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The effect of oils on PAH, PCDD, PCDF, and PCB emissions from a spark engine fueled with leaded gasoline

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Abstract

The effect of synthetic and mineral oils on the formation of polyaromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) in emissions from a spark ignition engine was studied on a Škoda Favorit engine fueled with leaded gasoline. The test cycle simulated urban traffic conditions on a chassis dynamometer, in accordance with the ECC 83.00 test. The data for selected PAHs as well as PCDDs, PCDFs, and PCBs congener profiles are presented. PCDD/Fs emissions for an unused oil and the oil after 10 000-km operation varied from 300 to 2000 fmol/m³, PCBs emissions from 75 to 178 pmol/m³, and PAHs emissions from 150 to 420 μ g/m³. The content of PCBs in oils varied from 2 to 920 mg/kg. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Spark engine; Oil; Emissions; PAH; PCB; PCDD/F

1. Introduction

In many industrial countries, PCDD/Fs as one of the most toxic components in traffic emissions make up only a few percent in the inventory of all known dioxin sources. However, in relation to environmental protection, the relevance of the emissions formed during gasoline combustion lies in the fact that a great number of these small-scale generators of these pollutants operate in regions with dense population and with the emissions close to the recipient. For that reason, traffic emissions were studied by a number of authors (Marklund et al.,

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1987, 1990; Bingham et al., 1989; Hagenmaier et al., 1990; Oehme et al., 1991; Schwind et al., 1991) who reported PCDD/Fs emission data. The conditions under which the just mentioned compounds are formed during combustion processes are well-known (Pekárek et al., 1995). The content of halogens and lead in the gasoline became the key aspect in these studies. In some countries (e.g., in Germany), the use of leaded gasoline containing halogenated scavengers has been banned, as PCDD/Fs emissions attained the values ranging from 30 to 520 pg I-TEQ PCDD/Fs per km (Marklund et al., 1987; Bingham et al., 1989; Hagenmaier et al., 1990; Schwind et al., 1991), while those for leaded and unleaded gasoline were 39-151 and 4-19 pg I-TEQ PCDD/Fs per km, respectively (Schwind et al., 1991). Hence, with regard to the environmental protection, replacement of leaded fuels

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by lead-free fuels is well-founded on both theoretical and experimental grounds.

However, reported PCDD/Fs emission data differ greatly, likely due to different conditions of the experiments and their difficult reproducibility (Schwind et al., 1991).

Nevertheless, the great difference in PCDD/Fs emissions reported in studies of Marklund (1987, 1990) dealing with the combustion of leaded gasoline containing scavengers cannot be explained solely on this ground. On the other hand, it might be probably stressed that the values by one order of magnitude lower were obtained (Marklund, 1990) on an engine lubricated by a semisynthetic oil.

Polyaromatic hydrocarbons (PAHs) in traffic emissions have been studied in detail by Parma and Novák (1994), Šebor et al. (1994), and by Mi et al. (1996).

The above facts prompted us to study the effect of synthetic and mineral oils on PAH, PCB, PCDD, and PCDF emissions generated during combustion of leaded gasoline. Determination of these noxious substances under identical experimental conditions using two different analytical methods and two successive experimental runs could render the mutual comparison of formation of these compounds for the oils under study possible. This would enable us to discuss factors that affect formation of these persistent organic pollutants (POP). Along with these experiments, the accumulation of PAH and PCB in motor oils has also been examined.

2. Experimental

2.1. Experimental arrangement

A Škoda Favorit passenger car (driven for about 118 000 km) with carburettor spark ignition engine of 1.3 l displacement without catalytic converter was used for these experiments. The emissions according to the EEC 83.00 test for CO, CH, and NO_x were below the EEC standard limits.

The experiments simulated urban traffic regime according to the EEC15 and 83 tests (Bratský and Stacho, 1993) on dynamometer rolls. The maximum, minimum, and mean velocities were 50, 0, and 19 km/h, respectively. One experiment (duration 2 h 44 min, ca 48-km

Table 1

The purification steps

distance) consisted of twelve engine testing runs. The consumption of gasoline was expressed by weight. For each oil type used, the engine was washed with toluene (total of 2 l) and conditioned by 6–20 min/running.

