

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

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Rykała, W., Fabiańska, M.J., Dąbrowska, D., Nourani, V., 2023. PAHs and organophosphorus substances in burnt landfill material as a potential source of water and soil pollution. *Geological Quarterly*, 2023, 67: 42; <http://dx.doi.org/10.7306/gq.1712>

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), Cu²⁺, Zn²⁺, Pb²⁺, Hg²⁺, Cd²⁺, Cr⁶⁺, 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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Received: June 19, 2023; accepted: September 8, 2023; first published online: December 14, 2023

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; Krzbiec et al., 2020). Because these compounds interact strongly with particulate matter (Bouزيد 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 an illegal landfill fire in southwestern 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

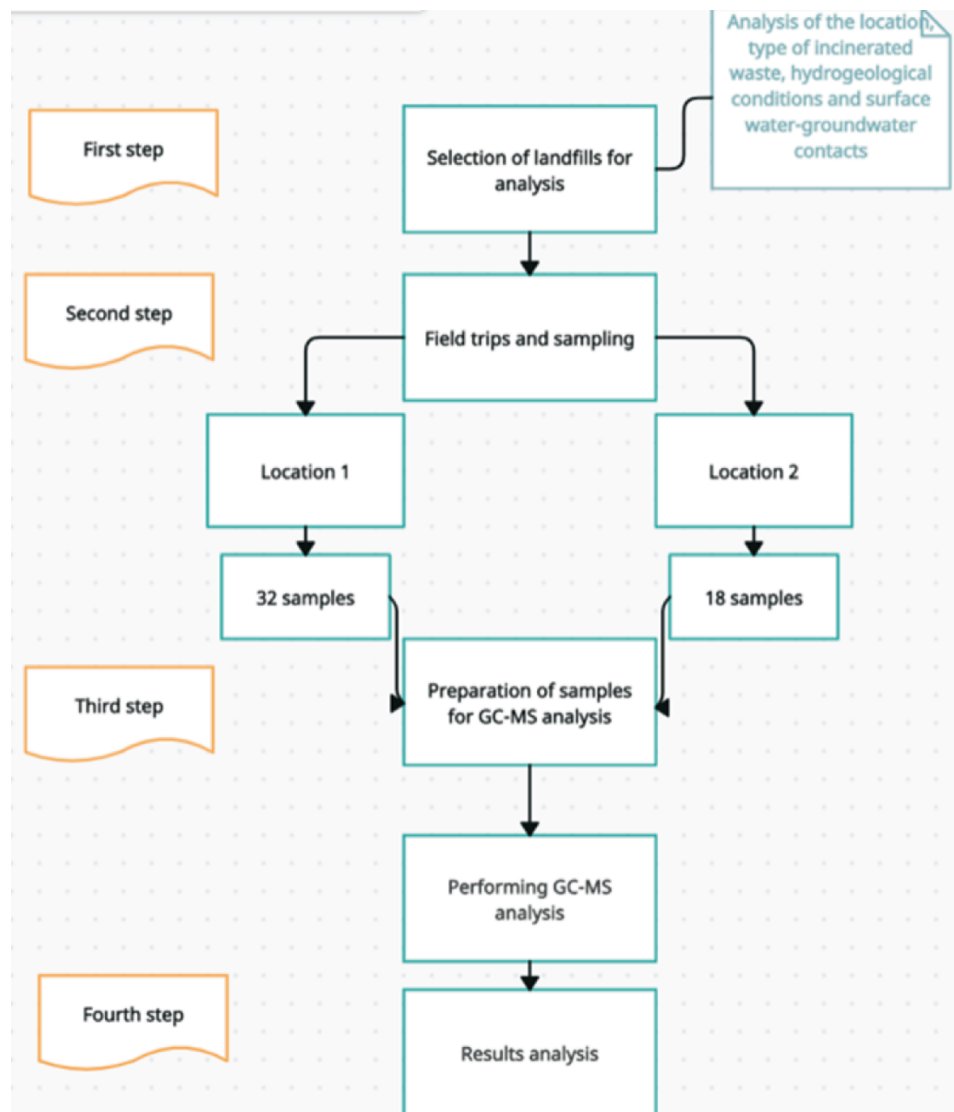


Fig. 1. Flowchart of the research

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 1.7×10^{-5} – 5.0×10^{-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 southwestern 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.

