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Research Article

Problems of Atmosphere Pollution in Cities with Carcinogenic Mutagen Supertoxins

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Abstract

The urgent problems of atmosphere pollution in cities with carcinogenic supertoxins are considered. On the basis of experimental data, the total levels of carcinogenicity of exhaust gases at application of various fuels including higharomatic fuels are analysed. The integral indices of carcinogenic danger caused by vehicles are presented and their comparison with admissible European standards is carried out.

Keywords: *motor transport, fuels, aromatic hydrocarbons, exhaust gases, nitric oxides, particulate pollutant, carcinogenic hydrocarbons, benzo(a)pyrene, ecological indices.*

Introduction

Among all the global problems, which have been ever solved by mankind, the most difficult have been problems of food and energy production. In recent decades one super problem was added to them, which chiefly belongs to ecology – environmental (E) pollution, especially pollution of the urban atmosphere by carcinogenic and mutagenic toxins (Luch A et al,2005; Seminogenko V.P et al,2003). Among ingredients, which occur in the E during human activities, there is a series of compounds, which is characterized by high chemical stability and which is extreme dangerous for all creatures on the Earth, primarily for human beings. These reagents belong to a category of persistent organic pollutants (POP). The most ecodangerous are polycyclic aromatic hydrocarbons (PAH), firstly carcinogenic hydrocarbons (CH). PAH consist of hundreds of chemical compounds, including such PAH derivatives as PAH with NO_2 group (nitroPAH), having even stronger mutagenic properties and heterocyclic aromatic compounds. Accumulated data shows that extreme low concentration of CH can promote progress of diseases of immune and reproductive systems, appearance of carcinomas, birth defects among children etc. Presence of just several molecules of such compounds is able to promote carcinogenic and mutagenic effects in the living body.

Publication analysis

Consequences of the extreme dangerous influence of the noted compounds on public health exacerbate year by year. Hence attention to the issue of carcinogenic and mutagenic environmental pollution in the world constantly grows, but unfortunately presence of these compounds grows faster (Chaclin A.V et al,1996; Gennadiev A.N et al,2003). Stockholm Convention, which was signed by Ukraine as early as in 2001 and its impact started in 2004, aims to health and E protection from POP and focuses on reducing the levels of carcinogenic contained emissions and their liquidation (Mischenko V.S. et al,2005).

Purpose and statement

In spite of a variety of PAH (by now it is about 500 have been identified), a series of toppriority groups has been emphasized, among them 16 PAH, including benzo(a)pyrene (BP), defined by United States Environmental Protection Agency to provide the measured data (US EPA, 1988); 4 PAH (benzo(b)fluoranten, benzo(k)fluoranten, benzo(a)pyrene, indeno(1,2,3cd) pyrene, which ought to be used as indicators for the emission inventory within PAH UNECE protocol. Then to analyze of carcinogenicity of exhaust gases (EG) of internal combustion engines (ICE), scientists and experts have defined a PAH priority group, including 12 PAH with different relative carcinogenic activity indexes (CAI). The PAH priority group for analyzing carcinogenicity EG ICE includes: benzo(a)pyrene ($C_{20}H_{12}$, CAI = 1,0); benzo(b)fluoranthene (CAI = 0,1); ben(a)anthracene , chrysene, benzo(g,h.i)perylen (CAI = 0,01); fluoranthene, pyrene, benzo(e)pyrene, perylen , indenopyrene, diben(a,h)anthracene, coronene (CAI < 0,01).

Among heavy (polycyclic) PAH, BP is the first studied and the most analyzed. That is why the most information

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about CAI of combustion gases and dispersion of PAH in the E mainly connects to the properties of this compound.

The main CH emission sources

There are combustion compounds of carboncontaining fuels (coals, oil or synthetic fuels, natural gases etc.) of which in everyday life, in manufacturing, in energetics, in transport facilities; hightemperature pyrolysis of organic materials, which is typical for several processes, using in manufacturing of iron and noniron metals, including in a primary aluminium smelter during production of anodes; in coke and byproduct process; and forest fires, burning agricultural wastes, rubbish etc.

Quasivolatile properties make CH highly dispersive in consequence of their sorption on finely divided solid debris and liquid aerosols. One of the main reason of long persistence of PAH in the E is their low water solubility and also they can bioaccumulate (amass). Since the most PAH are toxic for bacteria, they slow down biodestruction by microorganisms. Concentration of PAH in fish and shellfish is sometimes significantly higher than in the E. PAH can also be straight genotoxic; so it means that chemicals and their degradation products can directly react with genes of organisms and cause damages of DNA.
Information about the levels of CH emissions is limited in comparison with other toxic pollutants, an available data is usually represented in different configurations and it gets comparison of the data for the purpose of verification more complicated.