2.2. Sampling

The sampling (national standard CSN 124070) was made with the tube placed at 150 mm far from the prolonged (\emptyset 50 mm) end of the tail pipe. The measurements of emissions, flow rates, temperature (90– 110°C), and pressure were realized at the same sampling point. An absorption apparatus with heated probe was used. The coarse particles were collected on glass fibre filter Whatmann GF/F. The aerosols were absorbed in two impingers with 100 ml of ice-cooled 2-ethoxyethanol. The gas volumes were measured after a dry-tower by a gasometer. The volume of the withdrawn gas sample varied from 3.4 to 4.0 m³ at 0°C at the pressure 101.3 kPa.

2.3. Oils and chemicals

The synthetic Pennzoil Performax SAE 5W-40 oil and the mineral Mogul Forte GX SAE 15W-40 were used.

2.4. Analytical methods

A1 and A2. The purification steps in Table 1 were used both in the Czech and Swedish laboratory for PAH, PCB, and PCDD/F analysis for treating exhaust gas samples.

A3 and A4. The oil samples for PAH and PCB analysis in both laboratories were pretreated in accordance with the standard operational procedure (semipermeable membrane device) to remove substantial part of the oil and then analyzed as described above (A1).

2.5. Data presentation

To make comparison of our results with reported data, the outgas was calculated from the fuel consumption at its theoretical molar composition (C:H = 1:2). The volume of dry exhaust gases was estimated to 9.41 m³/kg fuel. The formation of 1 m³ of dry

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\downarrow			
10 ml volume adjustment \rightarrow 5%	6 aliquot for PAH ana	lysis, HPLC (A1)), GC/MS (A2)
↓			
Purification by H2SO4-SiO2 colur	nn-Al ₂ O ₃ column \rightarrow	2% CH ₂ Cl ₂ in h	exane-PCB fraction,
↓ GC/MS/MS and	alysis (A1), GC/HRMS	S analysis (A2)	
50% CH2Cl2/hexane-"C" column,	toluene-PCDD/F (GC	C/MS/MS analysis	s-A1, GC/HRMS-A2)

Extraction (glass filter with toluene-24 h. 2-ethoxyethanol/H₂O by hexane)

outgas (0°C, 101.3 kPa) thus corresponds to 1.73 ± 0.04 km for the Škoda Favorit car.

3. Results and discussion

3.1. Explorative experiments with synthetic oil

In our first trial experiment (experiment I), with the synthetic oil (see Section 2) we used the leaded gasoline 91 octane, containing 111 mg Cl/kg, 54.5 wt.% aromatic hydrocarbons (AH) and 0.13 g Pb/kg. The data obtained in this work are compared in Table 2 with the measurements by Marklund et al. (1990) of gasoline containing scavengers.

It is worth mentioning that the reported data were obtained with the GC/HRMS method (A2). Our finding and older results (Marklund et al., 1990) are in agreement with very low values of PCDD/Fs.

3.2. Effect of oil type on PCDDs and PCDFs emissions

The second experiment (experiment II) was carried out with the leaded gasoline 91 octane (Czech made) containing 0.13 g Pb/kg, 3.0 mg Cl/kg, 37.2 wt.% AH, and 8% MTBE. Three motor oils were studied: synthetic oil (*S*), mineral oil (*M*), and the same mineral oil after 10000-km operation (MR). Emission samples were analyzed in the Czech laboratory by the analytical method A1. The reproducibility of sampling, analytical methods, and PCDD determinations was evaluated from two successive runs (S_a and S_b) using GC/MS/MS technique.

In the third experiment (experiment III), we used the same gasoline of different production charge which contained 0.12 g Pb/kg, 1.0 mg Cl/kg, 34.4 wt.% AH, and 2.8% MTBE. Here the preparation of the samples for analysis and analytical determination of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) congeners were performed both in the Czech Republic (method A1) and in laboratories in Sweden (method A2) and samples were taken in two consecutive runs. Obtained data are presented in Table 3.

