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“Environmental fingerprinting” of waste combustion products based on polycyclic aromatic hydrocarbon concentrations

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Abstract. The design and construction of thermal waste disposal facilities (including energy production) faces a number of limitations when choosing the technologies used. One of the most important environmental requirements is to prevent the release of toxic compounds contained in the combustion products of household waste, including carcinogenic substances. One of the groups of these compounds is polycyclic aromatic hydrocarbons (PAHs): toxic hydrocarbon compounds that are persistent in the environment, which are present in the combustion products of many materials and may also be petrogenic in nature (they are formed during low-temperature processes not related to burning). An important property of PAHs is marker qualities: their presence in the studied objects indicates a certain source of their origin (linked to certain natural or man-made processes). PAH concentration ratios are used in many domestic and foreign studies to identify the source of contamination. However, the boundary values of the indicator ratios used do not always fully unambiguously characterize the source of pollution, and the ratios themselves are informative to varying degrees for different environments and different natural conditions. The purpose of the article is to substantiate the use of PAH indicator ratios for pollution control as a result of incineration of various categories of waste. The materials for the study are the results of analytical determinations of polyarene concentrations in waste incineration products at domestic and foreign thermal recycling facilities. Indicator ratios of PAHs (a method of “environmental fingerprinting” of pollution sources widely known in foreign practice) have been tested for these objects. Using the methods of multidimensional data analysis (the principal component method), the most informative indicator ratios that can be recommended for use have been determined. Identification of the genesis of PAHs makes it possible to control the amount of pollution in the components of natural environments caused by emissions and waste from the combustion of materials, which contributes to a more objective control of anthropogenic loads.

Keywords: polycyclic aromatic hydrocarbons (PAH), indicator ratios, petrogenic PAH, pyrogenic PAH, factor analyses, waste, combustion

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«Экологическое детектирование» продуктов сгорания отходов на основе концентраций полициклических ароматических углеводородов

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Аннотация. Проектирование и строительство объектов термической утилизации отходов (в том числе в целях получения энергии) сталкивается с рядом ограничений при выборе применяемых технологий. Одно из важнейших экологических требований — предотвращение выбросов токсичных соединений, которые содержатся в продуктах сгорания бытовых отходов, включая канцерогенные вещества. Одна из групп этих соединений — полициклические ароматические углеводороды (ПАУ): стойкие в окружающей среде токсичные углеводородные соединения, которые присутствуют в продуктах сгорания многих материалов, а также могут иметь петрогенную природу (образуются при низкотемпературных процессах, не связанных с горением). Важное свойство ПАУ — маркерные качества: их присутствие в изучаемых объектах свидетельствует об определенном источнике их происхождения (привязано к определенным природным или техногенным процессам). Соотношения концентраций ПАУ используются во многих отечественных и зарубежных исследованиях для идентификации источника загрязнений. Однако используемые граничные значения индикаторных соотношений не всегда в полной мере однозначно характеризуют источник загрязнения, а сами соотношения в различной степени информативны для разных сред и различных природных условий. Цель исследования — обосновать применение индикаторных соотношений ПАУ для контроля загрязнений в результате сжигания различных категорий отходов. Материалы для исследования — результаты аналитических определений концентраций полиаренов в продуктах сжигания отходов на отечественных и зарубежных объектах термической утилизации. Для этих объектов апробированы индикаторные соотношения ПАУ (широко известный в зарубежной практике метод «экологического детектирования» источников загрязнения). С применением методов многомерного анализа данных (метод главных компонент) определены наиболее информативные индикаторные соотношения, которые могут быть рекомендованы для использования. Идентификация генезиса ПАУ позволяет контролировать объемы загрязнений в компонентах природных сред, обусловленных выбросами и отходами при сжигании материалов, что способствует более объективному контролю антропогенных нагрузок.

Ключевые слова: полициклические ароматические углеводороды (ПАУ), индикаторные соотношения, петрогенные ПАУ, пирогенные ПАУ, факторный анализ, отходы, сжигание

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Introduction

Waste incineration is now practised in many countries with simultaneous production of electricity and heat. This trend has become the mainstream of most waste management programmes in the economically developed world. There is a real need to bury the waste that can be burned and to burn the waste that can be recycled. The wastes that can be incinerated include most of the MSW, and the wastes for which burning is recognized as the only civilized means of destruction are medical, biological and veterinary wastes. In this context, there is a problem of reliable identification and dispersion of toxic aromatic hydrocarbons (particularly PAHs) in the environment. In Russia, the technology of thermal treatment of domestic waste has not found widespread; burial in landfills is much more common. However, the capacity of many landfills is on the verge of exhaustion and thermal recycling becomes almost inevitable.