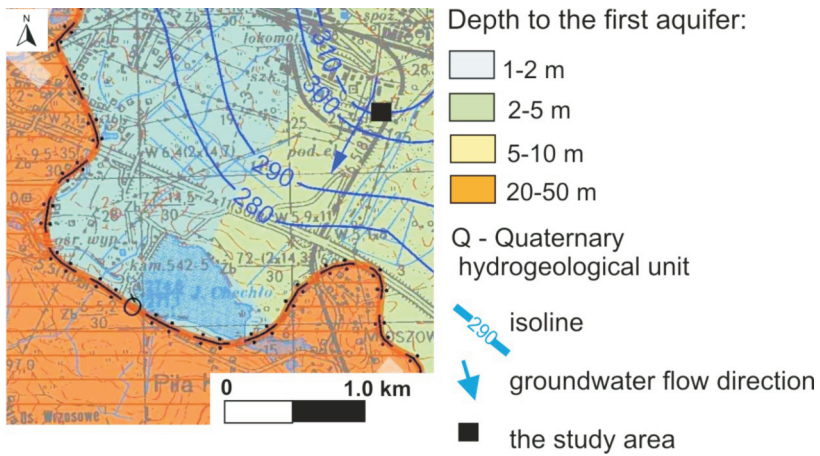


Fig. 2. Hydrogeological map of the first (Trzebinia) study area

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 (silylated) 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 illegal 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 (Fabińska et al., 2017; Suterio et al., 2018) and by organic phosphates (Fabińska 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

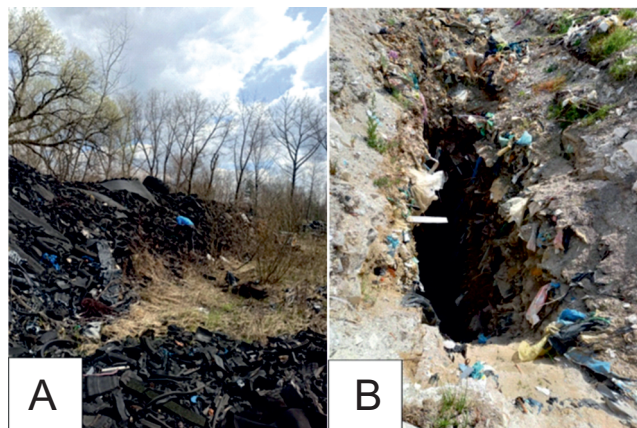


Fig. 4. Sampling places for testing

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

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).

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 ($S/N \geq 3$). 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, benzo(b+k)fluoranthene, benzo(a)fluoranthene, benzo(a)pyrene, benzo(e)pyrene and perylene. The U.S. 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