The I-TEQ values in Table 3 were calculated using WHO 25–29.5.1998 recommended TEFs. The sum of the PCDD/Fs is presented as the TEQ concentration interval. The lower values correspond to calculations

Table 2

The data obtained in comparison with the measurements by Marklund et al. (1990) of gasoline containing scavengers

pg I-TEQ PCDD/Fs per km	
Mineral oil (Marklund et al., 1987)	30-520
Semisynthetic oil (Marklund et al., 1990)	1.1 - 2.8
Synthetic oil (this work)	0.4

where non detected values in Table 3 were neglected. The higher values were calculated by the use of the half value of presented detection limits. The concentration range shows the uncertainty of these estimations.

Results obtained in experiment II prove that under the same experimental arrangement, PCDD measurements (S_a , S_b) in both runs yield well-comparable data. This confirms good reproducibility of the sampling method, analyses and of the state of the engine as well. The TEQs in emissions from synthetic oil (S_a) in experiment II shows lower concentrations than in emissions from mineral oils (M and MR).

The congener profiles in emissions from mineral oils in experiments II and III differ. However, within the experiment III similar profiles were found for M and MR oils. The content of PCDD/Fs in emissions for synthetic oils differ significantly not only in concentrations but in their congener profiles as well.

The differences in the experiments with the same car and under comparable experimental arrangement demonstrate well that how the emissions of PCDD/F might be influenced by the fuel, oil, and combustion conditions. The concentration of PCDFs in exhaust gases is higher than PCDDs in all experiments and the PCDD/PCDF ratio in experiments II and III show differences in chemical processes by fuel combustion in the same engine.

Our results present the possible concentration interval for PCDD/Fs which might be expected for leaded gasoline and engines of comparable type: 1.4–11 pg TEQ/m³. It may be of general interest that our results of urban air measurements in Prague during the winter period of 1996 are scattered between the values of 0.047– 0.39 pg TEQ/m³. PCDD/Fs here determined come of course from all urban sources.

3.3. Effect of oils on PCBs spark ignition engine emissions

The data of the content of polychlorinated biphenyls (PCBs) in emissions of spark ignition engines are rare in the literature. We found only the data of Parma and Novák (1994), however, information under which conditions these measurements were done is not available. During experiment III, PCBs content in emissions was measured in two laboratories (A1, A2) on different instruments. The results are summarized in Table 4.

The results are in fairly good agreement with respect to different analytical laboratories. The emissions do not contain remarkable amounts of octa- to deca-chlorinated biphenyls. Higher values of tetra- and hexachlorinated biphenyl congeners were found in emissions from synthetic oil.

The intake air for the engine was also analyzed on the PCBs content. Its concentration equaled to 0.3 pmol PCB/m³, in agreement with measurements in other parts of the Prague territory. In the exhaust gases, the PCB concentration is more than two orders of magnitude

