ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 34 no.3 pp. 41 – 47 2008

PL ISSN 0324-8461

LEACHING OF PAHS FROM FLY ASH – SLUDGE BLENDS

CZESŁAWA ROSIK-DULEWSKA[1], URSZULA KARWACZYŃSKA[2], TOMASZ CIESIELCZUK[2]

1. Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland
2.Opole University, Department of Land Protection, Opole, Poland
Corresponding author: T. Ciesielczuk, email: tciesielczuk@uni.opole.pl, tel. +48774016027

Abstract: This work presents results of the release of polycyclic aromatic hydrocarbons (PAH) from granules composed of fly ashes, which are the product of hard and coal combustion and sewage sludge. 3 types of granulates by a weight ratio of ash to sludge 3:7 and 1:1 were used. The research of PAH leaching was conducted within a simulated period of 24 months, with the examination of PAH washing out every three months. The highest amounts of PAH (297 – 330 µg/kg dw.) were obtained_from granulates containing 7 parts by weights of sewage sludge (3 times higher in comparison with the granulate containing ash and sludge in ratio of 1:1). The maximum PAH release from all the examined granulates took place in the 9th month of the research. Benzo(k)fluoranthene revealed the highest fraction (67.4-76.0%) of all examined compounds.

Key words: ash, sewage sludge, PAH, leaching

INTRODUCTION

An increase in the amount of produced waste is a characteristic [feature] of the civilization. This problem pertains both, the highly industrialized and developing countries. Presently, in Poland, there are growing amounts of industrial waste originating from natural resources mining and especially from hard coal mining. The amount, as well as the quality characteristics of post-exploitation and processing waste depends on several factors, among others on the characteristic of deposit rocks, the way of running the exploitation, and mining characteristics. Considerable amount of municipal waste and sludge are formed, especially for great urban agglomerations. Due to substantial level of sludge hydration as well as its chemical and microbiological composition, there are several limitations in waste disposal (Zheng 2007). In most cases, after preliminary dehydration, such sludge is stored at the landfill site.

However, this sludge might be a potential raw material, which can be used as fertilizer as it contains many components necessary for plants. Ash-sediment mixtures may appear especially useful, due to the fact that they enable natural waste recycling of sludge and fly-ashes formed during hard and brown coal combustion. Fly-ashes and sewage sludge may contain considerable amounts of minerals (heavy metals) and organic pollutants, including polycyclic aromatic hydrocarbons (PAH). Consequently using ash-sediment mixture as fertilizer may lead to PAH increase in soils (Oleszczuk 2006). Polycyclic hydrocarbons constitute a micro-pollution which belongs to the group of so-called persistent organic pollutants (POP), which are practically present in all environmental components. They can be of natural or anthropogenic origin. The natural sources of PAH are mainly pirolitic processes taking place during volcanic eruptions, forest fires and humus matter conversion in soils (Amir 2005, Atanassova 2004, Bojakowska 2003, Chen 2004,

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska i Gospodarki Wodnej w Katowicach

Lage 2005, Moretto 2005, Nadal 2004, Tang 2006, Thiele 2002, Verdin 2005, Wilcke 1999). Their main source in urban agglomerations are the processes of liquid and solid fuel combustion, wood processing and waste utilization (Amir 2005, Atanassova 2004, Bojakowska 2003, Moretto 2005, Nadal 2004, Verdin 2005, Wilcke 1999). A characteristic feature of such compounds are low water solubility and a long half-live. Due to their tendency towards accumulation in living organisms, it is commonly noted that there are higher concentrations of PAH in plant and animal tissues, then in the surrounding environment. As a result of high amounts of PAH in sludge and ash (Arditsoglou 2004) as well as potential possibility of underground water contamination, the process of washing out of these compounds from the applied ash-sedimentary mixture to the soil solution, is particularly significant. This work analyses the process of PAH washing out from ash-sedimentary granulates in the course of laboratory experiment.