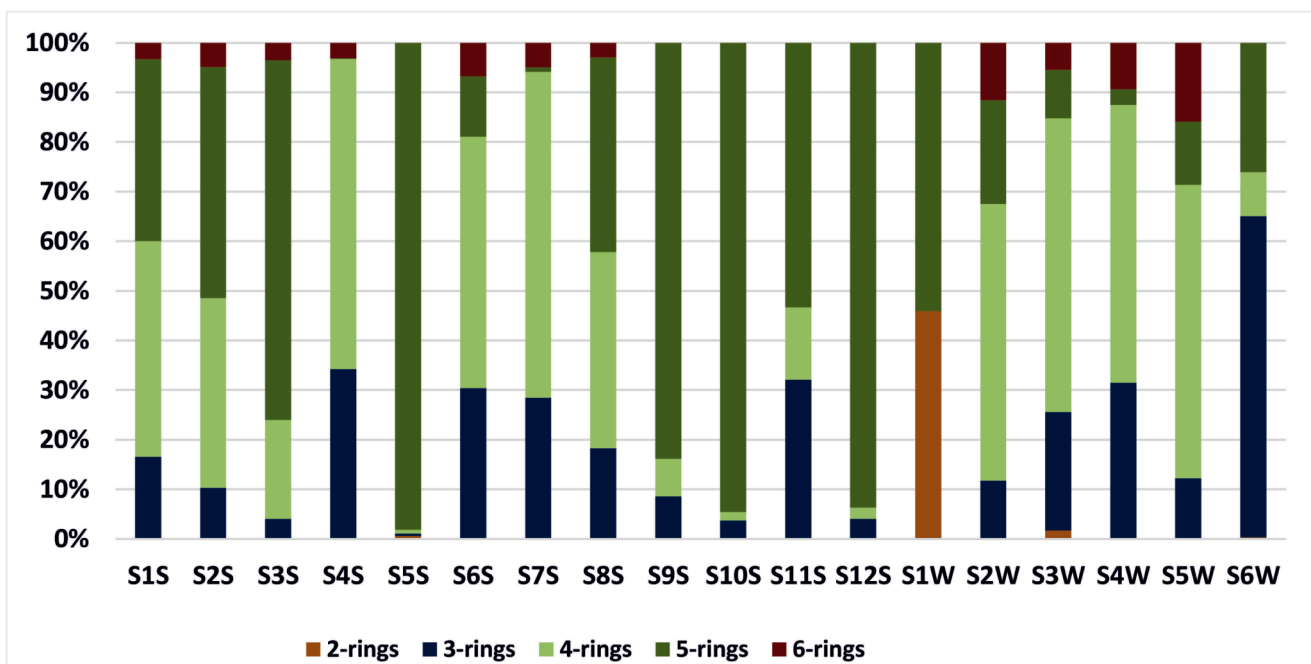


Fig. 5. Distribution pattern (%) of 2–6 ring PAHs around the city of Wrocław illegal landfill

HMW PAHs benzo(a)pyrene and benzo(ghi)perylene will remain in the water or settle in watercourse sediments (Malakhamad 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.

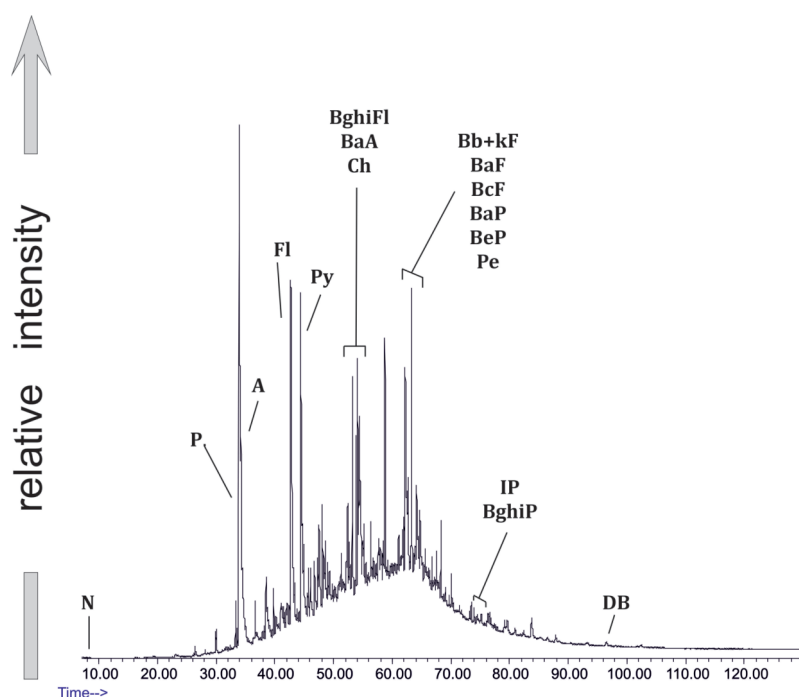


Fig. 6. Example PAH distribution in a soil sample

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 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 Maskouei, 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 – benzo(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).

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.

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

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. $\Sigma\text{PAH}_{\text{carc}}/\Sigma\text{PAH}$ 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 addition, 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.

Acknowledgements. The research and laboratory equipment used to analyze the samples in this paper were funded by the Doctoral School at the University of Silesia in Katowice (Poland) in 2022/2023.

