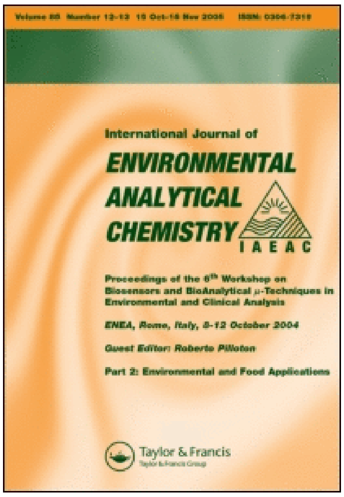

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FRACTIONATION AND CHEMICAL ANALYSIS OF URBAN AIR PARTICULATE EXTRACTS

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Urban air samples were collected using Hi-Vol PM_{10} samplers during 24 hours periods. Samples were collected from October 1993 to September 1994 both in Teplice and Prachatice and from October 1996 to April 1997 in Teplice, CR. Organic material (EOM) was extracted from filters with methylene chloride in a Soxhlet apparatus. Acid base partitioning of the crude extract was carried out and neutral compounds were further fractionated by silica gel column chromatography. More than one hundred and seventy compounds were identified by GC-MS in the fractions. Levels of PAHs and the distribution profile was similar at both sampling locations. Higher concentrations of PAHs, nitro-PAHs, polycyclic aromatic ketones and organic acids and bases were observed in winter period when the fuel consumption for home heating is high.

Keywords: Urban dust; extraction; fractionation; GC-MS analysis

INTRODUCTION

Urban air particles contain extractable organic matter (EOM) which has both mutagenic and carcinogenic activity[1–4]. Incomplete combustion products from various sources contain carcinogenic compounds and in several cases these combustion products have been recognized as human carcinogens (e.g. chimney soots, coal tars, diesel particles and cigarette smoke)[5–8].

Polycyclic aromatic hydrocarbons and mainly benzo(a)pyrene were for many years considered the best indicator of carcinogenity[9]. Recent improvements in analytical methods for measuring PAHs and other carcinogenic polycyclic organic matter (e.g. aromatic amines, substituted PAHs and heterocyclic com-

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pounds) have shown that B(a)P is not always well correlated with total exposure to carcinogenic organic matter[10,11]. Detection of the specific compounds responsible for this activity is limited by the complexity of these extracts. Since the extremely complex chemical nature of these products prevents ready detection and identification of individual compounds, fractionation of an extract according to class or type of hydrocarbons is essential.

The analysis of complex mixtures, such as ambient air or combustion source particulate extracts, to determine genotoxicity and to identify mutagens has been approached by using bioassay – directed fractionation[12–17]. High resolution gas chromatographic separation combined with mass spectrometric identification and quantification of single compounds or compound groups in fractions is frequently used[8,16,18–31]. The aim of this study was to characterize the fractions, identify major compounds, compare EOM composition in an industrial and a rural town in winter and summer periods and prepare individual fractions for biological tests to obtain an air quality assessment procedure. The sampling sites were Teplice, a typical town in an industrial region and Prachatice, a small town situated in the south-western region of the Czech Republic, chosen as the reference site.

In order to characterize biologically important organic compounds associated with urban aerosol, particle samples were run through a chemical fractionation scheme. Fractionation based on acid – base partitioning and silica gel chromatography was used for the separation of gram quantities of ambient air particulate extracts which were further submitted to chemical analysis using GC-MS.

EXPERIMENTAL

Sampling

The sampling of ambient air was carried out in Teplice which is situated in the north-western part of Czech Republic. Extensive strip mining of brown coal and numerous coal based industries (power plants, heavy engineering and chemical plants) is the main feature of this region. The district of Prachatice is situated in the south-western part of Czech Republic and the atmosphere in region is one of the cleanest in the Czech Republic. The sampling sites located in the centre of the towns were not subjected to a near source or intense vehicular traffic.

Ambient air samples about 1500 m^3 were collected using Andersen PM_{10} samplers-Ströhlein HVS 150 Hi-Vol pump during 24 hours periods. Samples were collected from October 1993 to September 1994 both in Teplice and Prachatice and from October 1996 to April 1997 in Teplice. Teflon coated glass filters Pallflex T60 20A were used and filters were kept in methylene chloride washed aluminium foil at 22°C and 30% relative humidity for 24 hours, weighted on Sartorius 1712 balances and stored in a deep freezer at −80°C.

Consecutively taken samples from winter and summer periods from boths sampling sites were combined and extracted.

Extraction and acid-base partitioning

Organic material (EOM) was extracted from filters with methylene chloride in a Soxhlet apparatus for 72 hours and three extracts were prepared from winter periods in Teplice and Prachatice TW93, TW96, PW93, (samples from October to March) and two from summer periods PS94 and TS94, (from April to September).

The total extracts were concentrated by rotary evaporation and fractionated according to the scheme shown in Figure 1.

