KSCE Journal of Civil Engineering (2023) 27(9):3694-3704
DOI 10.1007/s12205-023-2385-x

pISSN 1226-7988, eISSN 1976-3808
www.springer.com/12205

Environmental Engineering

Persistent Organic Pollutants in Sewage Sludge: Occurrence, Temporal Concentration Variation and Risk Assessment for Sewage Sludge Amended Soils

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ARTICLE HISTORY

Received 14 December 2022
Accepted 9 April 2023
Published Online 25 July 2023

KEYWORDS

Digested sewage sludge
Organochlorine pesticides (OCPs)
Polychlorinated biphenyls (PCBs)
Polycyclic aromatic hydrocarbons (PAHs)
Risk assessment
Soil-dwelling organisms
Soil amendment
Wastewater treatment plant

ABSTRACT

In this study, the occurrences, temporal concentration variations and ecotoxicological risks were determined for 18 polycyclic aromatic hydrocarbons (PAHs); 7 congeners of polychlorinated biphenyls (PCBs), and 18 selected organochlorine pesticides (OCPs) in the anaerobically digested sewage sludge samples obtained from a conventional wastewater treatment plant (WWTP) in Konya, Turkey. Flowrate of the evaluated WWTP was 200,000 m^3/day, with the production of 140 tons/day treated sewage sludge. Total 18 PAHs were in the range of 1,203 – 17,599 µg/kg of dry matter (dm); total PCBs were in the range of 51.26 – 561.37 µg/kg dm, and total OCPs were in the range of 4.90 – 13.11 µg/kg dm. The highest concentrations were determined for fluoranthene among PAHs, with 2445 µg/kg dm, PCB118 congener with 514 µg/kg dm, and δ-HCH among OCPs with 2.44 µg/kg dm. Considering the average daily production amounts of treated sludge, the highest mass loads were 1,785 g/day for total PAHs; 79 g/day for total PCBs; and 1 – 2 g/day for total OCPs, while the annual mass load was estimated to be approximately 7.3 kg. An ecotoxicological risk assessment was performed by estimation of risk quotients (RQs). High risk for soil ecosystem was identified due to PAHs and PCBs ingredient of sludge, while lower risk was determined for OCPs compounds. The highest RQ values were determined for pyrene (RQ: 1337) among PAHs, PCB118 congener (RQ: 7608), and γ-HCH (RQ: 5.23) among OCPs. Findings of this study show that sewage sludge can be an important source in the spread of persistent pollutants to the environment, and may pose a risk for soil ecosystem.

1. Introduction

Occurrence of persistent pollutants in sewage sludge used for soil amendment is an important issue due to the lack of information about the long term effect on soil fertility and ecotoxicology. Application of digested sewage sludge to agricultural soils, not only for nutrient enrichment, but also for enhancement of soil organic matter content, has become increasingly common. Digested sewage sludge is a good alternative to fertilizers to increase agricultural productivity, since it is inexpensive and effective (Ozdemir et al., 2019). However, most of the urban wastewater treatment plants (WWTPs) receive both domestic and industrial effluents. Therefore, urban wastewater and sewage sludge consist a variety of natural and synthetic organic pollutants, heavy metals, and pathogens. For over decades, great attention was paid to the occurrence of heavy metals and pathogenic bacteria in sewage sludge (Kowalik et al., 2021; Wojciula et al., 2021). Afterwards, it was understood that sewage sludge may contain various organic contaminants such as pharmaceuticals (Cespedes-Sánchez et al., 2011; Chen et al., 2013; Aydin et al., 2022), PAHs, PCBs, and OCPs etc. (Busetti et al., 2006; Clarke et al., 2010). PAHs, PCBs, and OCPs are characterized with their bioavailability, persistency, lipophilicity, and toxicity (UNEP, 2001; Alharbi et al., 2018). They are resistant to physical, chemical, and biological oxidation processes. PCBs are among the Persistent Organic Pollutants (POPs) dirty dozen list, which was announced in Stockholm Convention in 2001 (2001). PCBs have carcinogenic, mutagenic, endocrine disrupting, diabetic etc. effects on human (Plísková et al., 2005;

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Lee et al., 2018; Koukoulakis et al., 2020; Park et al., 2020; Galban-Velazquez et al., 2021).

Sources of PAHs are related to the incomplete combustion process of fossil products and vehicle emissions (Wild and Jones, 1995). They adsorb to airborne particles, transported over long distances and deposited on surfaces. PAHs are not specific wastewater pollutants, however they are ubiquous in urban environment. “16 EPA-priority PAHs were ranked by U.S. Environmental Protection Agency (US EPA), by considering their relative toxicity, abundance in the environment, and human exposure (Keith, 2015). The selected representative PAH compounds were; naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fuoranthene, benzo[k]fuoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and indeno [1,2,3-cd]pyrene (Khadhar et al., 2010).” Before 1980s PCBs were used as coolants and insulators in electrical capacitors and transformers (Diamond et al., 2010). Even the PCBs production has stopped four decades ago, some of the PCB containing capacitors and transformers are still in use and constitute historical contamination sources (Needham and Ghosh, 2019).

These persistent organic pollutants are ubiquitous in various environmental matrixes. Mansuy-Huault et al. (2009) analyzed 16 EPA PAH in sewage sludge samples taken from rural districts of France. 17 − 73 µg/g PAH was reported for eight samples. Maia et al. (2017) analyzed PCBs in sewage sludge samples obtained from a WWTP in Brazil. PCB 52 was the most quantified PCBs congener, with concentration range of 50 and 70 µg/kg. OCPs concentrations in sewage sludge has been determined generally in lower concentrations when compared with PAHs and PCBs. Clarke et al. (2010) reported 770, 290 and 270 µg/kg dieldrin, chlordane and DDE in sewage sludge samples, respectively.