MATERIALS AND METHODS

The research examined ash-sedimentary granulates extracted during mixing fly-ashes of brown coal from "Bełchatów" Power Station (Poland) (N41 granulate) or of hard coal from "Łaziska" Power Station, and sludge of sewage-treatment plant in Zabrze (Poland) (N42 and N43 granulates). The mixtures were prepared in a pelleting machine in the Institute for Chemical Processing of Coal in Zabrze. The granulation was carried out in humid conditions and no additional binding or process activating substances were used during granulate preparations. Subsequently, the granules were submitted to the process of drying. The weight ratios of ash to sludge in the mixtures used for granulation were 3:7 (N41), 3:7 (N42) and 1:1 (N43). In the first granulate, brown coal ash from Bełchatów was used, whereas in the second and third sample- the ash of hard coal form "Łaziska" Power Station. The N41 granulate which was characterized by dark grey colour and diversified grain-size distribution, as well as the N42 granulate, were characterized by weak mechanical resistance. Only the fine grained N43 granulate which had strong mechanical resistance. The research was conducted in vertical lysimeter of 75 mm diameter and 1000 mm long. Examination of PAH granulate leaching was carried out within simulated time, applying a dynamic method with immovable deposit in columns, where aeration conditions were simulated. The experiment was conducted within 24 days, with the assumption that 1 day was an equivalent of 1 month (i.e. the simulated time was 24 months). The flooding volume was calculated on the basis of average monthly rainfalls in Poland]; it was assumed that 246 cm^3 of water constitutes an equivalent of an average monthly rainfall on the granulate flooding surface in the lysimeter (44.2 cm^2). Once a day within a period of 24 days all lysimeters were flooded with water of pH = 5.5 at the volume of 246 cm^3/lysimeter. The tests were repeated three times. Refluxes obtained from three lysimeters containing the same kind of granulate were averaged and the PAH content was examined.

The PAH load was calculated according to the following formula:

$$q = C\ Vo/m\ [\mu g/kg\ dw.],$$

where:
C- compound concentration [$\mu g/dm^3$],
V_0- volume of the reflux obtained in the given month of research [dm^3],
m- banking sand of the column [kg].

The content of 16 PAH together with leached pollutants were marked in the collected eluates: naphthalene, acenaphthylene, acenaphthene, fluorene, phanthrene anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(l,2,3-c,d)pyrene, dibenzo(a,h)anthrecene, benzo(g,h,i)perylene (US-EPA list). The tests were conducted each 3 months (that is in the: 3rd, 4th, 9th, 12th, 15th, 18th, 21st, 24th month of the research). Samples of eluates were preserved with methanol, and extraction was carried out (Fig. 1).

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska i Gospodarki Wodnej w Katowicach

The PAH extraction from the elute was carried out with HPLC hexane by a 4-hour shaking. Hexane – water eluate ratio was 1 : 10 (v/v) and in the result of obtain eluates volume varied from 15 to 25 cm^3. Polycyclic aromatic hydrocarbons (PAHs) were determined in unrefined hexane extracts by a GC-FID method, using the VARIAN GC-3800 chromatograph on ZB-5 capillary column, at a constant helium flow of 1 cm^3/min through the column. The initial oven temperature program was 100°C, held for 2 min, and increased to 300°C at a rate of 5°C/min. The final temperature of 300°C was held for 10 min. The correlation coefficient was calculated for the y=ax+b linear model curve. Recoveries levels for this procedure was low for naphthalene (45-57%), and higher (68-89%) for the rest individual PAH. Recoveries procedure was based on dry samples of sewage sludge spiked with PAHs standard. The detection limits ranged between 0.05-0.1 µg/kg dw. for particular PAHs. The results uncertainly was calculated as standard deviation value.

