Research Articles: Air Pollution

The Variation of Street Air Levels of PAH and Other Mutagenic PAC in Relation to Regulations of Traffic Emissions and the Impact of Atmospheric Processes

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Abstract

The occurrence of particle associated PAH and other mutagenic PAC was determined in 1996 in the street air of Copenhagen. In addition, particle extracts were tested for mutagenicity. The measurements were compared with previous measurements in 1992/1993. The levels had decreased in this period. The decrease was caused by an implementation of light diesel fuels for buses and the exchange of older petrol-driven passenger cars with catalyst-equipped new ones. About 65% of the reduction was caused by the application of the light diesel fuels. Under special conditions, chemical processes in the atmosphere produced many more mutagens than the direct emissions. The concentrations of S-PAC and N-PAC were 10 times lower than those of PAH, while the levels of oxy-PAH were in the same order of magnitude as those of PAH. Benzanthrone, an oxy-PAH, is proposed to be formed in the atmosphere in addition to direct emissions. Benzo(a)pyrene, often applied as an air quality criteria indicator, was photochemically degraded in the atmosphere. A strong increase in the mutagenic activities was observed to coincide with a depletion of benzo(a)pyrene.

Keywords: Atmosphere; benzanthrone; benzo(a)pyrene; catalyst; city; degradation; diesel; formation; mutagenic activity; PAC; PAH; petrol; processes; regulations; Salmonella test; street; traffic; transport; vehicle

1 Introduction

The atmospheric content of polycyclic aromatic hydrocarbons (PAH) as well as the mutagenic activity of extracts of air samples can be applied as indicators for the presence of carcinogens [1,2]. In Denmark, traffic, domestic heating and long-range transport are important sources of PAH and other mutagens [3]. The traffic sources, however, are the dominant PAH sources in street air [1,4]. The purpose of this investigation was to determine whether the application of diesel fuel for buses having a low distillation end point had affected the air levels of PAH and mutagens. These new diesel qualities introduced in the summer of 1993 are expected to reduce the emissions of particulates and soot [5], and therefore probably also the emissions of PAH and other mutagens [6]. In addition, starting in October 1990, it was required by Danish legislation that all new petrol-driven passenger cars should be provided with closed-loop, 3-way catalysts. The new cars accounted for 10% of the total number of passenger cars in 1992, for 15% in 1993 and for 40% in 1996. This new technology will reduce the emission of CO, HC and NO_x from the individual car by 70-80%. The use of catalysts will probably also result in a significant reduction in the emission of PAH [7]. However, the application of catalysts appears to change the composition of polycyclic aromatic compounds (PAC) in favour of oxygenated PAC [7], either because the efficiency of the catalyst is less towards oxygenated PAH than towards PAH or because the PAH is transformed to oxy-PAH by the catalyst.

The paper evaluates the effects on the street air quality of the legislation of environmental authorities to regulate the emissions from the traffic by comparing measurements from 1996 with previous ones from 1992 and 1993 [1,2,4]. In addition, observations on the effects of atmospheric processes on the content of mutagenic compounds and the air quality criteria indicator, benzo(a)pyrene, during transport are presented and discussed.

2 Experimental Section

Location: The location was H.C. Andersens Boulevard, a busy street in Copenhagen close to the town hall. Measurements of NO, gaseous NO_y (NO_x + HNO_3 + HNO_2 + PAN + PPN + NO_3 + 2 x N_2O_5 + gas phase $RONO_2$) [8], SO_2, CO, ozone, soot, particulate matter and particulate inorganic elements have been performed for many years on a daily basis on location in Community and regional air quality programmes. The traffic intensity in the street is in the order of 60,000 cars each day. Most of the 1996 PAH and mutagenicity samples were collected in the winter (40%) and spring (45%), while measurements in 1992 and 1993 were performed in the months January-March [1,2,4].

Meteorological conditions: The average meteorological conditions for the 1996 and the 1992/1993 samples were comparable. Thus, the mean temperature and wind speed outside the city was 3.5 ± 2.9 °C and 5.9 ± 1.3 m/s, respectively, for the 1996 samples compared to 2.7 ± 0.6 °C and 5.5 ± 0.6 m/s, respectively, for the 1992/1993 samples. While the average temperature was almost the same, the temperature variation for the 1996 samples (range: -6.4 to 21.7 °C) was larger than for the 1992 - 1993 samples (range: -4.4 to 7.5 °C). A few of the samples in 1996 were collected in the summer and autumn.