PAHs, PCBs, and OCPs are end up in sewage sludge either by run-off on surfaces or by industrial discharges to sewer system. They partially degrade in WWTPs and eventually accumulate in sewage sludge. The fate of a chemical in a WWTP depends on the nature of the chemical and the type of the process applied (Margot et al., 2015; Man et al., 2017). It may be degraded, volatilized, sorbed to sewage sludge, or discharged in the effluent. Since organic pollutants have hydrophobic character, they bind to the particle fraction in wastewater media, and accumulate in the sewage sludge. The fate of pollutants in the sewage sludge also depends on the applied process for dewatering and reducing pathogens, such as anaerobic digestion, lime stabilization, composting, thermal drying, sludge cake production, or centrifugation (Patureau et al., 2021). While sludge treatment methods do not have reduction effect on heavy metals, they partly degrade organic pollutants (Mailler et al., 2014). Degradation of organic pollutants result in the formation of byproducts. The fate of organic pollutants after land application of sewage sludge also depends on the chemical structure of the pollutant, physicochemical characteristics of the soil, plant type cultivated in the soil, and environmental conditions. A positive correlation was recorded among sewage sludge PAHs concentration and soil PAHs content after sewage sludge amendment of soil (Paraiba et al., 2011). Concentration levels in vegetables, meat and milk were also linearly correlated to POPs occurrence in soil (Pasuello et al., 2010). Gworek et al. (2014) defined the relationship between the PAHs content of sewage sludge and the uptake amount by plant material cultivated in the sewage sludge amended area. An exponential accumulation of three-, four- and five-ring PAHs by *phragmites communis, bidens tripartite,* and *polygonum persicaria* was determined. Observed relationship was similar for three types of plants.

Authors determined mass loadings and toxic effect of pharmaceuticals on sludge amended soil in their previous publication (Aydin et al., 2022). Many publications point out PAHs, and PCBs content of sewage sludge (Włodarczyk-Makuła, 2005; Maia et al., 2017). Since there is a data about predicted no-effect environmental concentrations (PNECs) for water organisms, studies have been focused on ecotoxicological effects of synthethic organic pollutants on water organisms. A recent work determined ecotoxic potential of sewage sludge extract on *Aliivibrio fischeri* and *Daphnia magna* (Ahkola et al., 2021). However, there is no PNEC data for soil-dwelling organisms. Therefore, ecotoxicological risk assessment for soils, amended with sewage sludge containing PAHs, PCBs, and OCPs, is insufficient. This research study aims to fulfill this gap, via exampling a real WWTP sludge, being applied to agricultural soils.

The purposes of this work were;

1. To determine the occurrences and distributions of 18 PAHs, 7 congeners of PCBs, and 18 selected OCPs residues in the anaerobically digested sewage sludge produced by municipal WWTP,
2. To investigate the temporal variations in PAHs, PCBs, and OCPs residues over a period of 8 months, and
3. To determine the potential ecotoxicological risks caused by PAHs, PCBs, and OCPs residues in soils amended with that sewage sludge.

2. Materials and Methods

2.1 Chemicals and Reagents

All PAHs, PCBs, and OCPs standards used in this study were of analytical grade. Naphthalene, Acenaphthylene, Acenapthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Carbazole, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Chrysene, Pyrene, Benzo[g,h,i]perylene, Benzo[a]pyrene, Dibenzo [a,h]anthracene, and Indeno[1,2,3-c,d]pyrene were purchased from Accustandard (USA), and Benzo[j]fluoranthene was purchased from Dr. Ehrenstorfer (England). 7 congeners of PCB (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180), aldrin, α-HCH, β-HCH, γ-HCH, δ-HCH, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, p,p’-DDE, p,p’-DDD, p,p’-DDT, methoxychlor were also obtained from Accustandard (USA). The GC-grade solvents (e.g., acetone, dichloromethane, n-hexane, cyclohexane, ethyl acetate), silica gel (0.063 − 0.200

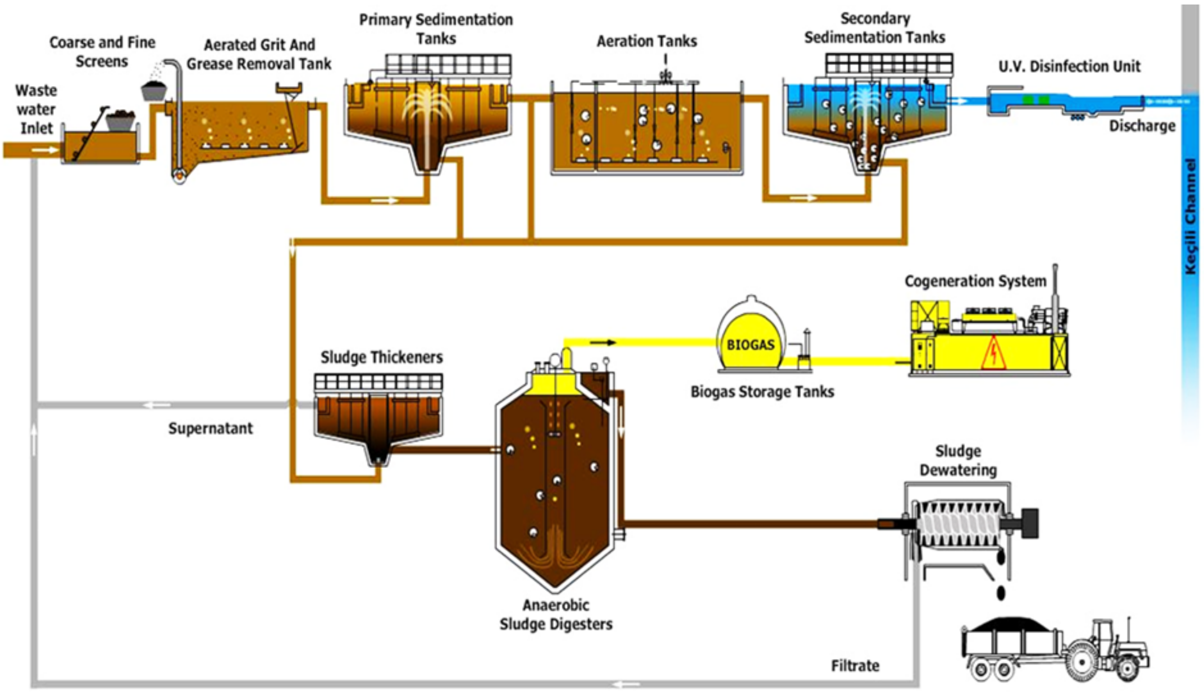

Fig. 1. Flow Diagram of the Wastewater and Sludge Treatments in WWTP

mm) were acquired from Merck (Darmstadt, Germany). Deionized water was provided by a Millipore Milli-Q Plus brand water purification system (Millipore, USA). Helium gas (99.999%) used in the gas chromatography device was obtained from BOS. Millipore Milli-Q Plus brand water purification system (Millipore, USA) were to obtain purified water for analytical studies.