Foreign literature contains numerous quantitative estimates of toxic emissions from waste incineration plants and individual incinerators, with the interest in this subject has not waned for several decades [9, 10, 15]. For example, the emission factors of PAHs (at least for the most common substances) are too high for many technologies. These compounds are monitored worldwide (16 PAHs compounds in the United States, only 3.4-benzenpyren in the Russian Federation), and there is strict regulation of their appearance and presence in the environment. In this context, the analysis of the origin of PAHs and their behaviour in the environment is very relevant. Knowing the processes of transformation and migration of these substances, it is possible to identify sufficiently reliably the causes of pollution, until the problem of finding the perpetrator of ecological damages is solved. In this case, PAHs act as geochemical markers of pollution.

The purpose of this article is a comparative analysis and evaluation of possibilities of adaptation of foreign experience of application of indicator ratios based on PAHs concentrations for identification of sources of pollution in natural and technological sites. The products of combustion of different materials are selected as research objects, which allows to consider the spectrum of PAHs concentration ratios depending on the combustion conditions.

Materials and methods

Like many compounds in the environment, PAHs can be natural, apart from their genetic origin. Conditionally, PAHs are substituted for pyrogenic (as a result of combustion processes), petrogenic (products of many geochemical processes involving carbohydrate-bearing, not related to combustion) and biogenic. The composition and structure of PAHs, as well as their stability depend on their genesis, temperature and environment in which they get into. Establishing the nature of PAHs is the most pressing environmental problem, as the question of determining who is responsible for the pollution is acute. The risk assessment of emissions and their effective management based on the knowledge of markers — the most representative taxonomy for combustion emissions. As markers, substances usually used that are sources of maximum risk to humans and biota. In order to identify sources of HC-contamination, environmental constituents use ratios of HC-isomer pairs [21], individual coefficients and biomarkers.

Advantages of using indicator ratios — relative simplicity of calculation and speed of estimation; use of data on a broad spectrum of toxic compounds (PAHs); clear presentation of the data. However, the coefficients used are in some cases not sufficiently informative and a number of coefficients previously introduced by Russian and foreign researchers have so far been inadequately implemented. This is often done mechanically, without assessing the temperatures and conditions of combustion of substrates and their physico-chemical properties.

Samples of ash from various wastes were examined to determine the presence of PAHs in the products of incineration of different types of waste. In addition to the “tuning of the method” of environmental fingerprinting (determination of optimal informative ratios), the relevance of the study of PAHs concentrations in ash residues is related to the fact that combustion products must subsequently be recovered for landfill.

This study focuses on PAHs sorbed in soot particles. These forms of bonding are most stable when the simultaneous oxidation is sufficiently strong. Confirmation of this is the supply during the combustion of medical waste in addition to incinerators air or oxygen, which provides a more complete combustion. The retention time in the combustion chamber and the oxygen content are also very important. By adjusting these parameters, it is possible to optimize the emission levels and concentrations of substances in waste gases, fly ash and soot, including PAHs content.

Ash from the Moscow MSZ No. 2. MSW (waste incineration plant) combustion technology assumed a temperature of 850°C. The characteristic feature of the process is the presence in the flue dust waste incineration plants of the maximum number of PAHs (by 8 orders higher than in the ash residue). This is due to both the combustion technology and the properties of PAHs: the ability to be separated in small-diameter fractions [2]. In the literature, it is believed that at high temperatures (more than 1200 degrees C) almost all PAHs are subject to combustion. In fact, the data show their adsorption on volatile ash fraction and the possibility of condensation nuclei in the atmosphere at lower temperatures.

Ash residue from incinerators for municipal waste incineration manufactured in Japan. The combustion temperature here was 850–900°C, after which it is planned to burn the waste gases at a temperature of 900–1200°C. The study [3] presents the characteristics of the 10 most typical plants that served as material for analysis:

a) with fixed grid;

b) semi-continuous furnaces, capacity from 9.6 to 600 t waste / day.