REFERENCES

- Abdel-Rasaq, S.M., 2012.** A study of aliphatic and aromatic levels of some waters and sediments at AL-Gabal AL-Akder coast regions. Diss. MSc thesis, Chemistry department, Omer EL-Mukthar University, Libya.
- Abdel-Shafy, H.I., Mansour, M.S.M., 2016.** A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, **25**: 107–123. <https://doi.org/10.1016/j.ejpe.2015.03.011>
- Adeniji, A.O., Okoh, O.O., Okoh, A.I., 2018.** Analytical methods for polycyclic aromatic hydrocarbons and their global trend of distribution in water and sediment: a review. In: *Recent Insights in Petroleum Science and Engineering* (ed. M. Zoveidavianpoor). IntechOpen, UK.
- Alk Jaffar, Y., LeeYook, H., Salmijah, S., 2009.** Toxicity testing and the effect of landfill leachate in Malaysia on behavior of common carp (*Cyprinus carpio* L., 1758; Pisces, Cyprinidae). *American Journal of Environmental Sciences*, **5**: 209–217. <https://doi.org/10.3844/ajessp.2009.209.217>
- Almouallem, W., Michel, J., Dorge, S., Joyeux, C., Trouvé, G., Le Nouen, D., 2023.** A comparative study of the sorption of O-PAHs and PAHs onto soils to understand their transport in soils and groundwater. *Journal of Environmental Sciences*, **124**: 61–75. <https://doi.org/10.1016/j.jes.2021.11.001>
- Bandowe, B.A.M., Bigalke, M., Kobza, J., Wilcke, W., 2018.** Sources and fate of polycyclic aromatic compounds (PAHs, oxygenated PAHs and azaarenes) in forest soil profiles opposite of an aluminium plant. *Science of the Total Environment*, **630**: 83–95. <https://doi.org/10.1016/j.scitotenv.2018.02.109>
- Benlahcen, K.T., Chaoui, A., Budzinski, H., Garrigues, Ph., 1997.** Distribution and sources of polycyclic aromatic hydrocarbons in some Mediterranean coastal sediments. *Marine Pollution Bulletin*, **34**: 298–305. <https://doi.org/10.1007/s11270-008-9904-8>
- Bojakowska, I., 1994.** The influence of anthropogenic factor on geochemical processes in the surface layers of the lithosphere (in Polish with English summary). *Instrukcje i Metody Badań Geochemicznych*, **53**: 1–199.
- Boruszko, D., Wojciula, A., 2022.** Heavy metals and polycyclic aromatic hydrocarbons in leachates from autothermal thermophilic aerobic digestion as a potential threat to the environment in north-eastern Poland. *Studia Quaternaria*, **31**: 15–22. <https://doi.org/10.24425/sq.2022.140882>
- Bouziid, I., Maire, J., Brunol, E., Caradec, S., Fatin-Rouge, N., 2017.** Compatibility of surfactants with activated-persulfate for the selective oxidation of PAH in groundwater remediation. *Journal of Environmental Chemical Engineering*, **5**: 6098–6106. <https://doi.org/https://doi.org/10.1016/j.jece.2017.11.038>
- Brandsma, S.H., de Boer, J., Leonards, P.E.G., Cofino, W.P., Covaci, A., Leonards, P.E.G., 2013.** Organophosphorus flame-retardant and plasticizer analysis, including recommendations from the first worldwide interlaboratory study. *TrAC Trends in Analytical Chemistry*, **43**: 217–228. <https://doi.org/10.1016/j.trac.2012.12.004>