2.2 Wastewater Treatment Plant and Sludge Sampling

Konya conventional WWTP was designed for 1,600,000 population equivalents, to remove organic matters, suspended solids and nutrients in urban wastewater of Konya City, located in the center of Turkey. The flow diagram for the WWTP is given in Fig. 1. The plant receives domestic wastewaters, rainwaters, and industrial wastewaters located out of the organized industrial zones in the city, which quantifies for 6% of total industrial wastewaters. Organized industrial zones have their own WWTPs, discharging their effluent to receiving water bodies. The average flowrate of the plant is 200,000 m^3/day. Activated sludge process is being used for organic matter removal from wastewater. Anaerobic (mesophilic) sludge digesters were designed to digest the pre-sedimentation sludge and biological sludge. For sludge dewatering, centrifugal decanters were installed. After conditioning with polyelectrolyte, the stabilized sludge is being dewatered averagely at 25% solid content. The daily produced 140 tons sludge is seasonally being applied to agricultural areas, poor of organic matter. For the present research, 1 kg sludge samples were monthly obtained from the dewatering process of the plant for eight months, from April to November. The samples were taken to amber colored jars, transferred and stored at 4°C until analysis.

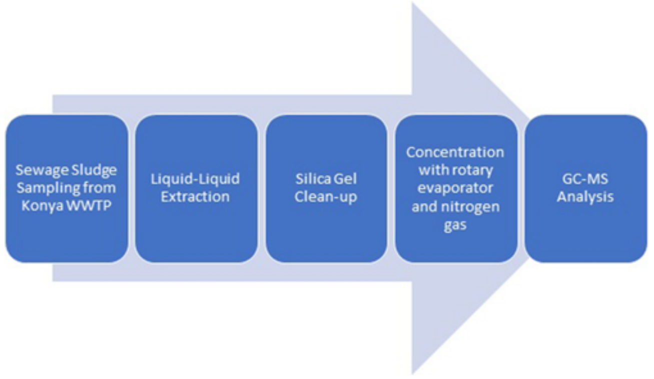

Fig. 2. The Experimental Flowchart

2.3 Analytical Procedures

The PAHs, PCBs, and OCPs ingredient of anaerobically digested sludge samples were analyzed. Experimental steps were given in Fig. 2. Analysis were performed by Agilent 6890 N gas chromatography (GC) with 5973 serial mass spectrometry (MS) detectors equipped with a 7663 B Autosampler. HP-5ms capillary column (film thickness 0.25 µm, inner diameter 0.25 mm, length 30 m) was used in the GC-MS system. For the analysis of target compounds, the optimum column, temperature program and carrier gas flow rates of the GC-MS system were determined by using PAHs, PCBs, and OCPs standards at a concentration of 1 ng/µL.

The PAHs, PCBs, and OCPs compounds were extracted according to the DFG (German Research Association) S19 multi-method (Their and Zeumer, 1987). 50 g sludge sample placed in the flask was shaken with a mixture of 150 mL acetone/pure water (2:1, v/v) with an orbital shaker at 221 rpm in the dark for 12 hours. A temperature-controlled horizontal shaker (Shin Saeng brand) was used for this stage. The amount of pure water was determined by considering the water content of the sludge sample. After the shaking process, 15 g NaCl and 100 mL cyclohexane were added, and the shaking process was carried out for 1 more hour under the same conditions. Subsequently, 25 g Na_2SO_4 was added and mixed for a few minutes, and the dewatering process was carried out. 100 mL of extract filtered through filter paper, concentrated to 2 mL in a rotary evaporator (Buchi rotavapor R-114), and the cleaning processes of the extract were carried out before GC-MS analysis. Extracts were cleaned up according to US EPA Metot 3630C - Silica Gel Clean-up. The column stationary phase was prepared according to the wet filling technique. Before packaging the 1.5 cm diameter and 14.5 cm long glass column with adsorbent, the glass wool placed on its base. The column was cleaned up by washing with 50 mL of elution solvent followed by 50 mL of acetone. The column containing 1 mL of n-hexane in the sorbent material suspended in n-hexane, was filled in such a way that no air bubbles were formed. After the filling process was completed, 50 mL of n-hexane was passed through the column, and the column was conditioned and made ready for the use. For the purification of sludge extracts, the column was given to the column containing 10 g of 5% deactivated silica and 2 g of Na_2SO_4 and the elution of the compounds was carried out with 70 mL of n-hexane followed by 100 mL of n-hexane/ethylacetate (1/1, v/v) mixture. The collected fractions were concentrated using a rotary evaporator and nitrogen gas and analyzed by GC/MS system. All sludge samples were analyzed in two replicates. A reagent blank was also treated in a manner similar to that of the sludge samples to detect potential contamination problems.

Standard spike procedure was used to determine the performance of the extraction and clean-up steps. Sludge samples were spiked with 100 µg/kg of PAHs, PCBs, and OCPs compounds, and stored at 4°C for 3 days. Afterwards, extraction and clean-up procedures were applied as described above. Spike-free sludge samples were used to control the background PAHs, PCBs, and OCPs residues. Obtained recoveries were 83 ± 18 – 98 ± 8% for PAHs, 98 ± 6 – 100 ± 6% for PCBs, and 74 ± 4 – 101 ± 4% for OCPs. Repeatability studies were performed for verification of the method. Relative standard deviation (RSD) of 12 experiments were 0.80 – 2.80%, 1.42 – 2.10%, and 1.60 – 3.80% for PAHs, PCBs, and OCPs, respectively. The verification parameters of the analytical method are given in Table S1.

