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TRANSFORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS
DURING SAMPLING IN AMBIENT AIR BY EXPOSURE TO
DIFFERENTOXIDIZED NITROGEN COMPOUNDS AND OZONE

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 It has been reported earlier that individual PAH can undergo chemical transformation when exposed to gases such as NO₂ and O₃. In this paper the possibility of artifact formation due to such transformations during sampling in ambient air is discussed. Addition of 1 ppm NO₂ or 120 ppb HNO₃ (g) during ambient air sampling caused degradation of reactive PAH on particles and formation of the corresponding mononitro-PAH. The degradation due to NO₂ exposure increased in the presence of acid on the particles. Addition of 100 ppb HNO₂ (g) had not detectable effect.

The results indicate that NO₂ concentrations within the range normally formed in urban air may cause degradation of some reactive PAH.

In the case of O₃ addition (200 ppb), degradation was obtained in one of the experiments only.

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Abstract

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Introduction

The concern about the occurrence of polycyclic aromatic hydrocarbons (PAH) in ambient air has increased during the last few years because of their potential for adverse biological effects. Thus sampling and analysis of airborne PAH have been accomplished all over the world. Together with the chemical analysis the mutagenic activity is often studied using Salmonella bioassays.

During the very last years several papers have been published concerning reactions between individual PAH and gases such as NO_2 , O_3 and SO_3 , e.g. benzo(a)pyrene (BaP) and perylene adsorbed on glass fiber filters form nitroderivatives by exposure to NO_2 and traces of nitric acid (1). In experiments where pyrene and BaP were

exposed to NO, NO₂, SO₂ or SO₃, degradation was obtained with NO₂ and SO₃ (2). It is thus evident that some PAH can react with NO₂ and SO₃ while NO and SO₂ seem to be without effect. Further experiments with BaP exposed to ozone demonstrated the production of directly mutagenic compounds, one of which was later reported to be benzo(a)pyrene-4,5-oxide (3).

The transformation rate has turned out to be dependent on what kind of carrier the individual PAH is adsorbed (2,4,5). Transformation of some of the most reactive PAH may take place during the transport in the atmosphere. As some of the transformation products are direct mutagens, this may explain the reported difference in mutagenic activity between ambient air samples and emission samples (6, 7, 8). On the other hand these reactions may also occur during the sampling and give rise to artifact formation leading to an erroneous conception of the mutagenic effect of the air sample.

In most of the experiments published previously, solutions of pure compounds have been sprayed on filters with or without particles. In this procedure either the whole amount of the compound or an unknown part of it will be in contact with the filter surface (run off effect). In ambient air samples the main part of the PAH collected on filters are adsorbed on particles, and consequently only a minor part will be in direct contact with the filter surface. The method with "spiking" filters is therefore inappropriate for studying sampling artifacts. Another way to obtain informations on sampling artifact processes would be to use different filters simultaneously. This was done by Lee et al. (5). They found that filters of glass fibers and micro glass fibers with Teflon binder

both gave a lower yield of PAH compared with the Teflon membrane filter.

The PAH emitted from incomplete combustion of organic material is formed together with soot and at least some of the PAH will thus be attached to soot particles. Recently, a study was published where soot and PAH were generated by combustion of ethene, transferred to a reaction chamber, and exposed to NO_x , about 10 ppm, during 5-51 days (9). Under these conditions the half-life of benzo(a)pyrene (BaP) was 7 days. Unfortunately, these experiments were carried out in dry air and thus the conditions are not comparable with those of stack gas. NO and NO_2 are acid anhydrides and form HNO_2 and HNO_3 in the presence of water vapour, which seems to play an important role in the degradation of PAH (1, 10).

In another set of experiments a smoke gas generator was adhered to a thermostat oven thus providing a relevant humidity. NO_x and SO_x were added just before the oven. The results indicate that degradation or transformation of reactive PAH take place under certain circumstances and that these reactions may occur during the sampling (11).

