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Polycyclic Aromatic Hydrocarbons as Priority Pollutants

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Many countries pay increasing attention to problems of environmental safety and control of pollutants emission. Thereat the problem of presence of polycyclic aromatic hydrocarbons (PAHs) in environment becomes urgent because this substances are ubiquitous pollutants and some of them have carcinogenic properties. PAHs and their derivatives appears in the processes of incomplete combustion of organic substances. PAHs concentrations vary considerably in urban and rural places under influence of vehicular traffic, heat power plant and industrial activity. Some countries set non-mandatory ambient air quality standards for the PAHs. This fact shows pollutants of this class is to be given significant attention. This paper presents some up-to-date data related with sources of atmospheric PAHs, methods of their determination and processes affecting their concentration.

Keywords: PAH, benzo[a]pyrene, sources.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds constituting only carbon and hydrogen, arranged in two or more aromatic rings. The biggest part of PAHs are hydrophobic substances which have low solubility in water. The best known PAH is benzo[a]pyrene (B[a]P) which contains 5 rings. Because of their low vapor pressure, some PAHs are present at ambient temperature in air, both as gas and associated with particles [1]. The lighter PAHs, such as phenanthrene, are found almost exclusively in gas phase whereas the heavier PAHs, such as B[a]P, are almost totally adsorbed on to particles. Seventeen priority PAH were chosen by Agency

for Toxic Substances and Disease Registry (USA) on the base of their toxicological profile[2]. Substances were included in priority List of PAH were chosen by following reasons: 1) there are more information on them than on others; 2) they are suspected to be more harmful than others, and they exhibit harmful effects that are representative of PAHs in general; 3) there is a greater chance for exposure to these PAHs than to the others; 4) these PAHs more abundant and have the highest concentrations in environment; 5) these PAHs are characteristic for some sources.

Sixteen PAHs have been specified by the United States Environmental Protection Agency (EPA) as priority pollutants. Table 1 lists the

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Table 1. USA EPA priority list of PAH

Substance	Total molecular formula	Molecular weight	Carcinogenic activity
Naphthalene	C ₁₀ H ₈	128	+
Phenanthrene	C ₁₄ H ₁₀	178	-
Anthracene	C ₁₄ H ₁₀	178	±
Fluoranthene	C ₁₆ H ₁₀	202	-
Pyrene	C ₁₆ H ₁₀	202	-
Chrysene	C ₁₈ H ₁₂	228	±
Benzo(a)anthracene	C ₁₈ H ₁₂	228	+
Benzo(b)fluoranthene	C ₂₀ H ₁₂	252	++
Benzo(k)fluoranthene	C ₂₀ H ₁₂	252	+
Benzo(e)pyrene	C ₂₀ H ₁₂	252	±
Benzo(a)pyrene	C ₂₀ H ₁₂	252	+++
Perylene	C ₂₀ H ₁₂	252	±
Benzo(ghi)perylene	C ₂₂ H ₁₂	276	±
Dibenzo(ah)anthracenes	C ₂₂ H ₁₄	278	+++
Indeno(cd)pyrene	C ₂₂ H ₁₂	276	+
Coronene	C ₂₄ H ₁₂	300	±

+ (++) - there is sufficient evidence that substance is carcinogenic to experimental animals;

± - the available data are inadequate to permit an evaluation of the carcinogenicity of substance to experimental animals.

- the available data provide no evidence that substance per se is carcinogenic to experimental animals.

priority PAHs their total molecular formulas and carcinogenic activity.

Adequacy of benzo[a]pyrene as indicator substance of total PAH concentration

Benzo[a]pyrene seems to be a reasonable choice, albeit an imperfect indicator, due to the strong correlation between B[a]P and other PAHs for a given set of conditions and due to the relative abundance of B[a]P exposure measurements [3]. Although B[a]P presents only 3-20% of total airborne PAH its part among carcinogenic PAHs is considerably higher - about 30-100 %. Role of B[a]P as indicator also is due to its characteristic and intensive fluorescence spectrum in visible spectral region.

But ratio of B[a]P to the other PAH varies considerably in different places. Furthermore

can't be reliable indicator because it is relatively unstable, poorly soluble in water and presents in low concentrations in emissions. For example its concentration in industrial exhausts usually is less than 10 % [4].