- Bruchajzer, E., Frydrych, B., Szymańska, J.A., 2015.** Fosforowe związki organiczne zmniejszające palność – toksyczność i wpływ na zdrowie ludzi (in Polish). *Medycyna Pracy*, **66**: 235–264. <https://doi.org/10.13075/mp.5893.00120>
- Castro-Jimenez, J., Berrojalbiz, N., Pizarro, M., Dachs, J., 2014.** Organophosphate ester (OPE) flame retardants and plasticizers in the open Mediterranean and Black Seas atmosphere. *Environmental Science and Technology*, **48**: 3203–3209. <https://doi.org/10.1021/es405337g>
- Chen, Y., Jia, R., Yang, S., 2015.** Distribution and source of polycyclic aromatic hydrocarbons (PAHs) in water dissolved phase, suspended particulate matter and sediment from Weihe River in northwest China. *International Journal of Environmental Research and Public Health*, **12**: 14148–14163. <https://doi.org/https://doi.org/10.3390/ijerph121114148>
- Chiedozie, C., Aralu, Patrice, A.C., Okoye, Hillary, O., Abugu, Victor, C., Eze., 2022.** Pollution and water quality index of boreholes within unlined waste dumpsite in Nnewi, Nigeria. *Discover Water*, **2**: 14. <https://doi.org/10.1007/s43832-022-00023-9>
- Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.J., Heron, G., 2000.** Biogeochemistry of landfill leachate plumes. *Applied Geochemistry*, **16**: 659–718. [https://doi.org/10.1016/S0883-2927\(00\)00082-2](https://doi.org/10.1016/S0883-2927(00)00082-2)
- Dąbrowska, D., Witkowski, A.J., 2022.** Groundwater and human health risk assessment in the vicinity of a municipal waste landfill in Tychy, Poland. *Applied Sciences*, **12**: 12898. <https://doi.org/10.3390/app122412898>
- Dąbrowska, D., Witkowski, A., Sołtysiak, M., 2018.** Application of pollution indices for the assessment of the negative impact of a municipal landfill on groundwater (Tychy, southern Poland). *Geological Quarterly*, **62** (3): 496–508. <https://doi.org/10.7306/gq.1420>
- Deng, W.J., Li, N., Wu, R., Richard, W.K.S., Wang, Z., Ho, W., 2018.** Phosphorus flame retardants and Bisphenol A in indoor dust and PM2.5 in kindergartens and primary schools in Hong Kong. *Environmental Pollution*, **235**: 365e371. <https://doi.org/10.1016/j.envpol.2017.12.093>
- Dobaradaran, S., Schmidt, T.C., Lorenzo-Parodi, N., Kazir-Cegla, W., Jochmann, M.A., Nabipour, I., Lutze, H.V., Telgheder, U., 2020.** Polycyclic aromatic hydrocarbons (PAHs) leachates from cigarette butts into water. *Environmental Pollution*, **259**: 113916. <https://doi.org/10.1016/j.envpol.2020.113916>
- Dreij, K., Lundin, L., LeBihanic, F., Lundstedt, S., 2020.** Polycyclic aromatic compounds in urban soils of Stockholm City: Occurrence, sources and human health risk assessment. *Environmental Research*, **182**: 108989. <https://doi.org/10.1016/j.envres.2019.108989>
- Fabiańska, M., Kozielska, B., Koniecznyński, J., 2017.** Differences in the occurrence of polycyclic aromatic hydrocarbons and geochemical markers in the dust emitted from various coal-fired boilers. *Energy Fuels*, **31**: 2585–2595. <https://doi.org/https://doi.org/10.1021/acs.energyfuels.6b03030>
- Fabiańska, J.M., Kozielska, B., Koniecznyński, J., Bielaczyc, P., 2019.** Occurrence of organic phosphates in particulate matter of the vehicle exhausts and outdoor environment, a case study. *Environmental Pollution*, **244**: 351e360. <https://doi.org/10.1016/j.envpol.2018.10.060>
- Goumaris, V., Anderson, P.R., Holsen, T.M., 1993.** Characteristics and environmental significance of colloids in landfill leachate. *Environmental Science and Technology*, **27**: 1381–1387. <https://doi.org/10.1021/es00044a013>
- He, M.J., Lu, J.F., Ma, J.Y., Wang, H., Du, X.F., 2018.** Organophosphate esters and phthalate esters in human hair from rural and urban areas, Chongqing, China: concentrations, composition profiles and sources in comparison to street dust. *Environmental Pollution*, **237**: 143e153. <https://doi.org/10.1016/j.envpol.2018.02.040>
- Hennerbert, P., Lambert, S., Fouillen, F., Charrasse, B., 2014.** Assessing the environmental impact of shredded tires as embankment fill material. *Canadian Geotechnical Journal*, **51**: 469–478. <https://doi.org/10.1139/cgj-2013-0194>