2.4 Determination of Organic Carbon Content of the Soil

Loss-on-ignition method was used for quantifying fraction of organic carbon in the soil (foc) (Hoogsteen et al., 2015). Soil samples were taken from 0 – 25 cm, 25 – 50 cm and 50 – 75 cm depths in the vicinity of sewage amendment area. Soil samples were sieved through 2 mm sieves before analysis. In order to determine the moisture content of the soil samples, 1 g sample was placed in a porcelain crucible and dried in an oven at 105 ± 5ºC for 1 hour, and after cooling in a desiccator, its mass was determined. The drying process was repeated for 30 minutes and this process was continued until the difference between the masses was less than 2 mg. In order to determine the amount of organic matter content of the soil samples, the sample, of which the amount of solid matter was determined, was kept in the muffle furnace at 550 ± 50ºC for 3 hours, then cooled in the desiccator and its weight was determined on a precision balance.

2.5 Ecotoxicological Risk Assessment

An ecotoxicological risk assessment was performed on the basis of risk quotients (RQs) determined for the sewage sludge-amended soils. The RQ values for each PAHs, PCBs and OCPs compounds were calculated as the ratio of maximum environmental concentrations ($MEC_{max,sludge}$) to predicted no-effect environmental concentrations ($PNEC_{sludge}$) (European Commission, 2003). Since there is no ecotoxicity data for soil-dwelling organisms, the $PNEC_{soil}$ were calculated based on aquatic ecotoxicity data. For this purpose, $PNEC_{water}$ values determined for algae, *Daphnia magna,* or fish were multiplied by soil-water linear sorption coefficients (Kd_{soil}) (Vlaardingen et al., 2003). The lowest $PNEC_{water}$ values reported for these three organisms were used so as to determine the worst scenario. Since experimental Kd values were not available, estimated Kd values were calculated by octanol-water partition coefficient (Kow) and organic carbon fraction of soil (foc) according to Lauridsen et al. (2000). The log Kd_{soil} values are provided in Table 2. $PNEC_{water}$ data for aquatic organisms (e.g., algae, *Daphnia magna*, and fish) of the investigated PAHs, PCBs and OCPs compounds are given in Table S3.

The predicted environmental concentrations in the soil (PEC_{soil}) were calculated with Eq. (1) (EC, 2003; Bastos et al., 2020; Mejías et al., 2021; Aydin et al., 2022).

$$PEC_{soil} = \frac{C_{sludge} \times APPL_{sludge}}{DEPTH_{soil} \times RHO_{soil}}, \tag{1}$$

where;

$APPL_{sludge}$ = Rate of sludge application to soil (0.5 kg/m^2 year),
C_{sludge} = PAHs, PCBs and OCPs concentration in dry sludge (µg/kg.dm),
$DEPTH_{soil}$ = Mixing depth of agricultural soil (20 cm)
RHO_{soil} = Bulk density of agricultural soil (1,700 kg/m^3).

The PEC_{soil} values were estimated by considering the worst possible scenario. Therefore, the maximum environmental concentrations (MEC_{max}) in the dry sludge samples were used for calculaion of the PEC_{soil} values. Risk ranking criteria was used to evaluate the estimated RQsoil values (Deblonde and Hartemann, 2013; Aydin et al., 2022). $RQ < 0.1$ was considered as low risk, $0.1 < RQ < 1$ was considered as medium risk, and $RQ > 1$ was considered as high risk.

3. Results and Discussions

3.1 Occurrence of PAHs, PCBs, and OCPs in Digested Sludge

The ranges, means, and median concentrations, and frequencies

Table 1. Ranges (minimum-maximum), Means, and Median Concentrations and Frequencies of Detection (n = 24 = 100%) for Each PAHs, PCBs and OCPs Compound in the Digested Sludge Samples and the Predicted Environmental Concentrations (PEC) of each PAHs, PCBs and OCPs Compound in the Digested Sludge-Amended Soils