Sampling and sample treatment: 24-hour samples of airborne particulate matter were collected using a conventional Hi-Vol sampler (Sierra Instruments Inc.) with glass fibre filters. The sampling volumes were typically about 2000 m^3. The filters were stored in a freezer (-18 °C) until analysed.

The filters were extracted ultrasonically twice with dichloromethane (*p.a.* Merck) and finally with acetone (p.a. Merck). The samples were protected against light, both in this and in the following steps, in order to avoid photolysis of the PAC. The combined extracts were divided into two equal parts. One part was concentrated to 5 ml and applied to the mutagenicity tests (see later).

The other part was added known amounts of d_8-dibenzothiophene, d_{12}-triphenylene, d_{12}-perylene and d_{12}-coronene (internal standards) and concentrated to 1 ml. Cyclohexane was added and the samples were concentrated to 1.0 ml. The PAH fraction of the solution was isolated by liquid-liquid extraction with a cyclohexane-dimethylformamide-water system [9]. The recoveries were 85-100% for a range of representative PAC, including the internal standards.

A few samples were analysed for N-PAC and the basic extracts of the samples were tested for mutagenicity. 25% of the collected dichloromethane-acetone extracts were added known amounts of d_7-quinoline, d_9-acridine and 10-azabenzo(a)pyrene and concentrated to 1.0 ml. 2.0 ml toluene was added and the mixture was concentrated to 2.0 ml. The basic N-PAC in the toluene solution was extracted with 2 x 2.0 ml of 8.25 M phosphoric acid [9]. The two phosphoric acid phases were combined and adjusted to a pH about 14 with ca. 9 ml of 11 M potassium hydroxide (p.a. Merck) in an ice bath. The N-PAC were extracted from the alkaline aqueous phase with 3 x 2.0 ml proportions of dichloromethane. The combined dichloromethane phases were dried with sodium sulphate, concentrated to 1.0 ml and analysed by GC-MS. The solutions for the mutagenicity tests of the N-PAC fraction were prepared in the same manner but without internal standards.

The samples were analysed by capillary gas chromatography (Varian STAR 3400 CX) using temperature programmable splitless injection, a RTX5-MS column (Restek) and ion trap mass spectrometric detection (Varian Saturn 4D).

Mutagenicity test: The dichloromethane was evaporated to near dryness under a gentle stream of nitrogen. Dimethyl sulfoxide (DMSO) was then added, followed by an evaporation of the remaining dichloromethane by means of nitrogen. The DMSO dissolved extracts were tested for mutagenic activity in the Salmonella/mammalian microsome assay. The assays were carried out by the standard plate incorporation method described by Maron and Ames [10] using the strains TA98 and TA98NR. The tests were performed with and without a rat liver homogenate (S9-mix) with the TA98 strain and without S9-mix with the TA98NR strain. The mutagenicity tests included a test of the total extracts and, in a minor number of cases, also tests of the basic fraction as described above. Positive and negative controls according to Maron and Ames [10] were included in all experiments. The spontaneous revertant frequencies per plate were in the range: TA98+S9: 26-74, TA98-S9: 12-62, and TA98NR: 7-31. The mutation rates with 2-aminoanthracene (positive control for TA98+S9) were 99-321 (0.21 mg/plate) and 303-469 (0.42 mg/plate). 2-nitrofluorene (positive control for TA98-S9) resulted in a mutation rate of 35-125 (0.1 mg/plate), 50-130 (0.2 mg/plate) and 39-87 (0.25 mg/plate). The positive control for TA98NR, 1,8-dinitropyrene (0.0002 mg/plate) resulted in a mutation rate of 597-2849 revertants/plate. The mutation rates for 2-nitrofluorene in TA98NR were 6-26 (0.1 mg/plate), 10-34 (0.2 mg/plate) and 10-46 (0.25 mg/plate) using the compound as a control for the lack of nitroreductase in TA98NR.