- Hisamuddin, N.H., Jalaludin, J., Bakar, S.A., Latif, M.T., 2022.** The influence of environmental polycyclic aromatic hydrocarbons (PAHs) exposure on DNA damage among school children in urban traffic area, Malaysia. *International Journal of Environmental Research and Public Health*, **19**: 2193. <https://doi.org/10.3390/ijerph19042193>
- Hoffman, K., Butt, C.M., Webster, T.F., Preston, E.V., Hammel, S.C., Makey, C., Lorenzo, A.M., Cooper, E.M., Carignan, C., Meeker, J.D., Hauser, R., Soubry, A., Murphy, S.K., Price, T.M., Hoyo, C., Mendelsohn, E., Congleton, J., Daniels, J.L., Stapleton, H.M., 2017.** Temporal trends in exposure to organophosphate flame retardants in the United States. *Environmental Science and Technology Letters*, **4**: 112–118. <https://doi.org/10.1021/acs.estlett.6b00475>
- Hsin-Chieh, K., Yen, Kung, H., Bo, Wun, H., Cheruiyot, N.K., Guo, Ping, Ch., 2022.** An overview: organophosphate flame retardants in the atmosphere. *Aerosol and Air Quality Research*, **22**: 220148. <https://doi.org/10.4209/aaqr.220148>
- Idowu, O., Semple, K.T., Ramadass, K., O'Connor, W., Hansbro, P., Thavamani, P., 2019.** Beyond the obvious: environmental health implications of polar polycyclic aromatic hydrocarbons. *Environment International*, **123**: 543–557. <https://doi.org/10.1016/j.envint.2018.12.051>
- Ishikawa, S., Taketomi, M., Shinohara, R., 1985.** Determination of trialkyl and triaryl phosphates in environmental samples. *Water Research*, **19**: 119–125. [https://doi.org/10.1016/0043-1354\(85\)90332-X](https://doi.org/10.1016/0043-1354(85)90332-X)
- Jiries, A., Rimawi, O., Lintelmann, J., Batarseh, M., 2005.** Polycyclic aromatic hydrocarbons (PAH) in top soil, leachate and groundwater from Ruseifa solid waste landfill, Jordan. *International Journal of Environment and Pollution*, **23**: 179–188. <https://doi.org/10.1504/IJEP.2005.006859>
- Kapsi, M., Tsoutsis, Ch., Albanis, T., 2020.** Simple analytical methodology based on solid phase extraction for monitoring pesticide residues in natural waters. *MethodsX*, **7**: 101011. <https://doi.org/10.1016/j.mex.2020.101011>
- Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., Christensen, T., 2002.** Present and long-term composition of MSW landfill leachate: a review. *Critical Reviews in Environmental Science and Technology*, **32**: 297–336. <https://doi.org/10.1080/10643380290813462>
- Kremser, K., Thallner, S., Strbik, D., Spiess, S., Kucera, J., Vaculovic, T., Vsiansky, D., Haberbauer, M., Mandl, M., Guebitz, G., 2021.** Leachability of metals from waste incineration residues by iron and sulfur-oxidizing bacteria. *Journal of Environmental Management*, **280**: 111734. <https://doi.org/10.1016/j.jenvman.2020.111734>
- Krzebietke, J.S., Mackiewicz-Walec, E., Sienkiewicz, S., Załuski, D., 2020.** Effect of manure and mineral fertilisers on the content of light and heavy polycyclic aromatic hydrocarbons in soil. *Scientific Reports*, **10**. <https://doi.org/10.1038/s41598-020-61574-2>
- Kumar, D., Alappat, B.J., 2005.** Evaluating leachate contamination potential of landfill sites using leachate pollution index. *Clean Technologies and Environmental Policy*, **7**. <https://doi.org/10.1007/s10098-004-0269-4>
- Lemieux, C.L., Lynes, K.D., White, P.A., Lundstedt, S., Öberg, L., Lambert, I.B., 2009.** Mutagenicity of an aged gasworks soil during bioslurry treatment. *Environmental and Molecular Mutagenesis*, **50**: 404–412. <https://doi.org/10.1002/em.20473>
- Li, J., Shang, X., Tanguay, R.L., Dong, Q., Huang, Ch., 2010.** Polycyclic aromatic hydrocarbons in water, sediment, soil, and plants of the Aojiang River waterway in Wenzhou, China. *Journal of Hazardous Materials* **173**: 75–81. <https://doi.org/10.1016/j.jhazmat.2009.08.050>
- Lundstedt, S., White, P.A., Lemieux, C.L., Lynes, K.D., Lambert, I.B., Öberg, L., 2007.** Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. *AMBIO*, **36**: 475–485. [https://doi.org/10.1579/0044-7447\(2007\)36\[475:sfatho\]2.0.co;2](https://doi.org/10.1579/0044-7447(2007)36[475:sfatho]2.0.co;2)
- Malakahmad, A., Xin, Law, M., Ng, Ka-Wy, Sabariah, Abd, Manan, T., 2016.** The fate and toxicity assessment of polycyclic aromatic hydrocarbons (PAHs) in water streams of Malaysia. *Procedia Engineering*, **148**: 806–811. <https://doi.org/10.1016/j.proeng.2016.06.572>