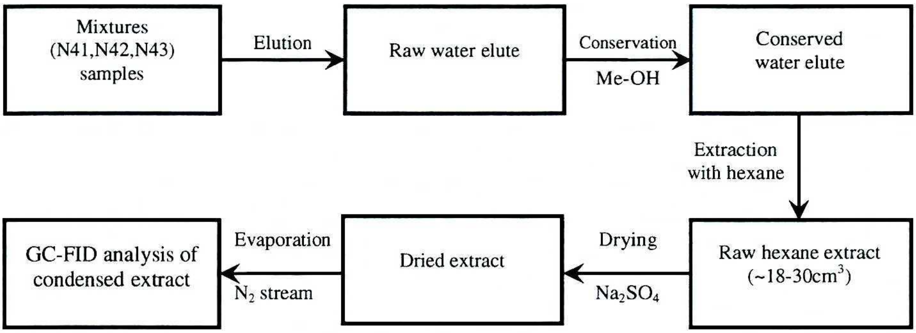

Fig. 1. Mixture elution experiment scheme

RESULTS AND DISCUSSION

The research which was conducted in simulated time proved a variability of generated PAH loads in different research periods. Initial amounts of PAHs in investigated materials were comparable except N43 granulate (Fig.2). In this case with lower charge of sewage sludge, detected PAHs content was mean 22% lower. Similar sums of washed out PAH loads from N41 and N42 mixtures (22.0 and 25.6 µg/kg dw. respectively) were noted at the beginning of the research (3^{rd} month), while the elute of N43 granulate contained a 3-times higher load (67.1 µg/kg dw.) what could be a result of finer granulometric size if it. One may observe there is a rapid growth of PAH load in the 9^{th} month of the research (Fig. 3) in case of all 3 tested granulates. A high PAH load of 222.7 and 224.5 µg/kg dw. was obtained from N41 and N42 mixtures, while only 58,1 µg/kg from N43. In this time a strong degradation of investigated granules was observed. However, it has to be taken into account that the ash/sediment quantitative ratio in the N43 granulate was 1:1 and mechanical resistance was higher, so ratio of released compounds was lower. High amount of PAHs in 9^{th} month of the research could be a result of anaerobic conditions inside of granules and creation of its during organic matter decomposition (Włodarczyk-Makuła 2003). In the following period of the research there is a clear decrease of noted PAH amounts in elutes up to do 24.8 µg/kg for N41 and 12.2 and 12.3 µg/kg dw. for N42 and N43 respectively. In the following months of the research the noted loads are low and do not exceed 10 µg/kg dw. BkFLA has the biggest fraction (76.0 and 75.8% respectively for N41 and N42, and 67.4% N43) from of all the examined compounds (Table

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska
i Gospodarki Wodnej w Katowicach

1).

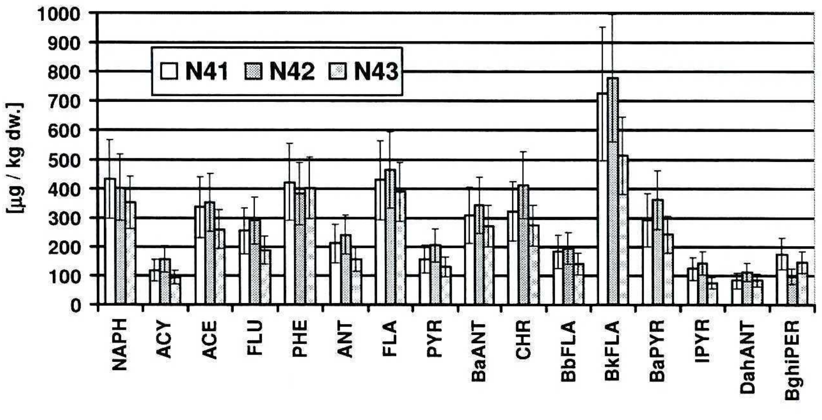

Fig. 2. The initial content of polycyclic aromatic hydrocarbons in granulates used in the experiment