3 Results and Discussion

Occurrence and intercorrelations: The levels of selected PAC, mutagenic activities and inorganic gases are presented in **Table 1**.

The PAH levels are within those found in street air in other cities in the western world [11-13]. The levels of the two oxy-PAH, anthraquinone and benzanthrone, were on the same order of magnitude as the most abundant PAH, e.g. benzofluoranthenes, benzopyrenes, benzo(ghi)perylene and coronene. The single PAH correlated with the other PAH. The correlation coefficients, r, were in the range 0.66-0.97 ($p<0.01$). The oxy-PAH, benzanthrone, had significant correlations with most of the PAH, r in the range of 0.49-0.83 ($p<0.05$). PAH in street air has previously been demonstrated to originate mainly from traffic emissions [4]. Traffic emissions also contribute strongly to NO, gas NO_y and soot and most of the linear correlations between PAC and these compounds were seen to be significant ($r = 0.49-0.71$, $p<0.05$). The mean mutagenic activity of the total extracts seen in TA98+S9 was 48±41 rev./m^3, 34±28 in TA98-S9 and 15±12 in TA98NR. The direct mutagenic activity measured in TA98-S9 was 70% of the activity seen with meta-

Table 1: 1996 levels of selected PAC, mutagenic activities and reference components. Results are given as mean levels ± 2 SD (n = 16)

PAH ng m^{-3}		N-PAC, S-PAC, oxy-PAH ng m^{-3}		Mutagenicity Rev. m^{-3}		Reference components	
Phen	1.4±0.3	AQ	4.1±1.6	TA98+S9	48±41	CO (ppm)	1.70±0.20
MePhen	4.0±0.4	BAO	3.7±1.2	TA98-S9	34±28	NO (ppb)	101±14
BaA	3.1±0.8	BfQ	0.23±0.01	TA98NR	15±12	gas NO_y (ppb)	133±16
BaP	2.2±0.6	BcAc	0.31±0.02			Soot (μg/m^3)	46±7
CP	2.4±2.3	DBT	0.10±0.02			SO_2 (ppb)	2.6±0.5
BeP	3.1±0.7						
BbjkF	6.5±0.4						
BghiP	5.1±1.1						
Cor	3.8±1.0						

Abbreviations: Phen: Phenanthrene, MePhen: Sum of methylphenanthrenes, BaA: Benz(a)anthracene, BaP. Benzo(a)pyrene, CP: Cyclopenteno(cd)pyrene, BeP: Benzo(e)pyrene, BbjkF: Sum of Benzo(b+j+k)fluoranthenes, BghiP: Benzo(ghi)perylene, Cor: Coronene, AQ: Anthraquinone, BAO: Benzanthrone, BfQ. Benzo(f)quinoline, BcAc: Benz(c)acridine, DBT: Dibenzothiophene, TA98+S9: Mutagenic activity with metabolic activation, TA98-S9: Mutagenic activity without metabolic activation, TA98NR: Mutagenic activity with nitro-reductase deficient strain, gas NO_y. see text

bolic activation. The mutagenic level of direct-acting nitro compounds ((TA98-S9)-(TA98NR)) makes up 56% of the total level of direct-acting mutagenicity (TA98-S9), which is not an unusual result for air samples [14]. Most of the correlations between the PAH and the mutagenicity were significant, but the mutagenicity increases much more than the PAH levels at high pollution levels (→ *Fig. 1*). An exceptionally high mutagenicity level was observed on April 22. It was associated with a significant increase in the level of sulphur dioxide, indicating a contribution from long-range transport from the Continent [8,15,16]. Even when including this episode, the intercorrelations between the results for the mutagenicity with and without metabolic activation were linear in contrast to the PAH-mutagenicity correlations (→ *Fig. 1*).