Formation

The principle formation mechanism for PAH occurs as part of the combustion process present in many different types of sources. Formation mechanism is not studied in details well enough today. Conventional theory claims that PAHs are formed by free radical mechanism in gas phase [5]. The biggest part of evidences shows that PAHs exist in the atmosphere as solids. It means that transformation of vapor into solid is to take place between point of PAHs formation and point of their release in atmosphere. It has been recognized that soot (a product of coal combustion) is similar

in some structural characteristics to polycyclic aromatic molecules and that both soot and PAH are products of combustion. Comparisons of the two types of molecules give rise to the first clue as to how PAH may be formed in combustion, namely by incomplete combustion and degradation of large fuel molecules such as coal. It is also known, however, that carbon black and soot are produced by burning methane (CH₄). Thus, it is believed that PAHs are not only produced by degrading large fuel molecules, but are also produced by polymerizing small organic fragments in rich gaseous hydrocarbon flames [6]. The question of how the polyacetylenes (that are produced by a sequence of rapid reaction steps) cyclize still remains. One theory is that the polyacetylene chain bends around the carbon atoms and eventually bonds into the condensed ring structures. The association shown requires minimum atomic rearrangements. Also, the formation of polyacetylene cycles is highly exothermic, thereby providing sufficient energy to dissociate terminal groups and the free valences to produce reactive and stable PAHs [7].

Sources of PAHs

PAHs are mostly formed during the incomplete combustion and pyrolysis of fossil fuels or wood, and from the release of petroleum products. Other sources of PAHs include petroleum spills, oil seepage, and diagenesis of organic matter in anoxic sediments. PAHs are also found in coal tar, crude oil, creosote, and roofing tar, and a few are used in medicine or to make dyes, plastics, and pesticides. PAHs produced for commercial use, include naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene. These pure PAHs usually exist as colorless, white or pale yellow–green solids. In general, there are five major emission sources of PAHs, i.e. domestic, mobile, industrial, agricultural, and natural [8]. Furthermore, some cosmic sources

of PAHs have also been proposed [9]. Different sources of PAHs are presented in Table 2 [10].

Source identification

Source markers. Some PAHs were suggested to be indicators for some processes which form PAH. These special PAHs are called source markers, tracers, or signatures. Profiles of concentrations and relative abundance concentrations could be used to determine the impact of different sources on total concentration. This approach makes possible to distinguish the sources in case when the lesser sources source contributed more than 10% of the total [11]. Table 3 presents PAHs groups which are suggested in literature as source markers [12].

Diagnostic ratio. Diagnostic ratio method means comparing ratios of pairs of frequently found PAH emissions. For example value of 0.35–0.7 of Ind/(Ind+B[ghi]P) ratio has been used for diesel emissions. The higher ratio (>0.5) of Flu/(Flu+Pyr) has been used for diesel emission, while a lower ratio (<0.5) for gasoline emission. The B[a]P/B[ghi]P ratio higher than 0.6 refers to the presence of traffic emission and contribution from other PAH sources. The PAH profile was also seen to perform as reliably as inorganic compound profiles in a multivariate PAHs source apportionment study. The diversity in PAHs sources could be described in terms of diagnostic ratios. At the same time Diagnostic ratio method should be used with caution because it is often difficult to discriminate between some sources. Ratio could change due to different reactivity of PAH against other atmospheric species, such as ozone and/or oxides of nitrogen. In addition to the atmospheric reactivity, degradation that may occur during the sampling process and can also modify the atmospheric PAHs levels and thus the ratios between PAHs. The other limitation of diagnostic ratio is that their interpretation greatly depends on the ratio considered and on