That is why following questions appear: how is it possible to reduce the pollution levels of the E by carcinogenic and mutagenic supertoxic agents, including how is it possible to provide their high efficient elimination, using for instance filter technologies for entrapment; what is happen in ecosystems, which have been already polluted by described ingredients and how is it possible to accelerate rehabilitation of such systems.

Carcinogenic environmental urban pollution by motor transport

It is determined that ~ 90% of PAH, containing in the atmosphere of big cities get done by sources based on fuel combustion processes and mainly by compounds which utilized with EG of cars with internal combustion engines (ICE). In big cities with strong traffic, average concentrations of BP vary in a range of more than 10 ng,m^3, but in rural areas these concentrations are lower than 1 ng,m^3. In the table 1 (Kanilo P.M et al,2000)a gradation of the main noxious substances (NS) in the common pollution in several cities of Ukraine is described, it is based on the exceeding levels of the daily average critical concentrations [CC].

The data shows that the main noxious ingredients for human beings are carcinogenic supertoxins (BP, HCHO formaldehyde) and oxides of nitrogen (NOx), as well as solid (carbonic) debris (SD), which sorb and carry CH. Notably the most dangerous The data shows that the main noxious ingredients for human beings are carcinogenic supertoxins (BP, HCHO formaldehyde) and oxides of nitrogen (NOx), as well as solid (carbonic) debris (SD), which sorb and carry CH. Notably the most dangerous for human beings are SD with the typical size of 0,2 – 1,0 μm, which penetrate in the human organism and promote PAH carcinogenic activity. Technical conditions of ICE has an extreme profound effect on carcinogenic danger of traffic EG (Kanilo P.M. et al,2000; Kutenev V.F. et al,1990)(see fig. 1).

Figure 1 shows that defects of fuel feeding systems and igniting systems, influencing on the process of fuel burning, can increase levels of BP emissions (and relatively SD) from traffic EG a sequence larger and more. And it will be emphasized, that with increase of mileage, their ecochemical (carcinogenic and mutagenic) figures are getting worse.

So, after mileage of a car of VAZ2105 in 100 thousand km, the limit pollution levels of hydrocarbons with EG have increased thrice and the emission levels of NOx have increased by half due to defects in quality of the working process in ICE cylinders (Korotkov M.V et al,2003). Usage of fuels with high concentrations of AH has the strongest influence on carcinogenic danger of traffic EG(Kanilo P.M et al,2008; Zvonov V.A et al,2005). Figures 2 and 3 show the average data according to the levels of emissions of NOx , BP, SD and EG of small cars with different ICE during their tests according to European urban drive circle depending on the concentration levels of AH in fuels. The shown data indicates that fuels and diesel oil fuels, produced from heavy fuel with modern technologies, are characterized by high concentration of AH, that leads during utilizing to the growing levels of NOx , BP, SD emissions with EG of motors.

Table 2 shows the experimental data about the results of the investigations with a series of GAZ cars with ZMZ motors according to European urban drive circle, using different fuels. Shown results indicate that usage of alternative fuels with high concentration of hydrogen (natural gas, mixture of benzene and hydrogen etc.) leads to decrease of the emission levels of NO_x and BP as well as SD and EG of cars. *NB.* The mass content of nitrogen oxide (NO) in EG of cars in relation to NO_x is 90%.