A lot of experiments reported so far thus indicate that artifact formation can take place during sampling. For that reason two series of experiments were accomplished: 1.) having the purpose to study the possible occurrence of degradation of PAH and the formation of mutagenic compounds through reactions with NO_2 and O_3 during sampling of particulate PAH from the atmosphere, 2.) investigating the reactions with NO_2 , HNO_2 and HNO_3 . The main purpose this time was to investigate the importance

of the active agent and to identify at least some of the reaction products.

To avoid false carrier effects and other disturbances we found it necessary to accomplish the studies in the way high-volume sampling of atmospheric PAH is usually made. The experiments were therefore carried out outdoors with existing particulate PAH. Two high-volume samplers were run in parallel (24 h sampling). One of them was equipped with different dosage systems which increased the concentration of the actual gas.

Experimental

In the first series of experiments sampling with NO_2 addition (~ 1 ppm) containing probably trace amounts of nitric acid, was carried out for five 24-h periods and with O_3 addition (~ 200 ppb) for three 24-h periods.

The experiments were carried out at an air quality monitoring station in central Göteborg, about 20 m above street level. The concentrations of SO_2 , NO , NO_2 , O_3 , NMHC, as well as some meteorological parameters were measured continuously.

After sampling, the filters were Soxhlet-extracted for 24 hours with acetone. 2-methylanthracene and 1-methylpyrene were added as internal standards and the extracts were diluted with water and shaken with cyclohexane. The cyclohexane phase was then subjected to a liquid-liquid extraction with dimethylformamide (DMF)/water (9:1), and a subsequent backextraction of PAH from the DMF phase by addition of water and cyclohexane. After

concentration the cyclohexane phase was analysed in a Carlo Erba gas chromatograph with a glass capillary column (SE-54). Beside the chemical analysis of the PAH content, additional tests for mutagenic activity in the Ames's Salmonella/microsome test and ability to displace 2,3,7,8-tetra-chlorodibenzo-p-dioxin (2,3,7,8-TCDD) from the rat liver receptor protein were made (12).

In the second serie eight experiments with each gas (NO_2 , HNO_2 and HNO_3) were accomplished. As in the first experiments NO_2 was delivered from a gas cylinder. Gaseous HNO_2 was prepared by adding, slowly and under intense mixing, a dilute solution of NaNO_2 to a dilute H_2SO_4 -solution. Purified air ventilated the reaction vessel continuously and the outlet air stream was mixed with ambient air just before the filter in the sampler. The concentration of gaseous HNO_2 in the total airflow passing through the filter was estimated to be 100 ± 20 ppb, based on experiments in the laboratory using a chemiluminescent detector. In the HNO_3 experiments 20 ml of concentrated HNO_3 was added to a 100 ml Pyrex glas cup placed in a circular acrylic frame, which was attached to the funnel of the high-volume sampler. The vapor pressure of HNO_3 was then sufficient high to obtain a concentration of HNO_3 (g) in the ambient air flow of 120 ± 15 ppb. This concentration was checked in a series of "blanc" experimental runs where a filter with high sampling efficiency of nitric acid were placed in the high-volume sampler instead of the glass fiber filter and then analysed for the nitrate content by ion chromatography. After sampling the filters were extracted separately, but the extracts were combined in order to

facilitate an identification of the reaction products. 12% of each of the combined extracts were submitted to the Ames' Salmonella/microsome test and 6% were used in an analysis of PAH as described above. The remaining 82% were fractionated with HPLC-technique. A Spectra Physics 8700 equipped with a precolumn (12 cm x 4.6 mm) and a preparative column (25 cm x 8 mm) both packed with Spherisorb 5 SP was used. With n-hexane as mobile phase this system gives one PAH-fraction followed by a mononitro-PAH fraction (13).

The individual mononitro-PAH were then identified with GC-MS single ion monitoring technique by means of the retention times.

Results and discussion

The amount and number of PAH detected varied from day to day, but in the first series of experiments eight PAH were found in detectable amounts in all samples. The concentration levels during the period were normal for the city and the time of the year (Table 1). In Table 2 air concentrations of continuously measured substances and the temperature for the sampling period are presented.