Table 2. Amount of PAHs emission from different industrial sources

Source	B[a]P concentration			
	Mass concentration $\mu\text{g}/\text{m}^3$	Mass emission $\mu\text{g}/\text{s}$	In fly ash $\mu\text{g}/\text{kg}$	In nonvolatile ashe $\mu\text{g}/\text{kg}$
Heat power engineering Products of coal and fuel oil combustion				
1. «Big» (50 MW),	0,005-0,150	0,2-8	0,1-0,3	1,4
2. «Medium» (5-50 MW)	0,6-50	4-250	(3-50)103	-
3. «Small» (до 5 MW)	1-10000	0,1-6000	(1,2-9)105	3100
4. Oil-burning boiler	0,1-1	1-6	5·103	-
Aluminum industry Products of combustion, excretion, decomposition of coal-tar pitch				
1. Electrolysis workshop	200-3000	(7-50)103	(9-10)105	-
2. Ventilation skylight	0,9-67	(4-8)104	7·105	-
3. Anodic mass workshop	10-100	(0,7-12)102	(3-8)103	-
Building technology Products of combustion, excretion, decomposition of fuel oil, bitumen				
1. Perlite burning furnace	0,05-50	2-80	(1-200)102	1-2
2 Asphalt-concrete installations	20-300	80-1100	(2-30)104	(2-3)103
Petrochemical industry Products of combustion, excretion, decomposition of natural gas, fuel oil, coke Combustion, pyrolysis and other installations.	0-15	0-40	-	-
Vehicle emissions gasoline engines	0,09-0,23	-	-	-
diesel engines	0,20-0,70	-	(4-10)103	-

Table 3. Source markers

Source	Characteristic PAHs
Coal Burning	Phenanthrene , Fluoranthene and Pyrene
Coking	Anthracene, Phenanthrene and B[a]P
Incineration of garbage	Pyrene , Phenanthrene and Fluoranthene
Wood burning	B[a]P and Fluoranthene ;
Fuel oil burning	Fluoranthene , Pyrene and Chrysene
Gasoline engines	Fluoranthene , Pyrene with high ratio of Benzo[b]fluoranthene
Dieseles engines	Fluoranthene, Pyrene with high ratios of Benzo[b]fluoranthene а и Benzo[k] fluoranthene

the source profile chosen. This may be a case, when the sampling is carried out in the vicinity of sources of particulate PAHs and for highly reactive compounds. Furthermore, the difference in chemical reactivity, volatility, and solubility of PAH species may introduce bias but to minimize this error, the diagnostic ratio with similar physico-chemical properties of PAHs should be used.

Principal component analysis (PCA). Using PCA, it is possible to simplify the interpretation of complex systems and to reduce the set of variables to few new ones, called factors. Each of these factors can be identified as either an emission source, or a chemical interaction. Many of these factors indicate more than one possible cause. In general, each factor from PCA is associated with a source characterization by its most representative PAH compound(s).

Radiocarbon analysis. Carbon has two stable, nonradioactive isotopes: carbon-12 (^{12}C), and carbon-13 (^{13}C). In addition, there are trace amounts of the unstable isotope carbon-14 (^{14}C). Carbon-14 is constantly generated in the atmosphere under impact of radiation (the main source of radiation is cosmic rays). Proportion of radioactive to non-radioactive carbon is constant in the atmosphere and biosphere at defined point and time, because all living organisms take part in carbon exchange and consume carbon from environment, and isotopes through their chemical identity take part in biochemical reaction by the same way. Once organism dies, this exchange stops, and the amount of carbon-14 gradually decreases through radioactive beta decay. This process determines difference in isotopic ratios in products of combustion of fossil fuels and biomass. Isolation of PAH and subsequent analysis by the method accelerative mass spectrometry makes possible to determine concentration of carbon isotopes in this substances and calculate

contribution of combustion of fossil fuels and biomass [13, 14].

Sampling artifacts

Representative PAHs sample should demonstrate their real concentration in ambient air. PAH monitoring is usually performed using high- or low-volume samplers (HVS, LVS) and is complex because of the reactive breakdown of PAHs between the gas and particulate phases. In HVS or LVS the particulate phase is first trapped on a filter and the gaseous phase is trapped on a solid adsorbent (e.g. polyurethane foam) located downstream from the filter. However, these sampling procedure have also been shown to be affected by several sampling artifacts. In the particulate phase, positive artifacts (overestimation of the particle phase concentrations) are mainly due to sorption of gaseous compounds on the filter, while negative artifacts (underestimation of the particle phase concentrations) result from the volatilization of particulate PAH from the filter. Moreover, chemical degradations of PAHs by oxidizing compounds such as nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), hydroxyl radical (OH), halogens, nitric acid (HNO_3), hydrogen peroxide (H_2O_2), and ozone (O_3) may occur during sampling reported that the atmospheric PAH concentrations measured using conventional samplers not equipped with an ozone trap can underestimate the PAH concentration by more than 200%.