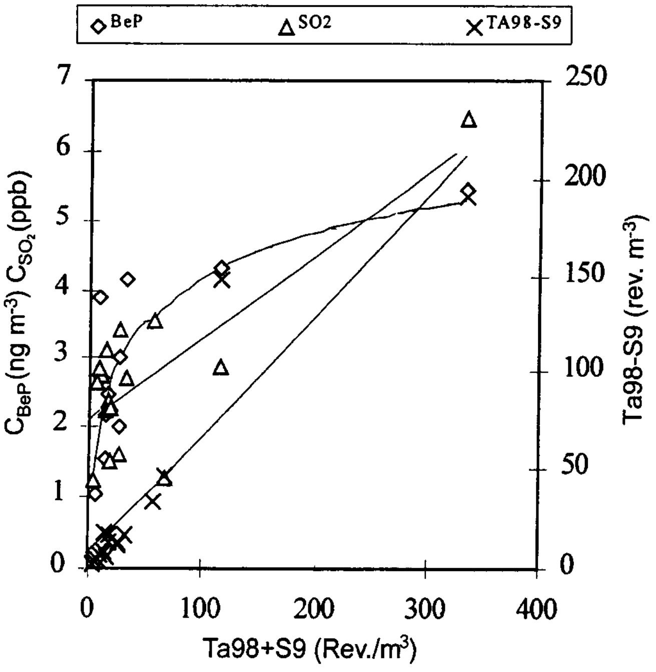

Fig. 1: 1996 TA98+S9 correlations with BeP, SO_2, and direct mutagenicity, TA98-S9. The full line is a logarithmic fit to the BeP data (R^2 = 0.59), the broken line is a linear fit to the mutagenicity data (R^2 = 0.86) and the dashed line is a linear fit to the SO_2 data (R^2 = 0.62)

The concentrations of S- and N-PAC were about one order of magnitude lower than those of PAH. The street air levels of N-PAC were higher than the roof levels observed recently in Liverpool and previously in Copenhagen [9,17], thus indicating that traffic is a major source of N-PAC. The TA98+S9 mutagenic activity in the basic extracts was about 3% of the activity in the total extracts in those samples collected on days with low activity of atmospheric photochemistry. This level is ascribed to the presence of N-PAC. The photochemical processes may produce water soluble, polar, indirect-acting mutagens ending up in the basic extract, as the mutagenicity of this fraction increased significantly with increasing atmospheric ozone concentrations ($r = 0.96$, $p<0.05$). The contribution of these compounds appears to be higher than the expected contribution of N-PAC in most of the samples.

Changes in composition and levels from 1992 to 1996: The PAH levels as well as the mutagenicity levels decreased from 1992 to 1996 (→ *Table 2* and *Fig. 2*). PAH levels decreased significantly more than the reference components (CO, soot, NO, gas NO_y) (t-test, $p<0.01$). If the long-range transport episode mentioned above is omitted, the mutagenicity levels decreased with 59% (TA98+S9), 54% (TA98-S9), and 71% (TA98NR). The corresponding PAH levels decreased 40%.

The PAH composition can be used to identify emission sources [4, 18]. From **Table 2** it can be seen that the PAH composition did not change significantly from 1992 to 1996, although the levels of reactive PAH (for example BaP and CP) have decreased slightly more than the other PAH as discussed later. By applying BghiP and Cor as traffic indicators [4] it has been calculated that the traffic contribution on working days was approximately the same in 1992 (90%) and 1996 (80-90%). The relative contribution of diesel vehicles can be estimated by the MePhen/Phen ratio [4]. Based on this method it is estimated that the diesel contribution was approximately 2/3 of the total traffic contribution in both 1992 and 1996. Thus, the relative reduction of emissions from diesel and petrol vehicles must have been about the same, and the absolute reduction of diesel vehicle emissions must have been twice the absolute reduction of petrol vehicle emissions. This indicates that the 35% reduction of the stable PAH, BbjkF and BeP,

Table 2: Ratios used to evaluate trend and impact of atmospheric processes

1996/1992 Ratio		LRT/1996_{rest} Ratio[1]		S/W ratio[2]	
Phen	0.60	BaP	1.5	BaP	0.64
MePhen	0.63	CP	0.6	CP	0.17
BaP	0.46	BeP	1.6	Perylene	0.72
CP	0.39	BbjkF	1.8	BbjkF + BeP	0.84
BeP	0.66	BghiP	1.4	Anthanthrene	0.46
BbjkF	0.65	Cor	1.2	BghiP + Cor	0.67
BghiP	0.61	BAO	2.0	BAO	1.33
Cor	0.63	TA98+S9	7.0	CO	1.02
TA98+S9	0.67	TA98-S9	5.7	gas NO_y	0.89
TA98-S9	0.67	TA98NR	5.2	Soot	0.99
TA98NR	0.40	CO	1.1		
CO	0.88	NO	1.1		
NO	0.76	gas NO_y	1.3		
gas NO_y	0.81	SO_2	2.5		
Soot	0.83				

[1] Levels during a long-range transport (LRT) episode relative to the average levels during the other sampling events.