Ash from medical waste incinerator in Taiwan [14]. Characteristics of incineration of general and specific copper-zinc wastes with the use of two types of periodically acting incinerators were considered:

— with mechanical grid is used for the destruction of crops and strains, blood and products based on it, used and unused cutting tools, insulating materials (general medical applications). The waste is pre-settled and incinerated in the front chamber at a temperature of 750–1000°C, and then transported by means of a mechanical grid to the second chamber for afterburning at a temperature of 1000–1200 °C.

— with a fixed grid for the elimination of pathogenic waste and animal waste (special medical waste). Special waste is placed in the centre of the first combustion chamber and destroyed at 700–1000°C without stirring. The waste gases are fed directly into a second combustion chamber with a temperature of 1000–1200°C. Ash residue is found only in the first combustion chamber.

The composition of combustion products is different. Samples of ash residues from the front chamber and second chamber of incinerators with mechanical grating, as well as fly ash, which has been subjected to electric filter and wet scrubber are analyzed. In both cases, diesel fuel is used as an auxiliary to combustion, which may also contribute to the possibility of generating additional PAHs.

Ash from incinerators used to produce energy (New York). The available materials do not give the characteristics of combustion technologies. Technologies are likely similar to those used in Japan's municipal waste incinerators [5].

Ash from an incinerator for burning sludge from biological treatment facilities, used for the removal of sludge from petrochemical production [20]. The characteristics of two incinerators with fluidized bed combustion technology (incineration temperatures of 870°C and 800°C) and one with a fixed bed (waste incineration temperature of 800°C) were assessed. Fuel oil was used as an auxiliary fuel in these three cases. The biosludge utilized here contains PAHs of 1 and 10 mg / kg; it is formed during the use of microorganism cultures for the utilization of petrochemical waste.

Ash from low-temperature combustion of materials in domestic stoves: aerosols from coal and peat burning; briquettes and firewood; fly ash and soot from firewood and (deposited on chimney walls) contaminated with varnish wood; ash and soot from leaf burning, forest litter, agricultural waste; ash and soot from a peat fire [2]. The highest concentrations of PAHs were found for fenantrene and fluore-na, while high concentrations were recorded for fluoranten and anthracene. Even in low-temperature combustion of agricultural wastes, the flue gases contain less PAHs than fly ash and soot.

Based on the concentrations of PAHs, the most "clean" ash was found in incinerators for disposal of biosludge. Low-temperature combustion of materials is on average slightly lower than PAHs content in waste incineration plant ashes, but seemingly "harmless" burning of firewood and grass may be a source of PAHs comparable to emissions from exhaust processes. In terms of the contents of polyarenes, PAHs clearly lead waste incineration plant ashes as well as some samples from incinerator plants with maximum concentrations also in fly ash. Considering the high adsorption capacity of PAHs by suspension, it can be argued that fly ash is an ideal sorbent at high temperatures. This is particularly evident in the case of ash from the electro filter of a fixed-grid medical waste incineration plant (Taiwan): the electric field ensures the maximum possible polyarene capture by particles, a concentrations of individual compounds reach record values compared to other samples and technologies. High concentrations of PAHs were also found in the waste incineration plant fly ash.

For the carcinogenicity of wastes from all samples examined, waste incineration plant No.2 fly ash should have a maximum effect (3,4-benzpyrene content is maximum compared to all other samples in the remaining plants). Given the carcinogenic effect of anthrancene, fly ash deposited on an electric filter at a Taiwan medical waste incineration plant is also characterized as a carcinogen.

Due to the different capacity of PAHs for transformation in surrounding environment, when justifying indicator ratios of PAHs for purposes of "environmental detection" ("environmental fingerprinting" in foreign practice) It is necessary to consider the relative thermodynamic stability of different source PAHs. To minimize the number of influencing factors (differences in volatility, water solubility, adsorption, etc.), indicator ratios of PAHs of one molecular mass are often calculated, that is isomers. The nature of PAHs (natural or man-made origin) can be determined by increasing the proportion of less stable PAHs isomers compared to more stable isomers.