We found that the effect of the O_3 addition was rather obscure (Table 3). Degradation occurred in one experiment only. On this occasion the ambient air concentration of NO_x was rather high (Table 2), but since O_3 was introduced very close to the filter only a minor part of the NO in the sampling air could have been oxidized leading to an estimated NO_2 concentration increases from 55 to 75 ppb

in the air sucked through the filter. An elevation in the NO_2 concentration of 20 ppb can hardly cause the degradation of 70% BaP obtained. In the biological tests there was no detectable influence as well (12).

The concentration of individual PAH with and without NO_2 exposure are plotted in co-ordinate systems with the exposed sample on the y-axis and the reference sample on the x-axis. The 1:1 line would be obtained if no reactions took place.

Exposure to 1 ppm NO_2 caused degradation of pyrene (P), benzo(a)pyrene (BaP) and benzo(a)anthracene (BaA) (Figure 1), while phenanthrene (PHE), chrysene/triphenylene (CHR) and benzo(b,j and k)fluoranthenes (BFL) seem to be resistant to chemical degradation (Figure 2). Of the two remaining compounds studied, benzo(e)pyrene (BeP) and fluoranthene (FL), benzo(e)pyrene is classified as medium reactive in electrophilic reactions (10), but any degradation in our experiments is masked by the great diversity of the values (Figure 3).

The increase in mutagenic effect was, on the average, fourfold, while the affinity to the receptor protein was unchanged (12). Thus, it is evident that exposure to NO_2 during sampling can lead to losses of some PAH. Since the losses are not related to any physical properties of the compounds, e.g. vapor pressure and are followed by a significant increase in the Salmonella mutagenicity, the most probable explanation is chemical transformation.

If we assume that the degradation has a first-order dependence on the concentration of NO_2 , the expected degradation at different levels of NO_2 in the atmosphere can be calculated from our data (Table 5). Within the range of NO_2 -concentrations normally formed in urban air (mostly less than 0.2 ppm) (14) the degradation of benzo(a)pyrene during sampling could amount to about 20% or even more under unfavourable conditions.

In the second series of experiments the concentrations of the eight PAH detected were somewhat lower, 0.3 - 3 ng/m^3 . As mentioned above, the filter extracts were combined and another clean-up procedure was used this time. Because of this, the concentrations obtained of individual PAH may be defective. Instead of comparing the concentrations of individual PAH from nonexposed and exposed filters directly, we therefore compared concentrations calculated relative benzo(e)pyrene (BeP), which was found stable throughout the experiments (Figure 4,5,6 and 7). We found that exposure to 100 ppb HNO_2 did not cause any degradation of PAH. The only nitro-PAH found, most probably 9-nitro-antracene, were found in all the other samples as well. Exposure to 1 ppm NO_2 gave rise to a degradation of BaA (20%), BaP (35%) and perylene (35%) and a corresponding formation of 10-nitro-BaA and 6-nitro-BaP (tentatively identified). Some nitro-pyrene was found as well, but no nitro-perylene could be detected.

The most pronounced effect was found in the experiment with HNO_3 . For BaP the loss was about 95% while the concentrations of BaA and perylene decreased with 55% and benzo(g,h,i)perylene with 20%. In the mononitro fraction

four of the corresponding reaction products: 1-nitropyrene, nitrofluoranthene- or pyrene, 10-nitro-BaA and 6-nitro-BaP (tentatively identified) were found.

The chemical changes were in accordance with the results of the Ames' Salmonella/microsome test (15). No effect of exposure to HNO_2 could be detected while both NO_2 and HNO_3 gave an increased number of revertants/ m^3 . The increase was greater in the test without addition of rat liver microsomes which indicates an increase of directly mutagenic compounds, e.g. mononitro-PAH.

It seems clear that exposure to NO_2 and HNO_3 during sampling causes degradation of individual PAH and a corresponding formation of mononitro-PAH. This degradation will probably also take place in the atmosphere during transportation.