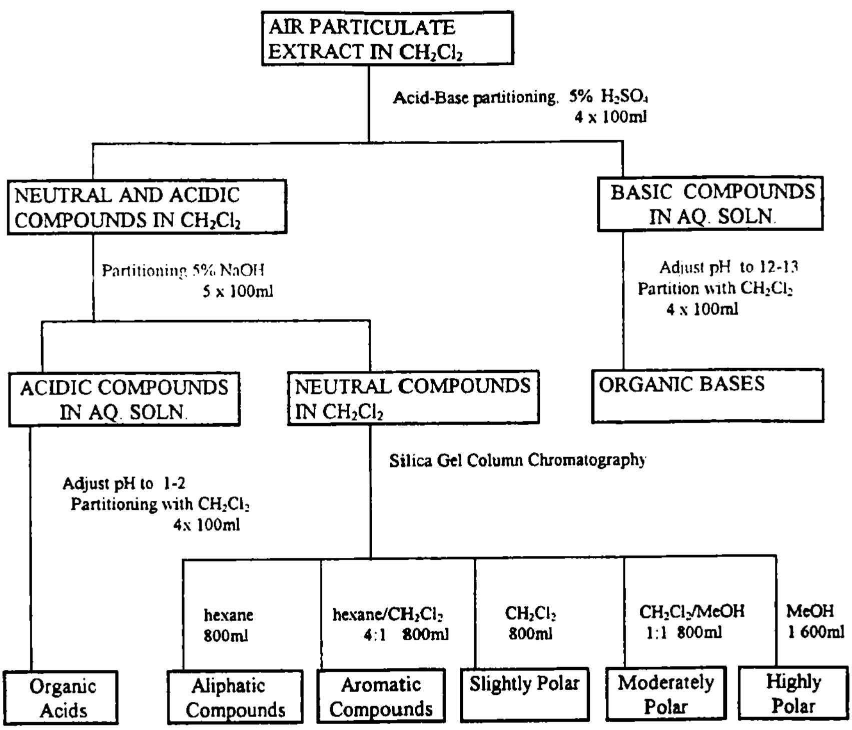

FIGURE 1 Fractionation scheme for gram quantities of EOM

First acid base partitioning[15] of the crude extract was carried out and the organic bases were removed from the extract by partitioning multiply with with 5% sulphuric acid.

Organic bases were re-extracted in methylene chloride after adjusting pH to 12–13 with 40% KOH.

The organic acids were extracted with 5% NaOH and recovered in methylene chloride after adjusting the aqueous phase pH to 1–2 with 6M sulphuric acid. Methylene chloride extracts were dried over natrium sulphate and concentrated to 100 mL by rotary evaporation.

Silica gel column chromatography of neutral compounds

Neutral compounds were further fractionated. Using model compounds, the chromatographic conditions were optimized to obtain the desired separation between the different classes of EOM. Standards used for the optimalization of fractions were pentacosane, hexachlorobenzene, naphthalene, fluoranthene, benzo(a)pyrene, 1-nitronaphthalene, 1-nitropyrene and dibutylphthalate.

Silica gel (0.063–0.200 mm, J.T. Baker, USA) was activated for 5 hours at 180 °C and 150 g was packed as a hexan slurry into a closed bed chromatography column (25 mm × 710 mm) with screw-type end fittings. For both column preparation and sample fractionation the solvent was introduced at the bottom of the column and collected at the top. The solvent flow rate 5 mL per minute was controlled by HPLC pump and the column was rinsed sequentially with 400 mL hexane, 400 mL methylene chloride, 400 mL methanol, 400 mL methylene chloride and 400 mL hexane. The column was equilibrated with hexane at a flow rate of 2 mL/min for three hours prior to sample introduction.

Sample material was injected using an Ultrasonic Bath Sampling Device (UBSD).

Stainless steel U tube (6 mm i.d., vol. 11 mL) was gradually filled with methylene chloride extract of neutral compounds under gentle stream of nitrogen. Solvent was evaporated (at 50 °C) and U tube was connected between pump and column and immersed into an ultrasonic bath. Neutral material was separated by sequentional elution with solvents of increasing polarity: 800 mL hexane, 800 mL hexane / methylene chloride (4:1 v:v), 800 mL methylene chloride, 800 mL methylene chloride / methanol (1:1 v:v) and 1600 mL methanol.

Ultrasonic bath was switched on for five minutes after every change of mobile phase and soluble part of the neutral fraction was subjected to chromatography.

Silica gel column chromatography fractions were concentrated by rotary evaporation.

Gravimetric analysis

Gravimetric analyses were perfomed on a Sartorius microbalance. Fraction masses were determined in duplicate by placing 1 mL fraction into each of two aluminium weight pans and evaporated under gentle stream of nitrogen. Five ambient blanks were measured, averaged, and used to adjust changing ambient conditions.

Material and methods blanks

All solvents (methanol, methylene chloride, n-hexane, p.a. quality, Merck, BRD) used in this study were distilled and the following blanks were prepared:

Solvent Blanks: A 100 mL of each solvent used was concentrated to 2 mL by rotary evaporator injected to the GS-MS and the material was used to determine residual mass.

Fractionation and Silica Gel Column Chromatography Blanks: A 100 mL aliquot of methylene chloride was carried out through the entire fractionation scheme using reagent quantities and methods identical to those used for separation.

High performance liquid chromatography

Additional cleaning was necessary for the determination of nitro-PAHs. Subfractionation of the slightly polar fraction was performed by using HPLC techniques (Figure 2). Semipreparative HPLC was undertaken on a 8 mm i.d. by 25 cm Separon SGX-CN 10 μm (Tessek, CR) normal phase column. The solvent program consisted of operating isocratically for the first 5 min. with n-hexane programming to 10% dichloromethane in n-hexane mixture in 19 min. and to 100% dichloromethane in 26 min. and then operating isocratically for 10 min. The flow rate was 1.5 mL/min. Sample injection was performed using a Rheodyne injector with a 500 μL loop.

