idzie - poniesienia ogromnych kosztów.

Dodatkowo stężenia WWA w próbkach z terenów po pożarze nielegalnych składowisk wykazują dużo wyższe poziomy w porównaniu z próbkami z niektórych lokalizacji miast w Aglomeracji Śląskiej: Katowice, Gliwice, Sosnowiec lub Zabrze (Kozielska et al., 2014; Fabiańska et a., 2015). Oznacza to znaczący wpływ katastrofy środowiskowej, jaką jest pożar składowiska na zanieczyszczenie środowiska przyrodniczego.

Wskaźnik MEQ w obu przypadkach pożarów (poza próbką glebową S5S) (Tabela 2 i 3) nie wykazywał zagrożenia dla mieszkańców znajdujących się w dalszej odległości od zapożarowania. Maksymalna wartość $\sum WWA_{carc}/\sum WWA$, jaką zaobserwowano w badanych próbkach, wynosiła 0.487. Oznacza to średni stosunek zagrożenia kancerogennych WWA dla zdrowia człowieka, gdzie najwyższy stosunek zagrożenia wynosi 1. Jednakże, przy ogólnie wysokim poziomie stężeń WWA w badanych glebach, należy zachować szczególne środki ochrony osobistej (strój ochronny, rękawiczki, maska) podczas prac na tych terenach, szczególnie w sytuacji, gdy ogólny poziom WWA jest wysoki.

Nie stwierdzono obecności WWA w badanych próbkach odcieków ze spalonych odpadów stałych, co wynika z ich słabej rozpuszczalności w wodzie.

Tabela 2. Wskaźnikami toksyczności środowiskowej z nielegalnego składowiska odpadów w Trzebini (ppm).

Sample code	PAH sum ppm/g	RTBaP	∑PAHcarc/∑PAH	MEQ	TCDD-TEQ	BaPE ppm/g	Sample code	PAH sum ppm/g	RTBaP	∑PAHcarc/∑PAH	MEQ	TCDD-TEQ	BaPE ppm/g
WR1G	26.174	5.042	0.410	3.198	0.01	2.53	WR12G	184.611	23.513	0.417	19.836	0.05	15.33
WR2G	89.850	9.366	0.234	6.211	0.02	4.87	WR6O	150.549	7.894	0.081	4.766	0.01	4.05
WR1O	7.795	0.080	0.066	0.098	-	0.06	WR13G	9.981	5.661	0.353	1.566	-	1.37
WR3G	37.884	5.559	0.393	4.231	0.01	3.31	WR7O	28.065	0.238	0.032	0.278	-	0.13
WR4G	0.964	0.139	0.440	0.164	-	0.13	WR1.O	50.458	2.664	0.102	2.938	0.01	2.46
WR2O	38.050	2.277	0.178	2.700	0.01	2.05	WR2.O	11.190	1.115	0.241	1.336	-	0.92
WR5G	149.558	4.127	0.046	2.320	-	1.89	WR3.O	8.927	0.541	0.129	0.661	-	0.42
WR6G	60.340	5.015	0.096	2.339	-	2.09	WR4.O	36.172	1.592	0.086	1.647	-	1.45
WR7G	33.757	3.783	0.159	2.267	-	1.93	WR5.O	27.402	1.592	0.157	1.792	-	1.50
WR3O	43.909	1.247	0.019	0.348	-	0.29	WR6.O	33.750	3.886	0.260	4.257	0.01	3.62
WR4O	212.045	0.465	0.010	0.483	-	0.17	WR7.O	-	-	-	-	-	-
WR8G	35.083	5.464	0.270	4.107	0.01	3.43	WR8.O	25.866	0.345	0.032	0.398	-	0.29
WR9G	7.981	2.339	0.391	1.065	-	0.89	WR9.O	10.504	0.447	0.078	0.516	-	0.40
WR10G	25.744	11.134	0.320	3.214	0.01	3.06	WR10.O	21.705	0.313	0.042	0.325	-	0.26
WR5O	34.022	0.145	0.022	0.139	-	0.10	WR11.O	74.640	0.386	0.013	0.341	-	0.27
WR11G	19.950	7.285	0.330	2.186	-	2.02	WR12.O	19.174	0.606	0.060	0.632	-	0.56

Tabela 3. Wskaźnikami toksyczności środowiskowej z nielegalnego składowiska odpadów we wsi koło Wrocławia (ppm).

Sample code	PAH sum ppm/g	RTBaP	∑PAHcarc/∑PAH	MEQ	TCDD-TEQ	BaPE ppm/g	Sample code	PAH sum ppm/g	RTBaP	∑PAHcarc/∑PAH	MEQ	TCDD-TEQ	BaPE ppm/g
S1S	88.747	34.701	0.372	10.454	0.03	9.60	S10S	101.411	57.447	0.411	13.691	0.05	13.18
S2S	12.607	10.464	0.454	2.003	0.01	2.18	S11S	15.308	11.516	0.487	2.699	0.01	2.60
S3S	7.758	4.441	0.455	1.375	-	1.26	S12S	72.240	31.656	0.378	7.693	0.03	7.40
S4S	2.483	0.725	0.421	0.437	-	0.35	S1W	13.417	0.745	0.304	0.778	-	0.60
S5S	853.532	246.366	0.344	75.176	0.27	66.92	S2W	3.387	0.344	0.234	0.403	-	0.33
S6S	20.049	12.255	0.415	2.465	0.01	2.54	S3W	9.330	0.309	0.087	0.372	-	0.28
S7S	4.117	0.273	0.244	0.317	-	0.25	S4W	9.013	0.562	0.163	0.674	-	0.52
S8S	86.884	43.879	0.366	10.143	0.04	9.88	S5W	2.648	0.183	0.253	0.252	-	0.17
S9S	167.742	61.842	0.355	16.897	0.06	15.62	S6W	8.144	0.676	0.252	0.842	-	0.62

4.2 Stężenia MPI w glebie i próbkach spalonych odpadów stałych

Metylofenantreny (*m/z* = 192) (Figura 3) wykryto w większości próbek glebowych i spalonych odpadów stałych. Wartości MPI-1 wykorzystano do obliczenia współczynnika refleksyjności witrynitu R_c spalanych paliw kopalnych w oparciu o wzór zaproponowany przez Radkego oraz poziomu ich przeobrażenia w wyniku temperatury pożaru (Radke 1988). Próbki o wskaźniku R_c powyżej 2.0 odpowiadają silnie przekształconym termicznie substancjom organicznym (Rykała et al., 2022). Wysokie wyniki R_c, ponad 2.0, zaobserwowano w próbkach glebowych z obu terenów badawczych, co może wskazywać po raz kolejny na oddziaływanie temperatury podczas pożaru na składowisku. Natomiast wskaźnik R_c w próbkach spalonych odpadów stałych występował w większości przypadków poniżej 2.0. Sugeruje to miejsca, w których dochodziło do niecałkowitego spalania, najprawdopodobniej przy zmniejszonym dostępie do tlenu. Średnie wartości MPI-3 i MPI-1 mogą odpowiadać wysokotemperaturowym przemianom termicznym próbek. Nie zaobserwowano wyników R_c w przedziale 0.7-0.9, który mógłby wskazywać na dopływ zanieczyszczeń ze spalania węgla w domach prywatnych i z ruchu samochodowego lub odpady ropo- i węglopochodne nieprzeobrażone termicznie (Radke 1986; Fabiańska et al., 2012). Wyniki te wskazują, że zanieczyszczenia organiczne obecne w badanych próbkach związane są z pożarem nielegalnego składowiska odpadów. Większość badanych próbek mieści się w przedziale mieszanym petro/pirogenicznym wartości MPI-1 i MPI-3 (Figura 6). Jednakże część wskazuje na pochodzenie petrogeniczne, które może być spowodowane spalaniem w niskiej temperaturze oraz zmniejszonym dostępem tlenu. Liniowa zależność MPI-1 i MPI-3 może świadczyć o pochodzeniu metylofenentrenów w glebie z jednego źródła, tj. z pożaru składowiska.

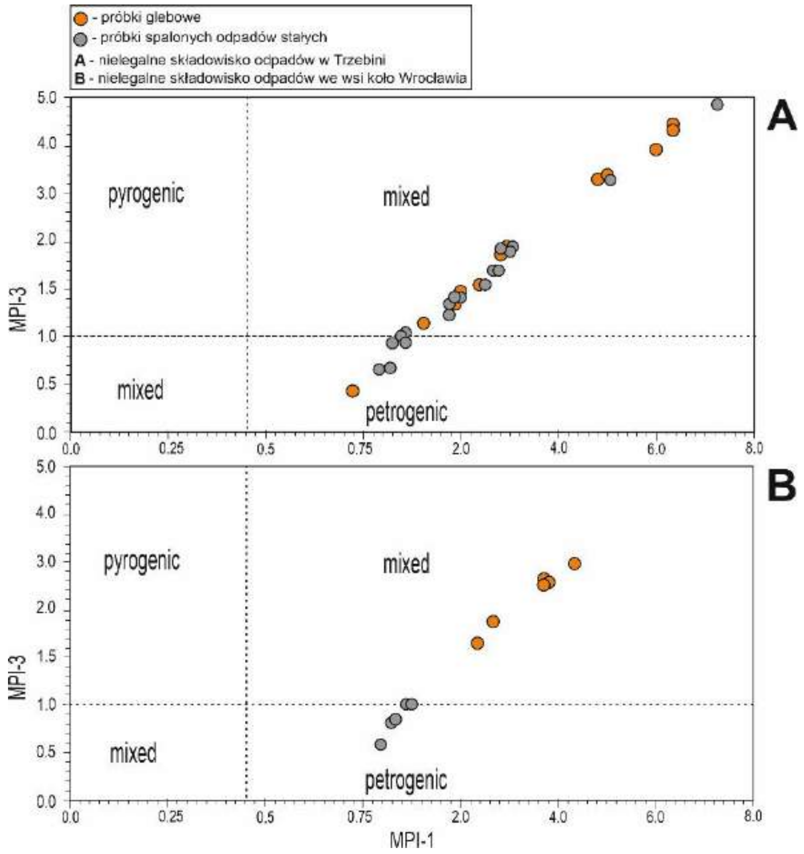

Fig. 6. Diagram diagnostyczny MPI-1 vs MPI-3 (Nádudvari et al., 2015).

4.3 Związki fosforoorganiczne w odciekach spalonych odpadów stałych

W ośmiu odciekach ze spalonych odpadów stałych wykryto trzy związki fosforoorganiczne (Figura 7): TCPP – fosforan tris(2-chloroizopropylu), TPP – fosforan trifenylu i TCEP – fosforan tris(2-chloroetylu). Każdy z tych związków posiada różne zastosowanie w przemyśle (Hsin-Chieh et al., 2022; Fabiańska et al., 2018):

- TCPP – dielektryk, środek ogniochronny m.in. pianek poliuretanowych;
- TPP – stosowany jest najczęściej jako plastyfikator, dodawany jest również do tworzyw sztucznych w celu zwiększenia elastyczności i łatwiejszej obróbki;
- TCEP – posiada doskonałe właściwości zmniejszające palność materiałów dzięki zawartości fosforu i chloru.

Związki fosforoorganiczne są stosunkowo dobrze rozpuszczalne w wodzie. Oznacza to, że stanowią potencjalne zagrożenie dla skażenia wód podziemnych na obszarach składowisk (Regnery et al., 2011; Huang et al., 2022). TCPP wykryto w odciekach spalonych czarnych gum, gąbek oraz tapet. Jednakże, jego największe stężenie wykryto w odciekach z próbek spalonych tekstyliów T8.L (0.037 µg/l) i T9.L (0.671 µg/l). Z kolei stężenie TPP było największe w odciekach ze spalonych tapet T7.L (0.024 µg/l). TCEP dominowały w dwóch próbkach odcieków ze spalonych czarnych gum T4.L (0.902 µg/l) i T5.L (1.366 µg/l). Nie wykryto żadnych OPEs w odciekach ze spalonych zużytych opon. Należy wspomnieć, iż nielegalne składowiska odpadów nie posiadają żadnego zabezpieczenia podłoża przed infiltracją odcieków w głąb gleby, co dodatkowo zwiększa ryzyko zanieczyszczenia. Dla człowieka są one niebezpieczne ze względu na drażniące działania na skórę, oczy oraz należą do związków kancerogennych.

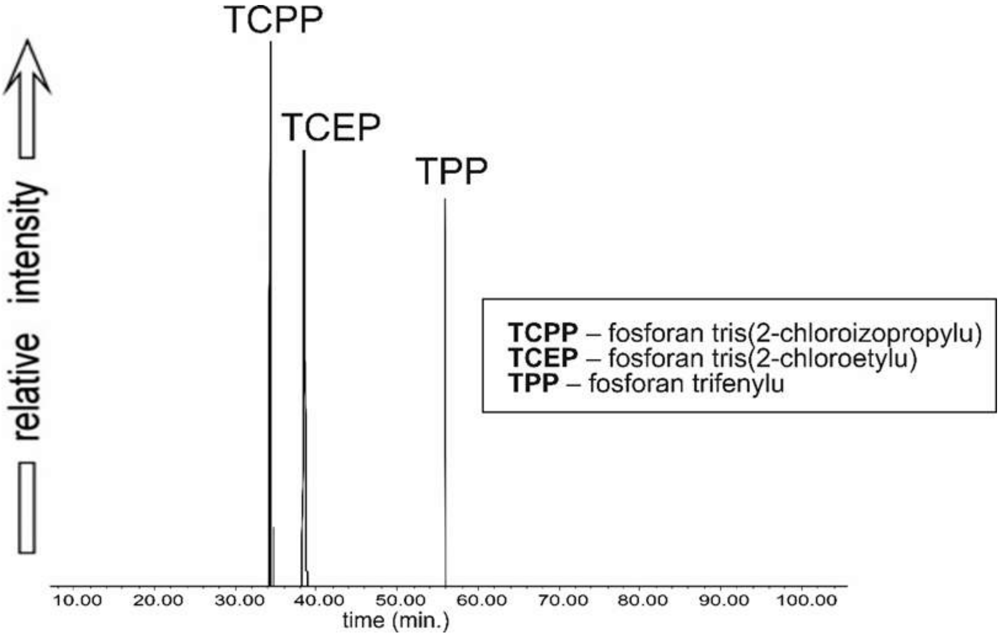

Fig. 7. Dystrybucja fosforanów organicznych w próbce odcieku T9.L ze spalonego odpadu stałego.

4.4 Związki nieorganiczne w odciekach spalonych odpadów stałych

Badane odcieki spalonych odpadów stałych były najbardziej zanieczyszczone przez jony takie jak siarczany i chlorki. Spośród metali ciężkich największe stężenie miał cynk (Tabela 4). Najwyższe stężenia zanieczyszczeń zaobserwowano w próbkach WR5.O i WR8.O. Są to głównie próbki spalonych czarnych gum oraz tekstyliów. Zawartości siarczków w tych próbkach przekraczały 1000 mg/l oraz chlorków odpowiednio: 85 i 320 mg/l. Próbka WR5.O miała również wysokie stężenie cynku 100 mg/l, natomiast WR8.O ponad 50 mg/l. Stężenia pozostałych badanych jonów: arsenu, boru, ołowiu, kadmu oraz miedzi były stosunkowo niskie w badanych próbkach odcieków (Tabela 4). Może to być związane z kilku czynnikami. Po pierwsze, badania prowadzono na składowiskach, które w przeważającej masie gromadziły odpady organiczne, stąd znikoma zawartość metali ciężkich w badanych odciekach. Metale te mogą jedynie pochodzić z rusztowania znajdującego się wewnątrz zużytych opon lub beczek metalowych w przypadku magazynowania w nich odpadów stałych. Dodatkowo, nie można stwierdzić, że w efekcie wpływu temperatury z czystych metali tworzą się rozpuszczalne ich formy. Najprawdopodobniej w efekcie pożaru metale lub sole przeszły w formy tlenkowe, które w większości są słabo rozpuszczalne w wodzie.

Odcieki powstające z przemywania spalonych czarnych odpadów gumowych i opon charakteryzowały się ciemno czarnym kolorem. Było to najprawdopodobniej spowodowane powstałą sadzą w procesie spalania tych odpadów stałych na składowisku. Takie same obserwacje zauważono w badaniach w Norwegii (Lemieux et al., 2004).

Tabela 4. Wyniki analiz chemicznych.

Unit No	**SO_4^{-2} [mg/l]**	**Cl^- [mg/l]**	**As [µg/l]**	**B [mg/l]**	**Cd [µg/l]**	**Cu [µg/l]**	**Pb [µg/l]**	**Zn [mg/l]**
WR1.O	239.0	13.0	64.0	0.6	28.0	12.0	12.0	12.0
WR2.O	534.0	38.0	82.0	1.0	0.1	4.9	13.0	1.9
WR3.O	397.0	8.1	85.0	1.1	0.4	70.0	15.0	1.6
WR4.O	255.0	76.0	59.0	3.1	1.5	50.0	9.6	2.9
WR5.O	1670.0	83.0	9.0	4.6	18.0	760.0	41.0	100.0
WR6.O	121.0	0.8	7.0	0.1	27.0	83.0	30.0	13.0
WR7.O	20.8	30.0	7.0	0.1	0.2	150.0	12.0	0.85
WR8.O	1240.0	320.0	14.0	0.4	35.0	300.0	13.0	56.0
WR9.O	43.5	2.7	8.0	0.1	4.6	37.0	110.0	2.9
WR10.O	220.0	16.0	6.0	0.2	0.5	68.0	16.0	30.0
WR11.O	58.2	15.0	10.0	0.1	0.1	20.0	6.7	0.22
WR12.O	17.9	20.0	35.0	0.1	0.9	59.0	33.0	0.25

W porównaniu do odcieków uzyskiwanych z legalnych składowisk odpadów zlokalizowanych w południowej Polsce (Dąbrowska i in., 2019), wartości zanieczyszczeń wymywanych odpadów stałych z Trzebini charakteryzują się mniejszą przewodnością elektrolityczną, ponieważ w odciekach z legalnych składowisk przewodność dochodzi do 30 mS/cm. Odcieki z Trzebini cechuje również mniejsza zawartość chlorków, gdyż w odciekach wartości te dochodzą do 2000 mg/l oraz żelaza (nawet 10 razy mniej niż w typowych odciekach) (Dąbrowska i in., 2022). W badanych próbkach zaobserwowano natomiast wyższą zawartość siarczanów. W przypadku niektórych odcieków z odpadów przemysłowych zawartość arsenu dochodzi nawet do 0.3mg/l, czego nie zaobserwowano w badanych próbkach. Można stwierdzić, iż otrzymane odcieki z wymywania spalonych odpadów stałych w Trzebini wykazują niższy poziom stężeń badanych metali i jonów.

5. Podsumowanie

Pożary na nielegalnych składowiskach odpadów stanowią poważne zagrożenie dla środowiska gruntowo-wodnego oraz zdrowia mieszkańców ze względu na ich nieprzewidywalny przebieg oraz brak wiedzy na temat odpadów stałych, jakie znajdują się na danym terenie. Obszary te dodatkowo nie są niczym zabezpieczone od podłoża, co prowadzi do infiltracji substancji z zalegających spalonych odpadów stałych i migracji związków organicznych, nieorganicznych w odciekach do warstwy wodonośnej. Konsekwencją pożarów jest również migracja zanieczyszczeń do atmosfery, które można zmierzyć w znacznej odległości od epicentrum pożaru składowiska.

Na potrzeby badań przeprowadzono analizy poziomów stężeń wielopierścieniowych węglowodorów aromatycznych, MPI, fosforanów organicznych oraz związków nieorganicznych w próbkach. Dokonano obliczeń wskaźników kancerogenności oraz mutagenicznośći WWA, które potwierdziły mniejsze zagrożenie dla zdrowia osób zamieszkujących dalsze tereny od epicentrum badanych miejsc pożarów, ale podwyższone dla potencjalnych pracowników oczyszczających teren. Wykazano potencjalne źródła i rodzaje zanieczyszczeń za pomocą wskaźników diagnostycznych WWA oraz MPI. Dodatkowo, określono dzięki nim potencjalnie możliwy rodzaj odpadu stałego jaki uległ zapożarowaniu na składowiskach.

Wyniki badanych próbek glebowych pochodzących z terenu nielegalnych składowisk odpadów po pożarze potwierdzają negatywny wpływ pożaru na środowisko. Miejsce potencjalnego pożaru nielegalnego składowiska odpadów oraz rodzaj odpadu zalegającego na nim ma wpływ na ostateczny poziom zanieczyszczenia pobliskiego terenu. Odpady pochodzenia ropopochodnego są istotnymi emitorami cięższych WWA, stanowiących substancje kancerogenne, co stanowi większe zagrożenia dla środowiska oraz zdrowia człowieka.

Zalecane jest prowadzenie stałego monitoringu terenów nielegalnych składowisk odpadów po pożarach pod względem potencjalnego wpływu zanieczyszczenia na środowisko przyrodnicze. Proponuje się pobór próbek glebowych z centrum, jak i otoczenia spalonego nielegalnego składowiska. Ma to określić siłę oddziaływania zanieczyszczeń i ustalić możliwą konieczność remediacji terenu celem uniknięcia wysokich kosztów w przyszłości. W przypadkach dużych obszarów nielegalnych składowisk odpadów, gdy nie jest możliwe ich szybkie usunięcie, zaleca się zamontowanie lizymetrów w celu stałego monitorowania zanieczyszczeń mogących przedostać się do warstwy wodonośnej. Dodatkowo proponuje się zakrycie odsłoniętych spalonych odpadów stałych folią nieprzemakalną oraz niepalną by zminimalizować oddziaływanie na otoczenie w postaci wymywania składników.

W ramach przyszłych badań dotyczących nielegalnych składowisk odpadów stałych po pożarze planuje się przebadanie gruntów na terenach, na których znajdowały się uprzednio spalone odpady. Pozwoli to określić możliwy długotrwały wpływ pozostałości zanieczyszczeń w środowisku i ich ciągłe oddziaływanie. Dodatkowo planowane jest przeprowadzanie kontrolowanych spalań wybranych rodzajów odpadów stałych celem określenia możliwych rodzajów zanieczyszczeń, jakie mogą powstać oraz w konsekwencji przedostać się do środowiska gruntowo-wodnego.

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Streszczenie rozprawy doktorskiej w języku angielskim

The increase in solid waste production is an ongoing problem around the world. Their number increases as the population increases. At the same time, illegal landfills are being created, which pose a potential threat to the environment and the health of the inhabitants of a given area. They are most often created in forests, on the outskirts of inhabited areas, or in private plots and vacant lots. The reasons for their creation include, among others: the lack of appropriate waste processing facilities or the desire to get rid of inconvenient waste cheaply.

One of the most serious dangers that may arise at illegal landfills is fire. This phenomenon may occur through spontaneous ignition, related to, among others, weather conditions, a chemical reaction of solid waste with oxygen, a spark from a machine operating in a landfill, or intentional ignition by third parties. Arson is usually done to get rid of solid waste that is expensive to dispose of quickly and cheaply. Data from the State Fire Service indicate that since 2012, the number of fires at waste collection sites in Poland has been increasing from 75 cases to 243 in 2018.

Solid waste that has undergone incomplete combustion during a fire becomes a new source of environmental pollution, often much more dangerous than substances originally deposited in a landfill. During rainfall, they are washed out from illegal landfills and the resulting leachates infiltrate deep into the ground. Depending on the geological structure of the substrate and the aquifer, the "cloud of pollutants" that forms moves in a manner specific to a given area. The quantity and quality of leachates produced, the rate of solid waste deposition in a specific area, and hydrogeological conditions have a significant impact on the extent of the spread of

pollutants. The consequences of such events may be long-term and costly contamination of the nearby soil and water environment and additional work related to monitoring groundwater in a given area.

The type and quantity of products from incomplete combustion of solid waste depend on the type of materials deposited. The most common substances include aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and their derivatives substituted with functional groups, e.g. phenols and chlorinated PAHs. The type of solid waste collected and burned also matters in the case of inorganic substances.

The presented research areas include the location: (i) in the southern part of Poland (Trzebinia) and (ii) in the southwestern part of Poland (village near Wrocław). In both cases, several dozen samples of soil and burned solid waste were collected. Additionally, using burnt solid waste in Trzebinia, their washing was simulated, resulting in leachates imitating the infiltration of water into the ground.