For larger PAHs molecules in work [21] the relative stability of isomers over relative heat of formation was estimated. This approach made it possible to rank substances according to their degree of stability: 276; 202; 252; 178; 278; 228. In other words, PAHs isomers with molecular masses 276 (benz(ghi)perylene, antanthrene, indeno(1,2,3-cd)pyrene, indeno(7,1,2,3-cdef)chrysene) and 202 (pyrene, fluoranthene, acephenanthrylene) have the highest degree of stability and, therefore have good prospects for considering them as indicators of petrogenicity or pyrogenicity, and substances with molecular masses 278 (dibenz(a,h)anthracene, picene, dibenz(a,j)anthracene, dibenz(a,c)anthracene, benz(b)chrysene, pentaphene) and 228 (triphenylene, hryzene, benz(a)anthracene) are much less suitable for this.

The PAHs have been shown to react easily with atomic oxygen, radicals and other active oxidants. However, these processes produce mutagenic and carcinogenic substances through interactions such as 3,4-benzenpyrene with ozone or nitrogen oxides and other oxides. In addition, PAHs interact with components of the cells of living organisms, which can provoke mutagenic and carcinogenic effects. Carcinogenicity of PAH is distributed as follows: 3,4-benzpyrene > anthracene > 2,3-benzfluoranthene > orthofenylpyrene > 11,12-benzphluorontene > 11,12-benzphluorontene.

Pyrolytic formation of PAHs at high temperatures 650–900°C occurs in flame with lack of oxygen. For individual PAHs, such as 3,4-benzenpyrene, lower formation temperatures are recorded in the relatively narrow range (300–350°C) that occur by a different mechanism. In addition, at relatively lower temperatures, PAHs derivatives (with side substitutes) are formed. For example, the chemical composition of soot from forest fires is significantly different from that of soot from anthropogenic sources with high PAHs accumulation due to low burning temperatures of wood and grass.

Changes in media concentrations may be due to both the PAHs themselves, and how they are extracted from samples, due to different waste incineration technologies (and therefore chemical processes for the formation of PAHs). Usually in combustion processes two stages of PAHs formation are separated:

1) thermal destruction of fuel occurs with the formation of relatively simple "fragments" of molecules of free radical type;

2) the recombination of radicals to form PAHs [4].

The composition of the resulting compounds is determined by the combustion conditions. In the environment, the behavior of PAH in the composition of emissions, their stability will also be determined by the geographical features of the area. In essence, given in the first part of the Table 1 coefficients represent the processes of transition of unstable hydrocarbon isomers to stable, and calculated ratios determine what stage of transition they are at the moment.

Table 1. **Indicator ratios of PAHs**

Value for petrogenic PAHs	Value for pyrogenic PAHs
Phenanthrene / Anthracene, *Ph / An*	
Ph / An > 10 [19]	***Ph / An*** <10 [19]; ***Ph / A*** ≈ 3 during the burning of wood and coal burning [4]
Anthracene / (Sume of isomers with a molecular mass 178), *An / (Ph + An)* or *An / 178*	
An / (Ph + An) > 0.10 ⇨ diesel oil. shale oil. coal. crude oil samples [21]	***An / (Ph + An)*** < 0.10 ⇨ lignite. diesel fuel and fuel oil combustion emissions [21]
Fluoranthene / Pyrene, *Flu / Py*	
Flu / Py > 1 petrogenic PAHs [21] ***Flu / Py*** < 0.4 – petrogenic PAHs [19]	***Flu / Py*** < 1 pyrogenic sources [21] ***Flu / Py*** < 1.4 coal burning; ***Fl u/ Py*** <1.0 wood burning [21]; ***Flu / Py*** > 0.4 burning [9]
Fluoranthene / (Fluoranthene + Pyrene), *Flu / (Flu + Py)**	
Flu / (Flu + Py) < 0.50 ⇨ most petroleum products and their combustion products [21]	***Flu / (Flu + Py)*** > 0.50 ⇨ burning kerosene and grass. most coals and wood; creosote [21]
Benzo[a]anthracene / (Benzo[a]anthracene + Chrysene (Triphenylene)), *BaA / 228*	
BaA / 228 <0.20 [18]	***BaA / 228*** > 0.50 [18] ***BaA / 228*** > 0.35 [21]
Indeno(1,2,3-cd)pyrene/ (Indeno(1,2 3-cd)pyrene + Benz(ghi)perylene), *IP/ (IP + Bghi)*	
< 0.20 [21 et al.]	***IP / IP + Bghi*** > 0.5 burning of grass. wood soot. creosote. wood and coal. bushfires. ***IP / IP + Bghi*** < 0.5 fires in the savannah; combustion products of NP and crude oil [18; 21]
The sum of Pyrene and Fluoranthene to the sum of Chrysene and Phenanthrene (*Py + Flu*) / (*Chr + Ph*)	
< 0.5 [21]	> 0.5 [21]