Gas chromatography-mass spectrometry

The electron ionisation (EI) GC-MS analyses were carried out by using Hewlett-Packard 5890 gas chromatograph interfaced with HP 5971 mass detector. For the EI analysis heated splitless injection (230 °C) was used and HP-5 column (30 m × 0.25 mm × 0.25 μm) was programmed from 70 °C to 300 °C at 10 °C/min. Helium (0.8 mL/min) was used as the GC carrier gas and spectra were acquired every 0.4 s from 40 to 350 daltons. Nitroarenes in the urban air extracts

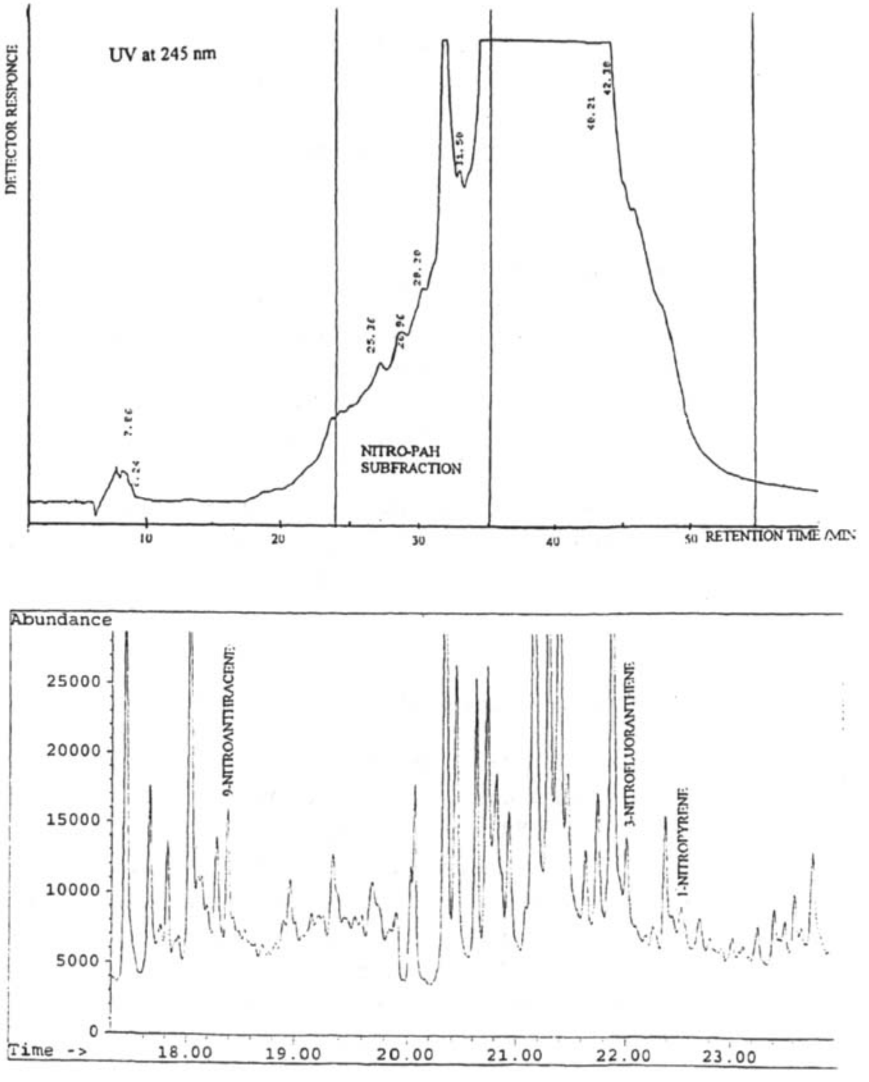

FIGURE 2 HPLC subfractionation of slightly polar fraction and SIM chromatogram of GC-MS analysis of the nitro-PAH subfraction. For HPLC and GC-MS conditions see text

eluted in the slightly polar fraction, this fraction was submitted to HPLC subfractionation and nitro-PAHs were quantified using selected ion monitoring at m/z 127, 165, 173, 176, 201, 211, 215, 217, 218, 223, 226, 227, 247, 250, 267, 273, 297.

Samples and Dr. Ehrenstorfer standards (1-nitronaphthalene, 2-nitronaphthalene, 2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene, 6-nitrobenzo(a)pyrene) were injected via on-column injection onto a HP-5 column.

RESULTS AND DISCUSSION

The samples from Prachatice exhibited lower mean PM and EOM values than the samples from Teplice. The ratio EOM / PM was on the other hand the same at both sites, there was no significant difference in winter samples from Teplice 93–94 and Teplice 96–97.

Sample volumes, particulate matter (PM) and EOM values for summer and winter periods are summarized in Table I. The total extracts were fractionated into seven compound class fractions by acid-base partitioning and silica gel column chromatography according to the scheme shown in Figure 1.

Mean recovery of organic mass was 74.3–92.3% (acid / base / neutral partitioning) and 65.5–92.2% (column chromatography partitioning). Neutral fractions were about 60% of the total extract in all samples. Very high values (28.1% and 24.4 %) exhibited acid fractions from both winter samples in Teplice.