Group	Compound	Digested sludge (μg/kg dm)			PEC in digested sludge-amended soil (μg/kg dm)			Frequencies of detection* (%)
		Ranges (min-max)	Means	Median	Ranges (min-max)	Means	Median	
PAHs	Naphthalene	599-1507	992	860	0.881-8.863	1.460	1.266	100
	Acenaphthylene	10-106	54.3	55.1	0.014-0.622	0.080	0.081	100
	Acenapthene	25-317	124	52.5	0.036-1.867	0.183	0.077	100
	Fluorene	7-387	182	155	0.010-2.278	0.269	0.229	100
	Phenanthrene	58-2176	989	886	0.085-12.80	1.455	1.303	100
	Anthracene	46-2037	498	244	0.067-11.98	0.733	0.360	100
	Carbazole	8-90	34,7	20.0	0.012-0.527	0.051	0.029	100
	Fluoranthene	105-2445	970	777	0.155-14.38	1.427	1.144	100
	Pyrene	201-2077	827	593	0.295-12.22	1.216	0.873	100
	Benzo[a]anthracene	9-884	270	235	0.014-5.198	0.398	0.346	100
	Chrysene	2-1458	407	126	0.002-8.577	0.600	0.185	100
	Benzo[b]fluoranthene	9-836	197	89.9	0.014-4.915	0.290	0.132	87
	Benzo[k]fluoranthene	nd -354	134	38.8	0.016-2.082	0.198	0.057	37
	Benzo[a]pyrene	14-174	78.7	72.4	0.020-1.026	0.116	0.107	100
	Indeno[1,2,3-c,d]pyrene	nd -59	27.7	25.2	0.002-0.348	0.041	0.037	87
	Dibenzo[a,h]anthracene	nd -11	6.96	6.47	0.005-0.065	0.010	0.010	37
	Benzo[g,h,i]perylene	nd -1829	544	177	0.137-10.75	0.801	0.260	87
	Benzo[j]fluoranthene	3-852	210	116	0.005-5.014	0.310	0.171	100
PCBs	PCB 28	4.15-171	47.70	18.08	0.0061-0.252	0.070	0.026	100
	PCB 52	1.79-25.21	10.63	9.68	0.0026-0.037	0.015	0.014	100
	PCB 101	nd-10.84	3.80	3.24	0.0002-0.015	0.005	0.004	87
	PCB 118	7.22-514	106	25.70	0.0106-0.756	0.157	0.037	100
	PCB 153	0.34-16.26	4.28	2.75	0.0005-0.023	0.006	0.004	100
	PCB 138	0.43-31.42	7.64	5.43	0.0006-0.046	0.011	0.008	100
	PCB 180	0.17-18.47	6.99	6.10	0.0002-0.027	0.010	0.009	100
OCPs	Aldrin	nd -0.22	0.04	0.00	0.00E+00-3.24E-04	6.25E-05	0.00E+00	37
	α-HCH	0.12-0.86	0.48	0.46	1.76E-04-1.26E-03	7.08E-04	6.69E-04	100
	β-HCH	0.17-3.04	1.07	0.92	2.50E-04-4.47E-03	1.57E-03	1.35E-03	100
	γ-HCH	0.36-2.88	1.61	1.58	5.29E-04-4.24E-03	2.37E-03	2.32E-03	100
	δ-HCH	0.13-6.93	2.44	2.18	1.91E-041.02E-02	3.59E-03	3.20E-03	100
	Chlordane I	nd-0.01	0.00	0.00	0.00E+00-1.47E-05	1.84E-06	0.00E+00	25
	Chlordane II	nd-0.04	0.02	0.01	0.00E+00-5.88E-05	2.39E-05	1.47E-05	87
	Dieldrin	nd-2.22	0.50	0.00	0.00E+00-3.26E-03	7.35E-04	0.00E+00	50
	Endosulfan I	nd-0.31	0.15	0.14	8.82E-05-4.56E-04	2.19E-04	2.06E-04	100
	Endosulfan II	nd-1.43	0.27	0.07	0.00E+00-2.10E-03	3.95E-04	9.56E-05	87
	Endosulfan sulfate	nd-0.46	0.16	0.05	0.00E+00-6.76E-04	2.35E-04	7.35E-05	87
	Endrin	nd-0.36	0.09	0.00	0.00E+00-5.29E-04	1.32E-04	0.00E+00	37
	Endrin aldehyde	0.05-1.36	0.40	0.22	7.35E-05-2.00E-03	5.85E-04	3.16E-04	100
	Endrin ketone	nd-0.40	0.06	0.00	0.00E+00-5.88E-04	8.09E-05	0.00E+00	25
	Heptachlor	nd-1.36	0.45	0.11	0.00E+00-2.00E-03	6.58E-04	1.54E-04	75
	Heptachlor epoxide	nd-0.13	0.07	0.09	0.00E+00-1.91E-04	9.56E-05	1.25E-04	62
	p,p’-DDE	nd-0.46	0.09	0.01	0.00E+00-6.76E-04	1.36E-04	1.47E-05	50
	p,p’-DDD	nd-0.40	0.08	0.02	0.00E+00-5.88E-04	1.14E-04	2.21E-05	87
	p,p’-DDT	0.01-0.26	0.08	0.05	1.47E-05-3.82E-04	1.10E-04	6.62E-05	100
	Methoxychlor	nd-0.28	0.14	0.18	0.00E+00-4.12E-04	2.00E-04	2.57E-04	87

nd: not detected
*Frequencies of detection: digested sludge concentration / PEC in digested sludge-amended soil

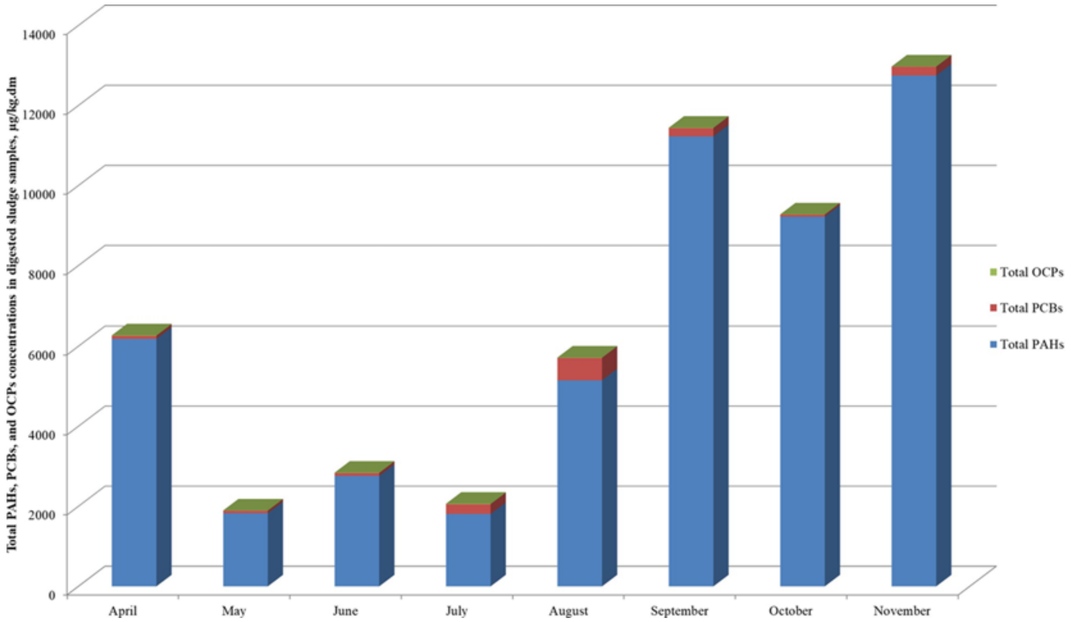

Fig. 3. The Distributions of Total PAHs, PCBs, and OCPs Detected in the Digested Sludge (µg/kg dm)

Table 2. Predicted No-Effect Concentrations (PNEC) of PAHs and PCBs in Water, Digested Sludge and Soil, Maximum Measured Environmental (MEC_{max}) in Digested Sludge and the Estimated Risk Quotients (RQs) in Digested Sludge and Soils (yellow: low risk; green: medium risk; red: high risk)