Integrated ecocarcinogenic indexes of cars with ICE

Motor transport, as mentioned earlier, is the main source of environmental pollution, especially of the atmosphere in big cities. Their integrated ecochemical indexes are mainly defined by operating fuel efficiency, by parametric reliability and by quality of used fuels, including by the concentration levels of hydrogen, AH, sulphur etc. The analysis of atmospheric pollution in big cities with heavy traffic shows that the most dangerous for human beings are NO_x and CH. Their quantity in making an assessment of ecochemical danger of car motors is 95% and more. Their derivatives such as nitrocarcinogenic compounds are especially dangerous; they have mutagenic properties due to synergism. Moreover, BP among the defined by the scientists group of CH has the highest carcinogenic activity index (CAI) and its daily average critical concentrations (CC) for cities is CC_{BP} = 10 ^{6} mg,m^3,which is one of the main factor in understanding of importance of carcinogenic urban pollution and of necessity to solve the problem urgently (Kanilo P.M et al,2000,2008,2007). The correlation dependence between the specific emission levels of BP (m_{BP}) with traffic EG and the priority group CH (m_{CH}) is defined experimentally taking into account their CAI $\Sigma(m_{CH}\cdot CAI)=1{,}3m_{BP}$, g,km (.Kanilo P.M et al,2006). German Transport Association in recent years formed so called ecological rating of cars according to the range of harmful influence on the human organism by different compounds of EG. The first place holds CH according to the association. Medics consider that their percent in the risk of carcinomas is ~85% in big cities. Federal Office of Environmental Control taking into account these criteria was ministerial to formulate the target by the government of FRG: to reduce in the coming years motor vehicle emissions by 90% (Petrov R.L et al,2001). The main carriers of carcinogens and nitrocarcinogens, which highly strengthen their activity (promoting influence) are finely divided SD as mentioned earlier.

On the taken experimental data basis, a specific integrated index of ecocarcinogenic danger of motor vehicles $(ECD)_j$ and an affinity index of specific integrated indexes to international standards $K_j = (ECD)_j$, $[ECD]_j$ were offered; it was done by taken into account sanitation standards for toxic and carcinogenic compounds $[CC]_{CC}$ and common carcinogenicity of EG. Aimed to measure of the combined and intense carcinogenic and toxic effects of NS on the human organism, experimental coefficients were defined: k_{NOx} = 3; k_{BP} = 4; k_{CH} =(4×1,3) = 5,2; k_{SD} = 2 [12, 15]. Integrated indexes $(ECD)_j$ of motor vehicles and allowed by European requirements $[ECD]_j$ can be represented in the following way:

$$(ECD)_J = \left\{3\cdot\left(\frac{0{,}9\cdot m_{NOx}}{[NO]_{cc}} + \frac{0{,}1\cdot m_{NOx}}{[NO_2]_{cc}}\right) + 5{,}2\frac{m_{BP}}{[BP]_{cc}} + 2\frac{m_{SD}}{[SD]_{CC}}\right\} \quad (1)$$

$$[ECD]_J = \left\{3\cdot\left(\frac{0{,}9\cdot [m_{NOx}]}{[NO]_{cc}} + \frac{0{,}1\cdot [m_{NOx}]}{[NO_2]_{cc}}\right) + 5{,}2\frac{[m_{BP}]}{[BP]_{cc}} + 2\frac{[m_{SD}]}{[SD]_{CC}}\right\} \quad (2)$$

The specific allowed rates of BP emissions $[m_{BP}]_j$ have been defined (taking into account common carcinogenic activity of CH) according to the following dependence:

$$3\cdot\left(\frac{0{,}9\cdot [m_{NOx}]}{[NO]_{cc}}\right) + \frac{0{,}1\cdot [m_{NOx}]}{[NO_2]_{cc}} \approx 5{,}2\frac{[m_{BP}]}{[BP]_{CC}} \quad (3)$$

Taken indications: m_i, $[m_i]$ – correspondingly experimental and allowed rates of NS emissions with EG of a traffic vehicle; $[CC_{NO}]_{cc}$ = 0,06; $[CC_{NO2}]_{cc}$= 0,04; $[CC_{BP}]_{cc} = 10^{-6}$; $[CC_{SD}]_{cc}$ = 0,05 mg,m^3. The allowed emission rates of toxic compounds with EG of cars according to EuroII (from 1996 to 2000): $[m_{NOx}]_B$ = 0,25; $[m_{NOx}]_D$ = 0,63; $[m_{SD}]_D$ = 0,08 g,km; according to EuroV (from September 2008): $[m_{NOx}]_B$ = 0,06; $[m_{NOx}]_D$ = 0,2; $[m_{SD}]_{B,D}$ = 0,005 g,km. The tentatively allowable emission levels of BP with EG of cars, which are defined according to (1) are: for EuroII is $[m_{BP}]_B = 2{,}5\cdot10^{-6}$; $[m_{BP}]_D = 6{,}4\cdot10^6$; for EuroV is : $[m_{BP}]_B = 0{,}6\cdot10^{-6}$; $[m_{BP}]_D = 2\cdot10^6$ g,km; B – benzine motors, D – diesel motors.

The calculation data about the limit values $[ECD]_j$ and $[m_{BP}]_B$; the specific index of carcinogenic danger (K_B) of the evaluated type of cars using different fuels is in the third table.