	Experiment II			Experiment III						
	Method A	A1			Method A1 Method A2				A2	
	S_{a}	$S_{ m b}$	М	MR	S	М	MR	S	М	MR
$PCDD/Fs \ pg/m^3$										
2378TCDD	<1.2	<1.3	<1.1	1.7	<2.2	<1.7	< 0.8	2.1	<1.7	<1.2
12378PeCDD	<1.2	<1.3	<1.4	<1.4	<2.5	<1.4	< 0.9	11	<4.0	<6.5
123478HxCDD	2.0	2.9	1.1	3.0	<2.4	<1.3	< 0.8	8.2	<8.7	<18
123678HxCDD	1.2	1.6	2.6	2.9	<2.2	<1.3	< 0.8	14	<7.2	<9.2
123789HxCDD	1.6	<1.3	1.2	2.2	2.2	<1.0	< 0.6	11	<5.8	<12
1234678HpCDD	3.5	5.6	6.9	7.2	15	< 0.9	0.7	21	<9.2	8.9
OCDD	11	15	27	18	57	47	28	56	20	39
2378TCDF	<2.7	NA	<4.0	4.9	5.7	2.8	4.0	7.0	4.3	7.7
12378PeCDF	<2.2	NA	<4.0	5.3	5.6	<1.1	1.0	15	2.9	5.0
23478PeCDF	<2.4	NA	<6.4	5.3	7.2	2.1	1.7	14	2.6	3.9
123478HxCDF	2.3	NA	6.3	8	7.8	1.0	0.4	18	4.3	5.0
123678HxCDF	2.7	NA	6.8	4.7	8.7	1.8	0.9	11	1.7	2.4
234678HxCDF	3.0	NA	11	8.7	8.6	4.0	4.5	16	3.5	6.8
123789HxCDF	<1.2	NA	<2.5	<1.8	0.5	1.2	0.7	5.3	<4.3	<3.9
1234678HpCDF	8.8	NA	24.0	39	69	19	8.8	41	6.6	19
1234789HpCDF	<1.3	NA	5.0	10	6.6	2.3	1.5	15	<12	<17
OCDF	<1.8	NA	<4.7	19	66.0	14.0	3.0	76	<66	59
$TEQ \ pg/m^3$										
$\sum PCDD/Fs$	1.4-3.5	_	3.3-6.5	6.9-8.6	8.2-11	2.4-4.1	2.1 - 3.0	30	2.9-7.2	4.7–11
Total PCDD/Fs fmo	l/m ³									
∑TCDD	50	62	81	93	150	21	11	140	<120	<78
\sum PeCDD	19	17	36	15	130	20	11	280	<160	<260
\sum HxCDD	64	61	95	72	84	43	22	280	<190	<310
\sum HpCDD	21	33	42	42	73	23	11	100	<40	66
OCDD	24	33	59	39	120	100	61	120	43	85
\sum TCDF	150	NA	300	420	420	85	110	72	52	98
\sum PeCDF	28	NA	320	210	270	91	38	320	94	110
\sum HxCDF	16	NA	250	200	250	45	19	370	86	100
$\overline{\sum}$ HpCDF	22	NA	69	170	240	61	29	250	23	110
OCDF	<4.1	NA	<11	43	150	32	7	<150	<150	130
$\sum PCDD/Fs$	390	_	1300	1300	1900	520	320	2000	300	700

Table 3 Effect of different oils on PCDD/Fs spark ignition engine emissions (experiments II and III)^a

^a S: synthetic oil; M: mineral oil; MR: mineral oil after 10000 km-operation; NA: not analyzed.

higher: 75–178 pmol PCB/m³. It is worthy to note that the concentrations of PCB congeners reported by Parma and Novák (1994) are of about one to two orders greater then our data. Because of the still great number of leaded gasoline-fed cars as emission resources in the highly populated urban regions in many countries, the PCBs values thus found are warning.

3.4. Effect of oils on PAHs spark ignition engine emissions (experiment III)

In experiment III, the selected PAHs were also determined in both laboratories (A1, A2). Results presented in Table 5 are compared with data reported in the literature for leaded gasoline.

In our experiments, we have observed in emissions the formation of the toxic dibenzo(a,h)anthracene and

benzo(a)pyrene with some less toxic PAHs. Benzo(a)anthracene was present in significant amounts. Our results agree with the reported data. The results of Parma and Novák (1994) are also in a good agreement with our findings.

Used mineral oils generate greater total amounts of PAHs.

3.5. Contents of PCBs and PAHs in motor oils

Biphenyls and polycyclic aromatic hydrocarbons generated during fuel combustion are characterized by their high solubility in lipophilic media. The oil on cooler walls of the combustion space contacts with formed persistent organic compounds. Preliminary analyses of PCBs and PAHs in oils (Table 6), support the presumptions. The relatively high PAHs and PCBs

Table 4 Effect of oils on PCBs content in spark ignition engine emissions (experiment III)^a

	PCB p	PCB pmol/m ³								
	Metho	od Al		Method A2						
	S	M MR		S	S M					
TriCB	28	28	62	NA	NA	NA				
TetraCB	66	28	27	30	24	15				
PentaCB	27	18	25	22	20	16				
HexaCB	58	29	39	40	27	23				
HeptaCB	24	13	12	17	28	21				
OctaCB	2.2	1.3	1.0	2.8	4.5	NA				
NonaCB	0.3	0.1	0.1	0.2	< 0.7	< 0.9				
DecaCB	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1				
\sum of PCB	178	89	104	112	104	75				
(tetra–										
decaCB)										

^a S: synthetic oil; M: mineral oil; MR: mineral oil after 10 000km operation; NA: not analyzed.

contents in used oil show that we deal with hazardous waste which requires proper care during its combustion or recycling. A potential presence of PCDD/F cannot be excluded from the theoretical standpoint.