Group	Compound	$PNEC_{water}$ (µg/L)	Log Kd soil	$PNEC_{soil}$ (µg/kg)	$MEC_{max, sludge}$ (µg/kg dm)	PEC_{soil} (µg/kg dm)	RQs_{soil}
PAHs	Naphthalene	3.4*	1.32	71.03	1507	8.86	21.22
	Acenaphthylene	10.62***	1.39	260.61	106	0.62	0.41
	Acenapthene	0.5*	1.39	12.27	317	1.87	25.84
	Fluorene	3.40*	1.42	89.42	387	2.28	4.33
	Phenanthrene	1.228*	1.46	35.42	2176	12.80	61.44
	Anthracene	1.777*	1.45	50.08	2037	11.98	40.68
	Carbazole	na	1.37	na	90	0.53	na
	Fluoranthene	1.068*	1.55	37.89	2445	14.38	64.52
	Pyrene	0.048*	1.51	1.55	2077	12.22	1337
	Benzo[a]anthracene	0.58*	1.63	24.74	884	5.20	35.74
	Chrysene	1.9**	1.62	79.19	1458	8.58	18.41
	Benzo[b]fluoranthene	0.269*	1.63	11.47	836	4.92	72.87
	Benzo[k]fluoranthene	0.271*	1.68	12.97	354	2.08	27.29
	Benzo[a]pyrene	0.212*	1.68	10.15	174	1.03	17.15
	Indeno[1,2,3-c,d]pyrene	0.133*	1.76	7.65	59	0.35	7.71
	Dibenzo[a,h]anthracene	0.469**	1.73	25.19	11	0.07	0.44
	Benzo[g,h,i]perylene	0.099*	1.75	5.57	1829	10.76	328.56
	Benzo[j]fluoranthene	na	1.68	na	852	5.01	na
PCBs	PCB 28	0.046*	1.61	1.88	171.97	0.25	91.36
	PCB 52	0.003**	1.68	0.14	25.21	0.04	176
	PCB 101	0.041*	1.78	2.47	10.84	0.02	4.39
	PCB 118	0.001**	1.83	0.07	514.31	0.76	7608
	PCB 153	0.093*	1.93	7.92	16.26	0.02	2.05
	PCB 138	0.057*	1.88	4.32	31.42	0.05	7.27
	PCB 180	0.001**	2.02	0.10	18.47	0.03	176

na: not available
*Algae, **Baetis, ****Daphnia magna*

Table 3. Predicted No-Effect Concentrations (PNEC) of OCPs in Water, Digested Sludge and Soil, Maximum Measured Environmental (MEC_{max}) in Digested Sludge and the Estimated Risk Quotients (RQs) in Digested Sludge and Soils (yellow: low risk; green: medium risk; red: high risk)

Therapeutic group	Compound	$PNEC_{water}$ (µg/L)	Log Kd soil	$PNEC_{soil}$ (µg/kg)	$MEC_{max, sludge}$ (µg/kg dm)	PEC_{soil} (µg/kg dm)	RQs_{soil}
OCPs	Aldrin	0.021*	1.77	1.24	0.22	3.24E-04	0.18
	α-HCH	10*	1.44	275.4	0.86	1.26E-03	nd
	β-HCH	10*	1.44	275.4	3.04	4.47E-03	0.01
	-HCH	0.02**	1,44	0.55	2.88	4.24E-03	5.23
	-HCH	3*	1.44	82.62	6.93	1.02E-02	0.08
	Chlordane I	0.056*	1.69	2.74	0.01	1.47E-05	nd
	Chlordane II	0.056*	1.69	2.74	0.04	5.88E-05	0.01
	Dieldrin	0.05*	1.58	1.90	2.22	3.26E-03	1.17
	Endosulfan I	2*	1.34	47.02	0.31	4.56E-04	0.01
	Endosulfan II	0.205***	1.34	4.48	1.43	2.10E-03	0.32
	Endosulfan sulfate	na	1.34	na	0.46	6.76E-04	na
	Endrin	0.384*	1,58	14.59	0.36	5.29E-04	0.02
	Endrin aldehyde	na	1.51	na	1.36	2.00E-03	na
	Endrin ketone	na	1.51	na	0.40	5.88E-04	na
	Heptachlor	0.038*	1.66	1.74	1.36	2.00E-03	0.78
	Heptachlor epoxide	1.020*	1.47	30100	0.13	1.91E-04	nd
	p,p'-DDE	0.069*	1.66	3.15	0.46	6.76E-04	0.15
	p,p'-DDD	0.232*	1.66	10.60	0.40	5.88E-04	0.04
	p,p'-DDT	0.059*	1.77	3.47	0.26	3.82E-04	0.07
	Methoxychlor	6*	1.62	250	0.28	4.12E-04	nd

na: not available
nd: not determined
*Algae, **Fish, ***_Daphnia magna_

of PAHs, PCBs, and OCPs in the digested sludge samples over eight months period are provided in Table 1. The total concentrations of PAHs, PCBs, and OCPs in the digested sludge samples were calculated for each month from April to November. The sum of PAHs, PCBs, and OCPs were given in Fig. 3 on a monthly basis. The most frequently detected group was PAHs, quantified 97% of the total organic groups. The sum of the 16 EPA PAHs was determined between 1,192 – 14,828 µg/kg dm. Total 18 PAHs were in the range of 1,203 – 17,599 µg/kg dm. The highest total PAHs, PCBs, and OCPs amount in the digested sludge was 12,975 µg/kg dm in November, while the lowest value was 1,897 µg/kg dm in May. Researchers show similar results for PAH concentration in sewage sludge samples. The highest amounts were recorded for PAHs compounds among the organic contaminants analyzed in sewage sludge samples obtained from a WWTP in Italy. Busetti et al. (2006) reported 1,440 – 1,260 µg/kg total 16 EPA PAHs in sewage sludge samples.