End of Table 1

Value for petrogenic PAHs	**Value for pyrogenic PAHs**
The ratio of concentrations of low molecular weight (LM) and high molecular weight (HM) PAHs	
LM / HM > 1 [18; 21]	***LM / HM*** < 1 [18; 21]
Pyrene / 3,4-benzpyrene, Py / BaP	
• 1.0…484.8 crude oil [1; 3; 5; 12; 13; 16] • 2.3…36.1 – slime [1; 3; 5; 12; 13; 16] • 0.0 – 7.3 – soils [1; 3; 5; 12; 13; 16]	• 0.3–16 – soot from home heating furnaces; • up to 23 – catalytic cracking; • up to 1000 – in TPP emissions; • up to 50 – diesel-fueled truck emissions; • up to 90 – emissions from gasoline-powered trucks; • 4–24 – passenger car emissions; • 0.18–8.17 – ash from the incineration of various categories of waste [1–6; 11–14; 16–17; 20]
Phenanthrene / 3,4-benzpyrene, Ph / BaP	
69.0 … 3040.0 – crude [1; 3; 5; 12; 13; 16]; 3.3 – 300.5 – slime [1; 3; 5; 12; 13; 16]; 1.92 – 12.01 – soils [1; 3; 5; 12; 13; 16]	1.8 – soot (wood burning); 10.6 – soot (burning of brown coal); 10.6…17.4 – exhaust gases 0.49…22.65 – ash from the incineration of various categories of waste [1–6; 11–14; 16–17; 20]
Fluoranthene / 3,4-benzpyrene, Flu / BaP	
• 0.0–303.0 – crude oil [1; 3; 5; 12; 13; 16]; • 0.0–114.4 – slime [1; 3; 5; 12; 13; 16]; • 0.64-2.38 – soils [1; 3; 5; 12; 13; 16]	• 1.8 – soot (wood burning); • 17.7 – soot (burning of brown coal); • 8.6…10.9 – exhaust gases; • 0.16… 8.97 – ash from the incineration of various categories of waste [1–6; 11–14; 16–17; 20]
Chrysene / 3,4-benzpyrene, Chr / BaP	
• 0.0–1454.5 – crude oil [1; 3; 5; 12; 13; 16*]; • 0.0–143.9 – slime [1; 3; 5; 12; 13; 16; • 0.01–2.12– soils [1; 3; 5; 12; 13; 16	• 4.9 – soot (wood burning); • 21 – soot (burning of brown coal); • 4.3…6.8 – exhaust gases; • 0.44…4.03 – ash from the incineration of various categories of waste [1–6; 11–14; 16–17; 20]

Source: compiled by A.P. Khaustov, M.M. Redina.

The lower part of the table shows the values of the indicator comparisons for PAHs with different molecular masses. In foreign and domestic literature, the predominance of low-molecular PAHs is attributed to petrogenic sources. Obviously, this principle is based on an approach that considers the ratios of different PAHs and 3,4-benzpyrene (the last 4 coefficients in the table). Unlike single-mass PAHs, for the last 4 indicator ratios there are no boundary values, which makes their application difficult. In addition, as will be shown, the informative coefficients vary for different objects.

Given the characteristics of the research objects, it is possible to distinguish 6 types of combustion technologies for different types of waste according to their genesis. The output gives different values of PAHs concentrations, as well as various coefficients based on their ratios: the range of changes and average values are shown in Table 2.

Table 2. **Indicator ratios for identifying the nature of PAHs (in the numerator – the range of data, in the denominator – the average value)**