Conclusions

Exposure to NO_2 and HNO_3 during sampling will cause degradation of individual PAH. If we assume that the degradation is due to nitration and has a first-order dependence on the concentration of NO_2 , the expected degradation at different levels of NO_2 in the atmosphere can be calculated from our data (Table 4). Within the range of NO_2 -concentrations normally formed in urban air (<0.2 ppm) the degradation of BaP during sampling could amount to 40%.

Acknowledgement

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Table 1.

The concentration of particle-associated PAH in ambient air (ng/m^3). Non-exposed filters.

Compound	1980 February				1980 March			1980 April
	25-26	27-28	28-29	4-5	5-6	26-27	27-28	31-1
Phenanthrene	1.9	1.0	0.48	0.42	1.7	1.1	2.2	1.5
Fluoranthene	22	2.3	1.6	0.64	2.4	2.0	3.4	1.7
Pyrene	8.0	2.9	2.3	1.2	2.5	1.1	3.5	2.1
Benz (a) anthracene	5.2	3.2	3.6	1.8	1.4	1.1	2.0	2.6
Chrysene/Triphenylene	4.0	2.5	2.2	0.8	1.6	0.82	2.0	2.3
Benzo (b, j and k) fluoranthenes	7.8	3.7	4.2	3.7	2.7	1.6	3.7	3.8
Benzo (e) pyrene	3.6	1.1	1.4	0.68	0.89	0.39	0.96	1.2
Benzo (a) pyrene	2.4	0.67	0.88	0.37	0.64	0.17	0.60	0.51

Table 2.

Air concentration of continuously measured substances and temperature for the sampling period.

Date	SO ₂	CH _x	NO _x	NO ₂	Temp.	Number of part. per l of air D = 0.4- 0.6 μm
	ppb	ppb	ppb	ppb	C ^o	
20-21/2	17	370	63	29	- 4.3	23307
21-22/2	47	1089	292	58	- 5.7	24324
25-26/2	44	860	205	55	- 5.2	20488
26-27/2	18	314	46	29	- 2.1	15558
27-28/2	26	739	114	40	- 3.9	21424
28-29/2	25	840	194	53	0.2	9468
4- 5/3	17	-	89	43	- 2.1	2951
5- 6/3	22	-	48	33	0.3	4978
26-27/3	5.3	-	39	31	- 1.7	23920
27-28/3	10	-	30	24	- 0.2	24542
31/3-1/4	29	-	131	55	2.0	24756

Table 3.

Concentrations of particle-associated PAH in ambient air (ng/m^3). Ozon-exposed and non-exposed (reference) filters.

Compound	March 1980 26-27		March 1980 27-28		March-April 1980 31/3-1/4	
	O_3	ref.	O_3	ref.	O_3	ref.
	Phenanthrene	0.73	1.1	2.0	2.2	0.66
Fluoranthene	1.7	2.0	3.6	3.4	2.3	1.7
Pyren	1.5	1.1	3.6	3.4	2.3	1.7
Benzo (a)anthracene	0.93	1.1	2.0	2.0	1.0	2.6
Chrysen/Triphenylene	1.1	0.82	2.1	2.0	1.4	2.3
Benzo (b, j and k)fluoranthenes	2.0	1.6	3.5	3.7	2.7	3.8
Benzo (e)pyrene	0.48	0.39	1.0	0.96	0.88	1.2
Benzo (a)pyrene	0.41	0.17	0.66	0.60	0.16	0.51

Table 4.

Calculated degradation of benzo(a)pyrene and benzo(a)-anthracene during high volume sampling by exposure to different concentrations of nitrogen dioxide at a temperature of -5 to 0°C . For further details, see the text.

Compound	Concentration of NO_2 in ppb	% degraded	
		mean	max
BaP	30	3	7
"	100	10	22
"	200	19	38
BaA	30	2	2
"	100	7	9
"	200	12	17

Figure 1. A comparison of the concentrations of reactive PAH on NO₂ exposed filters and non-exposed filters.