- Marklund, A., Andersson, B., Haglund, P., 2003.** Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere*, **53**: 1137e1146. [https://doi.org/10.1016/S0045-6535\(03\)00666-0](https://doi.org/10.1016/S0045-6535(03)00666-0)
- Marklund, A., Andersson, B., Haglund, P., 2005.** Traffic as a source of organophosphorus flame retardants and plasticizers in snow. *Environmental Science and Technology*, **39**: 3555–3562. <https://doi.org/10.1021/es0482177>
- Mass Spectral Database, 2014.** The Wiley Registry of Mass Spectral Data. Wiley, New York.
- Meyer, J., Bester, K., 2004.** Organophosphate flame retardants and plasticizers in wastewater treatment plants. *Journal of Environmental Monitoring*, **6**: 599–605. <https://doi.org/10.1039/b403206c>
- Miller, J.S., Olejnik, D., 2001.** Photolysis of polycyclic aromatic hydrocarbons in water. *Water Resources*, **35**: 233–243. [https://doi.org/10.1016/S0043-1354\(00\)00230-X](https://doi.org/10.1016/S0043-1354(00)00230-X)
- Mojiri, A., Zhou, J.L., Ohashi, A., Ozaki, N., Kindaichi, T., 2019.** Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. *Science of the Total Environment*, **696**: 133971. <https://doi.org/10.1016/j.scitotenv.2019.133971>
- Moqsud, M.A., Rahman, M.H., 2004.** Biochemical quality of compost from kitchen garbage in Bangladesh. *Environmental Informalities Archives*, **2**: 635–640.
- Mor, S., Ravindra, K., Dahiya, R.P., Chandra, A., 2006.** Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring Assessment*, **118**: 435–456. <https://doi.org/10.1007/s10661-006-1505-7>
- Mzoughi, N., Chouba, L., 2011.** Distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter, and sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). *Journal of Environmental Monitoring*, **13**: 689–698. <https://doi.org/10.1039/C0EM00616E>
- Nasr, I.N., Arief, M.H., AbdelAleem, A.H., Malhat, F.M., 2010.** Polycyclic aromatic hydrocarbons (PAHs) in aquatic environment at El Menofiya Governorate, Egypt. *Journal of Applied Sciences Research*, **6**: 13–21.
- Nisbet, I.C.T., LaGoy, P.K., 1992.** Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology*, **16**: 290–300. [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X)
- Ogunbisi, M.A., Olujimi, O.O., Sojину, O.S., Xian, Q., Arowolo, T.A., 2022.** Occurrence, source and risk assessment of polycyclic aromatic hydrocarbons in Ogun River and Lagos Lagoon, Southwest, Nigeria. *International Journal of Environmental Science and Technology*, **20**: 3. <https://doi.org/10.1007/s13762-022-04237-1>
- Öman, C.B., Junestedt, C., 2008.** Chemical characterization of landfill leachates – 400 parameters and compounds. *Waste Management*, **28**: 1876–1891. <https://doi.org/10.1016/j.wasman.2007.06.018>
- Paxeus, N., 2000.** Organic compounds in municipal landfill leachates. *Water Science and Technology*, **42**: 323–333. <https://doi.org/10.2166/wst.2000.0585>
- Philp, R.P., 1985.** Fossil Fuel Biomarkers. Application and Spectra. Elsevier, Amsterdam. <https://doi.org/10.1080/00908318708908703>
- PN-EN 12457-2:2006.** Charakteryzowanie odpadów. Wymywanie. Badanie zgodności w odniesieniu do wymywania ziarnistych materiałów odpadowych i osadów (in Polish). Część 2: Jednostopniowe badanie porcowe przy stosunku cieczy do fazy stałej 10 l/kg w przypadku materiałów o wielkości cząstek poniżej 4 mm (bez redukcji lub z redukcją wielkości).
- Quevauviller, P., Fouillac, A.M., Grath, J., Ward, R., 2009.** Groundwater monitoring. *Water Quality Measurements Series*, John Wiley and Sons, Ltd; **428**. <https://doi.org/10.1002/9780470749685.ch13>
- Øygard, J., Mage, A., Gjengedal, E., Svane, T., 2005.** Effect of an uncontrolled fire and the subsequent fire fight on the chemical composition of landfill leachate. *Waste Management*, **25**: 712–718. <https://doi.org/10.1016/j.wasman.2004.11.008>
- Regnery, J., Püttmann, W., Merz, C., Berthold, G., 2011.** Occurrence and distribution of organophosphorus flame retardants and plasticizers in anthropogenically affected groundwater. *Journal of Environmental Monitoring*, **13**: 347–354. <https://doi.org/10.1039/c0em00419g>
- Rogula-Kozłowska, W., Kozielska, B., Klejnowski, K., 2013.** Concentration, origin and health hazard from fine particle-bound PAH at three characteristic sites in Southern Poland. *Bulletin of Environmental Contamination and Toxicology*, **91**: 349–355. <https://doi.org/10.1007/s00128-013-1060-1>
- Roy, D., Ahn, S.H., Lee, T. K., Seo, Y.-C., Park, J., 2020.** Cancer and non-cancer risk associated with PM10-bound metals in subways. *Transportation Research Part D: Transport and Environment*, **89**: 102618. <https://doi.org/10.1016/j.trd.2020.102618>
- Rykała, W., Fabiańska, M.J., Dąbrowska, D., 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. <https://doi.org/10.3390/ijerph192013613>
- San Miguel, V., Peinado, C., Catalina, F., Abrusci, C., 2009.** Bioremediation of naphthalene in water by *Sphingomonas paucimobilis* using new biodegradable surfactants based on poly (ϵ -caprolactone). *International Biodeterioration and Biodegradation*, **63**: 217–223. <https://doi.org/10.1016/j.ibiod.2008.09.005>
- Sayyah, M., Azooz, R., 2011.** Electrosynthesis and characterization of adherent poly (2-aminobenzothiazole) on Pt-electrode from acidic solution. *Arabian Journal of Chemistry*, **9**: S576–S586. <https://doi.org/10.1016/j.arabj.2011.06.031>
- Schlanges, I., Meyer, D., Palm, W.U., Ruck, W., 2008.** Identification, quantification and distribution of PAC-metabolites, heterocyclic PAC and substituted PAC in groundwater samples of tar-contaminated sites from Germany. *Polycyclic Aromatic Compounds*, **28**: 320–338. <https://doi.org/10.1080/10406630802377807>
- Sheldon, S., Hites, R., 1978.** Organic compounds in the Delaware River. *Environmental Science and Technology*, **12**: 1188. <https://doi.org/10.1021/es60146a006>
- Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., Albaiges, J., 1987.** Aliphatic and aromatic hydrocarbons in the Mediterranean aerosol. *International Journal of Environmental Analytical Chemistry*, **29**: 73–94. <https://doi.org/10.1080/03067318708078412>
- Suterio, N.G., Carmo, S.N., Budziak, D., Merib, J., Carasek, E., 2018.** Use of a natural sorbent as alternative solid-phase micro-extraction coating for the determination of polycyclic aromatic hydrocarbons in water samples by gas chromatography-mass spectrometry. *Journal of the Brazilian Chemical Society*, **29**: 2417–2425. <https://doi.org/10.21577/0103-5053.20180119>
- Świetlik, R., Kowalczyk, D., Dojlido, J., 2002.** Influence of selected physicochemical factors on the degradation of PAHs in water. *Polish Journal of Environmental Studies*, **11**: 165–169.
- Theepharaksapan, S., Chiemchaisri, C., Chiemchairsi, W., Yamamoto, K., 2011.** Removal of pollutants and reduction of bio-toxicity in a full scale chemical coagulation and reverse osmosis leachate treatment system. *Bioresource Technology*, **102**: 5381–5388. <https://doi.org/10.1016/j.biortech.2010.11.091>