The highest amount was quantified for fluoranthene among PAHs, which was 2,445 µg/kg dm. Among 8 sampling periods, the highest standard deviation was also determined for fluoranthene, which was 848 µg/kg dm. Dibenzo[a,h]anthracene was below detection limit in most of the analyzed samples. The highest concentratios for naphtalene, fluorene, phenanthrene, anthracene, fluoranthene, benzo[g,h,i]perylene, and benzo[j]fluoranthene were determined in samples taken in November in rainy days. PAHs cumulate on the particulate matter in the air after releasing to atmosphere by gaseous emissions. They enter sewerage system by settling and urban run-off in rainy seasons. Since PAHs have low solubility, and hydrophobicity, they have tendency to accumulate in sewage sludge, sediment, and soil. PAHs removal performance of WWTPs is variable. The most toxic, high molecular weight PAHs are usually removed higher than 80% in conventional WWTPs (Margot et al., 2015). The sludge treatment process effect the fate of the PAHs. The best PAHs removal was reported for mesophilic aerobic digestion when compared with chemical and electrochemical processes (Zheng et al., 2007). Reduction of PAHs in sludge processing is also generally dependent on the hydrocarbon content of the compound. Biodegradation potential inversely correlated with the increasing number of rings (Trably and Patureau, 2006). Digestion of the sludge result in the decomposition of complex organic pollutants. Mesophilic and thermophilic digestion systems are generally used for stabilization of sludge. The studies have proved that PCBs can be biodegraded under aerobic and anaerobic conditions (Rosinska and Dabrowska, 2014).

Total PAHs was determined in the range of 1,809 µg/kg dm (in May) and 12,749 µg/kg dm (in November). PAHs contents of 50% of the sludge samples exceeded the reference value proposed by Turkish (MEU, 2010) and EU guide (86/278/EU), which is 6,000 µg/kg.dm for total PAHs. Rainy season samples taken in September, October, November, and December were not suitable to apply in soil.

In our research, 7-PCB congeners were quantified above detection limits for all samples, except PCB101 congener for a sample taken in July. Total PCBs were in the range of 51.26 – 561.37 μg/kg dm. None of the samples exceeded the reference value proposed by Turkish (MEU, 2010) and EU guide (86/278/EU), which is 800 μg/kg dm for total 7-PCBs. The patterns of congeners observed were similar in all samples taken for this study. The predominant congener was PCB118, which was in the range of 7.22 – 514.31 μg/kg dm. Since higher chlorinated congeners have less volatility, they have a tendency to bound to particles in sewage sludge (Meijer et al., 2003).

OCPs are not regulated compounds for sludge amendment of soil. However, most of the analyzed OCPs compounds were banned for agricultural use. Therefore, determination of their occurrence in sludge is important to evaluate overall risk for soil. Among OCPs, the highest concentrations were determined for δ-HCH, with 2.44 μg/kg dm mean value. Total OCPs were in the range of 4.90 – 13.11 μg/kg.dm. In addition to the sludge amendment of soil, OCPs compounds have layers of agricultural use. Therefore, they are likely to be higher in soil samples.

According to 30 years sewage sludge screening study held in China, organic contaminants content of sewage sludge obtained from WWTPs in the country were in the range of 100 – 170,000 μg/kg dm for PAHs; 3.14 – 1,400 μg/kg.dm for PCBs, and 9.0 – 3,200 μg/kg dm for OCPs (Meng et al., 2016). In a similar study, sewage sludge obtained from 14 WWTPs in U.K. were evaluated in the means of PAHs and PCBs. While total PAHs were 67 – 370 mg/kg dm, which were quite over the EU legislation, total PCBs were in the range of 110 – 440 μg/kg dm well below the proposed EU limit (Stevens et al., 2003).

3.2 Organic Carbon Content of the Soil

Foc value of sludge amended soil was used to determine Kd values of the compounds (Lauridsen et al., 2000). foc values of the soil samples ranged from 0.69 to 9.18%. It was determined that a few soil samples (3%) had low organic matter content (1%), while a significant portion of the soil samples (56%) had a good organic matter content (> 4%). Since, foc enhances the adsorption and accumulation of pollutants on soil particles, the highest foc value (9.18%) was used so as to determine the worst scenario.

3.3 Mass Loads of PAHs, PCBs, and OCPs in Digested Sludge

The mass loads of PAHs, PCBs, and OCPs in the digested sludge were determined by the average daily production amounts of treated sludge in the Konya WWTP. The total mass loads (g/day) of the studied persistent pollutants in the digested sludge is provided in Fig. 4. The highest mass load for total PAHs was 1,785 g/day in November. The highest value for PCBs was determined 79 g/day in August. Lower levels of PCB in winter time can be explained by dilution effect of snow and rain (Adeyinka et al., 2018). OCPs mass load was similar in all sampling period with 1 – 2 g/day. The total persistent pollutants loads were determined to be 4,720 g/day in autumn (e.g., September, October, and November); and 1,488 g/day in summer (e.g., June, July, and August); and 1,144 g/day in spring (e.g., April, and May).

The mass loads of the total persistent pollutants that were detected in the autumn season in the digested sludge were higher than those in the summer season. Since PAHs constitute the largest share among pollutants, possible pollution source is the air emissions. The annual mass loads of the analyzed total persistent