3.6. Influences on POPs formation in spark engines

3.6.1. The state of tested engine

De novo synthetic reactions are known to take place on carbon particles and/or particles with silicate structure. The incomplete combustion (i.e., cold start, technical state of the engine) leads to formation of carboniferous components, which will mix with dust

Table 5

Effect of different oils on PAH spark ignition engine emissions (experiment III)^a

	PAHs µg/m ³									
	I-TEF (Nisbet and LaGoy, 1992)	(Mi et al., 1996)	(Šebor et al., 1994)		Anal. method A1			Anal. method A2		
			Test ECE	Test at 90 km/h	S	М	MR	S	М	MR
Anthracene	0.01	54	19	46	26.5	19.9	55.3	21.0	14.0	36.0
Fenantrene	0.001	7	9	8	117.1	100.6	215.9	92.0	77.0	131.0
Benzo(a)anthracene	0.1	4	2	20	18.1	20.4	46.4	2.3	1.3	2.9
Chrysene	0.01	5	2	20	1.6	1.6	3.8	2.3	1.4	3.0
Pyrene	0.001	11	5	24	37.2	37.8	74.5	24.0	19.0	31.0
Dibenzo (a,h)-anthracene	5	0.4	NA	NA	ND	ND	ND	1.1	0.15	0.062
Fluorene	0.001	73	3	3	NA	NA	NA	31.0	26.0	44.0
Fluoroanthene	0.001	16	4	45	13.1	10.8	21.6	15.0	12.0	21.0
Benzo(b)fluoranthene	0.1	2	0.7	ND	0.6	ND	1.0	2.8	1.3	2.1
Benzo(k)fluoranthene	0.1	2	ND	ND	ND	ND	0.4	ND	ND	ND
Benzo(a)pyrene	1	2	ND	9	0.6	0.5	0.7	0.88	0.25	0.4
Benzo(g,h,i)perylene	0.01	2	1.4	8	1.6	1.4	1.3	1.6	0.46	0.55
Indeno(1,2,3-c,d) pyrene	0.1	2	0.5	3	0.5	0.6	0.5	1.2	0.24	0.21
$\sum PAHs$		180.4	46.6	186.0	216.9	193.6	421.4	195.2	153.1	272.2

^a S: synthetic oil; M: mineral oil; MR: mineral oil after 10000-km operation; NA: not analyzed; ND: not detected.

aerosol particles, passed through the air cleaner. These aerosol particles are very important for the formation of PCB and PCDD/F. This fact is in an agreement with Miyabara et al. (1999) findings, where the amounts of 26 ng PCDD/Fs/g on exhaust particles were found.

On the other hand, oxygen-rich fuel mixtures enhance the extent of de novo synthetic reactions (Grabic et al., 1999). Therefore, optimization of the oxygen content becomes also a successful approach to emission reductions. The oxygenous substances added to gasoline increase the content of oxygen utilizable for fuel combustion. Thus, 2.7 mass% of these compounds lead to a decrease of 15% of the hydrocarbons and a 25% decrease of CO in the exhaust gas (Šebor et al., 1995). However, the effect of oxygen and oxygenous compounds on PCDD/F distribution and their congener profiles has not as yet been determined, eventhough the presence of oxygen seems to be an important factor in the present knowledge about de novo synthetic reactions.

The technical state of some other parts of the car might affect the results too. Probably, the technical state of the engine including exhaust system was the reason of extremely high values of PAH and PCB which we met in one of our experiments. The same conclusion can be probably attributed for extremely high values of PCB presented by Parma and Novák (1994).

3.6.2. The effect of chlorine

The restriction of PCB and PCDD/F in emissions can be achieved by exclusion of the presence of halogens, especially of chlorine in the reaction system, regardless of whether it is organic- or inorganic-bond. The chlorine content of 3–4 mg Cl/kg in leaded gasoline and in oils of

1910		

	$\sum PCBs mg/kg^b$			\sum PAHs mg/kg ^c					
	Fresh oil	After 50 km run	Used oil	Used oil Fresh oil		After 50 km run		Used oil	
	A3	A3	A3	A3	A4	A3	A4	A3	A4
Synthetic oil	22	20	NA	2.8	2.0	51	25	NA	NA
Semisynthetic oild	NA	NA	47	NA	3.7	NA	NA	NA	361
Mineral oil	9.9	23	NA	56	1.8	77	63	926	605

Table 6 PCBs and PAHs in oils^a

^aA3 and A4 analytical method in the Czech Republic and Sweden, respectively.