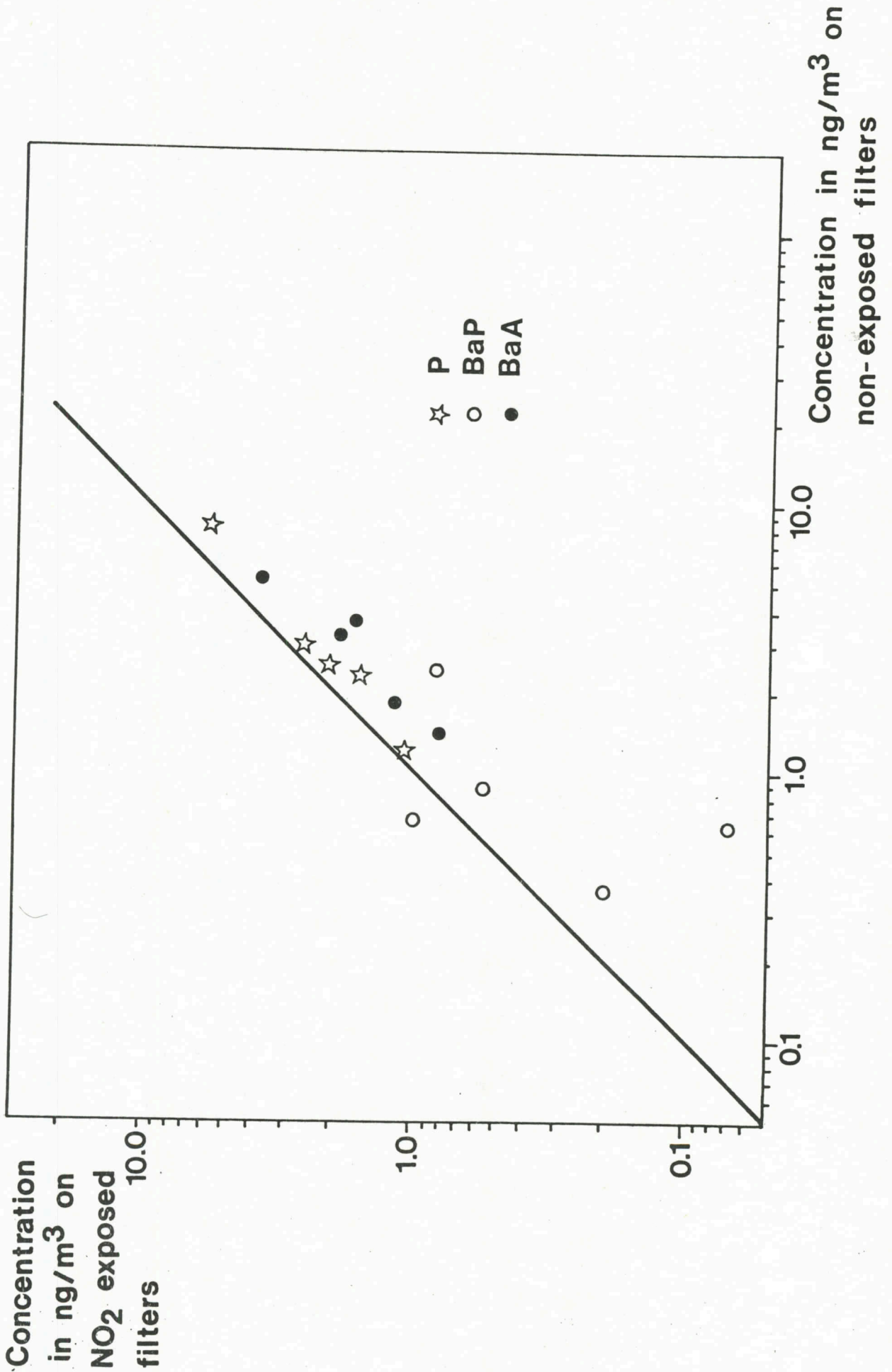


FIGURE 1.

FIGURE 2.

Figure 2. A comparison of the concentrations of low reactive PAH on NO_2 exposed filters and non-exposed filters.