- Thomas, S.D., Li, Q.X., 2000.** Immunoaffinity chromatography for analysis of polycyclic aromatic hydrocarbons in corals. *Environmental Science and Technology*, **34**: 2649.
<https://doi.org/10.1021/es991069d>
- Wilcke, W., Bandowe, B.A.M., Lueso, M.G., Ruppenthal, M., del Valle, H., Oelmann, Y., 2014.** Polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives (oxygenated PAHs, azaarenes) in soils along a climosequence in Argentina. *Science of the Total Environment*, **473–474**: 317–325.
<https://doi.org/10.1016/j.scitotenv.2013.12.037>
- Witkowski, A.J., Dąbrowska, D., 2017.** Diagnosis of the legal and organizational status of groundwater monitoring in Poland. *Przegląd Geologiczny*, **65**: 1393–1397.
- Wu, Y., Luo, Y., Zou, D., Ni, J., Liu, W., Teng, Y., Li, Z., 2008.** Bioremediation of polycyclic aromatic hydrocarbons contaminated soil with *Monilinia* sp.: degradation and microbial community analysis. *Biodegradation*, **19**: 247–257.
<https://doi.org/10.1007/s10532-007-9131-9>
- Zdarta, A., Pacholak, A., Galikowska, M., Smulek, W., Kaczorek, E., 2018.** Butylbenzene and tert-Butylbenzene-Sorption on sand particles and biodegradation in the presence of plant natural surfactants. *Toxins*, **10**: 154–196.
<https://doi.org/10.3390/toxins10090338>
- Zhou, J.L., Fileman, T.W., Evans, S., Donkin, P., Mantoura, R.F.C., Rowland, S.J., 1996.** Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber Estuary and Humber coastal zone. *Marine Pollution Bulletin*, **32**: 599–608.
[https://doi.org/10.1016/0025-326X\(96\)00014-8](https://doi.org/10.1016/0025-326X(96)00014-8)
- Zhou, J.L., Hong, H., Zhang, Z., Maskaoui, K., Chen, W., 2000.** Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. *Water Research*, **34**: 2132–2150.
[https://doi.org/10.1016/S0043-1354\(99\)00360-7](https://doi.org/10.1016/S0043-1354(99)00360-7)
- Zhou, J.L., Maskaoui, K., 2003.** Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. *Environmental Pollution*, **121**: 269–281.
[https://doi.org/10.1016/S0269-7491\(02\)00215-4](https://doi.org/10.1016/S0269-7491(02)00215-4)