It is important to emphasize that the quantity of NOx and CH in the integrated index of ecocarcinogenic danger of the evaluated cars, using carboncontained fuels is more than 90%.

According to the experimental data of a car kind of GAZ with a ZMZ402 motor on the stand with a chassis dynamometer according to European urban driving circle using benzine АИ92 (AH ≈ 40 %) it was defined that m_{NOx} = 2,4; $m_{BP} = 9\cdot10^6$ g,km; m_{SD} ≈ 0,01 g,km; m_{NOx} , $[m_{NOx}]$ ≈ 40; m_{BP} , $[m_{BP}]$ ≈ 15; m_{SD} , $[m_{SD}]$ = 2. The specific integrated index of ecocarcinogenic danger of the car was $(ECD)_B$ ≈ 200, but $[ECD]_B$ ≈ 6, so (K_B) = $(ECD)_B$,$[ECD]_B$≈ 33. So the specific integrated index of ecocarcinogenic danger of the car with a benzine ICE exceeded the normal rate of EuroV more than in 30 times.

Experimental investigations with a car kind of GAZ with a diesel motor GAZ560 (diesel fuel, AH ≈ 45 %) showed that m_{NOx} = 2,0; $m_{BP} = 32\cdot10^6$ g,km; m_{SD} ≈ 0,6 g,km; m_{NOx} , $[m_{NOx}]$ ≈ 10; m_{BP} , $[m_{BP}]$ ≈ 16; m_{SD} , $[m_{SD}]$ ≈ 100. The specific integrated index of ecocarcinogenic danger of the car was $(ECD)_D$ ≈ 300, but $[ECD]_D$ ≈ 21, so (K_D) = $(ECD)_D$,$[ECD]_D$≈ 14. So, the shown car kind of GAZ with a diesel motor in comparison with the shown car with a benzine motor pollutes the E more: by solid debris in 60 times, by carcinogenic compounds – in 4 times (with equal quantities of NOx and EG). That is why widespread presence of diesel cars can worsen solving the problems of reducing of the atmosphere contamination in cities by carcinogenic and mutagenic supertoxins. But the affinity index to international ecological standards (K_D) in comparison with K_B is lower more than in 2 times, that can be a sign of less severe («soft») ecological requirements EuroV to cars with diesel motors.

Conclusions

1. With usage in ICE of cars different hydrocarbon fuels, the most harmful compounds, utilized with EG are NOx and CH, which under the urban conditions synthesize extreme dangerous for the human organism nitrocarcinogenic ingredients, having mutagenic properties. Finelydivided SD, which absorb (amass) them remarkably strengthen their carcinogenic activity. Increased quantity of AH, that typical for modern fuels, sharply strengthens ecocarcinogenic danger of cars.

2. The limit rates of CH and SD emissions with EG of the evaluated type of cars with a diesel motor remarkably exceed the shown emission rates of the evaluated car with a benzine motor. The specific integrated index of ecocarcinogenic danger of the car with a diesel is higher than with a benzine motor in 1,5 times. But the affinity index to international ecological standards for the investigated car with a diesel motor (K_D), because of sensibly less severe rules EuroV ($[m_{NOx}]_D$, $[m_{NOx}]_B$ ≈ 3,3, and correspondingly ($[m_{BP}]_D$, $[m_{BP}]_D$ ≈ 3,3) is lower than for the car with a benzine motor (K_B) more than twice (K_B, K_D = 2,3).

3. For reducing of ecocarcinogenic danger of cars with ICE it is necessary: usage of fuels, including mixes, with the reduced levels of AH and sulphur and with the increased quantity of hydrogen; maximum increasing of exploitable economical efficiency of fuels, including keeping the parametric reliability of their work that will promote minimization in the emission levels of extreme harmful carbon contained ingredients (CH, SD); providing cars with ICE by modern filter systems for entrapment SD and correspondingly CH, that provides more efficient usage of both oxidative and bifunctional systems of catalytic neutralization of EG; usage of modern regeneration accumulative neutralizators (which have low hydraulic resistance) for reducing of the NOx and EG emission levels of cars, especially with diesel motors; usage of modern adaptive systems for adjusting the quality of working processes, including their ecocarcinogenic indexes and for providing the electronic controlled multiphase fuel supply straight to cylinders ICE and efficient fuel burning. Preparations and publication of these materials were done under the auspices of a grant of STC in Ukraine.