Ratio	Fly ash of Moscow waste incineration plant No. 2	Ash of incinerators for municipal waste incineration, Japan	Ash residue of incinerators for energy production, New York	Ash of incinerators for incineration of medical waste, Taiwan	Ash of incinerators for the combustion of bio–sludge, Taiwan	Low–temperature burning of biomaterials
Ph / An	8.38–20.6 14.8	5.5–10.8 7.8	4.75–5.31 5.03	0.23–2.43 1.20	1.15–9.80 5.83	1.46–6.84 4.7
Flu / Py	0.92–1.9 1.33	0.5–1.4 1.20	1.09–1.26 1.18	1.00–8.28 3.05	0.60–6.32 2.12	1.16–2.57 1.96
An / (An + Ph)	0.05–0.11 0.07	0.08–0.15 0.12	0.16–0.17 0.17	0.29–0.82 0.51	0.09–0.47 0.23	0.13–0.41 0.21
Flu / (Flu + Py)	0.48–0.66 0.57	0.34–0.58 0.53	0.52–0.56 0.54	0.50–0.89 0.67	0.38–0.86 0.58	0.54–0.72 0.65
(Py + Flu) / (Chr + Ph)	0.24–0.39 0.31	0.40–1.64 0.85	1.26–1.31 1.29	0.33–2.33 1.29	0.18–0.38 0.32	1.06–2.28 1.86
BaA / (BaA + Chr)	0.14–0.26 0.18	0.30–0.51 0.41	0.46–0.47 0.47	0.71–0.89 0.83	0.35–0.89 0.65	0.52–0.68 0.61
IP / (IP + B(ghi)P)	0.14–0.61 0.51	0.33–0.53 0.44	0.50–0.51 0.50	0.23–0.65 0.44	0.00–0.94 0.43	0.38–0.56 0.49
Py / BaP	0.37 – 1.25 0.58	3.70–13.9 8.17	1.65–1.75 1.70	0.19–6.72 2.67	0.01–0.59 0.18	0.84–4.75 2.43
Ph / BaP	0.26–0.72 0.49	4.08–72.6 22.6	1.68–2.14 1.91	1.86–5.40 3.57	0.17–0.91 0.54	0.38–28.75 11.02
Flu / BaP	0.40–1.76 0.78	4.38–18.0 8.97	1.80–2.21 2.00	1.55–7.86 4.31	0.06–0.35 0.16	1.16–6.49 4.46
Chr / BaP	2.19–11.4 4.03	0.84–6.60 3.29	0.95–1.00 0.97	0.37–3.40 1.66	0.00–1.71 0.44	0.74–2.00 1.40

Source: compiled by A.P. Khaustov, M.M. Redina.

The Table shows the values of the indicator ratios of PAHs, for which the limits given in Table 1 are maintained. As can be seen, despite the clearly pyrogenic nature of the PAH data, a number of widely used coefficients for them “did not work”.

Evaluate the informativity of the next group of indicator ratios. In Russia, when monitoring PAHs, one of the most “popular” compounds is 3,4-benzpyren, which is almost not involve in the indicator ratios given in the first part of the Table 1. It is the only PAHs compound in Russia that is mandatory for control. Previous work [14] has attempted to establish reference values for compounds of the pyrogenic nature, but no such data have been provided for compounds of petro-genetic origin. In the absence of monitoring data on other PAHs, the problem of establishing their genesis and assessing the informativity of the indicator ratios involving 3,4-benzpyrene is a central issue in identifying sources of pollution of natural media. Calculation was carried out for various samples of apparent petroleum nature (24 samples, i.e. mixtures of oils from the Volgo-Urals province, the West Siberian oil and gas province, 48 samples of oil from the United States of America, and samples of rock slags from collieries and reservoirs). This wide range of carbohydrate-bearing conditions suggests that the obtained ratios will cover all possible values characteristic for the petroleum-based conditions of PAHs formation.

The first ratio (***Py / BaP***) for petroleum samples has a very wide range of variations and is largely "intersected" with the range of values characteristic of pyrogenic PAH. However, the maximum value of this ratio for thermal power plant (up to 1000) given in work [14] is likely due to an error. Our research in the foreign and domestic literature has shown that this factor at high-temperature processes does not exceed 100 when burning coals of the most ruinous chemical composition (values vary from 0 to 97.4 with an average of 7.42). Thus, this coefficient can be considered as poorly informative with respect to both pyrogenic and petroleum-based PAHs, both in the case of ash and oily samples.

The following ratio, ***Ph / BaP***, is changed for oily samples ranging from 1.92 to 3040.0. Minimum values are typical for pure soil samples and one sample from a slurry barn. This may be due to either the total absence of oil contamination in clean soils and the minimum amount of petroleum products in the waste that fell into the slurry barn. For oil and sludge, the average values of this ratio are significantly higher than those of the pyrogenic birth. Thus, the indicator ratio, compared to the first one, is more informative when separating PAHs from pyrogenic and petrogenic nature.