^b PCBs No. 28, 52, 101, 138,153, 180.

^c Sum of PAHs content of compounds from column 1 in Table 5, excluding fluorene.

^d SAE 10 W/40, operated 15 000-20 000 km, Mazda.

15–40 mg Cl/kg in Mogul Forte and of 50 mg Cl/kg in Pennzoil Performax and at oil consumption of 0.4–1 g/km, results in 200–300 ng Cl/km levels. We have found that emissions amounts of 6–25 ng PCB/km and 0.1–0.7 ng PCDD/F/km. It is evident that the content of chlorine in the fuel and oil is high enough to form the experimentally found concentrations of PCB and PCDD in emissions.

Varying chlorine content in the materials of the same brand could be the reason of different results when determining the content of these substances in engine emissions. It is worth to mention that in the period following the dispersion of inorganic chlorides on roads in winter the entry of halogen rich aerosol by air suction into the combustion process is highly probable.

3.6.3. Effect of heavy metals

The presence of heavy metals is fundamental for de novo synthetic reactions to proceed. From this viewpoint, the restricted use of leaded gasoline is the right step leading to the reduction of PCB and PCDD/F emissions.

In the combustion processes taking place in motor vehicles, the effect of copper and its compounds has not yet been discussed. These compounds are known to be the most efficient catalysts of de novo synthetic reactions (Pekárek et al., 1995). The presence of copper in motor oils is due to the wear of metallic motor components. Hence, it seems likely that copper content in oils will increase with increasing degree of their wear, contributing thus to the formation of the above mentioned pollutants in the combustion space. Gasoline producers provide fuel analyses, which include data on the effect of fuel on copper corrosion. However, the effect of copper content in engine input materials on PCB and PCDD/F formation has not been examined.

3.6.4. Effect of precursors

The course of de novo synthetic reactions in the combustion system is significantly affected by the presence of PCBs precursors. The main input precursors which might be present at gasoline combustion are dienes, aromatic compounds such as benzene, chlorobenzenes, phenols, diphenyl ethers, and also PCB, the latter forming PCDF (Pekárek et al., 1995). The precursors formed by gasoline combustion involve carbonmonoxide, 1,3-butadiene, acrolein, and PAH. Carbonmonoxide is an "excellent" precursor in de novo synthetic reactions, since the formation of chlorinated POPs correlates well with its concentration. The addition of oxygenous components (e.g., MTBE or *tert*-butyl amyl ether) to gasoline causes also reduction of CO content in combustion gases. Analogously, benzene is formed during fuel combustion via dealkylation of aromatic C₇–C₁₂ hydrocarbons as well.

The important factor which affects POPs formation is gasoline composition. Gasoline contains among others alcohols, ethers, dienes, and AH. The AH content to adjust the corresponding octane number ranges from 30 to 50 mass%, while benzene content should not exceed 5 vol%. A recommendation for gradual replacement of leaded gasoline by reformulated unleaded fuels according to the American Clean Air Act - 1992 containing at maximum of 25 vol% AH, 1 vol% benzene, and 2.7 mass% oxygen (in the form of oxygenous components) is therefore the right step to a significant reduction of POPs precursors. The reproducibility of the experiments carried out with the gasoline of the same brand but of different production charges can be influenced not only by different chlorine and corrosion copper contents but also, and that mainly, by chemical composition and amount of AH.