[2] The LRT data is not included. Abbreviations, see *Table 1*

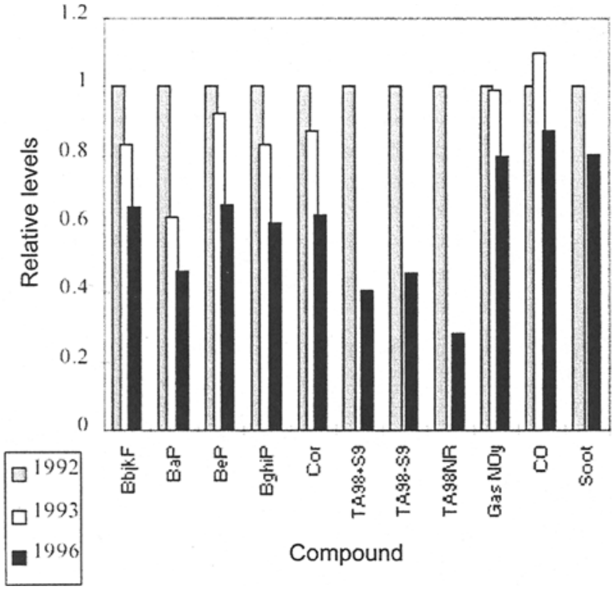

Fig. 2: Variation of the concentrations of different air pollution components in 1992, 1993 and 1996 normalised to 1992. Abbreviations: see *Table 1*

from 1992 to 1996 is caused by a 23% reduction of diesel vehicle emissions and a 12% reduction of gasoline vehicle emissions. Assuming that the effect of catalysts on CO and PAH emissions is the same, the decrease in CO levels can be used to estimate the catalyst contribution to reduction of PAH emissions. The CO level (and thus presumably the PAH level) decreased 13% corresponding to a 22% reduction of diesel vehicle emissions (total reduction = 35%), which is in excellent agreement with the estimates above. Furthermore, the 1993 measurements support this since the difference between the 1993-to-1992 ratio for CO and BbjkF was 22.5%.

Influence of atmospheric processes: On sampling days dominated by long-range transported air, atmospheric processes will have an impact on the occurrence of PAH and other mutagens. In 1996, such an episode took place on April 22. As shown in **Figure** 3 and Table 2, the composition of mutagenic PAC was affected by atmospheric processes on this date. Whereas the reactive PAH such as BaP and CP were depleted during transport relative to the stable PAHs, the mutagenicity levels were strongly increased. The mutagenicity increases were 3-5 times the BaP increase. Furthermore, a negative correlation between the sunlight intensity and the relative atmospheric content of BaP was found ($r = 0.66$, $p<0.05$). This supports the theory that photochemical processes represent a significant sink for BaP in the atmosphere as suggested in previous studies [19,20]. These observations are seriously questioning the validity of epidemiological studies and risk assessments [2] using BaP as an indicator for carcinogens in the air. Especially for people living or working at a distance from the source, the BaP level will underestimate the cancer risk. Also another recent study is questioning the application of BaP as an indicator [21].