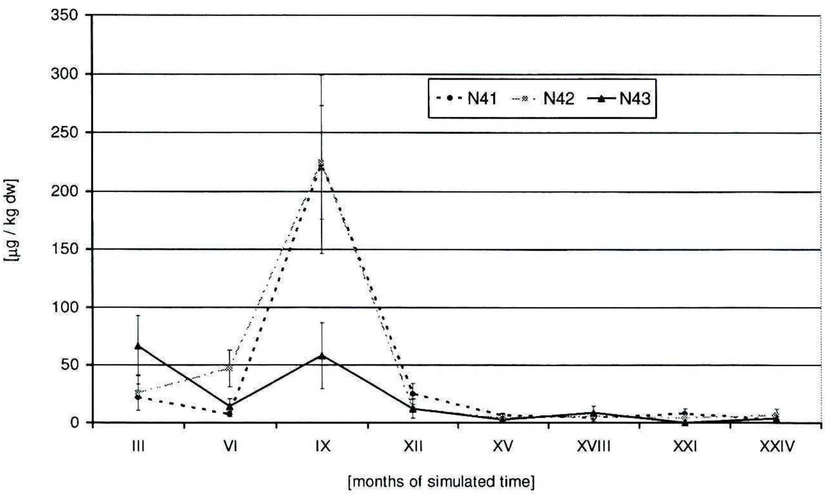

Fig. 3. Changes of 16 PAHs loads in elutes from investigated materials

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska i Gospodarki Wodnej w Katowicach

Table 1. Share of particular PAH in total loads eluted from examinated mixtures [%]

	N41	N42	N43
NAPH	2.45±1.2	1.24±0.6	8.74±3.2
ACY	0.49±0.	0.68±0.2	0.50±0.2
ACE	1.44±0.7	0.90±0.4	1.49±0.9
FLU	0.66±0.5	0.45±0.1	0.49±0.4
PHE	1.90±1.0	1.54±0.8	1.51±1.3
ANT	0.65±0.4	0.40±0.1	0.37±0.3
FLA	2.85±1.4	2.92±1.9	3.60±2.2
PYR	0.96±0.5	1.54±0.8	1.29±1.0
BaANT	2.37±1.5	2.49±1.6	2.62±1.6
CHR	3.64±2.1	3.65±2.0	3.45±1.9
BbFLA	2.15±1.5	2.14±1.3	1.34±0.5
BkFLA	76.0±9.6	75.8±8.2	67.4±7.1
BaPYR	3.19±1.7	4.27±3.2	3.95±2.2
IPYR	nd	nd	nd
DahANT	1.25±0.9	2.00±0,8	3.30±1.6
BghiPER	nd	nd	nd

nd – not detected; ± - standard deviation

Table 2. Sum of particular groups of PAHs obtained during experiment [μg/kg dw.]

	Granulate	III	VI	IX	XII	XV	XVIII	XXI	XXIV	Tot. load
	N41	0.7	1.6	3.7	3.8	1.3	1.2	2.1	0.9	15.3
Sum 3-ring	N42	0.6	1.4	2.6	2.7	1.3	1.0	0.8	2.7	13.1
	N43	1.6	0.8	1.2	1.6	0.5	1.2	0.1	0.2	7.2
	N41	2.1	2.2	13.9	5.0	1.2	1.3	2.8	0.8	29.2
Sum 4-ring	N42	2.9	8.4	12.1	5.6	1.4	1.9	0.9	1.6	35.0
	N43	6.9	2.3	4.2	2.0	1.5	1.0	nd	0.3	18.2
	N41	19.2	3.4	205	13.4	2.0	0.8	1.1	0.7	246
Sum 5-ring	N42	21.9	37.3	210	2.9	0.9	2.1	0.6	2.5	278
	N43	56.1	10.9	52.7	1.4	0.4	1.8	nd	3.0	126

nd – not detected. Mean value for 2 extractons.

A relatively high fraction (3.2 – 4.3%) was noted for BaPYR as well. This phenomenon lead to dominant group in eluted liquid – five ring PAHs (Table 2). The 6-ring PAHs (IPYR and BghiPER) were not noted in granulates, and the DahANT participation was 1.2 - 3.3%. The component fraction in mixtures may be particularly significant. Ashes from coal combustion contain mainly 3 and 4-ring PAH and small amounts of 5 and 6-cyclic PAH (up to 11% of the fraction). Consequently, sewage sludge (in which the amount of these compounds reaches up to 400-600 μg/kg) is the donor of the majority of carcinogenic PAHs (Oleszczuk 2006). The content of the examined 16 PAHs in unpolluted soils varies between 32.3 and 49.6 μg/kg dw. and increases after the application of sewage sludge as a fertilizer for 130 μg/kg dw. at the dose of 75t/ha reaching its maximum of 931 -1003 μg/kg dw. at 600t/h. (Oleszczuk 2006), which indicates a substantial role of sludge in the formation of PAH content in soils. However leachability of PAHs from contaminated soil could be very low and not exceed 0.3% of the initial amount of PAHs in soil (Enel et al. 2004). This research also noted three times higher values of released PAH loads in mixtures where the sewage/ash sludge ratio amounted to 3:7 in comparison to a mixture of 1:1 ratio.