This was especially found when the samples were collected in the vicinity of a point source of particulate PAHs and for highly reactive compounds such as B[a]P. To reduce artifacts induced by conventional samplers, denuder sampling devices were developed. The denuder sampler systems were designed to trap the gas phase on a solid sorbent coated on the surface of the trap prior to collecting the particulate phase on a filter. This methodology avoids the phenomenon

of adsorption of the gas phase on the filter and reduces the desorption artifact by collecting the volatilized fraction on a sorbent cartridge placed downstream from the filter. Finally, the chemical degradation of particulate PAHs may be reduced as the sorbent coated on the denuder tubes can remove the oxidizing species included in the gas phase.

Change of PAHs concentration in the atmosphere

PAHs concentration depends on a variety of factors like temperature, humidity, pressure, winds speed and direction, precipitation and so on [15]. Polycyclic organic matter emitted as primary pollutants present on particulate matter can be subject to further chemical transformation through gas-particle interactions occurring either in exhaust systems, stacks, emission plumes, or during atmospheric transport.

These include highly reactive intermediates (both free radicals and excited molecular species) and stable molecules. Seasonal variation in transformation reactions of PAH have been observed. During winter, with conditions of low temperature and low irradiation, the major pathway for PAH degradation is probably reactions with nitrogen oxides, sulfur oxides and with the corresponding acids.

Reactions with the ozone and free radicals have the most important influence on concentration of PAH in gaseous phase, while photolysis plays a minor role [16]. Seasonal variation in concentrations of particle phase PAH have similar trend in some large cities over the world. During winter PAHs concentrations are higher compared with those during summer[17]. Higher concentrations during winter (a) reduced vertical dispersion due to inversion[18]; (b) lower mixing layer and less intensive atmospheric reactions; (c) enhanced sorption to particles at lower temperature (d) increased emissions

from domestic heating and power plants during winter with low temperature [19]; (e) alteration of prevailing wind direction [20, 21]. Besides some big cities have diurnal variations of PAHs concentrations related with traffic [22].

It was found that PAHs transformation goes by different ways if it takes place on the surface of particles, in the solution or in the solid phase [23]. Gas/particles distribution depends on molecular mass of substance and ambient temperature. Usually, 2 to 4-ring PAHs are mainly gas-phase compounds, while PAHs with five or more rings tend to be mainly associated with particulate. It should be noticed that about 75% of total PAH accumulated with particles lesser than 0.6 μm [24].

Organic substances resulted from human activities could undergo long-range atmospheric transport to remote sites [25]. Water in clouds absorbs those substances and precipitation could lead to pollution of distant regions.

PAH are eventually removed from the atmosphere by sedimentation or washout, or due to their decomposition in surface of particles. It was found that dry sedimentation was usual for hydrophobic substances. For example up to 70% of B[a]P is present in precipitations in the surface of particles, while naphthalene due to its high solubility in water is present in precipitations as a solution.

Although the biggest part of pyrogenic PAHs precipitate near their source, considerable amounts of this substances could be transferred in atmosphere to distant regions. They are found in water of highland lakes and arctic ice [26].

Decrease of PAHs concentration in the atmosphere has three principal reasons:

- 1) photochemical modifications of PAH under irradiation from different sources;
- 2) non-photochemical degradation (spontaneous oxidation in the dark);
- 3) chemical modifications induced by reactions between atmospheric gas (NO_x ,

Table 4. Half-life of selected PAHs under simulated atmosphere conditions

PAHs	Half life in hours		
	Simulated sunlight	Simulated sunlight and ozone (0.2 ppm)	Dark reaction ozone (0.2 ppm)
Anthracene	0.20	0.15	1.23
Benzo(a)anthracene	4.20	1.35	2.88
Dibenzo(a,h)anthracene	9.60	4.80	2.71
Dibenzo(a,c)anthracene	9.20	4.60	3.82
Pyrene	4.20	2.75	15.72
Benzo(a)pyrene	5.30	0.58	0.62
Benzo(e)pyrene	21.10	5.38	7.60
Benzo(b)fluoranthene	8.70	4.20	52.70
Benzo(k)fluoranthene	14.10	3.90	34.90

SO_x, O₃) and various PAH adsorbed onto different substrates, in the absence or the presence of radiation.