TABLE I Samples collected in Teplice and Prachatice

Sample[a]	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
Air volume (m^3)	224369	286548	242985	261858	234452
Particulate Matter (mg)	15557	10449	7189	6186	14220
Extractable Organic Matter (mg)	3910	1516	1993	933	3695
EOM/PM_{10} (mg/mg)	0.251	0.145	0.277	0.160	0.260
PM_{10}/m^3 ($\mu g/m^3$)	69.3	36.5	29.6	23.6	60.6

a. TW93 – 205 filters collected from October 10. 1993 to March 31. 1994 in Teplice; TS94 – 180 filters collected from April 1. to September 30. 1994 in Teplice; TW96 – 169 filters collected from October 1. 1996 to March 31. 1997 in Teplice; PW93 – 154 filters collected from October 6. to March 31. in Prachatice; PS94 – 178 filters collected from April 1. to September 30. in Prachatice

A majority of the recovered mass from the neutral separation appears to be moderately polar compounds. The aromatic and slightly polar neutral fractions contributed more than two – fold to the total mass of the samples in the winter as compared to the summer. This result is in good agreement with the observation that concentration of polycyclic aromatic hydrocarbons is higher in winter period as a result of higher consumption of fossil fuels for heating purposes [26]. The per cent distribution and recovery of extract mass is in Table II.

TABLE II Per cent distribution and recovery of extract mass

Fraction (%)	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
Organic bases	1.4	2.4	1.3	2.2	1.3
Organic acids	28.1	10.6	12.6	19.5	24.4
Neutral compounds	62.8	61.3	62.6	55.4	57.5
Aliphatic compounds	13.6	15.1	13.6	12.6	11.8
Aromatic compounds	13.1	5.9	11.4	5.2	12.5
Slightly polar neutral compounds	15.3	8.5	10.2	4.4	14.0
Moderately polar neutral compounds	29.7	37.2	41.2	29.5	43.9
Highly polar neutral compounds	9.4	9.2	9.0	13.8	10.0
Recovery (%)					
Acid/Base/Neutral partitioning	92.3	74.3	76.5	77.1	83.2
Column chromatography separation	81.1	75.9	85.4	65.5	92.2
Overall recovery	80.4	59.5	67.3	58.0	78.7

GC-MS chemical characterization

The major compound class fractions that were identified from the EI GC-MS analyses are listed in Table III.

TABLE III Major compound class fractions

Fraction	*Compound Class*
Organic bases	N-heterocyclic aromatic compounds
Organic acids	carboxylic acids and anhydrides, hydroxy compounds
Neutral aliphatic	aliphatic hydrocarbons
Neutral aromatic	polycyclic aromatic hydrocarbons and alkyl substitued PAHs
Slightly polar	aromatic aldehydes, aromatics nitriles, aromatic ketones, aromatic diones, nitro-PAHs, phthalic acid ester
Moderately polar	aliphatic alcohols, aromatic ketones, phthalic acid ester
Highly polar	carboxylic acid ester, alkoxy alcohol

TABLE IV Identified basic compounds and acids

Fraction	*Rt min*	*EI m/z*	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
Basic Compounds							
quinoline	7.59	129	t	-	t	-	t
isoquinoline	7.91	129	t	t	t	-	t
methyl quinoline/isoquinoline	8.63	143	t	-	t	-	t
methyl quinoline/isoquinoline	8.77	143	t	-	t	-	t
methylquinoline/isoquinoline	9.09	143	t	t	t	-	t
pyridin,methyl-pyrrolidinyl	9.19	84	t	t	t	t	t
methylquinoline/isoquinoline	9.61	143	t	t	t	-	t
dimethylquinoline/isoquinoline	10.20	157	t	-	t	-	t
dimethylquinoline/isoquinoline	10.50	157	t	-	t	-	t
dimethylquinoline/isoquinoline	10.61	157	t	t	t	-	t
trimethylquinoline/isoquinoline	11.49	171	t	-	-	-	t
trimethylquinoline/isoquinoline	11.89	171	t	-	-	-	t
carbazole	13.05	167	t	t	t	-	t
acridine	14.80	179	t	-	t	-	t
benzoquinoline	14.92	179	t	-	t	-	t
benzoquinoline	15.19	179	t	-	t	-	t
phenanthridine	15.47	179	t	-	-	-	t
methylbenzoquinoline	15.96	193	-	-	-	-	t
indenoquinoline/isoquinoline	18.62	203	t	-	t	-	t
Organic acids							
carboxylic acid	7.34	73	t	-	-	t	t
carboxylic acid	8.81	73	t	-	-	t	t
benzaldehyde, hydroxymethoxy	9.91	152	t	t	t	-	t
1-hydroxynaphthalene	11.36	144	t	-	-	t	-
carboxylic acid	11.52	73	t	t	t	t	t
benzaldehyde, hydroxydimethoxy	13.26	182	-	-	-	-	t
biphenyl-ol	13.76	170	t	-	-	-	t
carboxylic acid	15.07	73	-	-	-	-	t
dibenzofuranol	15.66	184	t	-	-	-	t
1,8-naphthalic anhydride	17.50	198	t	-	-	t	t
carboxylic acid	19.99	73	t	-	-	-	t
unknown	22 63	285	t	-	-	-	t

t tenatively identified- based upon MS fragmentation only.
– not identified, not found.