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska i Gospodarki Wodnej w Katowicach

Moreover, the authors' research (Kim 2003) indicate a crucial role of the water-soluble organic matter in soil-to-soil transport of PAH solution. Mechanical resistance (including the resistance of granules to washing out) is an important factor here as well. A harder and more resistant N43 granulate released altogether three times less of PAH then brittle N41 and N42 granulates.

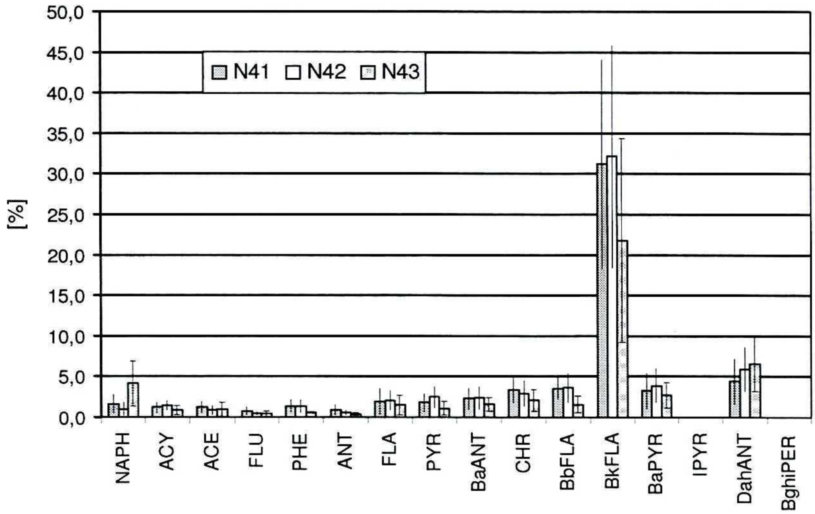

Fig. 4. Total PAHs elution ratio after 24 months simulated time experiment

CONCLUSIONS

In the obtained results of the ash-sludge granulates (N41, N42 and N43) research, distinct tendencies to release larger amounts of PAH, was noted only in the 9^{th} month of the experiment. The higher amounts of examined mixtures were noted in 6^{th} and 12^{th} months. Leaching, in the remaining months, was scant (8.4 μg/kg dw. max. for the N43 mixture). Such quantities of leached PAHs should not have any negative impact on the soil and water-soil environment. The amount of the released PAH considerably depends on granulate composition and its mechanical resistance. N43 mixture displaying high mechanical resistance gave twice lower PAH loads noted in elutes, in comparison to N41 and N42 blends. Thus, the ash/sludge ratio generating product resistance is a crucial parameter of the mixture. No differences were noted between the release of PAH from mixtures with brown and hard coal ash. The 4-cyclic PAHs (CHR) and 5-cyclic BkFLA and BaPYR- showed a prevailing participation in elutes. Moreover, large amounts of NAPH were noted in elutes as well. In the extracted elutes, 6-cyclic PAH IPYR and BghiPER were not noted in any of the research periods. The examined ash-sludge mixtures demonstrates a positive dependence of the amount of sludge and leaching to PAH soil solution. Chemical composition of the mixtures can show significant differences depending on the kind of combusted coal, combustion technology, place of taking the ash, way of storage, origin of the deposit and quality of the applied sewage sludge, which may exert some impact on changes in the intensity of compound leaching from granule. Granules which were qualified to natural use should undergo control tests on experimental beds in order to eliminate any potential hazard to the environment and to take a full advantage of the fertilizing potential.