There are three basic environmental categories for the consequences of fires at illegal landfills. The first is a situation in which, during waste combustion, some of the pollutants enter the atmosphere through the formation of thick, dark smoke that spreads hundreds of meters beyond the fire's epicenter. The level of toxic substances released into the atmosphere depends on the size of the fire, the type of solid waste, and atmospheric conditions during the incident. Another consequence is the threat to groundwater in the area of the illegal landfill. The reason may be the washing out of burnt solid waste by atmospheric precipitation and the subsequent infiltration of the resulting leachate into the aquifer. The final issue is soil contamination around the fire area, which can lead to costly and long-term negative consequences. The most common ones include the need to remediate contaminated soil and exclude the area from use for many months. Another very serious consequence of fires at illegal landfills is the threat to human health and life. Many of the pollutants generated during fires are toxic, carcinogenic, and mutagenic. Additionally, they can lead to skin irritation, asthma, heart attacks, and respiratory failure.

The conducted research allowed for the identification of organic substances released during fires in illegal landfills where solid waste of various origins was deposited. To determine the potential threat of fires from illegal landfills to the soil and water environment, the concentrations of PAHs, methylphenanthrenes, and their diagnostic indicators were determined in soils and samples of burned solid waste. However, concentrations of anthropogenic organic phosphates and inorganic compounds were detected in the leachates obtained from washing burned solid waste. Additionally, to assess the risk to human health, PAH toxicity indicators were determined, such as RTBaP toxicity equivalent (TEQ), mutagenicity equivalent (MEQ) and carcinogenicity equivalent (TCDD-TEQ), and the negative effect of PAHs ($\Sigma WWA_{carc}/\Sigma WWA$).

The results of the sum of PAH concentrations (ppm/g of soil) from landfills show their relatively higher content in soil samples than in samples of burned solid waste, most likely due to the strong accumulation of pollutants caused by the fire. However, lower sums of PAH concentrations in samples of burned solid waste may indicate a lower ignition temperature and, consequently, a less intense combustion process. The results of the PAH diagnostic coefficients used for calculations indicate that a fire at illegal landfills had a potential impact on the pollution of the nearby natural environment. However, attention should also be paid to the aspect of long-term pollution of areas by external factors. The MEQ index in both fire cases (except for the S5S soil sample) did not indicate any threat to humans further away. The maximum value of $\sum PAH_{carc}/\sum PAH$ observed in the tested samples was 0.487. This means an average risk ratio of carcinogenic PAHs to human health, where the highest risk ratio is 1. However, with the generally high level of PAH concentrations in the tested soils, special personal protective equipment (protective clothing, gloves, mask) should be used when working in these areas, especially when overall PAH levels are high. There was no presence of PAHs in the tested samples of leachate from burnt solid waste, which is due to their low solubility in water.

During examing methylphenanthrenes, high R_c values over 2.0 were detected in soil samples from both study areas. This may once again indicate strongly accumulated organic pollutants in the soil in and around the landfill site, caused by the fire. However, the R_c index in samples of burned solid waste was in most cases around 2.0 and lower. This suggests places where incomplete combustion occurred, most likely due to reduced access to oxygen. However, the average values of MPI-3 and MPI-1 may correspond to high-temperature thermal transformations of the samples. There were no R_c results in the range of 0.7-0.9, which could indicate pollution from coal combustion in private homes and car traffic, or oil and coal-derived waste that has not been thermally transformed. These results indicate that organic pollutants present in the tested samples are related to the fire of an illegal landfill.

Three organophosphorus compounds were detected in eight leachates from incinerated solid waste: TCPP - tris(2-chloroisopropyl) phosphate, TPP - triphenyl phosphate, and TCEP - tris(2-chloroethyl) phosphate. Organophosphate compounds are relatively soluble in water. This means that they pose a potential threat to groundwater contamination in such areas. TCPP was detected in leachates from burnt black rubbers, sponges, and wallpapers. However, its highest concentration was detected in leachate from samples of burned textiles T8.L (0.037 µg/l) and T9.L (0.671 µg/l). In turn, the TPP concentration was the highest in leachates from burned T7.L wallpapers (0.024 µg/l). TCEP was dominant in two samples of leachate from burnt black rubbers, T4.L (0.902 µg/l) and T5.L (1.366 µg/l). No OPEs were detected in leachate from burnt waste tires. These substances are dangerous to humans because they irritate the skin and eyes and are carcinogenic.

The examined leachates from burnt solid waste were mostly contaminated with ions such as sulphates and chlorides. Among the heavy metals, zinc had the highest concentration. The highest concentrations of pollutants were observed in samples WR5.O and WR8.O. These are mainly samples of burnt black rubber and textiles. The sulphide contents in these samples exceeded 1000 mg/l and the chloride contents were 85 and 320 mg/l, respectively. Sample WR5.O also had a high zinc concentration of 100 mg/l, while WR8.O had more than 50 mg/l. The concentrations of the remaining heavy metals tested: arsenic, boron, lead, cadmium, and copper were relatively low in the tested leachate samples. Most likely, as a result of the fire, the salts transformed into oxide forms, most of which are poorly soluble in water. Additionally, it cannot be stated that soluble forms of metals are formed as a result of the fire of pure metals. Another issue is the negligible content of heavy metals in this type of solid waste samples tested. They may originate most likely from scaffolding inside used tires or aluminum barrels if solid waste is stored in them. It can be concluded that the leachates obtained from washing out incinerated solid waste in Trzebinia are of better quality than other leachates

Fires at illegal landfills pose a serious threat to the land and water environment and nearby residents due to their unpredictable course and lack of knowledge about the solid waste that is present in a given area. These areas are additionally not protected from the ground, which leads to the infiltration of substances from the accumulated burnt solid waste and the migration of organic and inorganic compounds in the leachates into the aquifer. A consequence of fires is also the migration of pollutants into the atmosphere, which can be found at a considerable distance from the epicenter of the landfill fire.

The location of a potential fire in an illegal landfill and the type of waste lying there influence the final level of contamination of the nearby area. Petroleum wastes are larger emitters of heavier PAHs, which pose greater threats to the environment and human health.

It is recommended to constantly monitor illegal waste dumping sites after fires in terms of the potential impact of pollution on the natural environment. It is proposed to collect soil samples from the center and surroundings of the burned illegal landfill. This is to determine the impact of pollution and determine the possible need to remediate the area to avoid high costs in the future. In cases of large areas of illegal waste dumps, when it is not possible to remove them quickly, it is recommended to install lysimeters to constantly monitor pollutants that may enter the aquifer.

As part of future research on illegal solid waste dumps after a fire, it is planned to examine land in areas where previously burned waste was located. This will allow us to determine the possible long-term impact of residual pollutants in the environment and their ongoing impact. Additionally, it is planned to carry out controlled incineration of selected types of solid waste to determine possible pollutants that may arise and, as a result, be released into the ground and water environment.

Publikacja 1

Causes, Types and Consequences of Municipal Waste Landfill Fires—Literature Review

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Review

Causes, Types and Consequences of Municipal Waste Landfill Fires—Literature Review

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Abstract: The amount of municipal waste produced worldwide has seen a significant increase in recent years. The need to store waste is a significant problem in the context of environmental threats and spatial development. Due to the fact that the easiest way to reduce the amount of waste is to incinerate it, and despite the fact that waste incineration plants have existed since the late 1800s, the amount of illegal waste burning and landfills has also increased. Subsurface landfill fires are particularly dangerous, as they can affect the structure of the landfill. Methane also plays an important role in fires as it is flammable and contributes to the spread of fire. In addition, the leachate from incinerated waste is much more dangerous than the leachate from waste in its natural state. The effluents from incinerated waste include heavy metals and persistent organic pollutants, as well as sulphates, chlorides, and polycyclic aromatic hydrocarbons. Other pollutants also end up in the atmosphere. The aim of this article is to present the problem of landfill fires and their impact on air, soil, and water, based on a review of the selected documented fires as well as indicators of fires in the areas in which the authors of this article conducted their research. The article presents an overview of methods and tests, such as dynamic leaching tests, monitoring tests, and lysimetric tests, all of which can be implemented to prevent fires as well as for research purposes after a fire has occurred, so that this article can be utilitarian not only for researchers, but also for decision makers.

Keywords: landfill; fires; hydrogeology; waste; leaching

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1. Introduction

Due to its associated costs, landfill is one of the most common means of disposing of municipal waste [1,2]. Such costs mainly relate to the occurrence of three phases of waste transformation—physical, chemical, and microbial—and to the impact of waste on the environment. However, uncontrolled use of landfills is a major economic and environmental problem. Due to economic development and population growth, waste production continues to increase [3,4]. According to a forecast by the World Bank, by 2025, the global production of solid waste in cities will have increased by over 70%, amounting to as much as 6,100,000 tons per day [5]. The physical and chemical degradation of land is a typical consequence of uncontrolled landfills [6]. For this reason, landfill sites are at least potential (if not yet actual) sources of pollution, causing soil and groundwater contamination [7,8]. In order to reduce the amount of waste, numerous methods of waste disposal have been developed and used, such as incineration [9]. After incineration, the mass of waste may decrease by up to 70% [10]. This fact makes waste incineration the most popular type of disposal. Municipal waste that is incinerated in incineration plants undergoes compliance tests to determine whether it meets the necessary standards to be disposed of in this way. There are two types of incineration plant: refuse-derived fuel, and mass burning [11]. One of the significant advantages of incinerating waste in incineration plants is the possibility of producing energy [12]. Over 250 million tons of waste are burned worldwide annually [13,14]. Asian countries such as China incinerate the most waste, burning about 30% of this total. Data on waste management in the European Union indicate that incineration is one of the most common waste treatment strategies; approximately 70% of waste is dealt with in this way [15].

The situation is completely different when waste is burnt in an uncontrolled manner. The risk of spontaneous fires is not specific to any particular phase of disposal but exists both for fresh waste and for that deposited earlier. In addition to the negative impact on the aquatic environment [16], illegal landfills can also affect human health [17] and destroy natural habitats [18]. In conjunction with the introduction of regulations on waste management which have increased the costs of waste storage, the problem of people deliberately setting fire to landfills has also emerged. The problem of landfill fires is not a local one. For example, in Poland in 2019 there were 4.65×10^{-6} landfill fires per 1 million inhabitants [14], and in the USA there are 2.56×10^{-5} landfill fires per 1 million inhabitants annually [19]. In Serbia, only one district has around 1000 fires per year [20]. Landfill fires can be broadly divided into surface and subsurface fires [21]. The former is less dangerous because firefighters can react to it quickly as long as it does not cover a large area [22]. However, subsurface fires can have much more significant consequences, including those caused by damage to the structure of the landfill [23,24].

Municipal waste often contains various substances such as heavy metals, persistent organic pollutants, sulphates, chlorides, polycyclic aromatic hydrocarbons from batteries, treated wood discards, and discarded electronic devices [25]. Old disused landfills, the structure of which is heterogeneous, also pose a threat as the type of waste contained within them is difficult to determine [26]. Burnt waste contains residuals in the form of ash and slag [27]. Since these residuals are treated as hazardous waste, the leaching of pollutants from them is a threat to groundwater [28]. The leachate from waste incineration poses a much more significant threat to groundwater than the leachate from untreated waste, due to the higher mobility of the components of incinerated waste [29]. Among the most well-known pollutants released into the atmosphere during combustion, attention should be paid to carbon monoxide and dioxide, nitrogen oxides, hydrochloric acid, hydrogen cyanide, volatile organic compounds, persistent organic pollutants, ketones, aldehydes, and PM [30]. The leaching of pollutants into the aquatic environment (as well as emission of pollutants into the atmosphere) can be observed in various types of fires, e.g., tire dump fires [31], landfill fires [32], and long-lasting landfill fires [33]. Below is a photo showing an example of the waste from a dump (Figure 1).

Figure 1. Burnt waste (photo W. Rykala).

The aim of this article is to discuss the problem of landfill fires and their impact on the soil, water, and air, based on a review of the literature and of indications in the areas in which we, the authors of this article, chose to conduct our research. In recent years, many new landfills have been burned down in Poland. We selected three, where research was already being carried out; landfills in Trzebinia [34], Sosnowiec (southern Poland), and a landfill in Sobolew (in the south-western part of Poland). Samples of waste, soil and leachate were simultaneously collected in two series from, which were then subject to GC–MS analyses (performed at the University of Silesia). Physicochemical analyses (measuring electrical conductivity (EC), in addition to Cl^-, $SO_4{}^2$, nitrogen compounds, B, Cr^{6+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Co^{3+}, and Ni^{2+}) are being performed in an accredited laboratory, but these analyses are currently in progress. This article highlights the problem of the global environmental threat caused by the migration of pollutants from incinerated waste, indicates possible solutions to such fires, and brings it into the realm of current research.

2. Causes and Mechanisms of Landfill Fires

Unfortunately, landfills are increasingly a threat to the natural environment and its inhabitants as a result of fires. Uncontrolled fires in landfills can be caused, inter alia, by sparks from machinery being operated in the landfill, uncontrolled lightning, and self-ignition [24]. A fire in a landfill can spread because the resulting chemical reaction produces heat. This, in turn, leads to a situation where the waste is kept above the temperature needed for decomposition and incineration. High temperatures from an existing fire can heat the surrounding garbage to the point of pyrolysis. The biological and chemical degradation of the constituents of solid municipal waste leads to an increase in temperature within solid municipal waste landfills [35]. Many studies have observed that self-ignited fire is caused by heat generated from aerobic processes after oxygen has been introduced into anaerobic landfills [36]. In addition, it should be mentioned that anaerobic decomposition releases methane, which is explosive when its presence in the air reaches between 5.3 and 13.9% [37]. Methane emissions from landfills also are affected by site-specific factors such as waste composition, available moisture, and landfill size. The lack of a system for collecting gas from landfills increases the possibility of them producing methane, among other such things. This allows the uncontrolled migration of gas, enabling it to pose a fire and explosion hazard [38]. It is necessary to maintain good heat dissipation in landfills so that hot waste is not stored in one place and landfill fires can be avoided [35]. Intentional arson should also be included among the possible situations that may lead to fire in landfills. This is a very common reason for landfill fires around the world. The most common reason for this type of activity is to get rid of residual waste, which is most likely due to its being located in an unauthorized place, or whose contents are illegal and highly toxic. In addition, the widespread use of landfills, difficulties in waste disposal, costs, and improper storage methods all contribute to landfill fires [31].

When assessing the impact of incinerated waste on soil and water, it is important to control the chemical composition of the leachate. The possibility of carrying out a controlled incineration is extremely valuable, thanks to which it is possible to compare the chemical composition of the leachate from a landfill in its natural state with that resulting from incineration. Additionally, residues from waste incineration plants can be tested for leachability. Similar results can be obtained if a landfill with a groundwater monitoring system is burned. The worst situation is the case of uncontrolled waste fires in waste dumps. Almost 80% of all solid residue from the incineration of solid municipal waste is bottom ash [39]. This residue is alkaline and contains dioxins as well as oxides of silicon, iron, calcium, aluminum, sodium, and potassium [40]. Research on bottom ash is extremely important in the context of identifying the pollutants being leached from them.

3. Consequences of Spontaneous Landfill Fires

There are three categories of environmental consequences with landfill fires [32,41–43]. When waste is burned, some of the pollutants inside it are released into the atmosphere, some migrate to groundwater as a result of leaching, and some contaminate the land surrounding the landfill. Another negative effect of spontaneous landfill fires is the threat to human life. One example of such an eventuality occurred in 2005 in Indonesia, where the collapsed waste hit a nearby settlement and killed 147 people [44]. Indeed, it is possible to find a great many articles that focus primarily on determining the impact of fires on human health [45–47].

The easiest way to monitor this is to study changes in air quality, as it is much more time-consuming and costly to test the quality of soils and the soil–water environment [48]. The amount and degree of hazardous substances released into the atmosphere is dependent on the size of the fire, the type of solid waste involved, and the weather anomalies surrounding the event. Homeowners and business owners tend not to support the siting and development of landfills in their neighborhoods due to perceived notions about noxious fumes, health and environmental effects, and adverse influences on property values [49].

The problem of air pollution caused by fires in landfills is an annually recurring problem not only for a specific area in Poland, but on a regional scale, owing to the migration of toxic pollutants into neighboring areas. Consequently, landfill fires can cause adverse air pollution dispersion to the surrounding area [50]. Through open burning, we are exposed to the immediate impact of the problem as well as its subsequent consequences. Open burning of waste is a form of low temperature combustion with high contaminant emissions, particularly of black carbon (BC), which contributes significantly to air pollution and has both a health and an environmental impact [51]. Based on studies by the Environmental Protection Agency (EPA), one of the main end results is the emission of carbon monoxide and dioxide (CO and CO_2), nitrogen oxides (NOx), hydrochloric acid (HCl), hydrogen cyanide (HCN), volatile organic compounds (VOCs), persistent organic pollutants (POP), ketones, aldehydes, and PM. Moreover, the 2016 report by the European Environmental Agency [52] highlights the emission of metals, such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se), and zinc (Zn) during waste burning [33].

Higher temperature fires can cause the breakdown of volatile compounds which emit dense black smoke (New Zealand Ministry of Environment); one of the biggest threats to humans associated with this is the negative impact of PM10 [53–55].

However, there are fires in which the temperature reaches very high values. An example of such a fire was observed in the Dallas landfill. Shale deposits excavated from a calcareous bituminous marine shale formation spontaneously combusted in 2000. The temperature then exceeded 500 °C [56].

Some of the most common waste materials that are prone to fires are used tires. When ignited, tires burn with a higher per-pound heat output than most forms of coal, and they also produce large amounts of oil and smoke, which can cause serious air and water contamination [57]. Tire fires release a dark, thick smoke that contains carbon monoxide, sulfur dioxide, and the additional products of butadiene and styrene [58]. The emissions from the combustion of tires reflect their chemical composition, comprising 50% natural or synthetic rubber by weight, 25% black carbon, 10% metal (mostly in the steel belt), 1% sulfur, and 1% zinc oxide, in addition to containing trace quantities of other materials [59].

Another important issue is the threat to health resulting from the emission of hazardous substances into the air, which we then consequently breathe. As with all fires, those in landfills produce toxic smoke and gases which can result in headache, nausea, and fatigue (due to a lack of proper sleep) in exposed residents [38]. The associated danger and level of toxicity of these gases depend on both the duration of exposure one has to them and on the type of material that is burning (United States Fire Administration (USFA)). Suspended particulate matter from waste incineration is a major hazard. Particulates affect the environment as they contribute to greenhouse gases. Likewise, they can affect human health because they can easily reach the deepest recesses of the lungs, leading to respiratory ailments, according to the US Environmental Protection Agency [51]. Many pollutants emitted from tire burning are toxic, carcinogenic, and/or mutagenic. An accumulation of

Ni in the human body through inhalation, ingestion, or skin absorption may result in cancer of the lungs, larynx, or prostate [60]. Other effects include dermatitis, bronchial asthma, myocardial infarction, respiratory failure, and birth defects [61,62]. In addition, there is a strong link between exposure to BC and potentially severe health effects, such as cardiovascular disease, chronic respiratory illness, and premature mortality. The problem of air pollution caused by fire in landfills has been documented in several publications [30,31,33].

Analysis of the risks of leaching from waste into groundwater requires knowledge of the chemical and physical properties of the waste, its age, and the local geological and climatic conditions of the waste disposal site. The extent of these risks could be defined by determining the phase and chemical compositions, and by comparing various leaching methods. The use of many commonly used leaching methods has been described by Arain et al. [63], Delay et al. [64], Hesbach et al. [65], Hassett et al. [66], Kalembkiewicz and Sitarz-Palczak [67], Kim and Hesbach [68], Kosson et al. [69], and Menghini et al. [70].

The results from the above research [27] indicate that the amount of heavy metal present in waste ash is several times higher than in natural municipal landfill waste. Combustion of municipal waste in incineration plants is controlled in terms of the possibility of pollutants getting into the atmosphere or soil, but such control is not possible in the case of waste fires. The residues from waste incineration contain metals that are released either as a result of chemical reactions or as a result of infiltrating precipitation [71]. Such research covered the assessment of factors influencing the amount pollutants leaching from waste. Much attention has been paid to determining the ideal leaching pH [29,72].

One of the methods used to assess leaching is the Extraction Procedure Toxicity Test [73]. If the sample grains are larger than 9.5 mm, the sample of the waste is comminuted. It is then placed in an extractor, to which a volume of water is added corresponding to 16 times the weight of the sample. The pH of the solution is then reduced to 5.0 with the slow addition of acetic acid. A control of the pH is performed at 15, 30 and 60 min. If the pH rises above 5.2, some acetic acid is added until the pH drops to 5.0 ± 0.2; the pH control procedure is carried out for 6 h. The added volume of acetic acid may not exceed 4 mL per gram of sample. The sample is then subjected to leaching for 24 h. After this time, the pH should be greater than 5.2, and if it is not (despite the use of an acceptable volume of acetic acid), then extraction should be continued for the next 4 h with a pH adjustment every hour. After completion of the extraction, water is added to the solution in a volume corresponding to four times the weight of solids, minus the weight of CH_3COOH added. Then, the solution is filtered and subjected to chemical analysis. The chemical composition of the solution is then compared to the limit concentration values. If they are exceeded, it is assumed that the investigated waste is toxic.

In the case of incinerated waste, the bulk properties and geochemical characteristics of the ash will also affect the leaching of pollutants. Metal speciation in the ash also depends on the flue gas composition, such as the proportion of chlorine, moisture, sulfur, and inorganic particulates [74,75]. The typical components leaching from the ash are Ca, Cl, K, and, to a lesser extent, Si, Zn, Al, S, Ti, and Fe [76].

To prevent the leaching of pollutants from the ash, appropriate treatment is required. There are a few methods which are used for this, such as physical immobilization, solidification, or chemical (reagent) treatment. Some of the promoted methods are chelating treatment [77,78] and bioleaching [79,80].

There are several papers devoted to research on the possibility of using ash from municipal waste to seal landfills or recover metals [81,82]. Some studies have focused on the mineralogical composition of the ash. Such works include the Siddique studies from 2008 and 2010 [83,84]. This research also described the chemical composition of leachates and the influence of ash on the chloride shrinkage of concrete. Due to the fact that the incinerated waste is treated as a hazardous material and is also sometimes used in construction work or as a neutralizing agent for acid waste, it should undergo various tests in order to avoid negative impacts on the environment or human health [85,86].

4. Case Studies of Illegal Burning

In the literature, it is possible to find a number of examples of descriptions of landfill fires, such as fires in Spain [87], Greece [88], Brazil [89] or the USA [90].

One important example of such a landfill fire is an event that took place in Greece. An uncontrolled ignition took place on 15 July 2006 at the municipal waste storage site known as "Tagarades", situated 20 km from the city of Thessaloniki. The main waste materials in the landfill were household rubbish, with the addition of hospital and commercial waste and sewage sludge. The fire engulfed about 50,000 tons of garbage. The cause of the fire was most likely methane coming out of the storage area (methane in this area was not monitored), and a thick streak of smoke could be seen emitting from the smoldering waste for the next week [24].

The studies performed by Øygard et al. [24] on the site included a collection of soil and plant samples, both from inside and outside of the landfill site. They were collected 15 days after the fire was finally extinguished. In total, 10 soil samples (including one from the landfill) and nine plant samples (from outside the landfill area) were taken. When analyzing the samples, the researchers focused on detecting potential contaminants associated with polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), organochlorophenols (OCP) including hexachlorocyclohexanes (HCH) and DDT, as well as trace elements. The results of these studies showed that the level of PCB and trace elements inside the landfill were significantly higher than those reported in the remaining soil samples. The level of HCH was high inside the landfill, but also in places where the smoke plume may have reached. At agricultural sites, the DDT content of the soil exceeded that of the landfill. However, no exceedance of the relevant intervention values for soil reclamation were recorded. Only Cr exceeded the intervention value for soil reclamation, due to local geological occurrences. As far as the plant samples are concerned, no high concentrations were observed. In addition, the heavy metal content was similar to that recorded for vegetation species in other locations in Greece, meaning that the metals had not affected the vegetation as a result of the fire. The results of this study alone did not conclusively determine whether the landfill fire had an impact on the surrounding terrestrial environment.