It was found that PAHs could react with molecular oxygen in absence of irradiation, but speed of such reactions is very slow and they have no considerable effect on total degradation process. It seems that the ozone is the most important gaseous pollutant influencing PAHs concentration [27]. Ozone concentrations occurring in natural conditions lead to considerable decrease of half life of PAHs (Table 4).

Regulations and current levels of PAHs in different countries

Many countries have added PAHs to their hazardous air pollutants lists but till date there is no strict ambient air quality standard for PAHs (Table 5). The EPA (1994) has classified PAHs as a probable human carcinogen with sufficient evidence from animal studies but inadequate evidence from human studies and hence PAHs are among the list of hazardous air pollutants to be regulated under the US Clean Air Act Amendment, 1990. The Occupational Safety and Health Administration (OSHA) has set a limit of 0.2 mg/m⁻³ of PAHs. National Institute for

Occupational Safety and Health recommended a limit of 0.1 mg/m⁻³ of PAHs [28].

European union directive has proposed a target value of 1 ng/m⁻³ B[a]P for the total content in the PM10 fraction averaged over a calendar year. Furthermore, this directive also suggest to assess the contribution of B[a]P in ambient air, each Member State shall monitor other relevant PAHs, i.e. benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene. Monitoring sites for these PAHs should be selected in such a way that geographical variation and long-term trends can be identified.

Netherlands introduced an interim goal of reducing the annual average B[a]P concentration to below 5 ng/m⁻³ (Smith and Harrison, 1998), while a guideline of 10 ng/m⁻³ for the annual average B[a]P has been proposed by the German Federal Environmental Agency. The Dutch National Institute of Public Health and the Environment (DNIPHE) has determined values of maximum permissible concentrations (MPCs) and negligible concentrations (NCs) for about 200 toxic compounds including some PAHs (RIVM, 1999a). The MPCs and NCs represent risk limit of the substances in different compartments

Table 5. Non-mandatory ambient air quality standards for the PAHs

Countries	Limit value (ng/m ⁻³)	Guide value (annual average) (ng/m ⁻³)
Australia	–	1.0
Belgium	1.0	0.5
Croatia	2.0	0.1
Germany	–	10.0
India	–	5.0
Netherlands	1.0	0.5
France	0.7	0.1
Italy	1.0	–
Sweden	–	0.1
UK	–	0.25
WHO	–	1.0
EU*	6.0	–

* To be met in 2010.

of the environment-surface water, soil, air, groundwater, and sediments, and are calculated from available eco-toxicological data. These risk limits are used to derive environmental quality standards in the Netherland. Setting integrated environmental quality standards: environmental quality standards for soil, water and air. Dutch National Institute of Public Health and the Environment. However, ecotoxicological data available for only B[a]P out of the 7 PAHs has been reported. These MPCs and NCs for air were not available for the other 6 PAHs (anthracene, benz[a]anthracene, benzo[k]fluoranthene, fluoranthene, naphthalene, and phenanthrene) but DNIPHE has assigned a critical concentration value for each of these compounds. Critical concentrations are normally calculated for air and/or rainwater. They are theoretically derived steady state concentrations of the pollutants in air and/or rainwater that will not lead to exceedance of MPCs value for soil.

Russian Federation set up MPC for B[a]P 1 ng/m⁻³[29]. This value is lower than

corresponding European standards, but only B[a]P is under control. Limitations of this approach described above. Nowadays there is exceeding of B[a]P concentrations in some industrial cities in Russia [30-32].

Conclusions

Today biosphere suffers increasing anthropogenic influence. Considerable efforts are applied in the field of research and monitoring of hazardous or potentially hazardous substances. To control, predict and if possible to avoid negative effects of PAHs pollution it is necessary to have exact information about their nature, sources and amount of emission. Western countries pay increasing attention to problems of environment and living standards. Because Russia has large-scale industrial projects in the field of aluminum and petrochemical industry as well annually increasing traffic, analysis and use of up-to-date data about priority pollutants appears one of the chief elements of environmental safety ensuring.

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