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska
i Gospodarki Wodnej w Katowicach

REFERENCES

[1] Amir S., Hafidi M., Merlina G., Hamdi H., Reve J., 2005. Fate of polycyclic aromatic hydrocarbons during composting of lagooning sewage sludge. Chemosphere 58, 449-458.

[2] Arditsoglou A., Petaloti Ch., Terzi E., Sofoniou M., Samara C., 2004. Size distribution of trace elements and polycyclic aromatic hydrocarbons in fly ashes generated in Greek lignite-fired power plants. Science of the Total Environment 323, 153–167

[3] Atanassova I., Brummer G., 2004. Polycyclic aromatic hydrocarbons of anthropogenic and biopedogenic origin in a colluviated hydromorphic soil of Western Europe. Geoderma 120, 27-34.

[4] Biziuk M., Namieśnik J., Czerwiński J., Gorlo D., Makuch B., Janicki W., Polkowska Ż., Wolska L., 1996. Occurrence and determination of organic pollutants in tap and surface waters of the Gdańsk district. Journal of Chromatography A 733, 171-183.

[5] Bojakowska I., 2003. Charakterystyka wielopierścieniowych węglowodorów aromatycznych i ich występowanie w środowisku. Biuletyn Państwowego Instytutu Geologicznego 405, 5-28.

[6] Chen B., Xuan X., Zhu L., Wang J. J., Gao Y., Yang K., Shen X., Lou B., 2004. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. Water Research 38, 3558-3568.

[7] Enell A., Reichenberg F., Warfvinge P., Ewald G. 2004. A column method for determination of leaching of polycyclic aromatic hydrocarbons from aged contaminated soil. Chemosphere 54 707–715

[8] Kim Y.J., Osako M. 2003 Leaching characteristics of polycyclic aromatic hydrocarbons (PAHs) from spiker sandy soil. Chemosphere 51, 387-395

[9] Lage Yusty M.A., Cortizo Davina J.L., 2005. Supercritical fluid extraction and high-performance liquid chromatography-fluorescence detection method for polycyclic aromatic hydrocarbons investigation in vegetable oil. Food Control 16, 59-64.

[10] Moretto L.M., Silvestri S., Ugo P., Zorzi G., Abbondanzi F., Baiocchi C., Iacondini A., 2005. Polycyclic aromatic hydrocarbons degradation by composting in a soot-contaminated alkaline soil. Journal of Hazardous Materials B 126, 141-145.

[11] Nadal M., Schumacher M., Domingo J.L., 2004. Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environmental Pollution 132, 1-11.

[12] Oleszczuk P. 2006 Persistence of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge amended soil. Chemosphere 65, 1616-1626

[13] Tang X., Tang L., Zhu Y., Xing B., Duan J., Zheng M., 2006. Assessment of the bioaccessibility of polycyclic aromatic hydrocarbons in soils from Beijing using an in vitro test. Environmental Pollution 140, 279-285.

[14] Thiele S., Brummer G.W., 2002. Bioformation of polycyclic aromatic hydrocarbons in soil under oxygen deficient conditions. Soil Biology and Biochemistry 34, 733-735.

[15] Verdin A., Sahraoui A., Newsam R., Robinson G., Durand R., 2005. Polycyclic aromatic hydrocarbons storage by *Fusarium solani* in intracellular lipid vesicles. Environmental Pollution 133, 283-291.

[16] Wilcke W., Muller S., Kanchanakool N.,. Niamskul C., Zech W., 1999. Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. Geoderma 91, 297-309.

[17] Włodarczyk-Makuła M., Janosz-Rajczyk M., Zakrzewska E., Karwowska B., 2003. *Changes of PAHs contents In the sewage sludge and supernatants during anaerobic digestion process. Chemia i Inżynieria Ekologiczna* 10, 7, 687-694

[18] Zheng X.J., Blais J.F., Mercier G., Bergeron M., Drogui P. 2007. PAH removal from spiked municipal wastewater sewage sludge using biological, chemical and electrochemical treatments. Chemosphere 68, 1143-1152

Received: September, 2007; accepted: June, 2008.

Kolumna dofinansowana przez
Wojewódzki Fundusz Ochrony Środowiska i Gospodarki Wodnej w Katowicach