A second example is an uncontrolled fire at an illegal tire storage site in Spain, on the border between Castilla–La Mancha and Madrid. The site had been a wild landfill since 2002 and was then declared illegal by the authorities in 2015. The fire broke out on 14 May 2016, and was finally extinguished on 2 June. At that time, it is estimated that between 70,000 and 90,000 tons of tires were present at the scene (https://www.dailymail.co.uk/news/article-3589238/Giant-toxic-cloud-swamps-town-20-000-Spain-blaze-tyre-dump-expected-DAYS.html, accessed on 19 January 2023). The studies performed by Nadal [89] involved the collection of soil and ash samples in the area surrounding the landfill at two different intervals. The first occurred three days after the fire broke out at three distances (500, 1000, and 1500 m, for a total of three soil samples), while the second was carried out one month after the fire (3 soil samples, one ash sample). PAHs with 3–5 rings were the most common accumulations of PAH in the samples. However, in these studies, PWA levels did not appear to correlate with the distance from the tire storage site. The researchers suggested other potential sources of PWA near the samples taken, namely industrial activity, which occurred in a large proportion of the area. A comparison of the relative PMA calculated for the soils harvested during the second round indicates an overall decrease in EPA PVA levels as the distance from the fire increases. In addition, 16 non-primary PWAs and 29 alkylated PWAs were detected and identified in the analyzed samples. A number of heterocyclic PCs were also detected in the results of the studies. Among them, PAHs were the largest class, followed by O-PAH and PAH containing N heterocyclic compounds. Additionally, 20 PASHs were initially identified. The PASH levels in the samples showed a similar trend to that observed for previously discussed PAH derivatives. Elevated O-PAH concentrations were detected in the samples that were affected by the tire fire. Relatively low concentrations of PBDEs and DPs were found in the collected soil samples. This result was confirmed with an ash analysis, in which these compounds were not detected in significant quantities.

Another example of such a disaster is a fire that occurred at a landfill site in Norway [91]. The landfill was established in 1993 to collect solid municipal waste and some forms of industrial and construction waste. By 2003, a total of 230,000 m^3 of landfill leachates had been dumped there. The first fire in the area was observed on 10 March 2003. During the firefighting operations, the landfill reached a depth of up to 12 m, but by digging a deep ditch around them that reached the bottom of the landfill, the burning areas were isolated. The extent of the landfill where the fire was fought was about 8000 m^2 (10% of the total area of the landfill).

However, after the outbreak of this fire, liquid samples were tested daily for up to a week after the fire had ceased. Additional information was also collected on the macroscopic changes resulting from the event itself. The leachates after the fire had a fairly strong, unpleasant smell. In addition, it was black in color and contained relatively high levels of molecules. After the outbreak of the fire, the pH level and conductivity of the samples increased above the norm. The metal levels were also elevated in the cases of Cd, Cu, Cr, and Pb within the liquid samples. However, no PAH compounds were detected during the disaster. It is stated that a landfill fire extinguished with excavations can cause large increases in the concentration of certain substances, but only as a short-term effect if the fire is quickly extinguished.

Another example of a fire at a landfill is an incident that occurred in one of the largest landfills in Europe, located in Toledo (Spain). At this landfill, approximately 80,000 tons of tires had been illegally accumulated over 15 years [89]. The fire lasted 20 days. As part of the research, soil, crop, and air samples were collected. The research mainly focused on the level of PAHs, PCDD/Fs, PCBs, and toxic metals. Among PAHs, the contents of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, dibenzo (a, h) anthracene, benzo (g, h, i) perylene, and indeno (1,2,3-cd) pyrene were assessed. The mean levels of the analyzed PAHs in the soils ranged from 8.8 to 33.2 ng/g. The concentration of all PAHs in the air was determined to be 134 ng/m^3, with chrysene being the dominant compound. The concentrations of PCDD/Fs and dl-PCBs in the soils achieved 1.66 ng WHO–TEQ/kg. In the case of the air samples, the concentrations of these components did not differ from the air samples taken in this area before the fire (from prior monitoring tests). The highest concentrations of PCDD/Fs + dl-PCBs, and ndl-PCBs (0.33 ng, WHO–TEQ/kg, and 0.52 ng/g, respectively) were observed in lettuce.

It is worth mentioning that health risks were also assessed. Calculations indicate that the cancer risk due to exposure to environmental pollutants for the population living near the landfill was between three and five times higher than that estimated for the inhabitants of nearby towns.

In terms of controlled combustion, attention should be paid to, among other things, research in Denmark, wherein two examples of residues (bottom ash and air-pollution-control (APC) residues from municipal waste) have been tested for pollutant leaching [92,93]. Five different samples of individual residue types were taken into account in the research. Moreover, laboratory tests were performed in parallel for dried and non-dried samples of treated APC-residues. Bottom ash is a slag-like residue with a homogeneous composition collected from the combustion chamber. APC residues are carried away from the combustion chamber with the flue-gas. Three test methods were used to assess the leaching of pollutants: batch experiments with continuous pH control, up-flow percolation experiments, and static experiments without pH-control [94]. The leaching of Cd, Fe, Mg, Hg, Mn, Ni, Co, Sn, Ti, and P from both bottom ash and from APC was generally below the detection limits for those particular compounds. The highest leaching of pollutants was found for chloride, sodium, and potassium.

This type of waste can also be used as a landfill seal. An experiment was conducted in China on the use of incinerated waste as a sealant [95]. In this research, three simulated landfills were used: R1—typical landfill; R2—landfill with a mass proportion of the bottom ash layer to the municipal solid waste layer of 1:9; and R3—landfill with a mass proportion of the bottom ash layer to the municipal solid waste layer of 2:8. Each reactor was 287 mm in diameter and 1000 mm in height and had a volume of 65 L. Each reactor was equipped with five ports: one for exporting gas, three for the sampling of the bottom ash and waste, and the last one for leachate drainage and sampling. The leachate samples were analyzed for pH, dissolved organic carbon, and for Cu and Zn levels, while the waste samples were analyzed for Cu and Zn concentrations alone. The tested ash showed a high pH = 11.17. This is a consequence of the levels of $CaCO_3$, Al_2O_3, and Fe_2O_3. It was calculated that there were 6464.4 mg of Cu and 57,467.5 mg of Zn in R1, 7390.9 mg of Cu and 61,330.7 mg of Zn in R2, and 8317.5 mg of Cu and 65,193.0 mg of Zn in R3. The average concentration of DOC of the leachates from these three reactors was 28,481.5 mg/L.

The problem of landfill fires is still being investigated in Poland, in terms of the impact of the pollutants from precipitation on groundwater. One of the research areas on which we, the authors of this article, began our work is the landfill in Trzebinia (in southern Poland) [34], where a fire took place in 2018. The landfill contained, among other things, tires, black rubber, plastic packaging, and textiles. The landfill had not been used since 2013. As part of our preliminary studies, samples of soil and waste were collected and subjected to leaching tests, as well as PAHs and MPI analysis. The research showed that fluoranthene and pyrene were detected in all of the samples. Phenanthrene and anthracene were also detected in most of the samples. Among the inorganic pollutants, increased concentrations of sulphates and chlorides were observed. The obtained results have been systematized and analyzed. There are lots of challenges and different solutions connected with landfill fires. The most important aspects of these are presented in Table 1.

Table 1. Landfill fires problems and possible solutions.

Environmental Challenges Related to Landfill Fires	Proposal Solutions to Specific Problems of Landfill Fires
Pollution cloud created from infiltration of burnt waste in landfill [96]	Monitoring of the site by means of lysimeters installed in the region of the landfill site [16]
Damage to the top layer of the landfill [97]	Use of non-combustible materials covering the landfill
Mobile spread of the fire from the landfill to nearby areas [98]	Safer isolation of the site, inter alia, by means of sand shafts or excavations
Ignition of accumulated methane in landfill [99]	Accurate monitoring and discharge of collected methane from residual waste [21]
Production of toxic fumes into the atmosphere by the burning of waste [31]	Monitoring and investigation of the effects of air pollution [33]
Collection of flammable materials in a single landfill	Better segregation and ungrouping of flammable solid waste
The formation of wetlands in landfills	Use of terrain scanning to detect temperature rise [20]
Exposure of the health and life of landfill workers [50]	The right equipment and clothing for safe field work [100]
Containment of hazardous waste emitting permanent pollution over time [4]	Improving the technology for disposing of potential waste [101]

5. Conclusions

Fires in municipal landfills constitute a significant environmental problem in the context of air, soil, and groundwater pollution. Studies on the leaching of pollutants from incinerated waste indicate that such leachates are more toxic than for waste deposited directly into the landfill. Burnt waste not only contains Cu, Zn, Cd, Ni, and Mn, but due to its heavy metal content, ash and slag are also considered to be hazardous waste. The possibility of reusing such waste could be beneficial for the environment, providing that it is not possible for pollutants to migrate from this waste.

Due to the fact that a significant amount of waste is incinerated in wild or unsealed landfills, research on the leaching of pollutants (as well as the processes for the migration of these pollutants from various waste materials) should constantly be conducted. It is also important to identify as many factors as possible that may affect the size and type of the leached contaminants. Performing controlled incineration, reducing emissions from incineration plants, and, finally, securing waste against spontaneous combustion or arson are just a few examples of treatments that would reduce the development of fire-related problems. It is necessary to determine the type of pollution in relation to the type of waste incinerated, as well as the amount of pollution, the rate of migration, and the ability to clean the aquifer over time. It is worth remembering that it is possible to compare the leaching of pollutants from waste in the natural state with waste after incineration, e.g., with static or dynamic leaching tests.

Considering the numerous burnings of landfills, which occur due to increased fees for landfilling, it is necessary to consider whether these activities are expedient and to introduce new rates for landfilling and disposal. The issues discussed in this article can be used to prepare a report on the negative environmental effects of landfill fires. Additionally, they can also serve as a basis for conducting further research on burnt landfills.

Future research on the influence of leachates from burnt waste on groundwater should address the gaps in our current understanding of the differences between the toxicity of natural and burnt waste, between different waste and landfill processes, and fire prevention measures. These should be analyzed with new examples in different storage conditions.

The results of such research should be communicated to our political decision makers, in order to increase fines for those who intentionally burn landfills.

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My participation consisted of preparing the article, collecting materials for the preparation of the text, and translating the text

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The influence of a fire at an illegal landfill in Southern Poland on the formation of toxic compounds and their impact on the natural environment

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Article

The Influence of a Fire at an Illegal Landfill in Southern Poland on the Formation of Toxic Compounds and Their Impact on the Natural Environment

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Abstract: Landfill fires pose a real threat to the environment as they cause the migration of pollutants to the atmosphere and water sources. A greater risk is observed in the case of wild landfills, which do not have adequate isolation from the ground. The aim of this article is to present the results of studies on the toxicity of waste from a fire in a landfill in Trzebinia (southern Poland). Both soil and waste samples were investigated. The samples were analyzed using the GC-MS method and the leachates using ICP-OES. A total of 32 samples of incinerated waste and soil were collected. The organic compounds included naphthalene, fluorene, phenanthrene, anthracene, acenaphthene, acenaphthylene, fluoranthene, pyrene, benzo (c) phenanthrene, benzo (a) anthracene, chrysene, benzo (ghi) fluoranthene, benzo (b + k) fluoranthene, benzo (a) fluoranthene, benzo (c) fluoranthene, benzo (a) pyrene, benzo (e) pyrene, perylene, indeno[1,2,3-cd] pyrene, benzo (ghi) perylene, and dibenzo (a + h) anthracene. Among the inorganic parameters, sulfates, chlorides, arsenic, boron, cadmium, copper, lead, and zinc were taken into account. Phenanthrene reached values exceeding 33 mg/L. Fluoranthene dominated in most of the samples. Sulfates and chlorides were present in the samples in concentrations exceeding 400 and 50 mg/L, respectively. Compounds contained in burnt waste may have a negative impact on soil and water health safety. Therefore, it is important to conduct research and counteract the negative effects of waste fires.

Keywords: landfill; fire; contamination; PAHs; leachate; gas chromatography (GC-MS)

check for updates

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1. Introduction

The problem of landfill fires is becoming a more common and dangerous phenomenon worldwide every year [1–4]. Wild landfills occur most frequently, for example, on forest margins, in ditches, and on the peripheries of inhabited areas [5]. Since the oil, solvents, fuel, rusted metal, and batteries contained within them can cause severe environmental damage, they must be properly disposed of, which is expensive [6,7].

In 2012, the global generation of municipal solid waste (MSW) reached approximately 1.3 billion tons per year [8]. Although illegal dumping occurs for various reasons, one is thought to be the shortage of proper waste treatment facilities [9], while another could be the desire to dispose of waste cheaply. The problems with waste storage in Poland are influenced by economic and political factors [10].

Every day, about 10–30% of the MSW generated in metro cities and 30–50% in smaller cities and towns is left uncollected [11]. Another problem may be the low level of waste recycling. For example, the rate of recycling in Malaysia is as low as 15%, far behind developed countries such as Singapore, Germany, and South Korea, in which the annual rate is in the range of 50% to 75% [12].

One of the dangers that can arise from illegal landfills is fire, which can be caused by deliberate arson or spontaneous combustion resulting from the chemical reactions of waste, reactive materials, failure of landfill gas systems, smoking or sparks, landfill equipment, lightning strikes, or heated waste [13]. The main cause of fire is methane, as it is highly flammable [14]. It makes up about 40–60% of landfill gas. Carbon dioxide accounts for about the same amount, and the remainder is composed of nitrogen, oxygen, hydrogen, ammonia, sulphides, and other gases [15]. The amount of methane generated and migrating through a MSW landfill can lead to the increased intensity of the fire [16,17]. Over the years, according to the State Fire Service, there has been a consistently high number of landfill fires, which sometimes stayed active for days [18].

Higher temperature fires can cause the breakdown of volatile compounds which emit dense black smoke [19]. Such uncontrolled burning carries the risk of spreading rapidly beyond the landfill's perimeter and can lead to air pollution. In the aftermath, dense smoke can travel for several kilometers, threatening nearby residents. The consequences of a landfill fire can also produce a potential chemical hazard. Burnt waste on unprotected soil may lead to the physical and chemical degradation of the soil [20], which can cause it to migrate to aquifers [21].

An example of the most hazardous solid waste that can be found in wild landfills is used car tires. Approximately 240 million vehicle tires are discarded worldwide every year [22]. Only around 25% of the discarded tires are reprocessed/reused, while the remaining ones end up in landfills or illegal dumps [23]. These man-made products mainly consist of styrene-butadiene, poly (butadiene), bromated butyl rubber, carbon black, extender oils, nylon, and steel wire [24]. In open fires, tire emissions reflect their chemical composition, which is 50% natural or synthetic rubber by weight, 25% black carbon, 10% metal (mostly in the steel belt), 1% sulfur, 1% zinc oxide, and trace quantities of other materials [25].

After being landfilled, waste materials are subjected to a series of physicochemical and biological transformations, provided to create leachate [26]. The leachate composition varies among landfills depending on the type of waste buried, degradation stage, climate conditions, characteristics of the landfill site, socioeconomic factors, and landfill technology [27,28].

Heavy metals and polycyclic aromatic hydrocarbons (PAHs) pose a potential threat to the environment and nearby residents. PAHs have been reported to have carcinogenic properties, and 16 PAHs have been listed as priority pollutants by the US Environmental Protection Agency [29]. There is the potential for them to be generated in situ in municipal landfill fires [30–32].

Environmental aspects related to the impact of potential landfill fires have only been addressed in several scientific articles. In the work of Øygard et al. [4], landfill leachate collected during and after an accidental landfill fire was tested. Levels of selected metals and compounds were determined compared to compounds present in the leachate under normal conditions. Research conducted by Raudonyte-Svirbutaviciene et al. [33] focused on soil contaminated with PAHs and heavy metals after a tire landfill fire in Lithuania. Escobar-Arnanz et al. [34] used two-dimensional gas chromatography-time-of-flight mass spectrometry to analyze soil samples from an uncontrolled tire dump fire. In another work by Rim-Rukeh [35], five landfills in Nigeria, where fires are most common, were tested for air pollution. Precipitation leachate that washed away long-term burnt waste after a previous landfill fire was analyzed in Romania [36].

PAHs are among the pollutants hazardous to human health and have been included in the list of hazardous substances, with important factors being the quantity of the substance, the duration of exposure, the route of exposure, and the effects of other chemicals to which the body is exposed. PAHs can penetrate the body via the respiratory and digestive systems, and by direct skin contact with particular substances such as soot and tar [37]. As persistent compounds, PAHs do not have a carcinogenic or mutagenic effect themselves, but their metabolites do [38]. To determine the harmfulness of PAHs, indicators of the toxicity of individual PAHs were introduced. Benzo(a)pyrene (BaP) is used as a reference substance, and the carcinogenic strength of Toxicity Equivalence Factor (TEF) of other compounds is calculated against BaP. The toxicity equivalent RTBaP Toxic Equivalent (TEQ) is the sum of the concentrations of individual PAHs and their relative toxicity factors [39], and it is calculated using Formula (1):

$$\begin{aligned}\text{RTBaP} &= 0.001 \times [\text{Na}] + 0.001 \times [\text{Acy}] + 0.001 \times [\text{Ace}] + 0.001 \times [\text{Fl}] \\ &+ 0.001 \times [\text{Fen}] + 0.01 \times [\text{An}] + 0.001 \times [\text{Flu}] + 0.001 \times [\text{Pir}] + 0.1 \times [\text{BaA}] \\ &+ 0.01 \times [\text{Ch}] + 0.1 \times [\text{BbF}] + 0.1 \times [\text{BkF}] + 1 \times [\text{BaP}] + 5 \times [\text{DBA}] + 0.1 \times [\text{BghiP}] \\ &+ 0.1 \times [\text{IP}]\end{aligned} \tag{1}$$

A TEF value of 0 means that the compound is not carcinogenic. In a scientific paper [40], the calculation of mutagenicity equivalent (MEQ) and carcinogenicity (TCDD-TEQ) was suggested in order to assess the harmfulness of PAHs. The mutagenicity equivalent is given as the sum of the concentrations of the individual PAHs and their relative mutagenicity factors:

$$\begin{aligned}\text{MEQ} &= 0.00056 \times [\text{Acy}] + 0.082 \times [\text{BaA}] + 0.017 \times [\text{Ch}] + 0.25 \times [\text{BbF}] \\ &+ 0.11 \times [\text{BkF}] + 1 \times [\text{BaP}] + 0.31 \times [\text{IP}] + 0.29 \times [\text{DBA}] + 0.19 \times [\text{BghiP}]\end{aligned} \tag{2}$$

Carcinogenicity is equivalent to the sum of the concentrations of individual PAHs and their relative carcinogenicity coefficients:

$$\begin{aligned}\text{TCDD-TEQ} &= 0.000025 \times \text{BaA} + 0.00020 \times [\text{Ch}] + 0.000354 \times [\text{BaP}] \\ &+ 0.00110 \times [\text{IP}] + 0.00203 \times [\text{DBA}] + 0.00253 \times [\text{BbF}] + 0.00487 \times [\text{BkF}]\end{aligned} \tag{3}$$

The harmfulness of PAHs is also expressed as the ratio of PAHs classified as carcinogenic to the sum of all labelled PAHs:

$$\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH} = ([\text{BaA}] + [\text{BaP}] + [\text{BbF}] + [\text{BkF}] + [\text{Ch}] + [\text{DBA}] + [\text{IP}])/([\text{SWWA}]) \tag{4}$$

The closer the value of the ratio $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$ is to 1, the greater the risk posed to the population.

The purpose of this study is to investigate the toxic substances generated during a wild landfill fire. Such research has not yet been performed in Poland. Moreover, in the world's literature, the problem has not been sufficiently addressed, with such key information missing as the level of contaminants produced, their migration extent, and time present in the soil. A wildfire that occurred in the town of Trzebinia (Poland) (2016 y.) was examined to assess its potential threat to the nearby natural environment. The soil incinerated waste and the leachate generated by washing incinerated waste from the landfill were tested for compounds and elements hazardous to health and the environment. Compounds detected in all samples were identified, and their abundance and profiles were recalculated using appropriate quantitative methods.

2. Materials and Methods

2.1. Study Area

The wild dump (28,000 m^2) is located in the southern part of the town of Trzebinia (southern Poland). It is situated in a tree-lined space. To the west, there is the Trzebinia Penitentiary (approx. 130 m), to the north is an industrial area (approx. 284 m). The types of solid waste stored in the landfill included used tires, black rubber, plastic packaging, and textiles, among others.

Between 26 and 27 May 2018, a fire occurred at the wild landfill, at around 1:30 am (Figure 1). The fire spread at a swift pace, which made the firefighting operation difficult. The fire was extinguished by pouring water on it, and then the area was covered with firefighting foam to protect the nearby forest. For at least two days, the smell of the fire could be felt within a radius of 6–7 km. Children and the elderly living in the area were advised to stay inside their homes. No one was injured or killed in the fire.

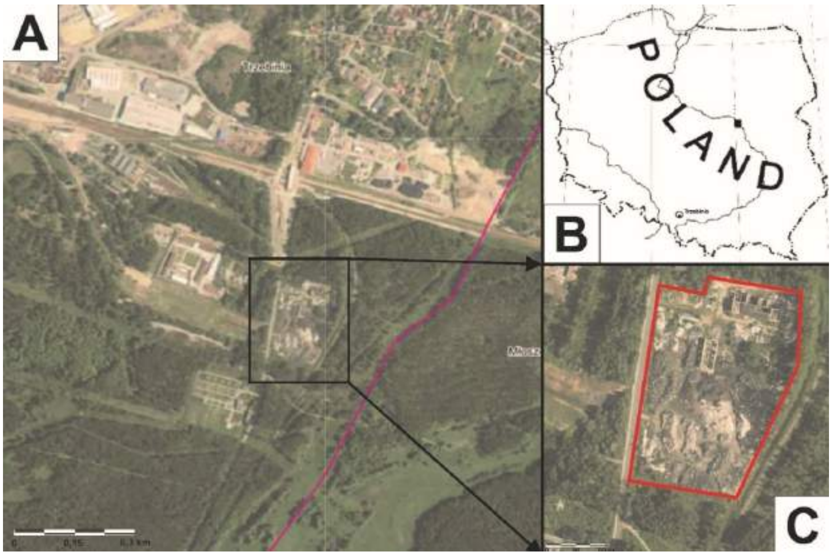


Figure 1. (**A**–**C**) Wild landfill fire location in Trzebinia on Słowackiego Street.

According to reports from nearby authorities, the landfill described had been unused since 2013. The owner was required to dispose of the waste stored there. However, for unexplained reasons, he abandoned the facility. Since then, waste has been a never-ending problem for the town government, nearby residents, and the natural environment.

The ensuing fire created a huge, dark cloud of smoke that spread to nearby neighborhoods. This garbage created very poisonous and dense fumes that could, among other things, impede firefighting operations in the area. According to data provided by "Airlyeu" on the fire, in Chrzanów, the PM 2.5 and PM 10 standards were exceeded by 336% and 260%, respectively.

The charred, leftover waste remains uncovered at all times, unprotected from the elements (Figure 2A,B). During rainfall, waste that was altered by the fire is systematically washed away. The resulting leachate then infiltrates deep into a nearby aquifer, creating a dangerous "pollution cloud".

Figure 2. (**A**,**B**) The present site of the burnt wild waste dump in Trzebinia on Słowackiego Street (April 2021).

2.2. Sampling

During two days of sampling in the morning hours of 24 April 2021, and 24 November 2021, a total of 32 soil and burnt solid waste samples were collected from the study area of the wild landfill in Trzebinia (Table 1). All samples included in the study were collected at an appropriate distance using a pre-planned route.

Table 1. Sample code and description.

Sample	Description of the Sample	Sample	Description of the Sample
WR1G	soil sample	WR12G	soil sample
WR2G	soil sample	WR6O	burnt waste sample
WR3G	soil sample	WR7O	burnt waste sample
WR1O	burnt waste sample	WR13G	soil sample
WR4G	soil sample	WR1.O	burnt tires
WR2O	burnt waste sample	WR2.O	burnt rubber black waste
WR5G	soil sample	WR3.O	burnt rubber black waste and brown sponge
WR6G	soil sample	WR4.O	burnt rubber black waste
WR7G	soil sample	WR5.O	burnt rubber black waste
WR8G	soil sample	WR6.O	burnt rubber black waste
WR3O	burnt waste sample	WR7.O	unburnt wallpaper
WR4O	burnt waste sample	WR8.O	burnt textiles
WR9G	soil sample	WR9.O	burnt textiles
WR10G	soil sample	WR10.O	burnt tires
WR11G	soil sample	WR11.O	burnt textiles
WR5O	burnt waste sample	WR12.O	burnt textiles

Samples of approximately 20 g of surface soil and waste were collected with a steel spatula in glass jars and then closed tightly and transported to the laboratory. Next, the soil samples were air-dried in a clean laboratory room.