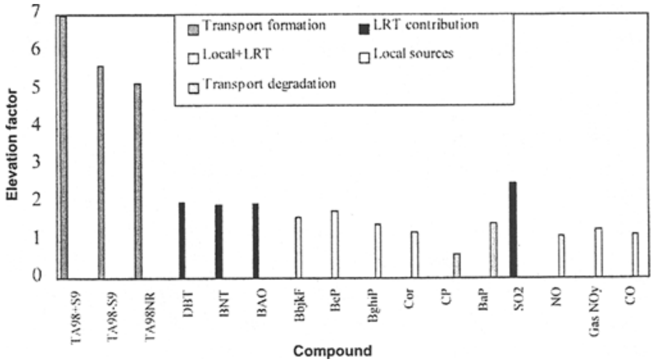

Fig. 3: The elevation of air pollutants during the long-range transport episode on 22 April 1996 normalised to the average levels. Abbreviations: see *Table 1*

The summer-to-winter (S/W) variation of PAC is also affected by atmospheric processes because of the higher photochemical activity during the summer months. In 1996 some of the samples were collected in the summer half-year. S/W ratios are listed in Table 2. As can be seen, BAO had higher atmospheric concentrations in the summer half-year than the winter half-year, suggesting that atmospheric formation is a source of BAO in addition to direct emissions. All the PAH show the opposite tendency of benzanthrone having the highest concentrations at winter-time. The S/W ratios for the reactive PAH (CP, BaP, perylene, anthanthrene) were lower than those for the non-source specific stable PAH, BbjkF and BeP. The ratios for CP and anthanthrene were especially low. However, the traffic PAH, BghiP and Cor, also had a lower ratio than BbjkF and BeP. It is not evident why the ratio for the traffic PAH is lower than that for the other PAH. Previous observations have been interpreted as higher PAH emissions at low ambient temperature than at summer-time conditions [1].

4 Conclusion and Future Outlook

The regulations to decrease the emissions of nitrogen oxides, carbon monoxide, soot and VOC from diesel and petrol engines are even more efficiently to reduce the levels of PAH and other mutagens. Both the emissions from diesel engines and petrol vehicles are reduced. About 65% of the reduction was caused by the regulation of diesel exhaust emissions from buses and the rest by the use of catalysts in petrol engines. The replacement of the remaining older petrol cars with catalyst-equipped new ones should bring the PAH air levels in street air down to about half of that in 1992. Although there has been an increase in the traffic intensity from 1992 to 1996, there was a clear decrease in the emissions in this period due to the regulations. In the future, an increasing number of diesel cars are probably going to use an oxidation catalyst or other technologies to reduce the emissions of VOC, PAC and soot particles. Another approach may be to remove the PAH in diesel fuels by catalytic technologies. Both kinds of approaches may further decrease the city air levels of PAH and other mutagenic PAC.

The mutagenic content of airborne particulates increases strongly during transport. The atmospheric processes cause a production of indirect mutagens, direct acting nitro-PAC and other direct acting mutagens. During long-range transport episodes, the contribution of mutagenic compounds formed by atmospheric processes may be larger than the contribution from direct emissions even in busy streets. The chemical processes cause a depletion in the content of reactive PAH, e.g. benzo(a)pyrene. The application of benzo(a)pyrene as an air quality criteria indicator for the presence of airborne carcinogens is being questioned as well as the results of risk assessments based on concentration differences without taking the impact of atmospheric processes into consideration. Benzanthrone – mutagenic itself, but also the parent compound for the potent mutagen, 3-nitrobenzanthrone [22] – has been demonstrated to be formed in the atmosphere in addition to the direct emissions.

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5 References

[1] Nielsen, T.; Jørgensen, H.E.; Larsen, J.C.; Poulsen, M.; Jensen, F.P.; Jensen, A.B.; Schramm, J.; Tønnesen, J. (1995): Traffic PAH and other mutagens in air in Denmark. Miljøprojekt no. 285. Danish Environmental Protection Agency, Copenhagen, Denmark

[2] Nielsen, T.; Jørgensen, H.E.; Larsen, J.C.; Poulsen, M. (1996): City air pollution of polycyclic aromatic hydrocarbons and other mutagens: Occurrence, sources and health effects. Sci. Total Environ. 189/190 41-49

[3] Nielsen, T.; Pilegaard, K.; Jensen, A.B. (1993): Occurrence and sources of atmospheric polycyclic aromatic hydrocarbons at an international airport. Polycyclic Aromatic Compounds 3 Suppl., 519-526

[4] Nielsen, T. (1996): Traffic contributions of polycyclic aromatic hydrocarbons in the centre of a large city. Atmos. Environ. 30, 3481-3490