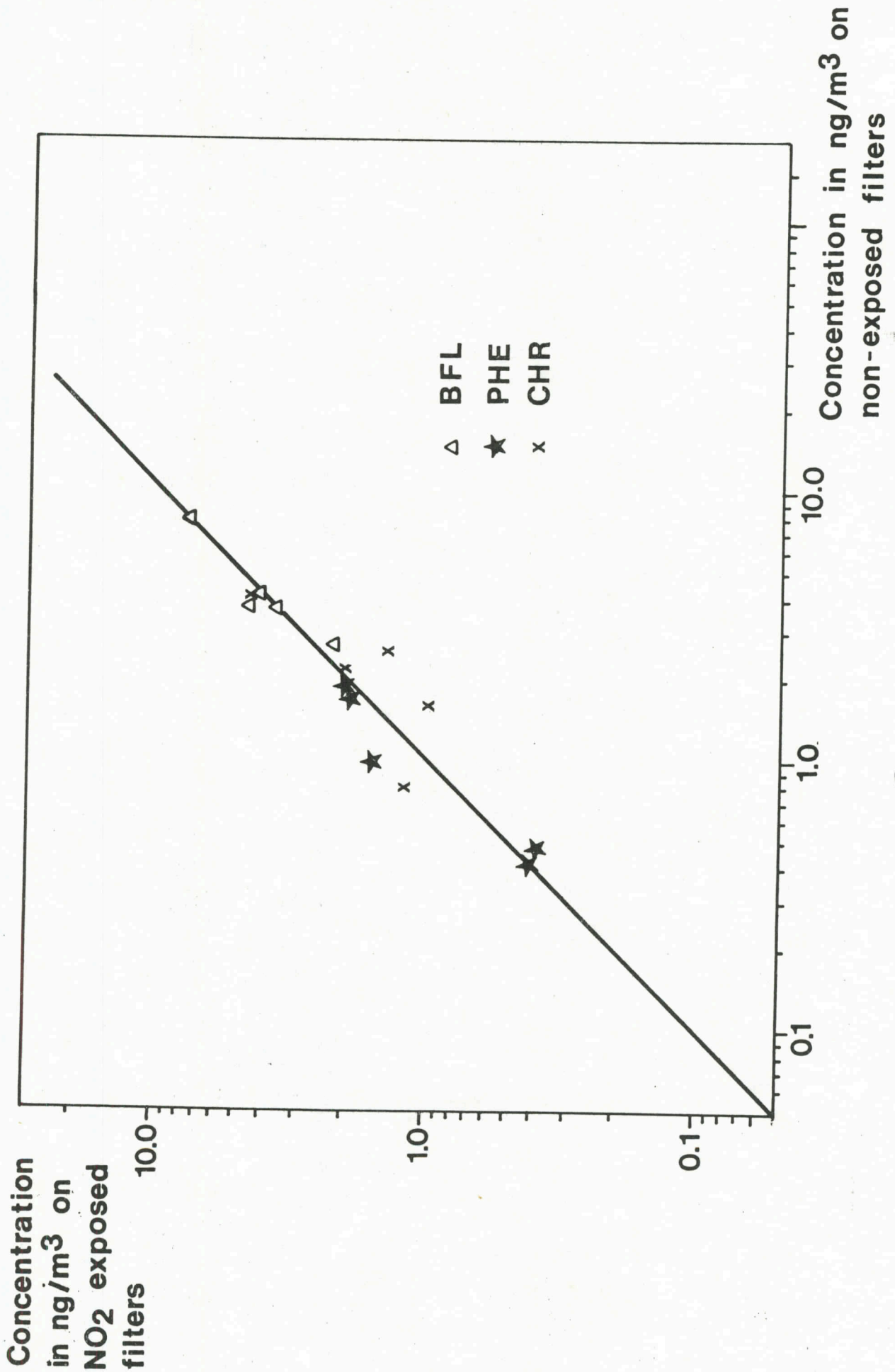


Figure 3. A comparison of the concentrations of medium-active PAH on NO_2 exposed filters and non-exposed filters.