The ***Flu / BaP*** ratio has a similar picture and a similar degree of informativity for the PAHs separation. This factor is also significantly higher for petroleum-derived PAHs compared to their concentrations in the products of combustion of various parent plants.

The indicator ratio of chrysin / 3,4-benzpyrene is also more vivid. Its values for petrogenic PAHs are significantly higher than those for pyrogenic PAHs. This is one of the most informative documents discussed. Note that the average values of this coefficient for crude oil exceed the values for pyrogenic PAH in 28 (for soot in case of brown coal burning) — 600 times (ash of MSW incinerators).

Another indicator ratio, (Py+BaP) / (Ph+Chr), does not yet show significant differences for petroleum and pyrogenic samples: all its values for soot and fly ash samples are in the range of 0.16 to 0.34; for petrochemicals — from 0.00 to 0.76.

Results and discussion

In order to analyse the behaviour of the coefficients calculated for pyrogenic and petrogenic formations, a factor analysis was carried out, which makes it possible to separate and group together similar dispersion features into factors. The signs that are in one factor have approximately the same dispersion and, therefore, genesis. For different factor values (correlation coefficient of feature with factor) on the sign, the location indicates opposite processes. There are several modifications of factor analysis with procedures for rotating orthogonal factor axes, down to coaxial. Such procedures are able to identify the maximum similarity or difference between features in multidimensional space. The most popular methods of implementing factor analysis procedures is the principal component method, which assumes maximising the total dispersion to the first major orthogonal components (factors). The rotation procedures themselves in factor analysis do not require as strict a regulation as in the main component method. The main criterion for rotation procedures is maximization of factor loads. For this purpose, we applied several rotation procedures from which the above criteria were selected. Calculations were performed for pyrogenic (Table 3) and petrogenic (Table 4) PAHs.

Table 3. **Factor loads for 12 indicator ratios of PAHs in combustion products**

Ratio	Factor 1	Factor 2	Factor 3	Factor 4
Ph / An	–0.19	**–0.92**	0.07	0.03
Flu / Py	–0.12	0.25	0.02	**–0.92**
An / (An + Ph)	–0.10	**0.89**	0.14	–0.20
Flu / (Flu + Py)	–0.16	0.18	0.02	**–0.93**
(Py + Flu) / (Chr + Ph)	**0.73**	0.06	–0.45	0.00
BaA / (BaA + Chr)	0.11	**0.85**	–0.33	–0.22
Ip / (Ip + BghiP)	–0.28	0.18	**0.77**	0.02
Py / BaP	**0.95**	0.01	0.05	0.20
Ph / BaP	**0.89**	–0.03	0.16	0.06
Flu / BaP	**0.95**	0.11	0.08	0.01
Chr / BaP	0.22	–0.47	**0.65**	0.02
(Py + BaP) / (Ph + Chr)	–0.27	0.21	**–0.77**	0.08
Expl. Var	3.42	2.76	1.97	1.86
Prp. Totl	0.29	0.23	0.16	0.15

Source: compiled by A.P. Khaustov, M.M. Redina.

The first factor is formed by the ratio “Py + Flu / Chr + Ph” and the ratios of pyrene, fenanthrene and fluoranthene to benzo[a]pyrene. It is interesting to note that the ratio of chrysene to benzo[a]pyrene has gone on to subsequent factors, indicating its independent behavior, which is expected from the estimates in the tables. 1 (maximum differences for pyrogenic and petrogenic PAHs among all the observed PAH ratios with benzo[a]pyrene). *The second factor* can be interpreted as predominantly formed by light PAHs ratios. However, the same group was also benz(a)anthracene. In this case, the opposite load signs of the coefficients Ph / An and An / (Ph + An) are due to the calculation technique (anthracene concentration — in the denominator). *The third factor* for pyrogenic PAHs is formed by the ratio of chrysene to benzo[a]pyrene, IP / (IP + Bghi) and (Py + BaP) / (Ph + Chr). Thus, the factor is formed by the ratios of the most “heavy” PAHs. A separate fourth factor for pyrogenic PAHs is the Flu and Py, as well as Ph / Py based coefficients popular in foreign literature. Obviously, the structure of this factor is determined by pyrene concentration.

The principle differences has a factoring structure of the matrix of indicator ratios for petrogenic objects (Table 4).