[5] Karonis, D.; Lois, E.; Stournas, S.; Zannikos, F. (1998): Correlations of exhaust emissions from a diesel engine with diesel fuel properties. Energy & Fuels 12, 230-238

[6] Westerholm, R.N.; Egeback, K.-E. (1994): Exhaust emissions from light- and heavy-duty vehicles: Chemical composition, impact of exhaust after treatment, and fuel parameters. Envir. Hlth. Perspec. 24, 1179-1186

[7] Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. (1993): Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27, 636-651

[8] Nielsen, T.; Egeløv, A.H.; Granby, K.; Skov, H. (1995): Observations on particulate organic nitrates and unidentified components of NO_y. Atmos. Environ. 29, 1757-1769

[9] Nielsen, T.; P.A. Clausen, P.A.; Jensen, F.P. (1986): Determination of basic azaarenes and polycyclic aromatic hydrocarbons in airborne particulate matter by gas chromatography. Analyt. Chim. Acta 187, 223-231

[10] Maron, D.M.; Ames, B.N. (1983): Revised methods for the Salmonella mutagenicity test. Mutat. Res. 113, 173-215

[11] Strandell, M.; Zakrisson, S.; Alsberg, T.; Westerholm, R.; Winquist, L.; Rannug, U. (1994): Chemical analysis and biological testing of a polar fraction of ambient air, diesel engine and gasoline engine particulate extracts. Envir. Hlth. Perspec. 102, 85-92

[12] Allen, J.O.; Dookeran, N.M.; Smith, K.A.; Sarofim, A.F.; Taghizadeh, K.; Lafleur, A.L. (1996): Measurement of polycyclic aromatic hydrocarbons with size-segregated atmospheric aerosols in Massachusetts. Environ. Sci. Technol. 30, 1023-1031

[13] Bini, G.; Vaio, V.D.; Liguori, E.; Marini, E.; L. Paglia (1998): Carcinogenic agents in the urban environment of Italian cities: benzene and benzo(a)pyrene. Fr. Med. Lav. 89, 177-187

[14] Finlayson-Pitts, B.J.; Pitts, J.N., Jr. (1986): Atmospheric chemistry: Fundamentals and experimental techniques. John Wiley & Sons, New York

[15] de Raat, W.K.; de Meijere, F.A. (1988): The mutagenicity of ambient air particles from local traffic and distant sources during episodes with moderate photochemical air pollution. Sci. Total Environ. 73, 159-179

[16] Nielsen, T.; Platz, J.; Granby, K.; Hansen, A.B.; Skov, H.; Egeløv, A.H. (1998): Particulate organic nitrates: Sampling and night/day variation. Atmos. Environ. 32, 2601-2608

[17] Chen, H.-Y.; Preston, M.R. (1998): Azaarenes in the aerosol of an urban atmosphere. Environ. Sci. Technol. 32, 577-583

[18] Bayona, J.M.; Casellas, M.; Fernandez, P.; Solanas, A.M.; Albaiges, J. (1994): Sources and seasonal variability of mutagenic agents in the Barcelona aerosol. Chemosphere 29, 441-450

[19] Nielsen, T. (1988): The decay of benzo(a)pyrene and cyclopenteno-(cd)pyrene in the atmosphere. Atmos. Environ. 22, 2249-2254

[20] Greenberg, A. (1989): Phenomenological study of benzo(a)pyrene and cyclopenteno(cd)pyrene decay in ambient air using winter summer comparisons. Atmos. Environ. 23, 2797-2799

[21] Matsumoto, Y.; Sakai, S.; Kato, T.; Nakajima, T.; Satoh, H. (1998): Long-term trends of particulate mutagenic activity in the atmosphere of Sapporo. 1. Determination of mutagenic activity by the conventional tester strains TA98 and TA100 during an 18 year period (1974-1992). Environ. Sci. Technol. 32, 2665-2671

[22] Enya, T.; Suzuki, H.; Watanabe, T.; Hirayama, T.; Hisamatsu, Y. (1997): 3-nitrobenzanthrone, a powerful bacterial mutagen and suspected human carcinogen found in diesel exhaust and airborne particulates. Environ. Sci. Technol. 31, 2772-2776

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