2.3. Sample Preparation and Characterization

2.3.1. Sample Preparation for Laboratory Analysis

The 12 waste samples (Appendix A Figure A1A–L) collected on 24 November 2021, were prepared for transport to the i2 Analytical Limited Sp. z o.o. Pionierów 39 Str. accredited laboratory in Ruda Śląska. The objective was to perform specific tests on the content of leachate generated from the aforementioned waste. The laboratory was commissioned to test the contents for inorganic compounds: chlorides, sulfates, and heavy metals: boron, arsenic, cadmium, copper, lead, mercury, and zinc.

Before being sent to the laboratory, the waste samples were dried, weighed, flooded with demineralized water, and then washed according to the PN-EN 12457-2 Norm. The resulting leachates were filtered and transported to an accredited laboratory in glass containers at room temperature.

Chlorides were analyzed using the colorimetric method using a Discrete Analyzer, while the other ordered compounds were analyzed using the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique. All analyses were performed using ISO 17025 accreditation and the procedure L039-PL.

2.3.2. Sample Preparation for GC-MS

Appropriately dried, cataloged, and aged transformed solid waste samples were extracted with dichloromethane in an ultrasonic bath for 15 min at 30 °C. The extracts were filtered, the solvent evaporated, and the extract yields calculated. All samples were derivatized (silanized) prior to gas chromatography-mass spectrometry (GC-MS) analysis.

2.3.3. Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS analyses were carried out using an Agilent Technologies 7890A gas analyzer chromatograph and Agilent 5975C network mass spectrometer with the triple-axis detector system at the Department of Natural Sciences, Sosnowiec, Poland, using helium (6.0 Grade) as the carrier gas at a constant flow rate of 2.6 mL/min. Separation was obtained with a J&W HP5-MS (60 m × 0.32 mm i.d., 0.25 µm film thickness) fused silica capillary column coated with a chemically bonded phase (5% phenyl, 95% methylsiloxane), for which the GC oven temperature was programmed from 45 °C (1 min) to 100 °C at 20 °C/min, then to 300 °C (hold 60 min) at 3 °C/min, with a solvent delay of 10 min [41]. Mass spectra were recorded from 45 to 550 da (0–40 min) and 50–700 da (>40 min) electron impact mode, with an ionization energy of 70 eV. Data were acquired in full scan mode and processed with the Hewlett Packard Chemstation software. The compounds were identified by their mass spectra, and a comparison of peak retention times with those of standard compounds was carried out, as well as an interpretation of MS fragmentation patterns, and literature data [42].

Peaks were integrated manually. Quantitative analysis was performed based on the 5-point calibration curves for the analytical standards. The linear correlation between the peak areas and PAH concentrations was checked within the range of 0.10–10 µg/mL, with correlation coefficient values within the range of 0.997–0.998. For quality assurance and quality control (QA/QC), the analysis of each sample series was accompanied by the analysis of a blank sample comprising the whole analysis procedure to assess possible contamination during the procedure. The method performance was verified by analyzing the NIST SRM 1649b reference material and comparing the results with the certified concentrations of the investigated PAHs. The limits of detection (LODs) were calculated as three times the standard deviation of background peaks in the procedural blanks repeated three times. The average LOD values were 2.0 ± 0.05 ng/mL. Concentrations below the LOD were considered zero for all calculations.

Gas chromatography coupled to mass spectrometry is a good, widely used analytical technique to assess the degree of contamination of soil and water, or the level of toxicity of waste where an assessment of chemical composition is required. It has been used in multifaceted ways in environmental and geochemical studies on various aspects of waste in scientific papers [41,43–45]. The method allows the identification of individual substances based on mass spectra and quantitative analysis.

3. Results and Discussion

3.1. PAH Concentrations in Soil and Combusted Solid Waste Samples from the Wild Landfill Fire

Among the PAHs of the Trzebinia samples, the following were identified (Table 2): naphthalene (N) (m/z = 128), fluorene (F) (m/z = 166), phenanthrene (P) (m/z = 178), anthracene (A) (m/z = 178), acenaphthene (Ace) (m/z = 154), acenaphthylene (Acy) (m/z = 152), fluoranthene (Fl) (m/z = 202), pyrene (Py) (m/z = 202), benzo(c)phenanthrene (BcPhe) (m/z = 252), benzo(a)anthracene (BaA) (m/z = 228), chrysene (Ch) (m/z = 228), benzo(ghi)fluoranthene (BghiFl) (m/z = 228), benzo(b + k)fluoranthene (Bb + kF) (m/z = 252), benzo(a)fluoranthene (BaF) (m/z = 252), benzo(c)fluoranthene (BcF) (m/z = 252), benzo(a)pyrene (BaP) (m/z = 252), benzo(e)pyrene (BeP) (m/z = 252), perylene (Pe) (m/z = 252), indeno[1,2,3-cd]pyrene (IP) (m/z = 276), benzo(ghi)perylene (BghiP) (m/z = 276), and dibenzo(a + h)anthracene (DB) (m/z = 278). PAHs have been reported to be among the most abundant classes of organic pollutants generated in many open burning processes [46,47]. The values of diagnostic PAH ratios in the Trzebinia samples are presented in Table 3.

Table 2. Polycyclic aromatic hydrocarbon concentrations in the Trzebinia samples (ppm).

Sample	N	F	P	A	Ace	Acy	Fl	Py	BcPhe	BaA	Ch	BghiFl	Bb + kF	BaF
WR1G	-	0.078	6.321	0.018	0.007	0.374	0.184	5.338	0.067	1.599	2.053	0.067	2.902	0.862
WR2G	5.045	0.076	33.445	0.025	4.247	9.319	0.427	12.036	0.267	3.628	5.658	0.267	6.053	1.360
WR1O	0.231	0.554	2.937	0.006	2.884	0.747	0.011	0.019	0.021	0.048	0.265	0.021	0.162	0.019
WR3G	0.002	0.045	8.766	0.042	0.002	0.019	0.464	9.113	0.231	2.469	2.754	0.231	4.085	1.281
WR4G	-	-	-	0.003	-	-	0.116	0.300	0.007	0.040	0.047	0.007	0.139	0.049
WR2O	4.740	0.913	6.562	0.201	0.166	6.442	1.836	9.638	0.920	0.522	2.015	0.920	2.295	0.773
WR5G	4.205	10.960	61.047	0.464	14.697	35.399	1.207	13.652	1.309	2.672	0.329	1.309	2.009	0.559
WR6G	4.700	3.441	27.542	0.180	7.209	6.462	0.255	5.421	0.739	1.367	0.512	0.739	1.831	0.379
WR7G	0.365	0.950	15.880	0.078	0.643	2.452	0.241	4.453	0.539	1.004	0.155	0.539	1.693	0.398
WR3O	9.310	2.769	24.653	0.202	4.949	6.208	0.793	2.661	0.009	0.163	0.338	0.009	0.113	0.040
WR4O	1.306	0.246	96.113	0.400	39.065	65.201	1.018	5.655	0.344	0.170	0.758	0.344	0.991	0.134
WR8G	0.406	0.537	11.149	0.084	0.240	1.388	1.835	5.954	0.629	1.049	0.355	0.629	3.401	0.890
WR9G	-	0.026	1.966	0.004	0.008	0.433	0.099	1.327	0.020	0.241	0.586	0.020	0.887	0.280
WR10G	-	0.379	7.225	0.030	0.014	0.392	0.636	5.407	0.084	0.712	0.643	0.084	2.004	0.666
WR5O	-	-	7.866	0.043	1.028	15.028	0.413	8.728	0.037	0.163	0.369	0.037	0.126	0.021
WR11G	-	0.115	5.749	0.006	0.327	0.690	0.299	3.852	0.088	0.764	0.800	0.088	1.744	0.588
WR12G	0.166	0.380	48.182	0.243	0.191	0.936	0.682	39.311	1.131	16.252	15.125	1.131	20.696	3.741
WR6O	31.277	7.159	74.291	0.017	20.191	0.049	0.164	25.577	1.956	4.122	1.567	1.956	4.390	0.704
WR13G	-	-	2.561	0.007	0.025	-	0.239	1.357	0.029	0.338	0.291	0.029	0.748	0.257
WR7O	0.659	3.180	21.739	0.032	1.298	0.075	0.074	0.063	0.011	0.505	0.126	0.011	0.188	0.059
WR1.O	13.455	-	20.564	1.125	6.286	-	4.956	6.552	0.791	0.880	0.868	0.791	1.969	0.572
WR2.O	1.743	-	0.827	0.189	0.352	-	0.886	3.250	0.078	0.354	0.920	0.078	0.538	0.377
WR3.O	3.945	-	2.434	0.130	1.265	-	0.826	1.454	0.028	0.552	0.212	0.028	0.362	0.098
WR4.O	12.840	-	16.321	0.591	4.407	-	4.873	4.355	0.055	1.276	0.836	0.055	0.654	0.346
WR5.O	1.539	-	9.871	0.403	0.610	-	5.559	4.802	0.412	0.256	1.125	0.412	1.493	0.209
WR6.O	2.448	-	9.387	0.250	-	-	6.721	5.475	0.039	2.100	1.079	0.039	2.200	0.625
WR7.O	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WR8.O	7.943	-	4.683	0.073	18.866	-	0.565	0.071	0.013	0.199	0.043	0.013	0.596	0.194
WR9.O	6.929	-	3.774	0.123	2.605	-	1.200	0.902	0.020	0.199	0.176	0.020	0.590	0.262
WR10.O	4.557	-	10.589	0.411	6.042	-	1.457	1.599	0.007	0.400	0.165	0.007	0.307	0.222
WR11.O	16.953	-	11.960	0.300	58.733	-	1.095	0.602	0.044	0.331	0.258	0.044	0.345	0.367
WR12.O	3.012	-	4.173	0.063	11.002	-	0.783	0.629	0.010	0.237	0.193	0.010	0.284	0.732

Sample	BcF	BaP	BeP	Pe	IP	BghiP	DB	PAH sum ppm/g	PAH sum µg/kg	RTBaP	$\sum$PAH$_{carc}$/ $\sum$PAH	MEQ	TCDD-TEQ	BaPE ppm/g
WR1G	0.347	1.908	1.964	0.407	0.239	0.931	0.507	26.174	26,173.7	5.042	0.410	3.198	0.01	2.53
WR2G	1.093	3.670	4.636	1.005	0.323	1.428	0.886	89.850	89,850.1	9.366	0.234	6.211	0.02	4.87
WR1O	0.020	0.049	0.033	-	-	-	-	7.795	7795.0	0.080	0.066	0.098	-	0.06
WR3G	0.715	2.602	3.026	0.508	0.203	0.899	0.429	37.884	37,883.9	5.559	0.393	4.231	0.01	3.31
WR4G	0.005	0.116	0.086	0.005	0.012	0.032	-	0.964	963.9	0.139	0.440	0.164	-	0.13
WR2O	0.783	1.844	0.794	0.440	0.117	0.869	-	38.050	38,049.8	2.277	0.178	2.700	0.01	2.05
WR5G	0.322	1.322	1.082	0.188	0.104	0.502	0.425	149.558	149,557.7	4.127	0.046	2.320	-	1.89
WR6G	0.319	1.501	1.242	0.235	0.085	0.261	0.620	60.340	60,340.4	5.015	0.096	2.339	-	2.09
WR7G	0.346	1.514	1.516	0.341	0.103	0.532	0.382	33.757	33,757.3	3.783	0.159	2.267	-	1.93
WR3O	0.020	0.149	0.164	0.022	0.052	0.400	0.194	43.909	43,908.8	1.247	0.019	0.348	-	0.29
WR4O	0.092	0.085	0.814	0.182	0.035	0.398	-	212.045	212,045.2	0.465	0.010	0.483	-	0.17
WR8G	0.431	2.873	1.976	0.447	0.158	0.650	0.408	35.083	35,082.6	5.464	0.270	4.107	0.01	3.43
WR9G	0.091	0.619	0.506	0.065	0.094	0.399	0.310	7.981	7981.2	2.339	0.391	1.065	-	0.89
WR10G	0.346	1.780	1.761	0.170	0.317	1.313	1.780	25.744	25,743.7	11.134	0.320	3.214	0.01	3.06
WR5O	0.010	0.079	0.033	0.039	-	-	-	34.022	34,021.9	0.145	0.022	0.139	-	0.10
WR11G	0.209	1.144	1.262	0.170	0.188	0.711	1.156	19.950	19,949.6	7.285	0.330	2.186	-	2.02
WR12G	4.335	11.982	12.421	3.330	0.676	2.407	1.457	184.611	184,611.0	23.513	0.417	19.836	0.05	15.33
WR6O	0.934	3.024	2.988	0.508	0.187	-	0.765	150.549	150,549.3	7.894	0.081	4.766	0.01	4.05
WR13G	0.118	0.727	0.516	0.053	0.135	1.623	0.928	9.981	9981.1	5.661	0.353	1.566	-	1.37
WR7O	0.029	0.087	0.021	0.037	-	0.530	-	28.065	28,064.6	0.238	0.032	0.278	-	0.13
WR1.O	0.515	2.260	1.590	0.273	0.082	0.384	-	50.458	50,458.1	2.664	0.102	2.938	0.01	2.46
WR2.O	0.257	0.853	0.574	0.116	0.090	1.450	-	11.190	11,189.7	1.115	0.241	1.336	-	0.92
WR3.O	0.064	0.357	0.231	0.090	0.112	0.684	-	8.927	8927.3	0.541	0.129	0.661	-	0.42
WR4.O	0.235	1.322	0.582	0.061	0.033	0.172	-	36.172	36,172.4	1.592	0.086	1.647	-	1.45
WR5.O	0.281	1.379	0.136	0.455	-	-	-	27.402	27,402.3	1.592	0.157	1.792	-	1.50
WR6.O	0.324	3.325	1.058	0.198	0.121	0.809	-	33.750	33,750.0	3.886	0.260	4.257	0.01	3.62
WR7.O	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WR8.O	0.058	0.232	0.260	-	-	-	-	25.866	25,866.4	0.345	0.032	0.398	-	0.29
WR9.O	-	0.350	0.283	-	-	-	-	10.504	10,503.9	0.447	0.078	0.516	-	0.40
WR10.O	0.139	0.212	0.147	-	-	-	-	21.705	21,705.1	0.313	0.042	0.325	-	0.26
WR11.O	0.159	0.223	0.177	-	-	-	-	74.640	74,639.7	0.386	0.013	0.341	-	0.27
WR12.O	0.094	0.526	0.292	0.089	0.012	0.047	-	19.174	19,173.9	0.606	0.060	0.632	-	0.56
WR6O	0.347	1.908	1.964	0.407	0.239	0.931	0.507	26.174	26,173.7	5.042	0.410	3.198	0.01	2.53
WR13G	1.093	3.670	4.636	1.005	0.323	1.428	0.886	89.850	89,850.1	9.366	0.234	6.211	0.02	4.87
WR7O	0.020	0.049	0.033	-	-	-	-	7.795	7795.0	0.080	0.066	0.098	-	0.06
WR1.O	0.715	2.602	3.026	0.508	0.203	0.899	0.429	37.884	37,883.9	5.559	0.393	4.231	0.01	3.31
WR2.O	0.005	0.116	0.086	0.005	0.012	0.032	-	0.964	963.9	0.139	0.440	0.164	-	0.13
WR3.O	0.783	1.844	0.794	0.440	0.117	0.869	-	38.050	38,049.8	2.277	0.178	2.700	0.01	2.05
WR4.O	0.322	1.322	1.082	0.188	0.104	0.502	0.425	149.558	149,557.7	4.127	0.046	2.320	-	1.89
WR5.O	0.319	1.501	1.242	0.235	0.085	0.261	0.620	60.340	60,340.4	5.015	0.096	2.339	-	2.09
WR6.O	0.346	1.514	1.516	0.341	0.103	0.532	0.382	33.757	33,757.3	3.783	0.159	2.267	-	1.93
WR7.O	0.020	0.149	0.164	0.022	0.052	0.400	0.194	43.909	43,908.8	1.247	0.019	0.348	-	0.29
WR8.O	0.092	0.085	0.814	0.182	0.035	0.398	-	212.045	21,2045.2	0.465	0.010	0.483	-	0.17

Table 2. *Cont.*

Sample	N	F	P	A	Ace	Acy	Fl	Py	BcPhe	BaA	Ch	BghiFl	Bb + kF	BaF
WR9.O	0.431	2.873	1.976	0.447	0.158	0.650	0.408	35.083	35,082.6	5.464	0.270	4.107	0.01	3.43
WR10.O	0.091	0.619	0.506	0.065	0.094	0.399	0.310	7.981	7981.2	2.339	0.391	1.065	-	0.89
WR11.O	0.346	1.780	1.761	0.170	0.317	1.313	1.780	25.744	25,743.7	11.134	0.320	3.214	0.01	3.06
WR12.O	0.010	0.079	0.033	0.039	-	-	-	34.022	34,021.9	0.145	0.022	0.139	-	0.10

N—naphthalene, F—fluorene, P—phenanthrene, A—anthracene, Ace—acenaphthene, Acy—acenaphthylene, Fl—fluoranthene, Py—pyrene, BcPhe—benzo(c)phenanthrene, BaA—benzo(a)anthracene, Ch—chrysene, BghiFl—benzo(ghi)fluoranthene, Bb + kF—benzo(b + k) fluoranthene, BaF—benzo(a)fluoranthene, BcF—benzo(c)fluoranthene, BaP—benzo(a)pyrene, BeP—benzo(e)pyrene, Pe—perylene, IP—indeno[1,2,3-cd]pyrene, BghiP—benzo(ghi)perylene, DB—dibenzo(a + h)anthracene.

Table 3. Values of diagnostic PAH ratios in the Trzebinia samples.

Sample	P/A	A/P	A/(A + P)	Fl/(Fl + Py)	Fl/Py	Fl/(Fl + P)	BaA/(BaA + Ch)	BaP/BghiP	IP/BghiP	IP/(IP + BghiP)	BaA/BaP	Py/BaP
WR1G	10.62	0.09	0.09	0.57	1.32	0.81	0.53	2.45	1.31	0.57	1.34	4.98
WR2G	6.12	0.16	0.14	0.54	1.19	0.62	0.24	3.08	1.15	0.54	1.58	5.83
WR3G	15.70	0.06	0.06	0.87	6.85	0.14	0.21	-	-	-	1.58	0.68
WR1O	8.04	0.12	0.11	0.54	1.19	0.82	0.56	3.46	1.15	0.53	1.52	6.24
WR4G	-	-	-	0.54	1.16	1.00	0.55	4.34	1.83	0.65	0.56	4.61
WR2O	8.22	0.12	0.11	0.34	0.51	0.74	0.27	2.53	0.69	0.41	0.45	9.31
WR5G	4.93	0.20	0.17	0.53	1.12	0.49	0.92	3.15	1.06	0.51	3.25	18.39
WR6G	4.79	0.21	0.17	0.50	0.98	0.42	0.79	6.86	1.66	0.62	1.46	6.43
WR7G	6.59	0.15	0.13	0.50	0.99	0.51	0.90	3.40	0.98	0.50	1.06	5.24
WR8G	6.21	0.16	0.14	0.59	1.43	0.37	0.41	0.44	0.66	0.40	1.76	31.85
WR3O	7.80	0.13	0.11	0.56	1.27	0.22	0.24	0.26	0.45	0.31	3.20	118.12
WR4O	12.42	0.08	0.07	0.55	1.22	0.71	0.81	5.28	1.24	0.55	0.59	3.69
WR9G	14.12	0.07	0.07	0.57	1.32	0.77	0.37	1.85	1.20	0.55	0.63	3.82
WR10G	8.73	0.11	0.10	0.55	1.24	0.78	0.61	1.62	1.23	0.55	0.64	5.41
WR11G	59.77	0.02	0.02	0.35	0.54	0.70	0.39	-	-	-	3.31	196.45
WR5O	8.57	0.12	0.10	0.56	1.28	0.76	0.58	1.92	1.35	0.57	1.07	6.00
WR12G	3.08	0.33	0.25	0.52	1.09	0.77	0.61	5.98	1.43	0.59	2.17	5.81
WR6O	4.30	0.23	0.19	0.42	0.73	0.49	0.79	3.73	0.98	0.50	2.19	15.05
WR7O	11.39	0.09	0.08	0.55	1.22	0.71	0.62	1.50	1.19	0.54	0.75	3.33
WR13G	22.52	0.04	0.04	0.95	20.53	0.18	0.85	-	-	-	9.32	1.28
WR1.O	5.39	0.19	0.16	0.41	0.71	0.46	0.59	1.35	1.09	0.52	3.27	26.97
WR2.O	1.29	0.77	0.44	0.20	0.25	0.79	0.65	0	0.32	0.24	-	-
WR3.O	5.53	0.18	0.15	0.35	0.53	0.55	0.79	0.62	0.84	0.46	2.49	7.26
WR4.O	8.14	0.12	0.11	0.51	1.04	0.51	0.69	9.19	0.98	0.49	1.55	5.87
WR5.O	7.23	0.14	0.12	0.52	1.08	0.67	0.24	-	-	-	0.30	6.20
WR6.O	11.06	0.09	0.08	0.53	1.14	0.72	0.74	4.91	0.76	0.43	1.01	2.93
WR7.O	7.74	0.13	0.11	0.52	1.08	0.47	-	-	-	-	-	-
WR8.O	18.92	0.05	0.05	0.88	7.45	0.30	0.87	-	-	-	1.38	0.54
WR9.O	9.05	0.11	0.10	0.55	1.24	0.53	0.62	-	-	-	0.92	4.60
WR10.O	7.60	0.13	0.12	0.46	0.85	0.33	0.78	-	-	-	3.02	13.41
WR11.O	11.74	0.09	0.08	0.63	1.70	0.24	0.65	-	-	-	2.38	4.80
WR12.O	19.63	0.05	0.05	0.54	1.16	0.40	0.64	13.31	1.25	0.56	0.72	2.13

P—phenanthrene, A—anthracene, Fl—fluoranthene, Py—pyrene, BaA—benzo(a)anthracene, Ch—chrysene, BaP—benzo(a)pyrene, BeP—benzo(e)pyrene, Pe—perylene, IP—indeno(1,2,3-cd)pyrene, BghiP—benzo(ghi)perylene.

In the samples analyzed, fluoranthene and pyrene were detected in 31 samples. The highest fluoranthene concentrations (ppm) were recorded in the following samples: WR6.O (6.721 ppm), WR5.O (5.559 ppm),WR1.O (4.956 ppm), WR4.O (4.873 ppm), WR2O (1.836 ppm), WR8G (1.835 ppm), WR10.O (1.457 ppm), WR5G (1.207 ppm), WR9.O (1.200 ppm), WR11.O (1.095 ppm), and WR4o (1.018 ppm), while pyrene concentrations were recorded in the following samples: WR12G (39.311 ppm), WR6o (25.577 ppm), WR5G (13.652 ppm), WR2G (12.036 ppm), WR2o (9.638 ppm), WR3G (9.113 ppm), WR5O (8.728 ppm), and WR1.O (6.552 ppm).

Phenanthrene and anthracene are among the co-extensive compounds, where the formation of anthracene is thought to result from combustion [48,49]. Lighter naphthalene (*m*/*z* = 128) was recorded in 24 samples: WR2G, WR1O, WR3G, WR2O, WR5G, WR6G, WR7G, WR3O, WR4O, WR8G, WR12G, WR6O, WR7O, WR1.O, WR2.O, WR3.O, WR4.O, WR5.O, WR6.O, WR8.O, WR9.O, WR10.O, WR11.O, and WR12.O. The average concentrations (ppm) of individual PAHs in the samples were as follows: N—4.305 ppm, F—0.994 ppm, P—17.455 ppm, A—0.18 ppm, Ace—6.48 ppm, Acy—4.738 ppm, Fl—1.257 ppm, Py—5.923 ppm, BcPhe—0.31 ppm, BaA—1.394 ppm, Ch—1.269 ppm, BghiFl—0.31 ppm, Bb + kF—2.056 ppm, BaF—0.533 ppm, BcF—0.396 ppm, BaP—1.504 ppm, BeP—1.318 ppm, Pe—0.295 ppm, IP—0.109 ppm, BghiP—0.545 ppm, and DB—0.32 ppm.