Table 4. **Factor loads for 13 indicator ratios of PAHs in oil-containing samples (Varimax raw rotation)**

Ratio	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Ph / An	0.07	–0.46	0.46	**–0.70**	–0.08
Flu / Py	0.37	–0.11	–0.13	0.01	**0.89**
An / (An + Ph)	–0.06	**0.92**	0.00	–0.04	0.06
Flu / (Flu + Py)	0.18	0.43	0.07	–0.09	**0.78**
(Py + Flu) / (Chr + Ph)	–0.17	–0.33	**0.80**	0.21	–0.16
BaA / (BaA + Chr)	–0.14	0.19	**0.94**	0.00	0.04
Ip / (Ip + BghiP)	0.12	–0.22	0.32	**0.86**	–0.08
Py / BaP	**0.84**	0.07	–0.08	–0.02	–0.45
Ph / BaP	**0.90**	–0.15	–0.10	0.03	0.37
Flu / BaP	**0.84**	0.12	–0.04	0.00	0.48
Chr / BaP	**0.94**	–0.08	–0.14	0.04	0.25
(Py + BaP) / (Ph + Chr)	–0.33	0.34	0.08	0.27	–0.16
Expl.Var	3.46	1.61	1.90	1.36	2.12
Prp.Totl	0.29	0.13	0.16	0.11	0.18

Source: compiled by A.P. Khaustov, M.M. Redina.

The first factor was formed with the ratio of all ratios involving 3,4-benzpyrene. In our opinion, this factor structure was formed due to the original composition of the PAHs compared to the pyrogenic ones.

The second factor was formed with the only indicative ratio of anthracene to its sum with pyrene. The third, fourth and fifth factors are predominantly indicative ratios based on light PAHs.

As it can be seen from the results of the factor analysis of the matrix, the indicators of the ratios of PAHs of pyrogenic and petrogenic nature have a fundamentally different structure. This indicates that widely used indicators such as the 3,4-benzpyrene concentration ratios can be quite informative. As a result, both matrices reflect the differences in PAHs formation processes, which is expressed by the difference in their concentration ratios.

Conclusion

Increased attention to waste incineration as a way of recycling requires the use of various methods of geo-ecological studies to determine the zone of influence of waste incinirating plants. The use of indicator ratios for this purpose may be of significant interest to confirm the role of thermal waste facilities in environmental pollution. However, the accuracy of these methods can and should be improved both by more precise methods for identifying the polyarens themselves in the media and by refined data processing procedures for analytical analyses.

1. The indicator ratios considered can be used effectively for identification of PAHs genesis, but their informativity is different. Part of the indicator ratios (for example, based on PAHs concentrations with four or more rings) does not allow to reliably distinguish between pyrogenic or petrogenic PAHs, which would not in practice substantiate the limits of influence of the object under study (combustion plant) on the surrounding area.

2. Of the indicators considered, it is most clearly possible to identify the genesis of PAHs in combustion products of various categories of wastes Py / Flu and Py / (Flu+Py). These same coefficients are most sensitive when separating the pyrogenic and petrogenic PAHs. However, the maximum effect is achieved by considering a set of coefficients.

3. For different media, it is impossible to offer universal (uniform) boundary values of the indicator ratios. Attempts to transfer them are shown in Table 1. The limits of the values of the coefficients for identifying the PAHs flow in different objects have shown that in each case their essential “individual setting” [8]. Otherwise, significant distortions and errors in the determination of pollution sources are possible.

4. Despite the significantly greater availability of data on 3,4-benzpyrene analysis in various natural and man-made objects, the indicator ratios with its

participation are less informative than the ratios of PAHs isomers within a single molecular mass (An / 178, BaA / 228 etc.).

5. The nature, composition and technologies of waste management determine not only the overall level of PAHs in combustion products, but also the values of the indicators of PAHs genesis. In some cases it is not possible to assign the PAHs definitely to petrogenic or pyrogenic. Calculations have shown that low-temperature products cannot always be clearly separated from high-temperature ones.

6. The "environmental fingerprinting" method, based on identification of PAHs sources, allows monitoring of pollution levels in natural environments caused by material combustion emissions and wastes, thus contributing to a more objective control of anthropogenic loads.

7. In low-temperature combustion of vegetation, despite full access to oxygen, PAHs may be generated in the products of combustion in concentrations exceeding the standards for specialized waste management facilities (including biomass). This requires a more detailed analysis and environmental justification of the application of these methods of waste management.

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