In the basic fraction were tenatively identified mainly nitrogen containing heterocyclic compounds. Azaarenes are like their parent compounds (PAHs) also the products of incomplete combustion processes. They are emitted into the the atmosphere in the vapour phase and may become sorbed onto the surface of the soot particles. Coal contains a variety of heterocyclic nitrogen compounds and through the extensive use of fossil fuels azaarenes have become widespread in the environment[28]. The authentic compounds were not available for establishing retention times and quantification. The identification via EI mass spectra is rather limited with regard to its ability distinguish between isomeric compounds, for a number of components only the basic chemical structure is given, but the exact position of functional groups is unknown. Compound with R_t 9.19 was identified as nicotine. To our knowledge smoking never occured in the vincinity of the samples and it is first time that this compounds was identified in urban air.

Carboxylic acids, aromatic aldehydes and hydroxy compounds were tenatively identified in the acid fraction. Identified compounds, retention time, EI characteristic ions in the fractions are summarized in Table IV. Analysis of the neutral fractions showed agreement with the chemical class fractionation predicted by the separation of standard reference compounds.

Aliphatic hydrocarbons C_{22} to C_{32} were identified in the aliphatic fraction. PAH mixtures encountered in air particulate samples are extremely complex because of the presence of alkylsubstitued PAHs, as well as the numerous isomeric parent compounds. More than 60 unsubstitued and methyl-substitued PAHs were identified based on GC retention and mass spectrometric data. The remaining compounds were tentatively identified as alkyl-substituted PAHs based on spectrometric data. The major PAH constituents were quantified in the aromatic fraction by using GC-MS as described previously[26].

Compounds identified in the neutral slightly polar fraction were mainly polycyclic aromatic ketones (PAK), diones and nitro-polycyclic aromatic hydrocarbons. The emission of PAK from combustion processes is not much less than the emission of PAH and in ambient air originates also by further atmospheric oxidation of methylene PAH[32]. The most abundant PAK in the emissions are 9H-fluoren-9-one, 4H-cyclopenta(def)-phenanthren-4-one, 7H-benz(de)anthracen-7-one and 6H-benzo(cd)pyren-6-one[27,30]. Compounds with molecular ions 180, 204 and 230 have shown the second most important $(M-28)^+$ ions, characteristic for loss of CO, were identified as 9H-fluoren-9-one, 4H-cyclopenta (def)-phenanthren-4-one and 7H-benz(de)anthracen-7one, see Figure 3.

Nitrated polycyclic aromatic hydrocarbons, a class of potent direct acting mutagens, are produced in trace concentrations from combustion processes or by the reaction of PAHs with NO_2. Nitro-PAHs have been demonstrated to be present in diesel exhaust gases and in ambient aerosol[33,34].

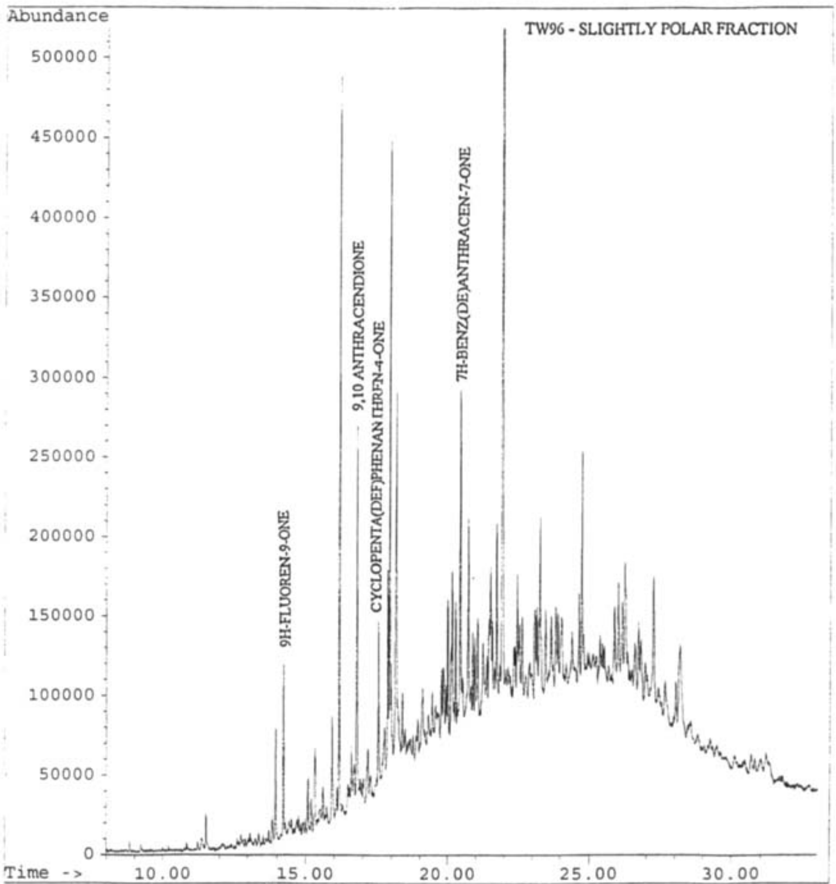

FIGURE 3 GC-MS total ion chromatogram and MS spectra of selected aromatic ketones and diones. Identified compounds are listed in Table V. For GC-MS conditions see text

Slightly polar fraction was cleaned by HPLC and the nitro-PAHs were determined by means of GC-MS in selected ion monitoring mode, see Figure 2.

The moderately polar fraction contained aliphatic alcohols, carboxylic acid esters, phenalen-1-one and traces of oxo- PAHs identified in the previous slightly polar fraction. Alkoxy ethanol and carboxylic acid esters were identified in the highly polar fraction. Identified compounds, retention times, EI characteristic ions in neutral fractions are summarized in Table V.