Some of the most abundant PAHs (except naphthalene) in controlled and uncontrolled landfill fire waste samples are reported to be phenanthrene, fluoranthene and pyrene [33]. In addition, the low-molecular weight PAHs, naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, and fluorene, are quickly transformed by many bacteria and fungi. Furthermore, high-molecular weight PAHs are more recalcitrant in the environment and resist both chemical and microbial biodegradation [50].

The diagram in (Figure 3) presents the distribution pattern (%) of 2–6-ring PAHs in the samples (ppm) from Trzebinia. The most dominant PAHs are 3-ring (P, A, Ace, Acy, F), which are present in 31. The sum of the 3-ring PAH values was 955.102 ppm. 4-ring PAHs (Fl, Py, BaA, Ch) represent the second value of the tested samples. These were observed in 31 samples, with a total value of 314.701 ppm. 5-ring-shaped PAHs (BghiFl, BcPhe, Bb + kF, BaF, BcF, BaP, BeP, Pe, DB) were observed in 31 samples, with a total value of 225.382 ppm. Naphthalene 2-ring PAH was observed in 25 samples, with a total value of 137.774 ppm. The lowest level of PAHs was 6-ring (IP, BghiP). These were observed in 24 samples. Naphthalene was more dominant in burnt waste than in soil samples. In contrast, 3-ring PAHs were more dominant in soil samples.

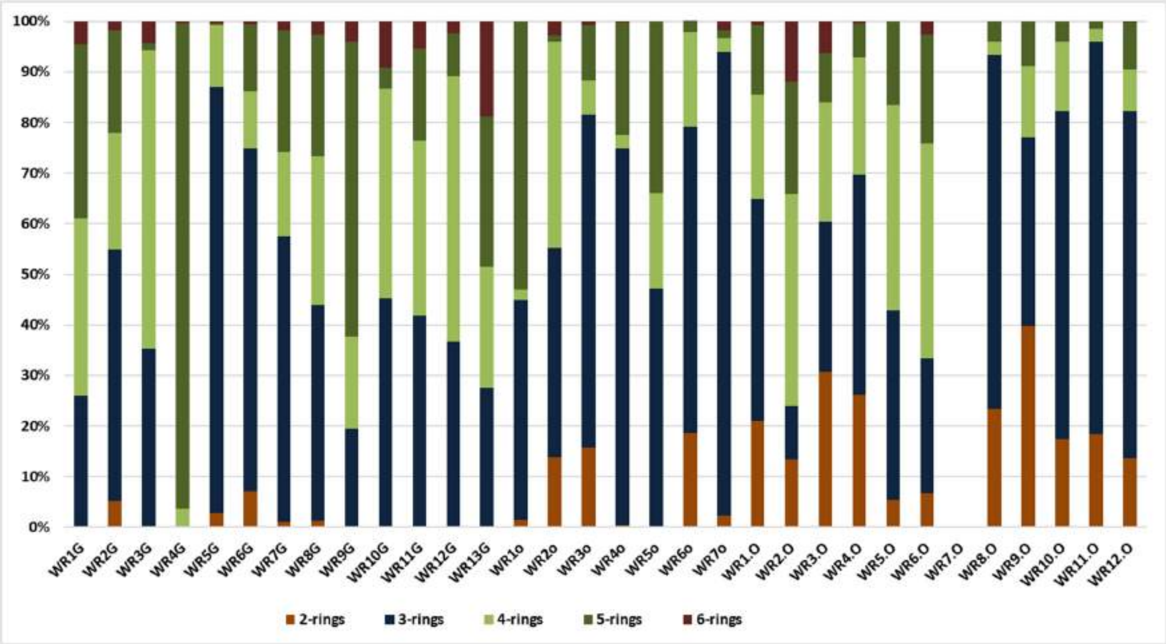


Figure 3. Distribution pattern (%) of 2–6-ring PAHs in the samples (ppm) from Trzebinia.

An important question to ask at the outset is whether the source of pollution is traffic, combustion of fossil fuels in nearby plants, or the wild landfill fire described here. For this purpose, PAH diagnostic coefficients were used (Figures 4 and 5). Several PAH diagnostic ratios were calculated based on quantitative analysis (Table 3) [51]. The origins of PAHs in soil may be identified by the phenanthrene/anthracene and the fluoranthene/pyrene ratios [52]. Three types of ratios of PAHs to their possible effects were compared: anthracene and phenanthrene to fluoranthene and pyrene, benzo(a)anthracene and chrysene to fluoranthene and pyrene, and indeno[1,2,3-cd]pyrene and benzo(g,h,i)perylene to fluoranthene and pyrene. In Figure 4, the distribution of the individual soil samples is presented, whereas Figure 5 presents the distribution of burnt waste from the wild landfill in Trzebinia. The soil samples in range (A/(P + A)) were plotted in the area corresponding to combustion and petroleum to biomass and coal combustion (Fl/(Fl + Py))—WR1G, WR2G, WR3G, WR4G, WR5G, WR8G, WR9G, WR10G, WR11G, WR12G, and WR13G. In the second case, most of the samples were recorded in the combustion range (BaA/(Ch + BaA)) to biomass and coal combustion (Fl/(Fl + Py))—except the WR2G sample. In the third case, most samples—except WR6G and WR7G, were recorded, with 11 samples in the range of biomass and coal combustion IdP/(IdP + BghiP)) to biomass and coal combustion (Fl/(Fl + Py)). Samples of burnt solid waste showed high separability compared to soil samples (A/(P + A)), (BaA/(Ch + BaA)), IdP/(IdP + BghiP)) to (Fl/(Fl + Py)). The production of PAHs will presumably be controlled by waste composition (concentrations have been shown to increase dramatically when the proportion of plastic in the waste increases) and combustion conditions [53]. Escobar-Arnanz et al. [34] suggested the potential of aromatic compounds with a wide range of rings to diffuse into the environment through, among other things, emission sources, the nature of the compounds produced, and meteorological conditions, where atmospheric deposition is considered the main source of PAHs in soil [54].

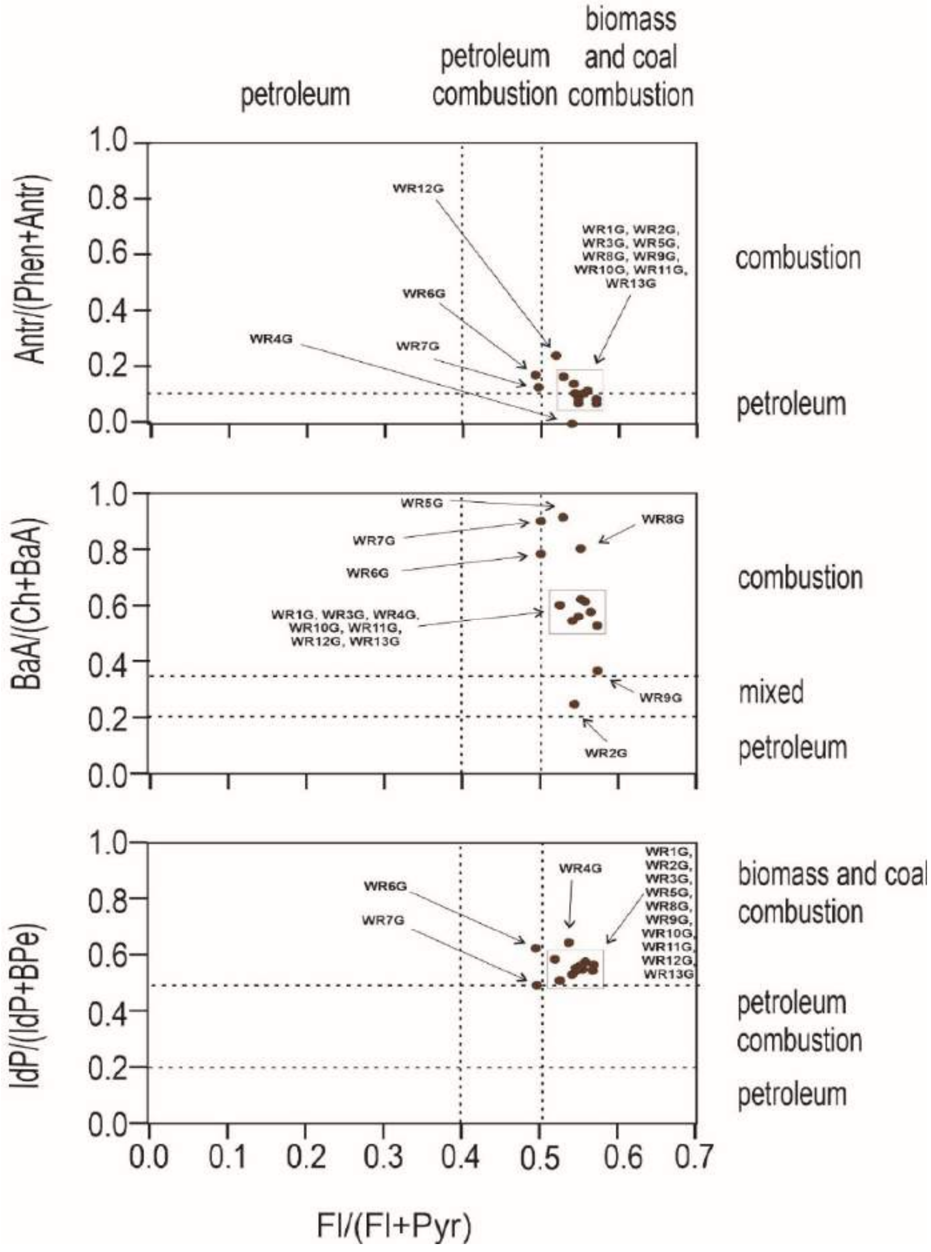


Figure 4. Diagnostics diagrams of PAHs in soils investigated from wild waste dump in Trzebinia on Słowackiego Street. A—anthracene, P—phenanthrene, Fl—fluoranthene, Py—pyrene, BaA—benzo(a)anthracene, Ch—chrysene, IP—indeno(1,2,3-cd)pyrene, BghiP—benzo(ghi)perylene.

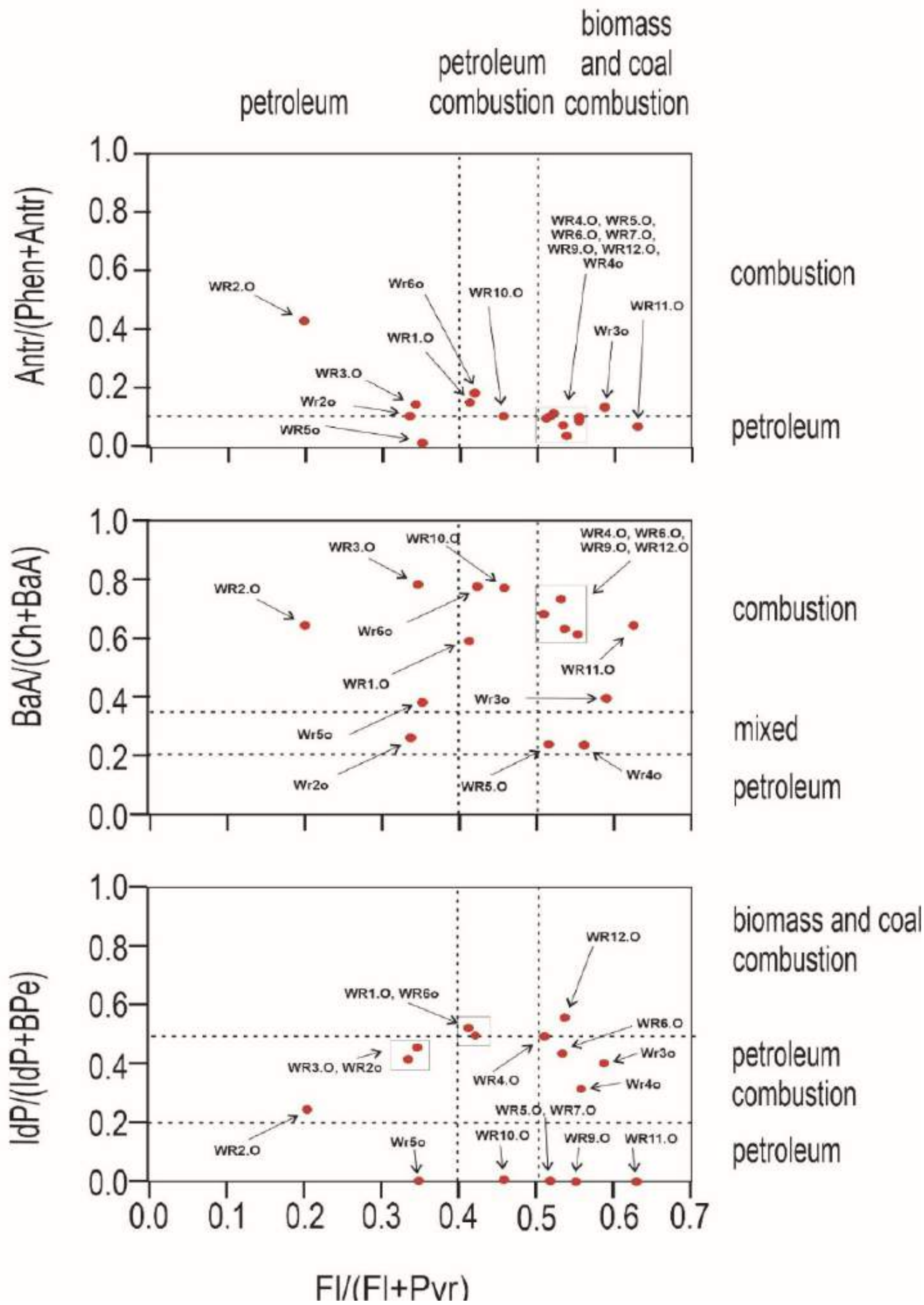


Figure 5. Diagnostics diagrams of PAHs in burnt waste investigated from wild waste dump in Trzebinia on Słowackiego Street. A—anthracene, P—phenanthrene, Fl—fluoranthene, Py—pyrene, BaA—benzo(a)anthracene, Ch—chrysene, IP—indeno(1,2,3-cd)pyrene, BghiP—benzo(ghi)perylene.

The mean RTBaP concentration of the samples tested was 3.571 ppm. Above-average results were observed in 13 samples (11 soil samples, 2 burnt waste): WR1G = 5.042 ppm, WR2G = 9.366 pmm, WR3G = 5.559 pmm, WR5G = 4.127 pmm, WR6G = 5.015 ppm, WR7G = 3.783 ppm, WR8G = 5.464 ppm, WR10G = 11.134 ppm, WR11G = 7.285 ppm, WR12G = 23.513 ppm, WR13G = 5.661 ppm, WR6O = 7.894 ppm, and WR6.O = 3.886 ppm. The highest concentration was found in soil samples WR12G and WR10G. The mean MEQ concentration of the samples tested was 2.386 ppm. Above-average results were observed in 10 samples (6 soil samples, 4 burnt waste): WR1G = 3.198 ppm, WR2G = 6.211 ppm, WR3G = 4.231 ppm, WR8G = 4.107 ppm, WR10G = 3.214 ppm, WR12G = 19.836 ppm, WR2O = 2.7 ppm, WR6O = 4.766 ppm, WR1.O = 2.938 ppm, and WR6.O = 4.257 ppm. The highest concentration was found in soil sample WR12G. The TCDD-TEQ were observed in 10 samples: WR1G, WR2G, WR3G, WR8G, WR10G, WR12G, WR2O, WR6O, WR1.O, and WR6.O—the highest in soil sample WR12G = 0.05 ppm. The average ratio $\sum PAH_{carc}/\sum PAH$ in the tested samples was 0.171 ppm. Above-average results were observed in 13 samples (10 soil samples, 3 burnt waste): WR1G = 0.41 ppm, WR2G = 0.234, WR3G = 0.393 ppm, WR4G = 0.44 ppm, WR8G = 0.27 ppm, WR9G = 0.391 ppm, WR10G = 0.32 ppm, WR11G = 0.33 ppm, WR12G = 0.417 ppm, WR13 = 0.353 ppm, WR2O = 0.178 ppm, WR2.O = 0.241 ppm, and WR6.O = 0.26 ppm. The highest concentration was found in soil samples WR4G and WR12G.

Studies related to PAHs under the influence of fire in landfills have also been conducted in several types of research—[4,18,33,55].

The sum of PAH concentrations in the soil samples investigated shows high variability in the range of 0.964–184.611 ppm. The same conclusion can be reached for samples of combusted waste 0.000–212.045 ppm. Only sample WR7.O (unburnt wallpaper) was below the detection limit of ppm. The highest content of the PAH sum was in the burnt waste sample WR4O: 212.045 ppm. However, while 6 more samples of combusted waste were analyzed than soil samples, the mean sum of PAHs is higher in the soil samples (52.452 ppm). The samples collected may be divided into three subgroups: (i) with a maximum concentration of PAHs > 100 ppm/g in samples: WR5G, WR12G, WR4O, and WR6O (4 samples), (ii) with a mean concentration of PAHs in the range 50–100 ppm/g, including WR2G, WR6G, WR1.O, and WR11.O (4 samples), and (iii) with the lowest PAH concentrations of < 50 ppm/g, including WR1G, WR3G, WR4G, WR7G, WR8G, WR9G, WR10G, WR11G, WR13G, WR1O, WR2O, WR3O, WR5O, WR7O, WR2.O, WR3.O, WR4.O, WR5.O, WR6.O, WR7.O, WR8.O, WR9.O, WR10.O, and WR12.O (24 samples). In the samples examined, a high cumulative PAH content was found, which is alarming even years after the fire in the wild landfill. The total concentrations of all carcinogenic PAHs (BaA, BaP, Bb + kF, Ch, DB, IP) are well above the permissible values. The highest sum was found in soil samples 153.324 ppm, with the largest amount found in sample WR12G = 66.189 ppm (Figure 6). In the combusted waste samples, 59.554 ppm were measured, with the WR6O sample having the highest value of 14.056 ppm. These results may be compared with the occurrence of PAH contaminants in other parts of Poland [56,57]. In addition, it can be seen that the sum results of PAHs correspond to highly contaminated industrial soils, although there is no industrial plant around the landfill [58,59]. This also shows that soil microorganisms cannot cope with the degradation of this amount of pollutant.

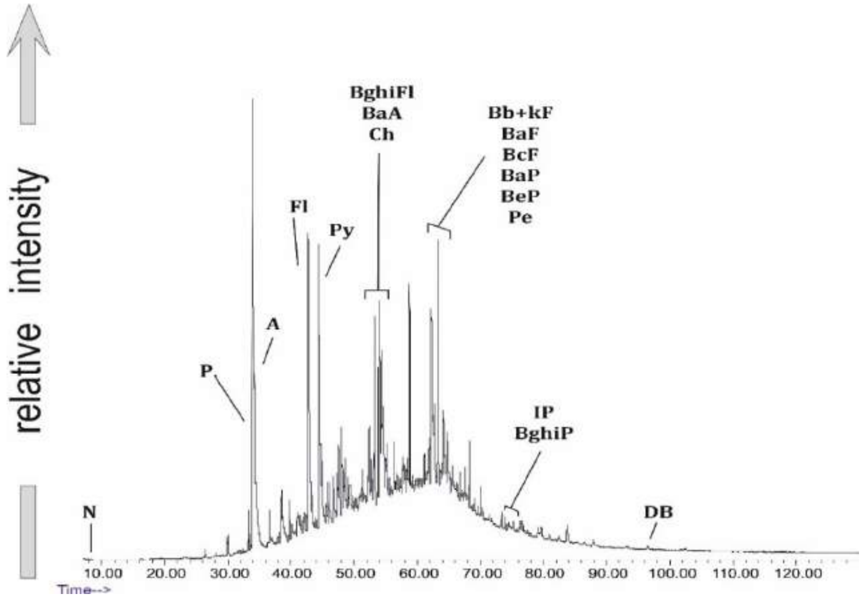


Figure 6. Generalized PAH distribution in sample WR12G.

To assess the effects of PAHs on health and the environmental, several indicators were calculated. They defined the toxicity of individual PAHs and the whole compound group to assess the risk caused by exposure to a PAH mixture. The reference contamination was BaP. Basically, the TEF factor for the other 16 PAHs was calculated using BaP. The toxicity value, TEQ, is the sum of individual PAH concentrations and their relative toxicity coefficients [60,61] (Table 2). The organization of carbon atoms as a bay region causes a high degree of biochemical reactivity to some PAHs and their metabolites [62]. The results showed an increased risk of carcinogenicity in the area of the fire, but no serious risk to the surrounding residents was identified. These results are comparable to other studies [33,55].

The mutagenicity equivalent MEQ and concentrations were also calculated [40]. This is one of the factors that may increase cancer risk [63]. MEQ concentrations were higher in soil samples than in combusted waste. Accordingly, WR12G recorded 19.836 ppm and WR2G 6.211 ppm. RTBaP and MEQ are quite different (RTBaP 114.26 ppm compared to MEQ 76.359 ppm).

BaPE was used to evaluate the toxicity of PAHs (Table 2). This method is often used to calculate toxicity in soil, air, and combusted waste in this article. The values of the indicator vary considerably between the soil samples and the combusted waste. Most soil samples exceeded 1.5 ppm/g, with the highest result in sample WR12G of 15.33 ppm/g. Almost all combusted waste samples (except WR6O, WR1.O, and WR6.O) did not exceed the limit value of 1.5 ppm/g, with the highest result in sample WR6O of 4.05 ppm/g.

PAH distribution transformations occur during migration in the air, which were not observed in the source material. A group of compounds emitted on particles exhibits a different distribution from the source material due to the sorption of the pyrolytic phase itself. The formation of hydrocarbons in fires in municipal waste occurs with oxygen or with severely restricted access. It is assumed that the formation of hydrocarbon groups is different from that of pyrolysis during complete or near-complete combustion. In addition, the use of diagnostic methods obtained from the landfill fire was not considered appropriate due to anomalies of high PAH levels in soils.

2-ring naphthalenes were found to be significantly higher in combusted waste than in soil samples. This may be related to a study [64], in which, in laboratory conditions, controlled heating and burning of coal spoils was carried out to determine PAH emissions with full access and without access to oxygen. Increased 2-ring concentrations in the range of 200 °C were observed. In addition, another paper [65] established that temperatures of up to 250 °F have been measured in municipal solid waste landfills when they are undergoing a subsurface reaction. This means that a firing temperature of about 200 °C may have contributed to the increase of naphthalenes in the combusted waste.

3.2. MPI Concentrations in Soil and Combusted Solid Waste Samples from the Wild Landfill Fire

Methylphenanthrenes (m/z = 192) were found in 30 samples (Table 4) from the wild waste dump in Trzebinia. The average values of MPI3 and MPI1 in the samples from this set were MPI3 = 1.97 and MPI1 = 2.95. The highest MPI3 above average was recorded in samples WR1G = 1.63, WR2G = 2.01, WR4O = 3.45, WR8G = 4.34, WR9G = 3.38, WR10G = 3.27, WR5O = 4.93, WR11G = 4.39, WR13G = 3.91, and WR5.O = 2.01. On the other hand, MPI1 index above the mean was recorded in samples WR2G = 3.02, WR4O = 5.18, WR8G = 6.52, WR9G = 5.07, WR10G = 4.90, WR5O = 7.39, WR11G = 6.59, WR13G = 5.86, and WR5.O = 3.01. The mean R_c was 2.84. The MPI1 values were used to calculate the theoretical reflectivity value of fossil fuel vitrinite Rc based on the formula proposed by Radke [66].

Table 4. Values of geochemical ratios found in DEP extracts ratios in the Trzebinia samples.