4. Effect of oils

As to POPs formation by fuel combustion, the effect of oil seems to be absolutely unknown. Its composition, so important in regard to the components affecting de novo synthetic reactions, has not been as yet unambiguously resolved. Thus, for example Fourier transform of IR spectra of semisynthetic and synthetic oils which we used exhibit, according to our analytical results, similarity to the spectrum of mineral oil used. Furthermore, synthetic oils can contain chemically unknown additives. The differences between studied oils found by us could thus not be expected to be large, because all the oils under study contain the same mineral component. In our view, the emission changes observed are mainly due to the different degree of the lubricating ability decrease. The formulation of the oil composition such that it would minimize its effect on de novo synthetic reactions is one way to improve spark engine emissions. On this topic we did not find any information in available literature sources.

5. Conclusions

- The spark ignition engine emissions contain not only PCDD/F and PAH but also PCB.
- The higher PAH emissions were found for 10 000-km operated oils as compared with new oils.
- The contents of PCB and PAH in oils increase with the time of their operation.
- The discussion about possible effects influencing the PCB, PCDD, and PCDF formation applied to the combustion conditions in cars is outlined.
- The effect of oil on PAH, PCB, and PCDD/F formation is of general interest and should be therefore studied to obtain more data on simplified systems under more defined conditions.

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References

Bingham, A.G., Edmunds, C.J., Graham, B.W.L., Jones, M.T., 1989. Determination of PCDDs and PCDFs in car exhaust. Chemosphere 19, 669–673.

- Bratský, D., Stacho, D., 1993. Examination of car gasolines. Ropa a uhlie 35 (2) 122–131 (in Slovak).
- Grabic, R., Marklund, S., Pekárek, V., Punčochář, M., Ullrich, J., 1999. Effects of oxygen, sulphuric acid and peroxides on formation of PCBs, PCDDs and PCDFs on the MWI fly ash. Organohalogen Compounds 41, 251–254.
- Hagenmaier, H., Dawidowski, N., Weberuss, U., Hutzinger, O., Schwind, K.H., Thoma, H., Essers, U., Buehler, U., Greiner, R., 1990. Emission of polyhalogenated dibenzodioxins and dibenzofurans from combustion-engines. Organohalogen Compounds 2, 329–334.
- Marklund, S., Andersson, R., Tysklind, M., Rappe, Ch., Egebaeck, K.E., Bjoerkman, E., Grigoriadis, V., 1990. Emissions PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20, 553–561.
- Marklund, S., Rappe, Ch., Tysklind, M., 1987. Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars on leaded gasoline. Chemosphere 16, 29–36.
- Mi, H.H., Lee, W.-J., Wu, T.-L., Lin, T.Ch., Wang, L.-Ch., Chao, H.-R., 1996. PAH emissions from gasoline-powered engine. J. Environ. Sci. Health A 3 (8), 1981–2003.
- Miyabara, Y., Hashimoto, S., Sagai, M., Morita, M., 1999. PCDD and PCDF in vehicle exhaust particles in Japan. Chemosphere 39, 143–150.
- Nisbet, J.C., La Goy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons. Reg. Tox. Pharm. 16, 290–300.
- Oehme, M., Larssen, S., Brevik, E.M., 1991. Emission factors of PCDD and PCDF for road vehicles obtained by tunnel experiment. Chemosphere 23, 1699–1708.
- Parma, Z., Novák, L., 1994. Monitoring of POPs in Prague territory (in Czech). Report of Mega Ltd., Stráž pod Ralskem and of the Institute of Municipal Informatics (IMIP) Prague.
- Pekárek, V., Hetflejš, J., Kaštánek, F., 1995. Polychlorinated dibenzo-p-dioxins and dibenzofurans in combustion processes. Chem. Listy 89, 343–353.
- Schwind, K.H., Thoma, H., Hutzinger, O., Dawidowski, N., Weberuss, U., Hagenmaier, H., Buehler, U., Greiner, R., Essers, U., Bessey, E., 1991. Emission halogenierter dibenzodioxine und dibenzofurane aus verbrennungsmotoren. Z. Umweltchem. Őkotox. 3, 291–298.
- Šebor, G., Pospíšil, M., Maxa, D., Blažek, J., Černý, J., Vaňura, J., 1994. Emissions from combustion of gasolines. Project MŽP ČR No. 1677–94, Czech Republic (in Czech).
- Šebor, G., Kozák, P., Pospíšil, M., Blažek, J., 1995. Properties of gasolines and their effects on the environment. Chem. Listy 89, 233–244 (in Czech).