TABLE V Identified neutral compounds

Fraction	*Rt min*	*EI m/z*	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
Aliphatic Compounds							
C_{22}-C_{32} n-alkanes		71	+	+	+	+	+
Aromatic Compounds [a]							
2,6 dimethylnaphthalene	10.00	156	+	-	+	-	-
2,7 dimethylnaphthalene	10.19	156	+	-	+	-	+
1,7 dimethylnaphthalene	10.26	156	+	-	+	-	+
1,3 dimethylnaphthalene	10.47	156	+	-	-	-	-
2,3 dimethylnaphthalene	10.51	156	+	-	+	-	-
acenaphthylene	10.61	152	6.6	-	5.2	-	2.6
1,2-dimethylnaphthalene	10.68	156	+	-	+	-	-
acenaphthene	11.06	154	+	-	+	-	+
dibenzofuran	11.47	168	0.9	-	3.5	-	3.0
trimethylnaphthalene	11.68	170	t	-	t	-	-
trimethylnaphthalene	11.89	170	t	-	t	-	-
trimethylnaphthalene	11.92	170	t	-	t	-	t
1H-phenalene	12.07	165	+	-	+	-	-
trimethylnaphthalene	12.09	170	-	-	t	-	-
fluorene	12.32	166	4.8	-	5.6	-	8.3
trimethylnaphthalene	12.42	170	t	-	t	-	t
methyldibenzofuran	12.78	182	t	-	t	-	t
methyldibenzofuran	12.94	182	t	-	t	-	t
ethyldimethylazulene	13.39	184	-	-	t	-	-
dimethylpropylnaphthalene	13.49	198	t	-	t	-	-
2-methylfluorene	13.71	165	0.8	-	2.1	-	2.3
1-methylfluorene	13.79	180	0.8	-	4.5	-	2.2
methylfluorene	13.92	180	-	-	t	-	t
dibenzothiophene	14.31	184	2.8	-	3.9	-	5.2
phenanthrene	14.68	178	32.4	3.8	95.0	8.3	60.5
anthracene	14.77	178	4.5	0.8	17.6	1.7	10.7
1-phenylnaphthalene	15.51	204	3.2	-	13.1	1.0	5.4

Fraction	*Rt min*	*EI m/z*	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
3-methylphenanthrene	15.91	192	4.8	1.0	15.4	1.9	10.2
2-methylphenanthrene	15.97	192	3.2	1.4	27.4	2.7	16.2
2-methylanthracene	16.07	192	1.6	0.5	12.9	1.4	3.7
cyclopenta(def)phenanthrene	16.16	190	12.8	2.1	45.5	4.2	26.4
4-methylphenanthrene	16.29	192	12.8	2.1	33.0	3.4	20.3
2-phenylnaphthalene	16.67	204	-	-	30.9	-	+
dimethylphenanthrene/anthracene	17.12	206	t	-	t	-	t
3,6-dimethylphenanthrene	17.21	206	+	-	+	+	+
3,5-dimethylphenanthrene	17.26	206	-	-	+	-	+
2,6-dimethylphenanthrene	17.40	206	+	+	+	+	+
2,7-dimethylphenanthrene	17.47	206	+	+	+	+	+
1,7-dimethylphenanthrene	17.53	206	+	-	+	+	+
fluoranthene	17.65	202	112.4	13.2	209.7	21.0	143.6
acephenanthrylene	17.87	202	47.4	3.5	100.8	5.3	51.7
pyrene	18.17	202	123.8	16.9	220.7	26.3	128.0
benzo(b)naphtho(2,3d)furan	18.21	218	5.8	3.1	37.9	6.9	9.4
trimethylphenanthrene/anthracene	18.58	220	t	t	t	t	t
8-methylfluoranthene	18.87	216	+	+	+	+	+
7-methylfluoranthene	18.90	216	+	+	+	+	+
benzo(a)fluorene	19.13	216	46.2	3.5	81.8	5.6	35.2
retene	19.16	219	43.2	4.4	65.4	4.6	42.0
benzo(a)fluorene	19.26	216	20.2	0.9	32.7	2.2	23.5
4-methylpyrene	19.29	216	+	+	+	+	+
2-methylpyrene	19.29	216	+	+	+	+	+
1-methylpyrene	19.31	216	28.7	2.0	40.9	4.2	19.6
methylpyrene	19.59	216	-	-	t	-	t
dimethylpyrene	20.59	230	-	-	t	-	-
benzo(ghi)fluoranthene	20.70	226	85.9	6.3	108.7	14.4	130.3
cyclopenta(def)pyrene	21.21	226	54.4	9.4	95.3	5.8	42.8
benzo(a)anthracene	21.21	228	83.7	8.9	112.5	30.2	80.0
chrysene/triphenylene	21.30	228	107.8	13.2	145.9	16.8	106.2