Sample	MPI3 (1)	MPI1 (2)	R_c (3)	Sample	MPI3 (1)	MPI1 (2)	R_c (3)
WR1G	1.63	2.45	2.61	WR12G	0.46	0.69	1.02
WR2G	2.01	3.02	3.12	WR6O	1.02	1.53	1.78
WR1O	1.23	1.85	2.06	WR13G	3.91	5.86	5.68
WR3G	1.16	1.75	1.97	WR7O	1.89	2.83	2.95
WR2O	1.07	1.60	1.84	WR1.O	0.93	1.40	1.66
WR5G	1.86	2.78	2.90	WR2.O	0.74	1.10	1.39
WR6G	1.44	2.16	2.35	WR3.O	1.29	1.93	2.14
WR7G	1.29	1.93	2.14	WR4.O	1.46	2.19	2.37
WR3O	1.65	2.48	2.63	WR5.O	2.01	3.01	3.11
WR4O	3.45	5.18	5.06	WR6.O	1.89	2.84	2.95
WR8G	4.34	6.52	6.26	WR8.O	1.65	2.47	2.62
WR9G	3.38	5.07	4.96	WR9.O	0.69	1.03	1.33
WR10G	3.27	4.90	4.81	WR10.O	1.27	1.90	2.11
WR5O	4.93	7.39	7.05	WR11.O	1.79	2.68	2.81
WR11G	4.39	6.59	6.33	WR12.O	0.90	1.35	1.61

(1) MPI-3 = (2-methylphenanthrene + 3-methylphenathrene)/(1-methylphenathrene + 9-methylphenathrene); m/z = 192; thermal maturity [67]. (2) MPI-1 = 1.5(2-methylphenanthrene + 3-methylphenanthrene)/(phenanthrene + 1-methylphenanthrene + 9 methylphenanthrene); thermal maturity [66]. (3) R_c = 0.60 MPI-1 + 0.40; calculated according to the [67] formula.

R_c values above 2.0 correspond to a thermally highly transformed organic substance, while significant parameter variations indicate heterogeneous temperatures during the fire. At the same time, it was noted that the location of the samples taken affects the index value. In the case of soils, these high values indicate that a fire is the cause and not car traffic. An example R_c of car traffic and coal combustion in private fireplaces would be about 0.7–0.9 [66–69]. The mean MPI3 and MPI1 values also correspond to a high thermal transformation of the samples.

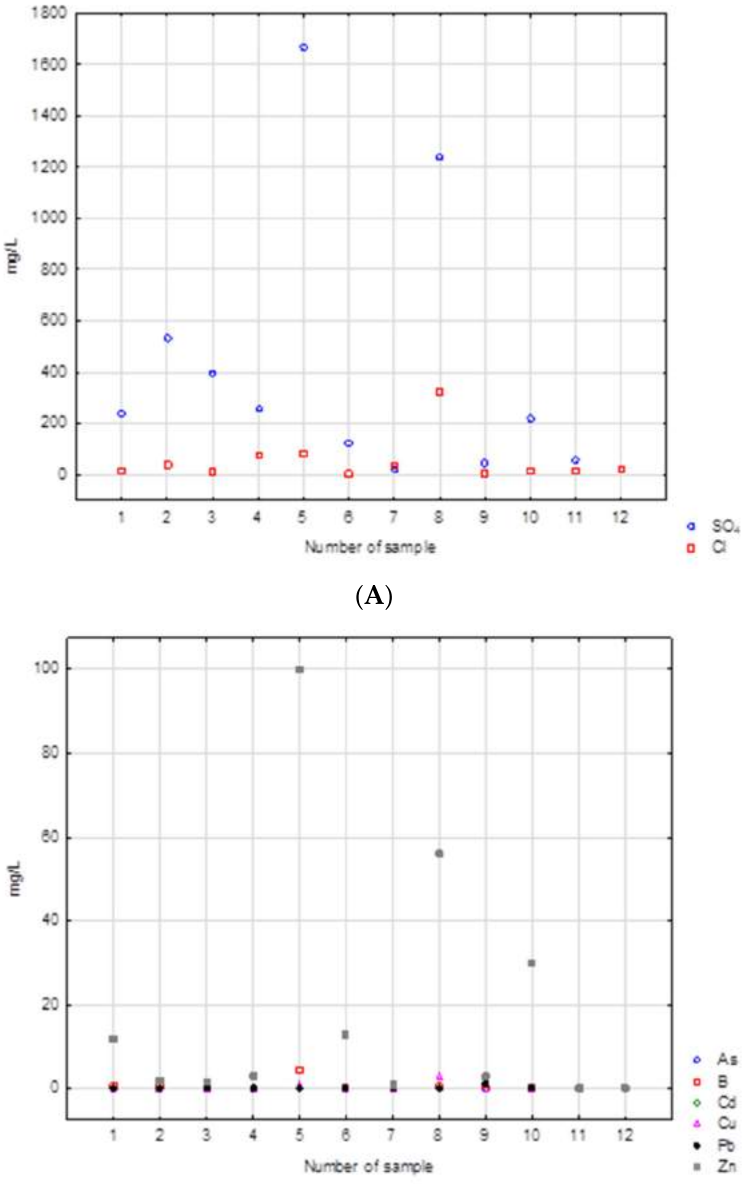
3.3. Compound Contents in Leachate Samples of Burnt Solid Waste from the Wild Landfill Fire

Physical and chemical results indicate that the leachates analyzed were most contaminated by major ions, namely sulfate and chloride (Table 5).

Table 5. Results of physicochemical analyses of the leachates analyzed.

Ions [mg/L]	Mean	Min	Max	St. Dev
SO_4	401.367	17.900	1670.00	524.607
Cl	51.881	0.7700	320.00	88.540
As	0.032	0.0062	0.09	0.031
B	0.960	0.0770	4.60	1.430
Cd	0.008	0.0001	0.04	0.012
Cu	0.359	0.0049	3.00	0.857
Pb	0.108	0.0067	1.10	0.312
Zn	18.468	0.2200	100.00	30.570

Of the metals, zinc is the most significant contributor. The highest concentrations of sulfate were observed in samples 5 and 8. These include samples of burnt tires and rubber and foam. Both samples had sulfate contents exceeding 1000 mg/L. These samples have the highest concentrations of most contaminants. This is also true for the chloride content in these samples: 85 and 320 mg/L, respectively. Sample 8 also had a high concentration of zinc, over 50 mg/L. In this case, the highest concentration was found in sample 5 (100 mg/L). There were few arsenic, lead, cadmium, or copper concentrations in the samples tested. The concentrations of each constituent in the leachate are shown in (Figure 7A,B). The leachate produced by washing burnt rubber black waste and tires displayed a dark black color. This was most likely caused by very fine soot from the combustion process.



(**A**)

(**B**)

Figure 7. (**A**,**B**) Concentrations of main ions in the leachates analyzed.

The results obtained from the leachate tests show that the contamination caused by metals and major ions is low compared to organic compounds (Appendix A Table A1). Similar results regarding the amount of contaminant leaching from such waste has been documented in other studies such as Hennerbert et al. [70]. Burnt tires also had significant concentrations of sulfate and zinc in the leachate, but the other parameters tested did not indicate high contamination.

The results of the physicochemical analyses were compared with the permissible values of these parameters in groundwater based on the Regulation of the Minister of Maritime Economy and Inland Navigation of 11 October 2019, on the criteria and method of assessing the state of groundwater bodies. In the case of sulfates, three samples (WR2.O, WR5.O, and WR8.O) would be classified as water quality class V (poor chemical status). Samples WR7.O, WR9.O, and WR12.O would be classified as quality class I (good chemical condition). It should be noted that the V class of water quality includes water samples with sulfate concentrations higher than 500 mg/L. In this context, samples with concentrations exceeding 1200 mg/L seem particularly dangerous. Typical sulfate levels in fresh water range from 0 to 630 mg/L in rivers, from 2 to 250 mg/L in lakes and from 0 to 230 mg/L in groundwater [71].

It is assumed that the chloride concentration in unpolluted waters can reach 10 mg/L. The concentration of this component in precipitation fluctuates around 1 mg/L. The high chloride content in waters and soils is a result of anthropogenic activity. It is also a typical indicator of groundwater pollution in the area of landfills [72]. The upper limit of the hydrochemical background for this component is 60 mg/L. In the case of sample numbers WR4.O, WR5.O, and WR8.O, these values are much higher. In the last one, it would be classified as water quality class IV. The high chloride content of this sample may come from dyes in the textiles.

In the case of arsenic, the acceptable concentration value for the first class is 0.01 mg/L. On the other hand, the upper limit of the natural hydrochemical background is twice as high. The arsenic content in the samples tested ranges from 0.0062 (WR10.O) to 0.085 mg/L (WR3.O). This suggests that the most contaminated samples would be classified in quality class IV.

Only two samples (WR4.O and WR5.O) have the content of boron ions appropriate for the V quality class. In other cases, these are concentrations characteristic of quality class III and higher. Boron is an important pollution indicator for municipal waste, but it is also a component of paints.

In the event of contamination with copper, cadmium, or lead, most samples would be graded into third and fourth quality classes. However, there are also samples whose concentration of the mentioned components suggests that they belong to class V. For example, the concentration of lead in sample WR9.O is ten times higher than the lower limit for class V, and in the case of copper ions, a concentration six times higher was found in sample WR8.O.

In the case of zinc ions, the natural hydrochemical background is in the range 0.005–0.050 mg/L. Only two of the samples tested could be classified as class II of water quality. Most, however, are classified in the fourth and fifth quality class. For samples WR10.O and WR5.O, the concentrations of zinc ions are 15 times and 50 times higher, respectively, than the fifth-class limit. It should be borne in mind that high zinc contents in the waste tested may be, among other things, the effect of the use of zinc oxide in tire vulcanization.

The results from the laboratory were also compared with the acceptable standards for leaching pollutants specified in the Regulation of the Minister of Economy of July 16, 2015, on allowing waste to be deposited in landfills [73]. The values were converted depending on the size of the waste sample collected. For all samples tested, except for sample number 3 (sponge), the limit values were reduced by 10 times, and for this sample by 20. When comparing the results obtained with the standards, for all parameters, except for lead and zinc, the requirements for depositing non-municipal waste are met. In the case of lead, only one sample (WR9.O) slightly exceeds the allowed concentration. The situation is much worse with zinc. For this sample size, the acceptable value limit is 5 mg/L. In the set of analyses obtained, as many as 5 samples exceed this value. One of the samples (WR5.O) was up to 20 times higher. It should also be noted that these are the results of leachability tests obtained from small samples of waste. These values should be properly recalculated depending on the total mass of waste located in the wild landfill.

It is also possible to constantly monitor changes in soil or water quality in the vicinity of such facilities with the use of sensors and artificial intelligence [74,75].

The concentrations of the individual components are not too high compared to the typical values that can be recorded in soils. A similar lack of increased concentration of inorganic compounds in soils in the vicinity of the fires was also observed in other studies [55,76,77].

4. Conclusions

Soil samples and incinerated waste were analyzed to determine how a wild landfill fire may affect the environment and the health of the surrounding inhabitants. The most significant finding of the research is that the currently deposited burnt solid waste in the wild landfill poses a potentially permanent hazard to the environment. Samples taken even a long time after the fire started in the study area contain significant concentrations of hazardous organic compounds, in particular PAHs. This includes both soil samples and solid waste transformed by the fire. The results obtained show a high total concentration of the PAHs found in the samples. These results show that these soils are at similar pollution levels to soils heavily polluted by industry, although there are no industrial installations on the site itself or in the surrounding area. However, lower levels of mutagenicity and carcinogenicity were observed. $\Sigma PAH_{carc}/\Sigma PAH$ did not approach 1, which is considered a potential health risk, in any of the samples tested. However, since the general summary PAH level is high, it follows that carcinogenicity is also high.

No significant spikes in heavy metal content were observed in leachate collected from the incinerated waste samples. This may be justified because, during the incineration of solid waste such as tires and black rubber, more organic compounds are formed by high temperature and oxidation.

Personal protective measures (gloves, protective clothing, and protective masks) are required for workers in all future work on the site of a burnt wild landfill. They aim to reduce skin contact with dust and reduce the risk of contaminated dust particles being breathed into the body, which could increase the risk of lung cancer.

Research of this type must be carried out in conjunction with environmental monitoring to identify potential threats to the environment and human health early. This is important since the amount of illegal waste stored in previously unsecured and unattended places is growing year by year.

It is worth mentioning that similar tests are currently being carried out at sites after fires in Sosnowiec and Sobolew to obtain a larger database of results for contaminant tests.

In addition, future research could be complemented by the development of a pollutant migration model and geochemical modeling using appropriate programs.

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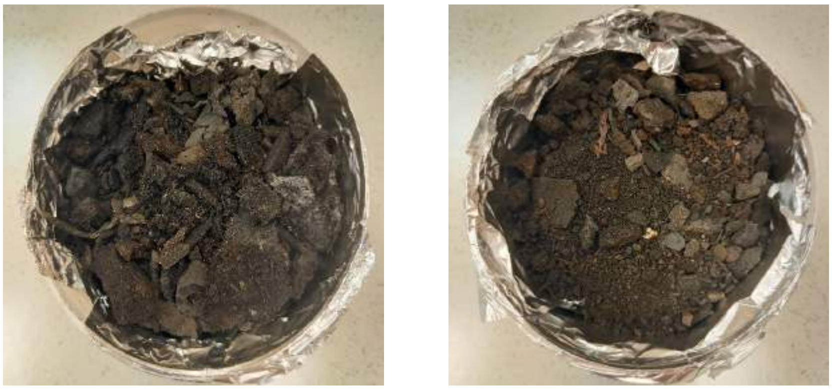
Nomenclature

A—anthracene
Ace—acenaphthene
Acy—acenaphthylene
BaA—benzo(a)anthracene
BaF—benzo(a)fluoranthene
BaP—benzo(a)pyrene
Bb + kF—benzo(b + k)fluoranthene
BcF—benzo(c)fluoranthene
BcPhe—benzo(c)phenanthrene
BeP—benzo(e)pyrene
BghiFl—benzo(ghi)fluoranthene
BghiP—benzo(ghi)perylene
Ch—chrysene
DB—dibenzo(a + h)anthracene
DMR—Dimethylnaphthalene Ratio
Fl—fluoranthene

F—fluorene
IP—indeno[1,2,3-cd]pyrene
MNR—Methylnaphthalene Ratio
MPI—Methylphenanthrene Index
N—naphthalene
PAHs—Polycyclic aromatic hydrocarbons
Py—pyrene
TEQ—Toxic Equivalent
GC-MS—Gas chromatography-mass spectrometry
ICP-OES—Inductively Coupled Plasma Optical Emission Spectrometry
MOE—Ministry of Environment
MSW—Municipal solid waste
P—phenanthrene
Pe—perylene
TEF—Toxicity Equivalence Factor
TNR—Trimethylnaphthalene Ratio

Appendix A

(**A**) Burnt tires—WR1.O. (**B**) Burnt rubber black waste—WR2.O.



(**C**) Burnt rubber black waste and brown sponge—WR3.O. (**D**) Burnt rubber black waste—WR4.O.

(**E**) Burnt rubber black waste—WR5.O. (**F**) Burnt rubber black waste—WR6.O.

Figure A1. *Cont*.

(**G**) Unburnt wallpaper—WR7.O. (**H**) Burnt textiles—WR8.O.

(**I**) Burnt textiles—WR9.O. (**J**) Burnt tires—WR10.O.

(**K**) Burnt textiles—WR11.O. (**L**) Burnt textiles—WR12.O.

Figure A1. (**A**–**L**) Presentation of 12 solid waste samples subjected to the leaching process.

Table A1. Results of chemical analyses.

Unit No.	SO_4 [mg/L]	Cl [mg/L]	As [µg/L]	B [mg/l]	Cd [µg/L]	Cu [µg/L]	Pb [µg/L]	Zn [mg/L]
WR1.O	239.0	13.0	64.0	0.6	28.0	12.0	12.0	12.0
WR2.O	534.0	38.0	82.0	1.0	0.1	4.9	13.0	1.9
WR3.O	397.0	8.1	85.0	1.1	0.4	70.0	15.0	1.6
WR4.O	255.0	76.0	59.0	3.1	1.5	50.0	9.6	2.9
WR5.O	1670.0	83.0	9.0	4.6	18.0	760.0	41.0	100.0
WR6.O	121.0	0.8	7.0	0.1	27.0	83.0	30.0	13.0
WR7.O	20.8	30.0	7.0	0.1	0.2	150.0	12.0	0.85
WR8.O	1240.0	320.0	14.0	0.4	35.0	300.0	13.0	56.0
WR9.O	43.5	2.7	8.0	0.1	4.6	37.0	110.0	2.9
WR10.O	220.0	16.0	6.0	0.2	.5	68.0	16.0	30.0
WR11.O	58.2	15.0	10.0	0.1	0.1	20.0	6.7	0.22
WR12.O	17.9	20.0	35.0	0.1	0.9	59.0	33.0	0.25

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OŚWIADCZENIE OSOBY UBIEGAJĄCEJ SIĘ O WŁASNYM WKŁADZIE W POWSTAWANIE PRACY

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Rykała Wojciech, Fabiańska J. Monika, Dąbrowska Dominika, 2022. The influence of a fire at an illegal landfill in Southern Poland on the formation of toxic compounds and their impact on the natural environment. International Journal of Environmental Research and Public Health, 19, 13613.

Mój udział w przygotowanie artykułu polegał na: prowadzeniu badań terenowych oraz laboratoryjnych, analizie, interpretacji i opisywaniu otrzymanych wyników badań, jak również przygotowaniu Rycin 1, 2, 3, 4, 5, 6 oraz Tabel 1, 3, 4.

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A STATEMENT OF THE APPLICANT'S AUTHOR OF THEIR CONTRIBUTION TO THE WORK

I declare that for the following work:

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My participation in the preparation of the article consisted of: conducting field and laboratory research, analyzing, interpreting and describing the obtained research results, also preparing Figures 1, 2, 3, 4, 5, 6 and Tables 1, 3, 4.

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OŚWIADCZENIE

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(autorzy, rok wydania, tytuł, czasopismo lub wydawca, tom, strony)

Mój udział polegał na konsultacjach podczas prac laboratoryjnych i interpretacji wyników, w tym obliczeniach stężeń WWA na podstawie krzywych kalibracji (Tabela 2) oraz opracowaniu końcowego manuskryptu do publikacji w czasopiśmie naukowym.

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Rykała Wojciech, Fabiańska J. Monika, Dąbrowska Dominika, 2022. The influence of a fire at an illegal landfill in Southern Poland on the formation of toxic compounds and their impact on the natural environment. International Journal of Environmental Research and Public Health, 19, 13613.
(authors, year of publication, title, journal or publisher, volume, pages)

My participation consisted of consultations during laboratory work and interpretation of results, including calculations of PAH concentrations based on calibration curves (Table 2) and preparation of the final manuscript for publication in a scientific journal.

Monika Fabiańska
....
Signature of the co-author of the publication

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Załącznik nr 10
do pisma okólnego nr 2
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OŚWIADCZENIE

WSPÓŁAUTORA OSOBY UBIEGAJĄEJ SIĘ O WŁASNYM WKŁADZIE W POWSTAWANIE PRACY

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Rykała Wojciech, Fabiańska J. Monika, Dąbrowska Dominika, 2022. The influence of a fire at an illegal landfill in Southern Poland on the formation of toxic compounds and their impact on the natural environment. International Journal of Environmental Research and Public Health, 19, 13613.

Mój udział polegał na przygotowywaniu artykułu, zbieraniu materiałów do przygotowania tekstu, tłumaczeniu tekstu

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STATEMENT

I declare that for the following work:

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My participation consisted of preparing the article, collecting materials for the preparation of the text, and translating the text

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Signature of the co-author of the publication

* applies to co-authors

Publikacja 3

PAHs and organophosphorus substances in burnt landfill material as a potential source of water and soil pollution

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PAHs and organophosphorus substances in burnt landfill material as a potential source of water and soil pollution

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Illegal landfills pose a potential threat to the aquatic environment due, in part, to the unprotected subsoil beneath them. We describe the toxicity of soil samples and incinerated solid waste from two illegal landfills in Poland, and discuss the potential negative impact on groundwater. Fifty samples were taken, including 32 from an illegal landfill in Trzebinia (southern Poland), and analysed by GC-MS. The PAHs detected included naphthalene, fluorene, phenanthrene, anthracene, acenaphthene, acenaphthylene, fluoranthene, pyrene, benzo(c)phenanthrene, benzo(a)anthracene, chrysene, benzo(b+k)fluoranthene, benzo(a)fluoranthene, benzo(c)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo(ghi)perylene and dibenzo(a+h)anthracene. The organophosphates detected were tris-(2-chloroisopropyl) phosphate, trisphenyl phosphate, tri-cresyl phosphate, tri(butoxyethyl)phosphate and tris(2-chloroethyl) phosphate. PAHs at <50 ppm/g predominate in the samples, though samples with total PAHs ranging to >100 ppm/g were also identified in both study areas. Among the organic phosphate concentrations in the leachates, tris-(2-chloroisopropyl) phosphate was most frequently observed, with concentrations reaching ~0.7 μg/l. These compounds within burnt waste and soil can negatively impact the safety of groundwater. Constant monitoring and research is needed to assess the negative effects of waste fires on unsealed ground beneath, and to help prevent further instances.

Key words: landfill, fire, contamination, PAHs, organic phosphates, leachate.

INTRODUCTION

Landfills, especially those that are illegal or not isolated from the ground, are a potential source of threats to the soil and water environment (Moqsud et al., 2004). These risks are mainly related to the possibility of fire (Øygard et al., 2005; Kremser et al., 2021) and leachate generated from waste (Gounaris et al., 1993; Christensen et al., 2000; Paxeus, 2000; Alk Jaffar et al., 2009; Boruszko and Wojciula, 2022). Leachates are formed as a result of physical, chemical, and biological changes taking place in the landfill and infiltration of rainwater through waste (Bojakowska, 1994; Theepharaksapan et al., 2011). Leachate composition is influenced by many factors, including types of waste deposited in a landfill, moisture content, particle size, geomorphology of the area, climate, and time of disposal (Kjeldsen et al., 2002; Kumar and Alappat, 2005). The chemical composition of the leachate is variable, but typical components include dissolved organic matter, inorganic macrocomponents, heavy metals, and xenobiotic organic compounds, e.g. aromatic hydrocarbons (Mor et al., 2006).

In Poland, the requirements for monitoring and the conditions for designing, building, and operating landfills are regulated by legal acts, such as the Journal U. 2021 item 673, Regulation of the Minister of Climate and Environment of March 19, 2021, amending the regulation on landfills. This regulation specifies the minimum number of monitoring points per aquifer and the basic range of parameters that should be measured in groundwater and leachate (Dąbrowska et al., 2018; Dąbrowska and Witkowski, 2022). The minimum scope of field and laboratory tests comprises the specified EC, pH, total organic carbon (TOC), Cu^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+}, Cr^{6+}, and PAHs. The range of parameters has been questioned because it does not reflect the actual composition of groundwater in the area analysed (Quevauviller et al., 2009; Witkowski and Dąbrowska, 2017).

Polycyclic aromatic hydrocarbons (PAHs) are compounds with two or more benzene rings that have many negative consequences related to environmental, water or food pollution. They

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are ubiquitous through incomplete combustion of materials (Hisamuddin et al., 2022). In addition, they can be identified at long distances from the epicentre of combustion. Importantly, PAHs are easily dispersed in the atmosphere due to their physical and chemical properties. PAHs also pose a risk to human health and are therefore included in lists of hazardous substances.

The study of PAH content in groundwater around municipal waste landfills is often controversial because their migration to soils and waters is primarily associated with incomplete combustion of fossil fuel, biomass, or biofuel (Almouallem et al., 2023). Therefore, their concentrations in the area of municipal waste landfills are small. However, PAHs are known to be toxic (Abdel-Shafy and Mansour, 2016), and are classified as mutagenic and carcinogenic substances (Wu et al., 2008). Pollutants entering the soil with leachate cause transfer of PAHs to the lichens, and then also to waters (Jiries et al., 2005; Öman and Junestedt et al., 2008; Chiedozie et al., 2022).

The accumulation of PAHs in soil occurs very quickly as they are hydrophobic (Abdel-Shafy and Mansour, 2016), making it important to study the risk from them to human health and groundwater. Sensitivity analysis is a tool that can be helpful in such calculations (Roy et al., 2020) taking into account the age, body weight, duration of exposure, frequency of exposure, and skin surface area of people who may be at risk. The content of PAHs in soils and groundwater has been documented in many studies over the years (e.g., Lundstedt et al., 2007; Schlanges et al., 2008; Lemieux et al., 2009; Wilcke et al., 2014; Bandowe et al., 2018; Idowu et al., 2019; Dreij et al., 2020; Krzebietke et al., 2020). Because these compounds interact strongly with particulate matter (Bouzid et al., 2017), they pose a significant threat to groundwater (Zhou et al., 2000). The concentration of PAHs in the aquatic environment is influenced by factors such as evaporation and biological degradation. Compounds with a lower molecular weight are additionally degraded by microorganisms, such as bacteria (Thomas and Li, 2000).