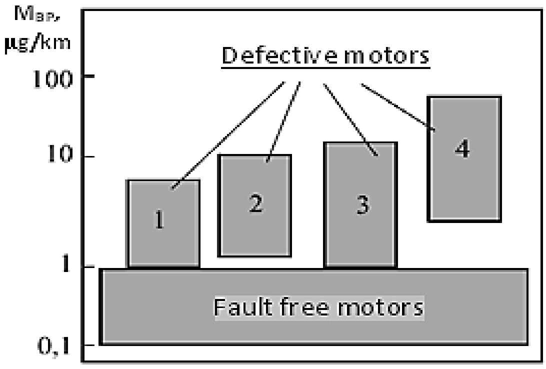

Fig 1 The emission levels of benzo(a)pyrene with traffic EG under different defects of gasoline engines: 1 misalignment of free run; 2 oil loss; 3 defects of a feeding system; 4 – defects in an igniting system.

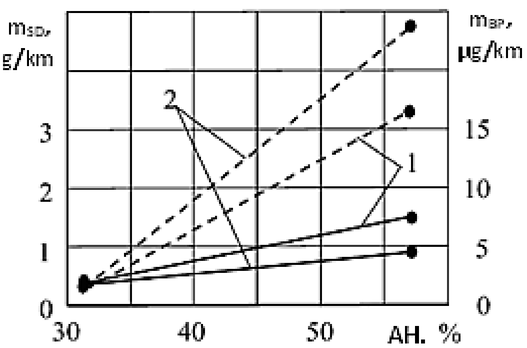

Fig 2. Dependence of the emission levels of SD (—) and BP () on the increasing concentrations of AH in diesel oil fuels. The cars are: 1 – Oldsmobile Delta 88 diesel, 2 Peugeot 505 D

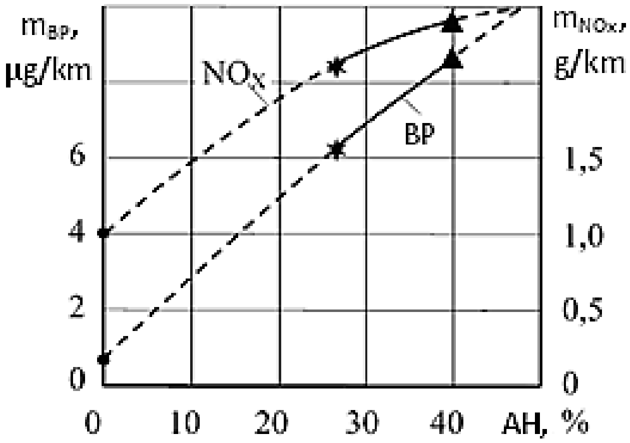

Fig 3 Influence of the AH concentration in fuels on the levels of NO_x and BP emissions with EG of cars kind of GAS: ● – methane, – benzine A76, ▲ – benzine АИ92

Table 1 Gradation of the NS based on the exceeding levels of CC

City	Noxious substances
Basraha	BP, HCHO, NO_x, dust
Diwaniyaha	BP, dust, phenol, ammonia
Babylon	BP, NO_x, HCHO, phenol
Kerbala	BP, HCHO, NO_x, carbon bisulphide
Najaf	BP, NO_x, dust
Dialla	BP, HCHO, NO_x
Muthana	BP, HCHO, fluorine hydride, ammonia
Anbar	BP, HCHO, fluorine hydride, phenol
Baghdad	BP, NO_x, HCHO, phenol, dust

Table 2 Experimental data

S.No	Fuels	m_{NOx}	$m_{BP} \cdot 10$
		g,km	
1	Benzine АИ92	2,4	8,9
2	Benzine АИ76	2,2	6,3
3	Propanebutane	1,0	1,2
4	Benzine +30% of hydrogen	0,9	0,8
5	Natural gas	1,0	0,6
6	Benzine +10% of hydrogen	0,5	0,6
7	Methanol	0,8	0,6
8	Hydrogene	0,2	

Table 3 Limit and specific ecocarcinogenic values of cars

Motor fuels	**EuroII**	**EuroV**
	[ECD]·10–3, нм3,км	
(see table 2)	27	6
	$K_Б$ = (ECD)B , [ECD]B	
1	6,5	26,3
2	5,6	22,5
3	2,3	9,3
4	2,0	7,9
5	0,6	2,5
6	0,6	2,2
7	0,6	2,2
8	0,1	0,4

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