Fraction	*Rt min*	*EI m/z*	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
1-methylchrysene	21.80	242	+	+	+	+	+
methylchrysene/benzo(a)anthracene	21.84	242	t	-	t	-	t
methylchrysene/benzo(a)anthracene	21.99	242	t	-	t	t	t
methylchrysene/benzo(a)anthracene	22.15	242	t	t	t	t	t
1-methylbenzo(a)anthracene	22.22	242	+	-	+	+	+
10-methylbenzo(a)anthracene	22.33	242	+	+	+	+	+
3-methylchrysene	22.35	242	-	-	-	-	+
6-methylbenzo(a)anthracene	22.38	242	-	-	-	-	+
2-methylchrysene	22.41	242	+	+	+	+	+
5-methylchrysene	22.51	242	+	+	+	+	+
methylchrysene/benzo(a)anthracene	22.55	242	t	t	t	t	-
4-methylchrysene	22.64	242	+	+	+	+	+
benzo(b)fluoranthene	23.75	252	89.2	18.2	148.4	16.6	83.6
benzo(k+j)fluoranthene	23.80	252	58.0	24.7	75.3	15.2	84.6
benzo(a)fluoranthene	23.98	252	34.8	8.8	146.0	9.7	77.8
benzo(e)pyrene	24.32	252	68.4	15.1	96.1	18.6	65.0
benzo(a)pyrene	24.42	252	87.3	15.5	124.4	17.5	78.6
perylene	24.60	252	15.9	4.6	54.6	24.1	24.1
indeno(7123cdef)chrysene	26.45	276	+	-	+	-	+
dibenz(aj)anthracene	26.88	278	+	-	+	-	+
indeno(123cd)pyrene	26.88	276	86.9	23.9	77.5	20.7	62.2
dibenz(ah)anthracene	26.96	278	30.4	6.7	33.7	5.1	44.4
benzo(b)chrysene	27.21	278	+	+	+	+	+
picene	27.30	278	22.4	6.21	30.8	5.1	15.4
benzo(ghi)perylene	27.51	276	76.9	19.1	98.9	20.5	74.2
anthranthrene	27.84	276	19.2	3.9	15.3	2.5	13.6
methyldibenzoanthracene	28.66	292	t	-	t	-	t
methyldibenzoanthracene	29.16	292	t	t	t	t	t
quaterphenyl	30.45	306	t	-	t	-	-
quaterphenyl	30.84	306	t	t	t	t	-
naphtho(def)chrysene	31.13	302	+	-	+	-	+

Fraction	*Rt min*	*EI m/z*	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
coronene	32.59	300	23.3	3.6	15.7	5.1	20.9
Slightly polar compounds							
naphthalene carbonitrile	11.23	153	-	-	-	-	t
carboxylic acid ester	13.98	74	-	-	-	-	t
9H-fluoren-9-one	14.21	180	-	-	t	-	t
9(10H)-anthracenone	15.19	194	-	-	-	-	t
carboxylic acid ester	16.14	74	t	-	t	-	t
9,10-anthracendione	16.76	208	t	t	t	t	t
4H-cyclopenta(def)-phenanthren-4-one	17.53	204	t	t	t	-	t
carboxylic acid ester	17.92	97	t	-	t	-	t
anthracene carbonitrile	18.18	203	-	-	-	-	t
9-nitroanthracene[b]	18.35	223	0.26	0.04	0.18	0.08	0.55
anthracene carboxaldehyde	18.37	206	-	-	-	-	t
carboxylic acid ester	19.99	74	t	-	t	-	t
dimethylpyrene	20.44	230	t	-	-	-	t
7H-benz(de)anthracen-7-one	20.72	230	t	-	t	-	t
carboxylic acid ester	21.69	74	t	t	t	-	t
bis(ethylhexyl)phthalate	21.89	149	+	+	+	+	+
3-nitrofluoranthene[b]	21.95	247	1.3	0.26	0.44	0.13	2.3
1-nitropyrene[b]	22.40	247	0.79	0.22	-	0.23	0.80
benz(a)anthracen-7,12-dione	22.44	258	-	-	-	-	+
carboxylic acid ester	23.27	74	t	t	t	-	t
unknown	23.45	254	t	-	-	-	t
carboxylic acid ester	24.72	74	t	t	t	-	t
unknown	26.77	278	-	-	-	-	t
Moderately polar compounds							
benzoic acid ester	10.64	163	t	-	-	-	t
benzoic acid ester	13.89	163	t	-	t	-	t
pentadecanol	15.62	97	t	-	-	-	t
1H-phenalen-1-one	16.08	180	t	t	-	t	t
carboxylic acid	16.46	73	t	-	-	-	t

Fraction	*Rt min*	*EI m/z*	*TW93*	*TS94*	*PW93*	*PS94*	*TW96*
dibutylphthalate	16.58	149	+	+	+	+	+
benzoic acid ester	17.25	163	t	-	-	-	t
unknown	18.44	223	t	-	t	-	t
7H-benz (de)anthracene-7-one	20.72	230	t	-	t	-	t
bis(ethylhexyl)phthalate	21.89	149	+	+	+	+	+
unknown	23.35	135	t	-	-	-	t
unknown	24.45	254	t	-	t	-	t
unknown	25.41	161	t	-	-	-	t
Highly polar compounds							
carboxylic acid ester	9.05	71	t	-	-	-	-
carboxylic acid ester	9.28	71	t	-	-	-	-
unknown	15.35	179	t	-	-	-	-
unknown (alkoxy alcohol)	18.40	223	t	-	t	-	-
unknown	20.98	237	t	-	t	-	-

+ identified by matches with NHS 54 k library and on GC retention data
t tenatively identified- based upon MS fragmentation only
– not identified, not found

a. PAHs were quantified using SRM 1647c, SRM 1597 (NIST) and Dr. Ehrenstorffer standards, concentrations are in ng/mg PM_{10}.
b. Analysis of HPLC subfraction II, nitro-PAHs were quantified using GC-MS (SIM) and Dr. Ehrenstorfer standards, concentrations are in ng/mg PM_{10}.