Monitoring the formation and migration of PAHs is an important part of the protection of the soil and water environment. PAHs are very mobile (Zhou et al., 1996), and the reclamation of sites contaminated by PAHs is a complex and lengthy process (San Miguel et al., 2009). Therefore, it seems essential to monitor their content in soils and waters.

The second type of chemical compound that deserves attention when monitoring groundwater quality in the area of pollution hotspots is organic phosphates. These are compounds commonly added to lubricants, hydraulic fluids, and also to reduce the flammability of some products (Hoffman et al., 2017; Deng et al., 2018; He et al., 2018). Organophosphates easily migrate to other environments by volatilization and leaching (Marklund et al., 2003). These compounds are considered toxic and cause eye and skin irritation, neurotoxicity, reproductive toxicity, endocrine-disrupting effects and carcinogenicity (Castro-Jimenez et al., 2014).

The first records of these compounds in water date back to the 1970s (Sheldon, 1978). For some time, however, they were overlooked in research, but in the late 1990s their importance in the environment was rediscovered. The occurrence of organophosphate triesters and diesters in groundwater, surface water, and leachate has been reported since the 1980s (Ishikawa et al., 1985; Meyer and Bester, 2004), albeit only rarely (Marklund et al., 2005; Sayyah and Azooz, 2011). Monitoring these components as well as studying their distribution and migration is extremely important due to their increasing presence in the environment. This, in turn, can overcome the diffusion limitation of substrates into cells and increase bioavailability (Zdarta et al., 2018).

Our research assesses the degree of environmental and health risk from PAHs and OPEs in municipal waste and soil samples collected in the area of a illegal landfill fire in south-western Poland, and compares the results obtained with those from a landfill in Trzebinia city (southern Poland) using the mutagenicity equivalent (MEQ) and carcinogenicity (TCDD-TEQ), the toxicity equivalent RTBaP, Toxic Equivalent (TEQ) and ratio PAH$_{carc}$/ PAH. This comparative analysis allows assessment of the impact of fires on the soil and water environment in both regions. Although assessment of the degree of risk from PAHs and OPEs is important due to the widespread existence of them in the environment, identification of these compounds in the areas of landfills affected by fire is still rarely performed. A comprehensive approach to assessing the risk of these two groups of compounds is a novel aspect of this article.

MATERIALS AND METHODS

GENERAL DESCRIPTION OF STUDY AREA

Both illegal landfills are in Poland. The first (Trzebinia city) is located in the southern part of the country. The landfill is surrounded by a forest and a nearby road. Industrial areas are farther away. The fire occurred in 2018, and it took all night to extinguish it. Solid waste that was burnt comprised used tyres, plastic packaging, textiles and black rubber.

The second illegal landfill is located around the city of Wrocław, in the southwestern part of Poland. It is surrounded by meadows and farmland, while in the distance there are individual households. The fire occurred in 2021, and 20 fire brigades took part in extinguishing it. Plastics, textiles and plastic car parts were burnt at this place.

In both cases, the fire produced thick, poisonous black smoke, which covered the neighbouring area and then migrated downwind. The nearby residents were advised to close windows for the duration of the fire and of the ongoing fire-fighting operation. In both cases, no firefighter was injured while putting out the fire.

Our research was carried in several stages. The research plan is shown in Figure 1.

While researching these two landfills in Poland, we focused on determining the potential negative impact of a landfill fire on the natural environment and groundwater, and on the health of nearby residents. The data collected helped detail this impact and determine possible future consequences from the pollution produced in the epicenter of the fire. Examples of negative effects include pollution of nearby agricultural areas and groundwater, and long-term health threats to nearby inhabitants. However, our studies were restricted to the illegal landfills themselves, with no sampling of sites beyond.

HYDROGEOLOGY OF THE STUDY AREAS: AQUIFER SYSTEMS AND GROUNDWATER STATUS

The hydrogeological features of the two areas differ significantly from each other. The illegal landfill in Trzebinia is located on a Triassic aquifer, in an area where two aquifer tiers are separated from each other by a poorly permeable unit of marl and limestone. Cracks, fissures and karst channels between these two tiers lead to close hydraulic contact between them. Groundwater in overlying Quaternary deposits occurs within sands and gravels of both Holocene and Pleistocene age. The Quaternary units vary in thickness and are discontinuous. The groundwater

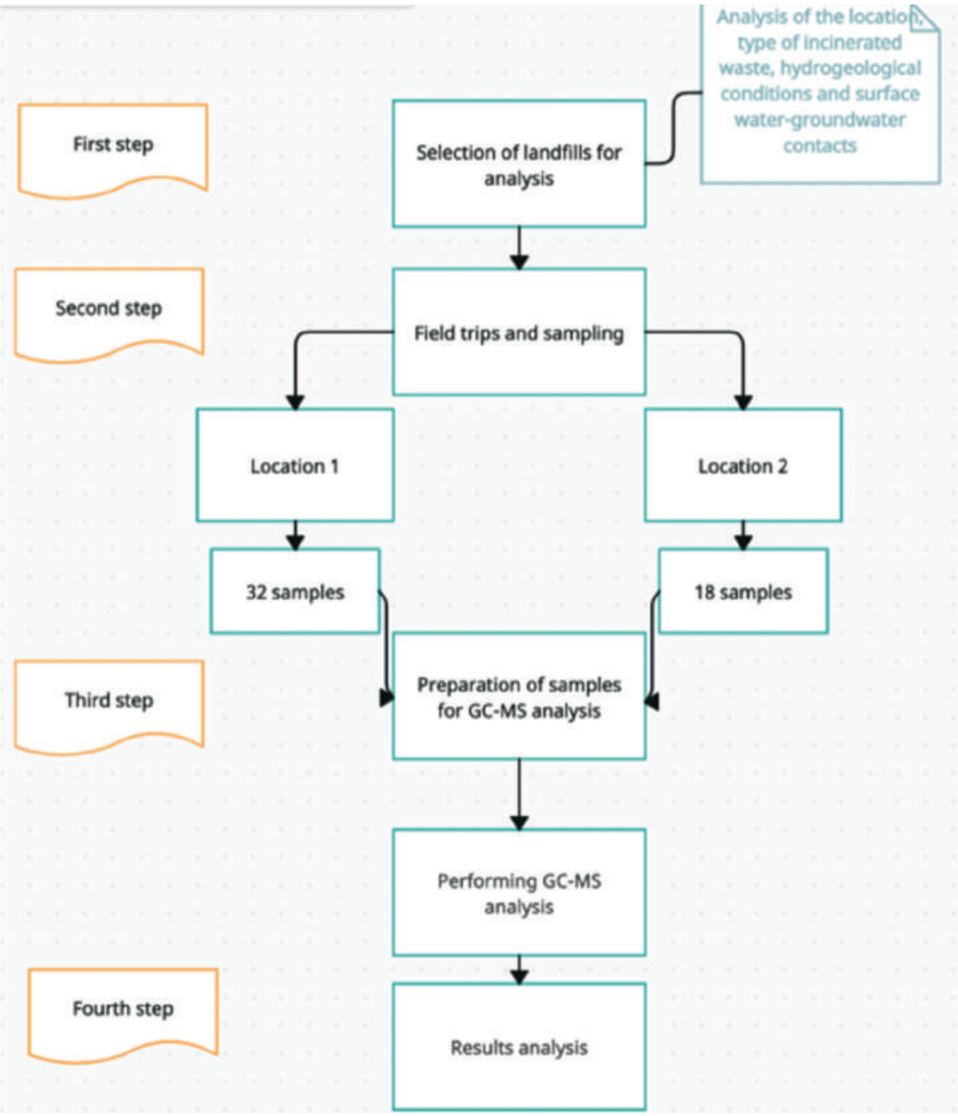

Fig. 1. Flowchart of the research

table within the Quaternary level is unconfined and occurs at depths from 0 to ~20 m b.g.l. (Fig. 2). The hydraulic conductivity of the Quaternary deposits are in the range of 1.7 x 10^{-5} – 5.0 x 10^{-5} m/s. The water supplying the Quaternary aquifer originates from both infiltration of precipitation and surface watercourses.

By contrast, in the area of illegal landfill, groundwater occurs in sandy Quaternary deposits, Neogene sands, and within tectonized zones in underlying fractured crystalline rocks. The groundwater table in the sands and gravels of river terraces has typically stabilized at a depth of over 2 m. Within local Miocene clays, there are several aquifers with different parameters. Outcrops of Neogene clays, boulder gravels and silty clays are very poor in groundwater.

DATA COLLECTION PROCEDURES

At the Trzebinia locality, 32 samples of soil and incinerated solid waste were collected during two days of fieldwork (Fig. 3). The samples were described in detail by Rykała et al. (2022). In addition, leachates were obtained from 12 incinerated solid wastes, which simulated precipitation infiltrating deep into the aquifer (Table 1).

In the Illegal landfill around the city of Wrocław in the south-western part of Poland, 18 soil and incinerated solid waste samples were collected during the fieldwork (Table 2), to a predetermined plan (Fig. 4).

Samples of 20 g of surface soil and waste were collected with a steel spatula, placed into glass jars that were then closed tightly and transported to the laboratory. Next, the soil samples were air-dried in a clean laboratory room.

Samples of soil and incinerated solid waste at both illegal landfill sites were taken at distances of several metres between each other, from both from the landfill centres and adjacent to them. 32 samples were taken from the Trzebinia site, 13 of which were soil samples, and 19 of different types of incinerated solid waste. 18 samples were taken from the around the city of Wrocław, 12 of soil and 6 of various incinerated solid waste.

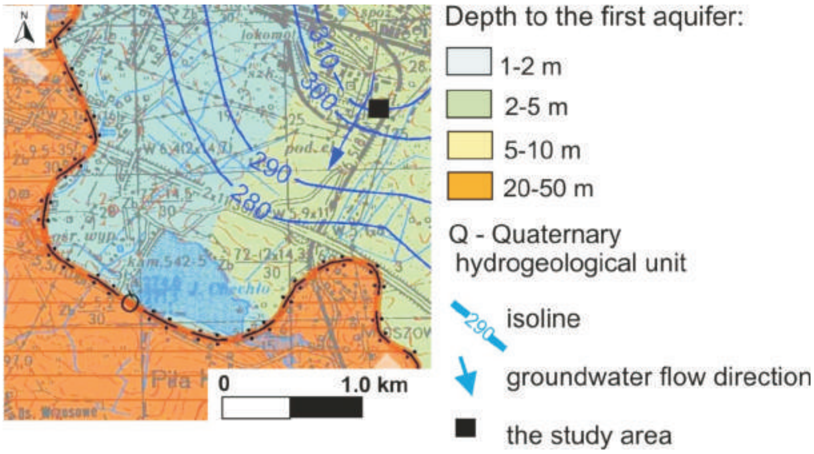

Fig. 2. Hydrogeological map of the first (Trzebinia) study area

LABORATORY ANALYSIS

All soil and incinerated solid waste samples were dried, cataloged, and extracted with dichloromethane in an ultrasonic bath for 15 min at 30°C. The extracts were filtered, the solvent evaporated, and the extract yields were calculated. All samples were derivatized (silanized) prior to gas chromatography mass spectrometry (GC--MS) analysis.

For leachate preparation, the incinerated solid waste was previously dried, cured, flooded with demineralized water, and then washed according to the PN-EN 12457-2 Norm. The effluents were then subjected to solid phase extraction (SPE), with the following procedure (Kapsi et al., 2020):

I. Vacuum-filter the water sample through 1 µm glass fibre filters GF/B (Whatman, UK) prior to analysis, in order to remove

Fig. 3. Location of the samples collected

Table 1

Sample code and description of burnt wastes at the Trzebinia illegall landfill

Sample	Description of the sample	Sample	Description of the sample
T1W	burnt tyres	T7W	unburnt wallpaper
T2W	burnt rubber black waste	T8W	burnt textiles
T3W	burnt rubber black waste and brown sponge	T9W	burnt textiles
T4W	burnt rubber black waste	T10W	burnt tires
T5W	burnt rubber black waste	T11W	burnt textiles
T6W	burnt rubber black waste	T12W	burnt textiles

W – burnt solid waste sample

Table 2

Sample code and description from the southwestern part of Poland in a illegal landfill

Sample	Description of the sample	Sample	Description of the sample
S1S	soil sample	S10S	soil sample
S2S	soil sample	S11S	soil sample
S3S	soil sample	S12S	soil sample
S4S	soil sample	S1W	burnt waste sample
S5S	soil sample	S2W	burnt waste sample
S6S	soil sample	S3W	burnt waste sample
S7S	soil sample	S4W	burnt waste sample
S8S	soil sample	S5W	burnt waste sample
S9S	soil sample	S6W	burnt waste sample

S – soil sample, W – burnt solid waste sample

suspended solid matter, avoiding in this way potential interferences during the analysis;

II. Precondition the C18 columns with 10 mL of methanol, and 10 mL of deionized water;

III. Before the column becomes dry, pass the water samples (500 mL) through the SPE columns, at a flow rate of 10 mL/min, using a vacuum manifold that maintains a constant pressure differential between the inlet and the outlet of the column;

IV. Once the total sample is percolated, rinse the columns with 2 × 5 mL of deionized water;

V. Dry the columns under vacuum for 10 min to remove residual water;

VI. Elute the analytes with 9 mL of ethyl acetate/dichloromethane (85:15), drop-by-drop, at a flow rate of 1 mL/min;

VII. The final result of the extraction was also the transfer of the resulting bituminous mass into 2 ml amber vials for gas chromatography-mass spectrometry (GC-MS) analysis.

Gas chromatography with mass spectrometry (GC-MS) is a method widely used in the analysis of environmental samples as regards water and soil contamination, where assessment of chemical composition is required. Assessments of contamination by PAHs (Fabiańska et al., 2017; Suterio et al., 2018) and by organic phosphates (Fabiańska et al., 2019) have been described. The method allows the identification of individual substances based on mass spectra, and quantitative analysis.

Samples were analysed using an *Agilent Technologies 7890A* gas analyser chromatograph and *Agilent 5975C* network mass spectrometer with a triple-axis detector system at the Faculty of Natural Sciences (University of Silesia in Katowice, Poland). Helium (6.0 Grade) as the carrier gas was used at a constant flow rate of 2.6 mL/min. Separation was obtained with a *J&W HP5-MS* (60 m x 0.32 mm i.d., 0.25 µm film thickness) fused silica capillary column coated with a chemically bonded phase (5% phenyl, 95% methylsiloxane), for which the GC oven temperature was programmed from 45 (1 min) to 100°C at 20°C/min, then to 300°C (hold 60 min) at 3°C/min, with a solvent delay of 10 min. Mass spectra were recorded from 45 to 550 da (0–40 min) and 50–700 da (>40 min) electron impact mode, with an ionization energy of 70 eV. *Hewlett Packard Chemstation* software was used to process previously acquired data in a full scan model. The compounds were identified by their mass spectra, and a comparison of peak retention times with those of standard compounds was carried out, as well as an interpretation of MS fragmentation patterns, and published data (Philip, 1985; Mass Spectral Database, 2014).

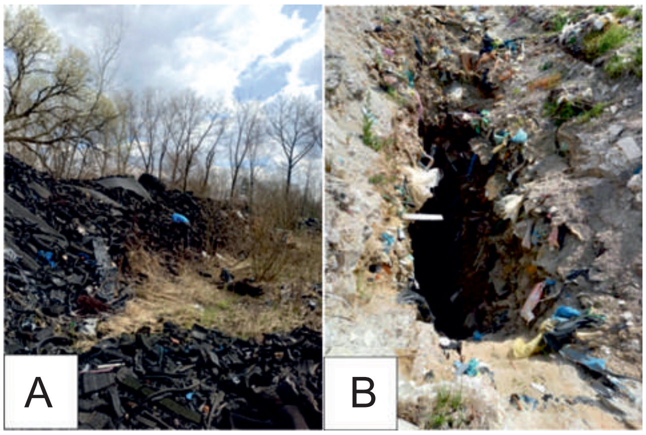

Fig. 4. Sampling places for testing

A – illegal landfill in Trzebinia; **B** – illegal landfill around the city of Wrocław

PAH peaks were integrated manually. The 5-point calibration curves for the analytical standards were used for quantitative analysis. The linear correlation between the peak areas and PAH concentrations was checked within the range of 0.10–10 µg/mL, with correlation coefficient values within the range of 0.997–0.998. The method performance was verified by analysing the NIST SRM 1649b reference material and comparing the results with the certified concentrations of the PAHs investigated. The limits of detection (LODs) were calculated as three times the standard deviation of background peaks in the procedural blanks repeated three times. The average LOD values were 2.0 ±0.05 ng/mL. Concentrations below the LOD were considered zero for all calculations. For quality assurance and quality control (QA/QC), the analysis of each sample series was accompanied by the analysis of a blank sample comprising the whole analysis procedure to assess possible contamination during the procedure.

For organophosphate, peaks were also integrated manually. The following analytical OPEs standards were used (prod. Sigma-Aldrich): TCiPP (a mixture of isomers), TPhP, TCEP, TBEP, and Sigma Aldrich reagents for synthesis: TCP, TBP, and TEP 99%. All standards purity was checked prior to calibration curves preparation in the same analytical conditions as used for extract analyses. The linear correlations between peak areas and OPE concentrations were checked within the range of 0.10–10 µg/mL (correlation coefficients: 0.997–0.998). For quality assurance and quality control (QA/QC), the analysis of each sample set was accompanied by blank sample analysis to assess possible contamination during the analytical procedure. Contamination of the chemicals used was not observed because no blank values were detected. The instrumental limitations of detection (LOD) were calculated as three times the background noise level (S/N ≥3). The limits of detection (LODs) were 3.5 ±0.05 ng/mL. Concentrations below LOD were considered zero for all calculations.

RESULTS AND DISCUSSION

DISTRIBUTION OF PAH COMPOUNDS IN THE SUBSOIL

The results of concentration studies of individual PAHs from the Trzebinia locality were published by Rykała et al. (2022),

Table 3

Polycyclic aromatic hydrocarbon (PAH) concentrations in the southwestern part of Poland in illegal landfill samples [ppm]

Sample	N	F	P	A	Ace	Acy	Fl	Py	BcPhe	BaA	Ch	Bb+kF	BaF
S1S	–	0.269	12.969	0.536	–	0.926	14.642	11.958	0.299	5.350	6.640	9.718	2.810
S2S	–	–	1.174	0.032	0.093	–	1.836	1.506	0.049	0.723	0.751	1.392	0.358
S3S	–	0.005	0.589	–	–	–	1.050	0.870	0.036	0.380	0.532	1.092	0.250
S4S	–	0.001	0.207	–	–	–	0.388	0.336	0.011	0.106	0.200	0.358	0.103
S5S	1.400	4.628	166.920	10.850	6.799	19.473	134.405	108.268	3.306	53.639	85.016	77.793	25.190
S6S	–	0.093	2.691	0.095	0.080	0.376	3.028	2.395	0.080	1.115	1.743	2.142	0.562
S7S	–	0.001	1.328	–	–	–	0.740	0.586	0.022	0.217	0.245	0.328	0.097
S8S	–	0.585	15.934	0.793	0.420	1.488	12.012	9.549	0.269	4.417	6.052	8.607	2.563
S9S	–	0.232	27.662	1.823	0.784	2.592	28.003	23.227	0.660	10.777	14.395	15.513	4.962
S10S	–	0.020	15.141	0.452	0.077	3.968	12.538	9.634	0.302	5.132	7.670	11.955	3.590
S11S	–	0.421	0.221	0.077	–	0.301	1.707	1.489	0.056	0.577	1.167	2.287	0.637
S12S	–	0.602	12.003	0.480	0.172	1.344	11.533	8.967	0.316	4.455	6.655	7.025	2.081
S1W	1.520	0.943	2.380	0.045	2.012	–	1.453	0.207	0.267	2.979	0.090	0.630	0.130
S2W	–	0.857	0.471	0.031	0.250	–	0.451	0.185	0.016	0.030	0.050	0.416	0.078
S3W	0.240	1.750	0.772	0.058	4.205	–	0.599	0.248	0.019	0.045	0.039	0.484	0.238
S4W	–	1.741	1.426	0.098	1.560	–	1.429	0.566	0.042	0.114	0.090	0.807	0.166
S5W	–	0.593	0.421	0.007	–	–	0.349	0.147	0.015	0.031	0.035	0.473	0.099
S6W	0.037	1.258	0.700	0.046	1.319	–	1.135	0.563	0.042	0.246	0.107	1.168	0.277

Sample	BcF	BaP	BeP	Pe	IP	BghiP	DB	PAH sum ppm/g	RTBaP	PAH_{carc} / PAH	MEQ	TCDD-TEQ	BaPE ppm/g
S1S	1.118	5.250	6.239	1.556	0.526	2.436	5.507	88.747	34.701	0.372	10.454	0.03	9.60
S2S	0.159	0.917	0.949	0.193	0.089	0.533	1.852	12.607	10.464	0.454	2.003	0.01	2.18
S3S	0.080	0.737	0.709	0.144	0.094	0.493	0.698	7.758	4.441	0.455	1.375	–	1.26
S4S	–	0.275	0.198	0.042	0.028	0.153	0.076	2.483	0.725	0.421	0.437	–	0.35
S5S	10.516	34.534	43.103	9.697	3.435	15.480	39.079	853.532	246.366	0.344	75.176	0.27	66.92
S6S	0.252	1.019	1.151	0.305	0.148	0.613	2.161	20.049	12.255	0.415	2.465	0.01	2.54
S7S	0.041	0.213	0.245	0.055	–	–	–	4.117	0.273	0.244	0.317	–	0.25
S8S	1.036	4.436	5.591	1.318	0.771	3.523	7.520	86.884	43.879	0.366	10.143	0.04	9.88
S9S	1.883	7.719	9.208	2.348	1.041	4.779	10.133	167.742	61.842	0.355	16.897	0.06	15.62
S10S	1.154	6.078	6.507	1.559	1.015	4.829	9.791	101.411	57.447	0.411	13.691	0.05	13.18
S11S	0.100	1.206	1.377	0.382	0.238	1.092	1.975	15.308	11.516	0.487	2.699	0.01	2.60
S12S	0.651	3.394	4.062	0.737	0.445	1.963	5.354	72.240	31.656	0.378	7.693	0.03	7.40
S1W	0.066	0.374	0.268	0.052	–	–	–	13.417	0.745	0.304	0.778	–	0.60
S2W	0.076	0.296	0.156	0.022	–	–	–	3.387	0.344	0.234	0.403	–	0.33
S3W	0.092	0.247	0.186	0.109	–	–	–	9.330	0.309	0.087	0.372	–	0.28
S4W	0.139	0.462	0.321	0.053	–	–	–	9.013	0.562	0.163	0.674	–	0.52
S5W	0.287	0.130	0.018	0.042	–	–	–	2.648	0.183	0.253	0.252	–	0.17
S6W	0.173	0.528	0.473	0.074	–	–	–	8.144	0.676	0.252	0.842	–	0.62

N – naphthalene, F – fluorene, P – phenanthrene, A – anthracene, Ace – acenaphthene, Acy – acenaphthylene, Fl – fluoranthene, Py – pyrene, BcPhe – benzo(c)phenanthrene, BaA – benzo(a)anthracene, Ch – chrysene, Bb+kF – benzo(b+k)fluoranthene, BaF – benzo(a)fluoranthene, BcF – benzo(c)fluoranthene, BaP – benzo(a)pyrene, BeP – benzo(e)pyrene, Pe – perylene, IP – indeno[1,2,3-cd]pyrene, BghiP – benzo(ghi)perylene, DB – dibenzo(a+h)anthracene, "–" compound not found who showed the similarity of the results obtained to the data of contaminant leaching obtained by Hennerbert et al. (2014). In the samples from the illegal landfill around the city of Wrocław, 20 different types of PAHs were identified (Table 3): naphthalene (N) ($m/z = 128$), fluorene (F) ($m/z = 166$), phenanthrene (P) ($m/z = 178$), anthracene (A) ($m/z = 178$), acenaphthene (Ace) ($m/z = 154$), acenaphthylene (Acy) ($m/z = 152$), fluoranthene (Fl) ($m/z = 202$), pyrene (Py) ($m/z = 202$), benzo(c)phenanthrene (BcPhe) ($m/z = 252$), benzo(a)anthracene (BaA) ($m/z = 228$), chrysene (Ch) ($m/z = 228$), benzo(b+k)fluoranthene (Bb + kF) ($m/z = 252$), benzo(a)fluoranthene (BaF) ($m/z = 252$), benzo(c)fluoranthene (BcF) ($m/z = 252$), benzo(a)pyrene (BaP) ($m/z = 252$), benzo(e)pyrene (BeP) ($m/z = 252$), perylene (Pe) ($m/z = 252$), indeno[1,2,3-cd]pyrene (IP) ($m/z = 276$), benzo(ghi)perylene (BghiP) ($m/z = 276$) and dibenzo(a + h)anthracene (DB) ($m/z = 278$).