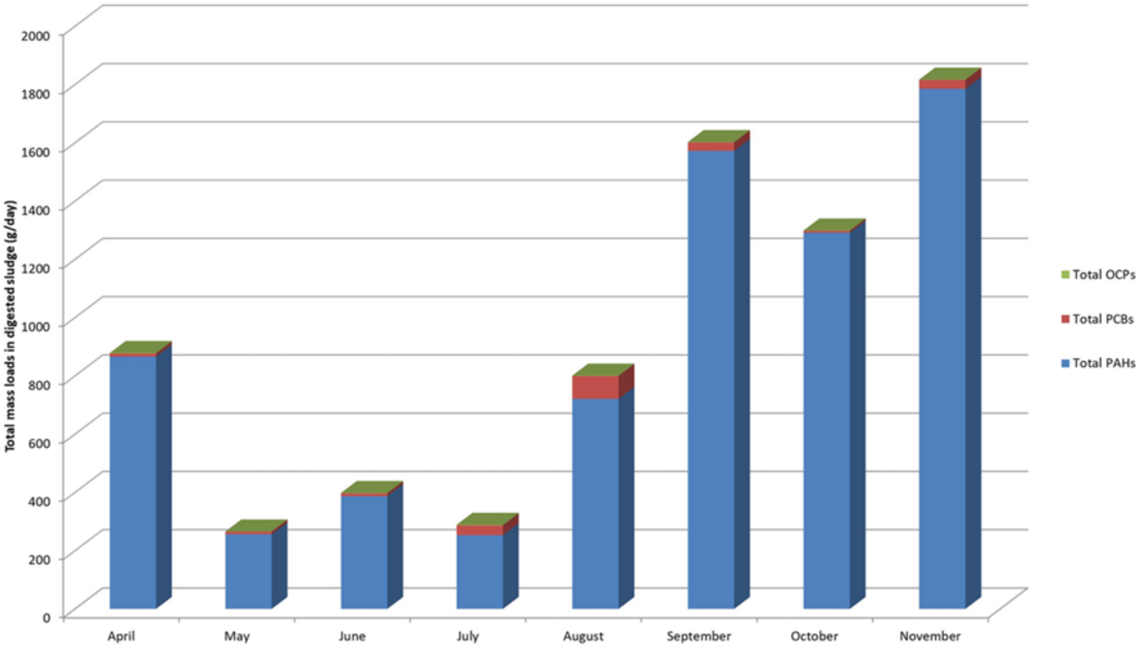

Fig. 4. Total Mass Loads in the Digested Sludge (g/day)

pollutants were 7.3 kg for the studied period. Since this sludge was applied to agricultural areas in Konya city, 7.3 kg of PAHs, PCBs, and OCPs were also applied to these lands annually. As a result of this application, persistent pollutants can be transported to the whole area and may enter the food chain.

3.4 Risk Assessment

The potential environmental risks posed by each PAHs, PCBs, and OCPs compounds in the digested sludge-amended soils were evaluated by using the RQ values, which were provided in Tables 2 and 3. The RQ values were determined to be within the range of 0.41 – 1337 for the PAHs compounds; within the range of 2.05 – 7608 for the PCBs compounds, and 0.01 – 5.23 for the OCPs compounds in the digested sludge. All of the PAHs compounds, except Acenaphthylene and dibenzo[a,h]anthracene, pose high risk for soil ecosystem. The highest RQ value was determined for pyrene (RQ: 1337). Besides, all of the PCBs compounds pose high risk for soil ecosystem, and the highest RQ value was determined for PCB118 (RQ: 7608). On the other hand, most of the OCPs compounds determined to have low ($RQ < 0.1$) or moderate ($0.1 < RQ < 1$) risk for soil, except g-HCH (RQ: 5.23) and dieldrin (RQ: 1.17). There is an insignificant risk for a-HCH, chlordane I, heptachlor epoxide, and methoxychlor. RQ values could not be calculated for endosulfan sulfate, endrin aldehyde, and endrin ketone since PNEC values were not available. These results show that digested sludge amendment of soil may pose high risk for soil ecosystem. Even none of the samples exceeded the reference PCBs value proposed by Turkish guide, RQ values determined for PCBs compounds were quite high. It must also kept in mind that, continuous application will result in accumulation of these compounds in soil as a result of their physicochemical properties.

Ahkola et al. (2021) evaluated ecotoxic potential of PAHs and some other selected chemicals containing sewage sludge on some bioassays. Digestion or composting of the sludge affected its toxic effect potential. While digested sludge caused toxic effect on *Aliivibrio fischeri*, no toxic effect was observed after composting. On the other hand, all sludge treatment types caused acute or chronic toxic effect on *Daphnia magna*. Urbaniak et al. (2020) estimated growing inhibition effect of PCB containing sediment amendment of soil on cucurbit species. While no phytotoxic effect was observed at the beginning of the amendment, an inhibition effect was observed at the end of four weeks. There are some studies reveal that cultivation of plants decreases the PCBs content of soil, contaminated with sewage sludge amendment (Wilson et al., 1997; Wyrwicka et al., 2019), however these studies do not give any data whether PCBs adhere to vegetation, which can be an exposure route for human.

According to the environmental risk analysis in this study, PAHs, PCBs, and OCPs compounds present in digested sludge pose high risk for sludge amended soils. Even the sludge has been applied for enhancement of soil fertility, it was proved that it had a potential ecotoxicological risk for soil organisms. Chronic ecotoxicological risks could be expected as a result of long term sludge amendment of soil, which may result in the inhibition of soil fertility.

4. Conclusions

18 PAHs, 7 PCBs, and 18 OCPs were determined in the anaerobically digested sewage sludge samples obtained from a conventional WWTP. It has been revealed that currently applied anaerobic sludge treatment processes cannot provide the complete elimination of the analyzed persistent pollutants. PAHs were the dominant group in the sludge. The highest concentrations of PAHs were determined in November in rainy days, and fluoranthene was determined in peak concentration among PAHs, which was 2,445 µg/kg dm. The patterns of PCBs congeners were similar in all samples. The predominant congener was PCB118, determined in the range of 7.22 – 514 µg/kg dm. OCPs were determined in lower concentrations when compared with PAHs and PCBs. Among OCPs, the highest concentrations were determined for δ-HCH, with 2.44 µg/kg dm mean value. Konya province is a city with large agricultural lands. Since the treated sludge meet the regulations, it has been used for soil amendment in the region. However, findings of this research study show that there is an ecotoxicological risk for the soil. The RQ values goes up to 1337 for the PAHs (e.g., pyrene); 7608 for the PCBs (e.g., PCB118); and 5.23 for OCPs (e.g., γ-HCH). RQ values are the indication of high toxicity for soil organisms, that may result in inhibition of soil fertility in the course of time.

While the sewage sludge has been applied to the soil to benefit from its organic carbon and nutrient content, it may adversely affect the soil-dwelling organisms, because of its pollutants content. Vitality of soil organisms is related to the soil fertility. Annual application of sewage sludge to soil may affect sustainability of agriculture. It should be kept in mind that sewage sludge consists not only organic contaminants investigated in this study, but also a variety of others, that may cause toxic effects on soil-dwelling organisms. Therefore, alternative methods other than soil amendment should be preferred to re-use sewage sludge. Studies in the field have revealed that sewage sludge can be added to clay bricks (Areias et al., 2020); can be used as raw materials to produce lightweight aggregates (Souza et al., 2020); and can be used as landfill liner barrier (Liu et al., 2023) etc.

Acknowledgments

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