Quantitative analysis of seven EPA priority pollutants – carcinogenic PAHs[35] revealed that concentrations of these compounds were comparable in the winter periods in the years 1993 and 1996 in Teplice (544 and 540 ng/mg PM). Higher concentration was found in winter in Prachatice (718 ng/mg PM). Samples from the summer period exhibited about 5–6 times lower values 111 ng/mg PM in Teplice and 122 ng/mg PM in Prachatice.

Carcinogenic PAHs expressed in ng/m^3 air were on the other hand lower in Prachatice due to lower PM_{10} concentration, see data in Table VI. Concentrations 38 and 33 ng/m^3 were found in winter in Teplice 1993 and 1996 respectively, in Prachatice (winter 1993) was found 21 ng/m^3. Concentrations in the summer period were 4.1 ng/m^3 in Teplice and 2.9 ng/m^3 in Prachatice.

Characterization of urban air aerosol, seasonal variation of genotoxic air pollutants and differences between the Teplice and Prachatice towns[26,36] will help to better understand the Program Teplice health studies[37–40] and to assess the impact of air pollution on the health of the population.

TABLE VI Concentration of PAHs and nitro-PAHs in air, Teplice and Prachatice

Compound (ng/m^3)	*TW93*	*TS94*	*PW93*	*PW94*	*TW96*
acenaphthylene	0,46	–	0,15	–	0,16
dibenzofuran	0,62	–	0,10	–	0,18
fluorene	0,33	–	0,17	–	0,50
2-methylfluorene	0,06	–	0,06	–	0,14
1-methylfluorene	0,06	–	0,13	–	0,13
dibenzothiophene	0,19	–	0,12	–	0,32
phenanthrene	2,25	0,14	2,81	0,20	3,67
anthracene	0,31	0,03	0,52	0,04	0,65
1-phenylnaphthalene	0,22	–	0,39	0,02	0,33
3-methylphenanthrene	0,33	0,04	0,46	0,05	0,62
2-methylphenanthrene	0,22	0,05	0,81	0,06	0,98
2-methylanthracene	0,11	0,02	0,38	0,03	0,22
cyclopenta(def)phenanthrene	0,89	0,08	1,35	0,10	1,60
4-methylphenanthrene	0,89	0,08	0,98	0,08	1,23
2-phenylnaphthalene	–	–	0,92	–	–
fluoranthene	7,79	0,48	6,21	0,50	8,70
acephenanthrylene	3,29	0,13	2,99	0,13	3,13
pyrene	8,58	0,62	6,53	0,63	7,76
benzo(b)naphtho(2,3d)furan	0,40	0,11	1,12	0,16	0,57
benzo(a)fluorene	3,20	0,13	2,42	0,13	2,13
retene	2,99	0,16	1,94	0,11	2,55
benzo(a)fluorene	1,40	0,03	0,97	0,05	1,42
1-methylpyrene	1,99	0,07	1,21	0,10	1,19
benzo(ghi)fluoranthene	5,95	0,23	3,22	0,34	7,90
cyclopenta(def)pyrene	3,77	0,34	2,82	0,14	2,59
benzo(a)anthracene	5,80	0,33	3,33	0,71	4,85
chrysene/triphenylene	7,47	0,48	4,32	0,40	6,44
benzo(b)fluoranthene	6,18	0,66	4,39	0,39	5,07
benzo(k+j)fluoranthene	4,02	0,90	2,23	0,36	5,13
benzo(a)fluoranthene	2,41	0,32	4,32	0,23	4,72

Compound (ng/m³)	*TW93*	*TS94*	*PW93*	*PW94*	*TW96*
benzo(e)pyrene	4,74	0,55	2,85	0,44	3,94
benzo(a)pyrene	6,05	0,57	3,68	0,41	4,76
perylene	1,10	0,17	1,62	0,10	1,46
indeno(123cd)pyrene	6,02	0,87	2,29	0,49	3,77
dibenz(ah)anthracene	2,11	0,25	0,10	0,12	2,69
picene	1,55	0,23	0,91	0,12	0,93
benzo(ghi)perylene	5,33	0,70	2,93	0,48	4,50
anthranthrene	1,33	0,14	0,45	0,06	0,82
coronene	1,62	0,13	0,47	0,12	1,27
9-nitroanthracene	0,018	0,002	0,005	0,002	0,033
3-nitrofluoranthene	0,090	0,009	0,013	0,003	0,139
1-nitropyrene	0,055	0,008	–	0,005	0,048

– not identified, not found

CONCLUSIONS

A broad range of semivolatile and nonvolatile compounds were collected using a conventional PM_{10} High Volume sampler at "Program Teplice" sites in the Czech Republic during years 1993 – 1994 and 1996–1997. By means of fractionation of gram quantities of EOM and GC-MS analysis of the fractions more than one hundred and seventy compounds were identified in air inTeplice and Prachatice. Levels of PAHs and the distribution profile is very similar at both sampling locations. Higher concentrations of PAHs, nitro-PAHs, polycyclic aromatic ketones and organic bases and acids were observed in winter period when the fuel consumption for home heating is high. Very similar distribution profiles and concentrations of PAHs were in air in Teplice in winter 1993 and 1996. This result is surprising as coal combustion was replaced by gas for heating purposes in the years 1994–1995 in this region.

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