In all samples analysed the following PAHs were detected: phenanthrene, fluoranthene, pyrene, benzo(c)phenanthrene, benzo(a)anthracene, chrysene, ben-zo(b+k)fluoranthene, benzo(a)fluoranthene, benzo(a)pyrene, benzo(e)pyrene and perylene. The U.S. The Environmental Protection Agency has classified seven PAH compounds as probable human carcinogens: benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene (Nasr et al., 2010). The highest concentrations of these PAHs (ppm) were detected in samples S5S (293.496) and S9S (59.579). Naphthalene was detected in the following samples: S5S (1.400 ppm), S1W (1.520 ppm), S3W (0.240 ppm) and S6W (0.037 ppm). The highest fluoranthene and pyrene concentrations (ppm) were recorded in 6 soil samples.

Figure 5 shows the distribution (%) of 2–6 cyclic PAHs (ppm) in all samples from the around the city of Wrocław illegal landfill. The largest % share in the samples had 4-ringed PAHs (Fl, Py, BaA, Ch) with a total concentration of 627.757 ppm in 18 samples. In second place are 5-ring PAHs (BcPhe, Bb + kF, BaF, BcF, BaP, BeP, Pe, and DB) with a total concentration of 461.417 ppm in 18 samples. Then, 3-ring PAHs (P, A, Ace, Acy, and F) with a total concentration of 337.351 ppm in 18 samples, where phenanthrene was dominant, as also indicated by Jiries et al., (2005). The 6-ring PAHs (IP, BghiP) represent a value of 43.724 ppm in 11 samples. Finally, 2-ring naphthalene reached values of 3.195 ppm in 4 samples. Low molecular weight PAHs may likely have higher concentrations and be released in less time in water than high molecular weight PAHs (Dobaradaran et al., 2020).

The RTBaP index is the sum of the concentrations of individual PAHs and their relative toxicity factors (Nisbet and LaGoy, 1992). The RTBaP index value in the samples analysed was 518.384 ppm. The average content was 28.799 ppm. Results higher than the average concentration were recorded in the 6 soil samples. The cumulative health hazard from a PAH mixture is expressed quantitatively as the carcinogenic equivalent (CEQ) or mutagenicity equivalent (MEQ) relative to the carcinogenicity or mutagenicity of BaP (Rogula-Kozłowska et al., 2013). The total mutagenicity equivalent MEQ was 146.673 ppm. The average content was 8.148 ppm. Results higher than the average concentration were recorded in 5 soil samples. The TCDD-TEQ index was calculated in 11 samples. In the remaining ones, the TCDD-TEQ index was not calculated due to the lack of one of the six PAHs needed to calculate this index (BaA, Ch, Bb+kF, BaP, IP and DB). These were mainly samples of incinerated solid waste. Great emphasis is placed on the study of carcinogenicity and mutagenicity indicators of PAHs (Abdel-Rasaq, 2012). The average content PAH_{carc}/ PAH was 0.333. Results higher than the average concentration were recorded in the 11 soil samples.

The average PAH concentration per sample in the soils was 45.940 ppm, and in incinerated solid waste 7.657 ppm. Higher total concentrations of 4–5-ring PAHs were recorded in soil samples than in samples of burnt waste. In addition, 6-ringed PAHs (IP, BghiP) were not observed in samples of incinerated waste, whereas they were present in 11 soil samples. Low molecular weight (LMW) and high molecular weight (HMW) PAHs behave differently when released into water. LMW PAHs, e.g. naphthalene, are usually emitted to the atmosphere, while

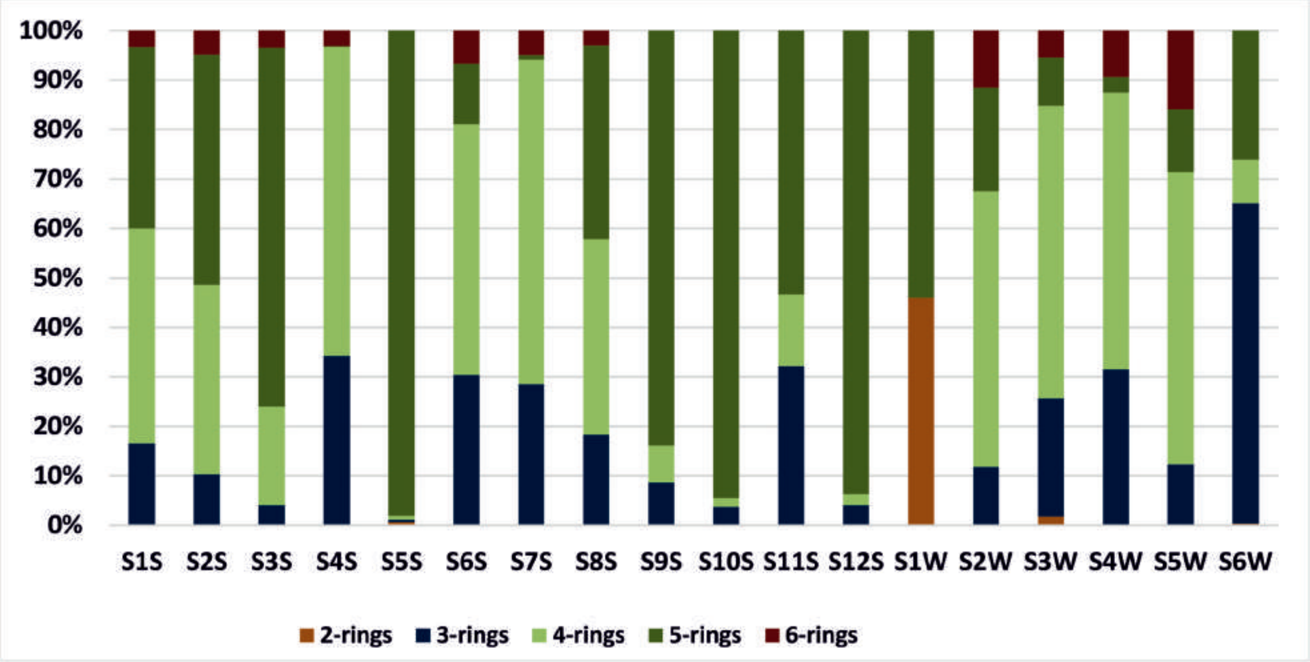

Fig. 5. Distribution pattern (%) of 2–6 ring PAHs around the city of Wrocław illegal landfill

HMW PAHs benzo(a)pyrene and benzo(ghi)perylene will remain in the water or settle in watercourse sediments (Malakahmad et al., 2016). The sums of individual PAHs in soil and water samples have been given in various studies (Li et al., 2010; Chen et al., 2015; Ogunbisi et al., 2022).

In the samples from both study areas, a similar number of PAH types was detected. Naphthalene was detected more frequently at both sites in the burnt waste samples than in the soil samples. Of the 3-ring PAHs, the most dominant was phenanthrene with the highest concentration in samples T4W 96.113 ppm (Trzebinia) and S5S 166.920 ppm (sample from around the city of Wrocław). Among 4-ringed PAHs, fluoranthene and pyrene predominated in both areas. Above-average concentrations of 5-ringed PAHs in the samples in both areas were statistically slightly different. In the Trzebinia landfill, they were: T1S = 9.031 ppm, T2S = 19.238 ppm, T4S = 13.108 ppm, T6S = 8.768 ppm, T7S = 8.525 ppm, T8S = 7.604 ppm, T9S = 7.266 ppm, T12S = 11.684 ppm (8 soil samples with an average value of 7.113 ppm) and T1W = 8.675 ppm, T4W = 60.225 ppm, T5W = 17.224 ppm, T1.W = 8.762 ppm, T6.W = 7.808 ppm (5 samples of incinerated waste above the average value of 6.996 ppm). In the around the city of Wrocław illegal landfill: S5S = 243.219 ppm, S9S = 52.426 ppm, S10S = 40.935 ppm (3 soil samples above the average value of 37.617 ppm), and S1W = 1.788 ppm, S4W = 1.989 ppm, S6W = 2.734 ppm (3 samples of combusted waste above the average value of 1.668 ppm). In the Trzebinia illegal landfill, the average concentration exceeded that found in soil samples, while in the around the city of Wrocław illegal landfill, the concentrations in soils were comparable to those in the burnt waste samples. Concentrations of indeno[1,2,3-cd]pyrene and benzo(ghi)perylene (BghiP) were detected in both study areas. In the Trzebinia illegal landfill, the concentrations of IP in soil samples were within the range of 0.012–0.676 ppm, BghiP 0.032–2.407 ppm, while in the samples of incinerated solid waste, the concentration of IP ranged from 0.012 to 0.187 ppm, BghiP 0.047 to 1.450 ppm. In the illegal landfill, the concentration of IP in the soil samples was within the range of 0.028–3.435 ppm, BghiP 0.153–15.480 ppm, while in the samples of incinerated solid waste, no IP and BghiP were detected.

According to the total content of PAHs, the samples were classified in the following way, (i) the total range of PAHs >100 ppm/g, (ii) the range of total PAHs 50–100 ppm/g, and (iii) the range of total <50 ppm / g (Fig. 6). Samples S5W, and S9-10W, belonged to the (i) group, samples S1S, S8S, and S12S to the (ii) group, whereas the S2-4S, S6-7S, S12S, S1-6W samples belonged to the (iii) group. The samples from the Trzebinia locality (Rykała et al., 2022) can be assigned to the particular groups in the following way, (i) 4 samples, (ii) 4 samples, and (iii) 24 samples. The samples of incinerated waste dominated group (iii) in both research areas. The carcinogenicity level is calculated using PAHs, e.g. BaA, BaP, Bb + kF, Ch, DB, IP. In the Trzebinia illegal landfill, the sum of these PAHs oscillated within the range of 0.35466.189 ppm in soil samples and 0.000–14.056 ppm in samples of incinerated waste. By contrast, in the illegal landfill in the around the city of Wrocław, there was found to be 1.003–293.496 ppm in soil samples and 0.669–4.074 ppm in samples of incinerated waste. In both cases, higher concentrations of these PAHs can be observed in soil samples than in incinerated solid waste. The MEQ index in the illegal landfill in soil samples ranged from 0.317 to 75.176 ppm. 3 of these samples (S5S, S9-10S) exceeded the average value of 11.946 ppm. In the samples of incinerated solid waste, the MEQ ranged from 0.252–0.842 ppm, where 3 of these samples (S1W, S4W, S6W) exceeded the average value of 0.553 ppm. The BaPE index in the illegal landfill in soil samples ranged from 0.249 to 66.920 ppm. 3 of these samples (S5S, S9S, S10S) exceeded the average value of 10.982 ppm. In the samples of incinerated solid waste, the indicator ranged from 0.165 to 0.625 ppm, where 3 of these samples (S1W, S4W, S6W) exceeded the average value of 0.420 ppm. Soil samples from the illegal landfills both in Trzebinia and in around the city of Wrocław showed higher MEQ and PaPE values than did the samples of incinerated solid waste.

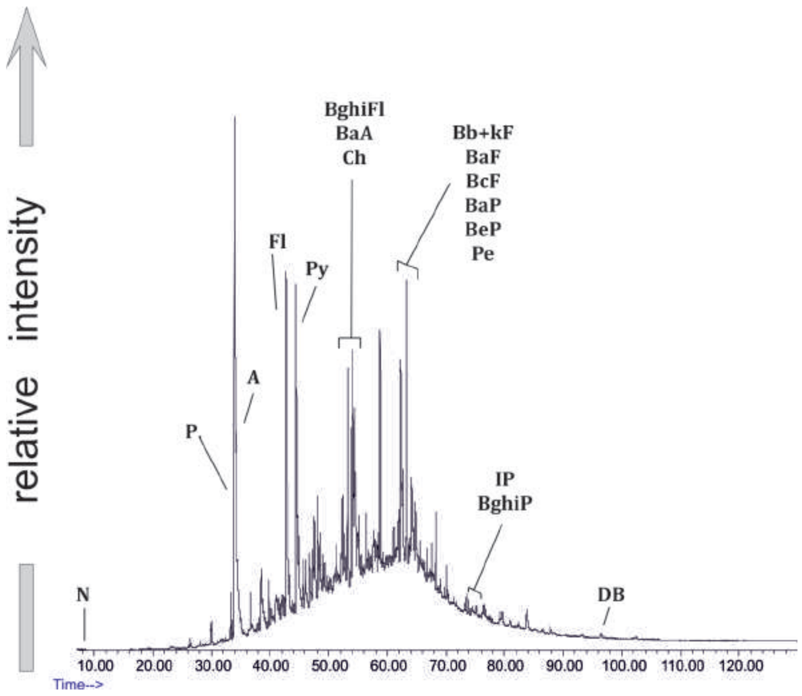

Fig. 6. Example PAH distribution in a soil sample

Anthropogenic PAHs come mainly from the combustion of fossil fuels and the spillage of petroleum (Mzoughi and Chouba, 2011). Table 4 shows the relationship of individual PAHs to each other. PAH contamination caused by combustion is indicated by the ratios of phenanthrene/anthracene <10 and fluoranthene/pyrene >1 (Benlahcen et al., 1997). Such a relationship was observed in almost all soil samples but in none of the combusted solid wastes from around the city of Wrocław. A similar dependence was observed in the samples from Trzebinia. In samples T3S, T11S, T13S, T8.W, T12.W (Trzebinia), and S5W (around the city of Wrocław), the P/A ratio was higher than 15, which may suggest smaller pyrolysis sources in this place (Zhou and Maskaoui, 2003). On the other hand, a fluoranthene/pyrene ratio >1 indicates a pyrolytic origin and values 1 indicate a petrogenic source (Sicre et al., 1987). Contaminants of PAHs in the aquatic environment can occur in dissolved form and as adsorbed particles forming a suspension. Condensed aromatic compounds are usually non-polar or very weakly polar; their solubility in water is very low (Miller et al., 2001). Photodegradation of PAHs, and also other light-induced pro-

Table 4

Values of diagnostic PAH ratios around the city of Wrocław illegal landfill samples

Sample	P/A	A/P	A/(A+P)	Fl/(Fl+Py)	Fl/Py	Fl/(Fl+P)	BaA/ (BaA + Ch)	BaP/BghiP	IP/BghiP	IP/ (IP + BghiP)	BaA/BaP	Py/BaP
S1S	7.14	0.14	0.12	0.53	1.14	0.80	0.53	2.58	1.10	0.52	1.63	4.05
S2S	10.72	0.09	0.09	0.53	1.14	0.85	0.58	2.06	0.85	0.46	1.27	2.92
S3S	–	–	–	0.53	1.13	1.00	0.50	1.78	0.97	0.49	0.83	2.10
S4S	–	–	–	0.52	1.08	1.00	0.43	2.14	0.94	0.48	0.62	2.17
S5S	4.54	0.22	0.18	0.54	1.16	0.74	0.47	2.71	1.13	0.53	2.45	5.49
S6S	8.37	0.12	0.11	0.54	1.18	0.80	0.48	1.99	1.23	0.55	1.76	4.18
S7S	–	–	–	0.54	1.18	1.00	0.56	–	–	–	1.63	4.90
S8S	5.93	0.17	0.14	0.54	1.17	0.73	0.51	1.51	1.11	0.53	1.60	3.83
S9S	4.48	0.22	0.18	0.53	1.12	0.78	0.52	1.94	1.11	0.53	2.23	5.34
S10S	9.88	0.10	0.09	0.55	1.21	0.75	0.49	1.51	1.07	0.52	1.35	2.82
S11S	0.17	5.73	0.85	0.52	1.07	1.00	0.41	1.32	1.11	0.53	0.77	2.20
S12S	7.38	0.14	0.12	0.55	1.20	0.77	0.49	2.07	1.15	0.54	2.10	4.70
S1W	7.47	0.13	0.12	0.50	0.99	0.35	0.30	–	–	–	1.05	5.33
S2W	13.82	0.07	0.07	0.55	1.20	0.32	0.12	–	–	–	0.48	6.01
S3W	12.14	0.08	0.08	0.54	1.19	0.28	0.21	–	–	–	–	–
S4W	13.20	0.08	0.07	0.55	1.24	0.33	0.22	–	–	–	1.14	11.79
S5W	51.37	0.02	0.02	0.54	1.17	0.29	0.17	–	–	–	1.11	10.85
S6W	13.80	0.07	0.07	0.50	0.99	0.44	0.34	–	–	–	2.15	10.25

P – phenanthrene, A – anthracene, Fl – fluoranthene, Py – pyrene, BaA – benzo(a)anthracene, Ch – chrysene, BaP – ben-zo(a)pyrene, BeP – benzo(e)pyrene, Pe – perylene, IP – indeno(1,2,3-cd)pyrene, BghiP – benzo(ghi)perylene, "–" compound not found

cesses occurring in water, can contribute to a reduction in the concentration of dissolved PAHs (Świetlik et al., 2002). Watercourses and water bodies in the vicinity of a given landfill are most susceptible to PAH contamination. 4-ringed PAHs (Ch, BaP) are almost insoluble in water (Adeniji et al., 2018). This can lead to the deposition of particulate matter on the surface, which in turn is noticeable mainly through the transport of PAHs from land and air to water systems (Mojiri et al., 2019).

Table 5

Organic phosphate concentrations of leachates from the illegal landfill in Trzebinia [ppm]

Sample	TCPP [μg/l]	TPP [μg/l]	TCP [μg/l]	TBEP [μg/l]	TCEP [μg/l]
T1.L	–	–	–	–	–
T2.L	0.005	–	–	–	–
T3.L	0.031	0.004	–	–	–
T4.L	–	0.002	–	–	0.902
T5.L	0.013	–	–	–	1.366
T6.L	0.001	–	–	–	–
T7.L	0.014	0.024	–	–	–
T8.L	0.037	–	–	–	–
T9.L	0.671	0.009	–	–	0.011
T10.L	–	–	–	–	–
T11.L	–	–	–	–	–
T12.L	–	–	–	–	–

TCPP – tris-(2-chloroisopropyl) phosphate, TPP – trisphenyl phosphate, TCP – tri-cresyl phosphate, TBEP – tri(butoxyethyl)phosphate, TCEP – tris(2-chloroethyl) phosphate, "–" compound not found, L – leachate sample

Our research has provided data reflecting the behaviour of PAH pollutants produced through the influence of fire, and their potential impact on the environment, including on groundwater. The results help determine the negative impacts arising from the unsealed base of the illegal landfill, and constrain the migration of pollutants over time. In addition, the research helps assess possible negative impacts of the landfill burning on the health of local inhabitants.

DISTRIBUTION OF ORGANIC PHOSPHATE COMPOUNDS IN THE LEACHATES

Among the 12 leachates obtained from the washing of incinerated solid waste from the Trzebinia locality (Table 5), three types of organic phosphates were detected: tris-(2-chloroisopropyl) phosphate (TCPP), trisphenyl phosphate (TPP) and tris(2-chloroethyl) phosphate (TCEP). TCPP was detected in 7 leachate samples (T2-3L, T5-9L). The concentration levels oscillated between 0.005 and 0.671 ppm. TPP was detected in 4 leachate samples (T3-4L, T7L, T9L) at levels of 0.002–0.024 ppm. Additionally, TCEP was found in 3 leachate samples (T4-5L, T9L), at 0.011–1.366 ppm.

When it comes to applications of organic phosphates, we can distinguish (Hsin-Chieh et al., 2022):

- TCPP – flame retardant, dielectric;
- TPP – plasticizer;
- TCP – flame retardant for PVC film, epoxy, and phenol resins, plasticizer, and lubricant oil additive;
- TBEP – plasticizer, flame retardant, antifoam agent;
- TCEP – flame retardant, plasticizer.

Organic phosphates are soluble in water. They are used as a starting material of plastics. TCPP and TBEP are irritating to the skin and eyes and have been classified as potentially carcinogenic (Bruchajzer et al., 2015). These compounds can infiltrate into the aquifer from unprotected landfill sites (Regnery et al., 2011). Organophosphorus Flame Retardants (OPFRs) are not chemically bound in products and may be released into the environment by abrasion, volatilization or leaching (Marklund et al., 2005). OPFRs are mainly used as flame-retardant plasticizers in engineering plastics (Brandsma et al., 2013). This may indicate the presence of a number of such wastes in the study area due to their appearance in the leachates. In addition, OPFRs are industrially added to all kinds of plastics and materials, leading to easy release into the environment through heat and/or fire.

SUMMARY

Soil and incinerated solid waste samples from two illegal dumps in Poland were analyzed and compared. The incinerated solid waste deposited in illegal landfills poses a potential threat to the soil and water environment. This is mainly due to the unsealed landfill bed in these areas, which in turn leads to waste leaching and leachate infiltration into the ground. In both research areas, high sums of PAH content in the samples were noted, with higher contents being recorded in the soil samples. $\Sigma PAH_{carc}/\Sigma PAH$ in soil samples was recorded as higher than in burnt solid waste samples, which is taken into account when determining carcinogenicity and potential adverse effects on human health. However, the total concentrations of all PAHs in the samples are high. Monitoring the presence of organophosphates in leachates from landfills should be statutory due to their adverse impact on human health. One of the factors that may affect their presence in leachates is their resistance to degradation. Concentrations of OPEs in leachates from an illegal landfill can also be caused by firefighting activities (lubricants, diesel engines). However, the fire in question happened a few years ago, which may mean a long period of deposition in the aquatic environment.

Personal protective equipment is required for future employees who carry out cleaning activities in the areas of illegal landfills, i.e.: gloves, protective clothing, and protective masks. These are designed to reduce the negative impact of skin contact and reduce the risk of polluted dust particles entering the body, which can lead to lung disease.

Research of this type should be carried out systematically due to the impossibility of determining which type of waste is found in a given area of an illegal landfill. Ultimately, such waste will have a negative impact on groundwater. In additional, there is a constantly growing number of illegal landfills in the country.

The results obtained from these two illegal landfills can lead to important findings with potential future consequences. Concentrations of both PAHs and OPEs may pose potential risks to groundwater treatment. Although the concentrations of some PAHs are not very high, due to the influence of time and storage, they can lead to continuous environmental pollution, which may last until the disposal of these landfill wastes. Our results help determine which type of waste may have a more negative impact on the environment. We show that, without proper sealing of the ground, such illegal landfills are a constant emitter of hazardous substances into the environment.

Similar research is currently being carried out at a illegal landfill site following a fire in Sosnowiec. In future, these issues may be expanded to include the detection of inorganic elements.

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OŚWIADCZENIE OSOBY UBIEGAJĄCEJ SIĘ O WŁASNYM WKŁADZIE W POWSTAWANIE PRACY

Oświadczam, że w pracy:

Rykała Wojciech, Fabiańska J. Monika, Dąbrowska Dominika, Nourani Vahid, 2023. PAHs and organophosphorus substances in burnt landfill material as a potential source of water and soil pollution. Geological Quarterly, 67: 42.

Mój udział w przygotowanie artykułu polegał na: prowadzeniu badań terenowych oraz laboratoryjnych, analizie, interpretacji i opisywaniu otrzymanych wyników badań, jak również przygotowaniu Rycin 3, 4, 5, 6 oraz Tabel 1, 2, 4, 5.

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My participation in the preparation of the article consisted of: conducting field and laboratory research, analyzing, interpreting and describing the obtained research results, also preparing Figures 4, 5, 6 and Tables 1, 2, 4, 5.

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