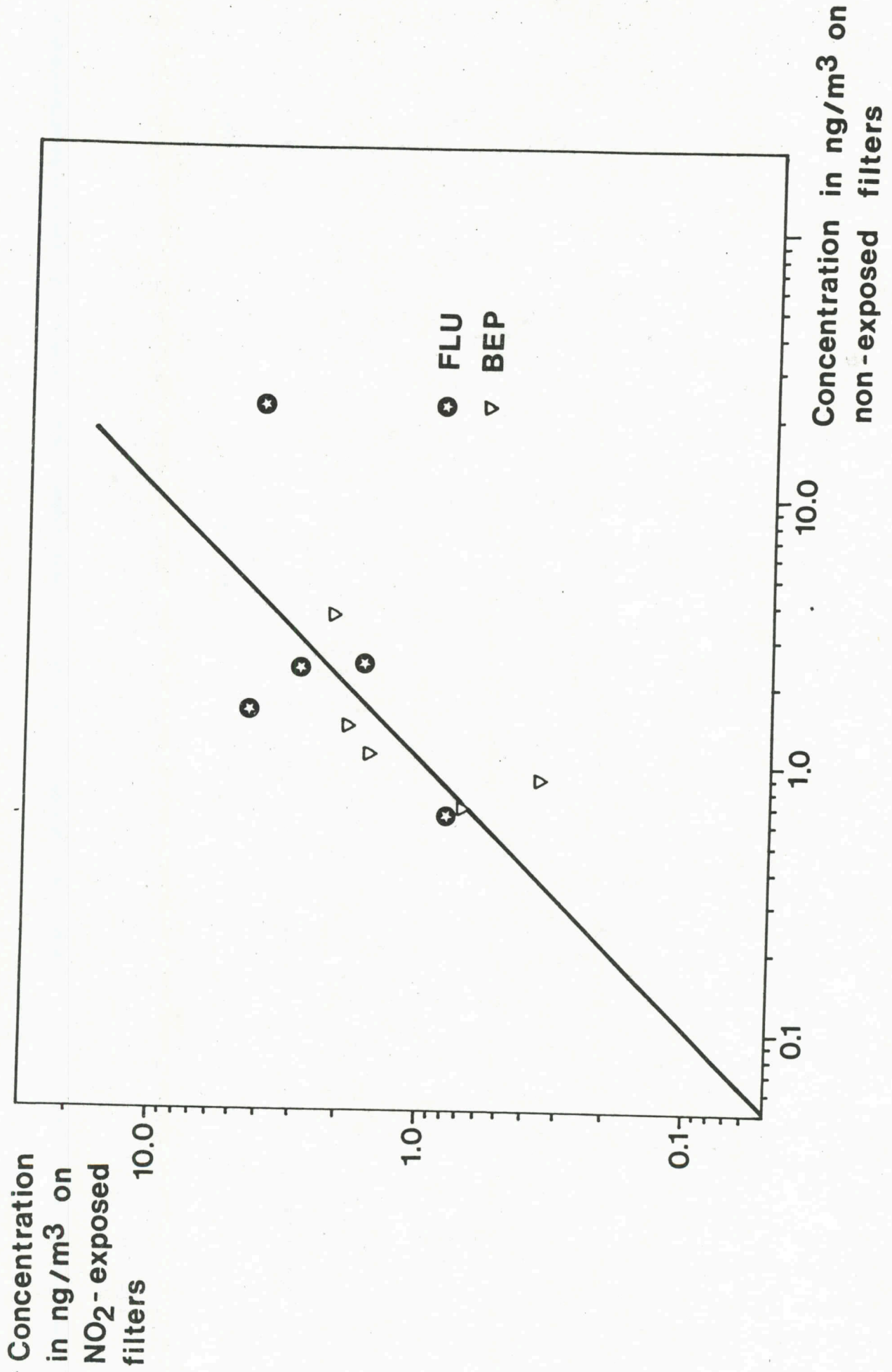


FIGURE 3.

Figure 4. A comparison of the concentration of individual PAH relative to the concentration of benzo(e)pyrene on HNO₂ exposed filters and non-exposed filters.

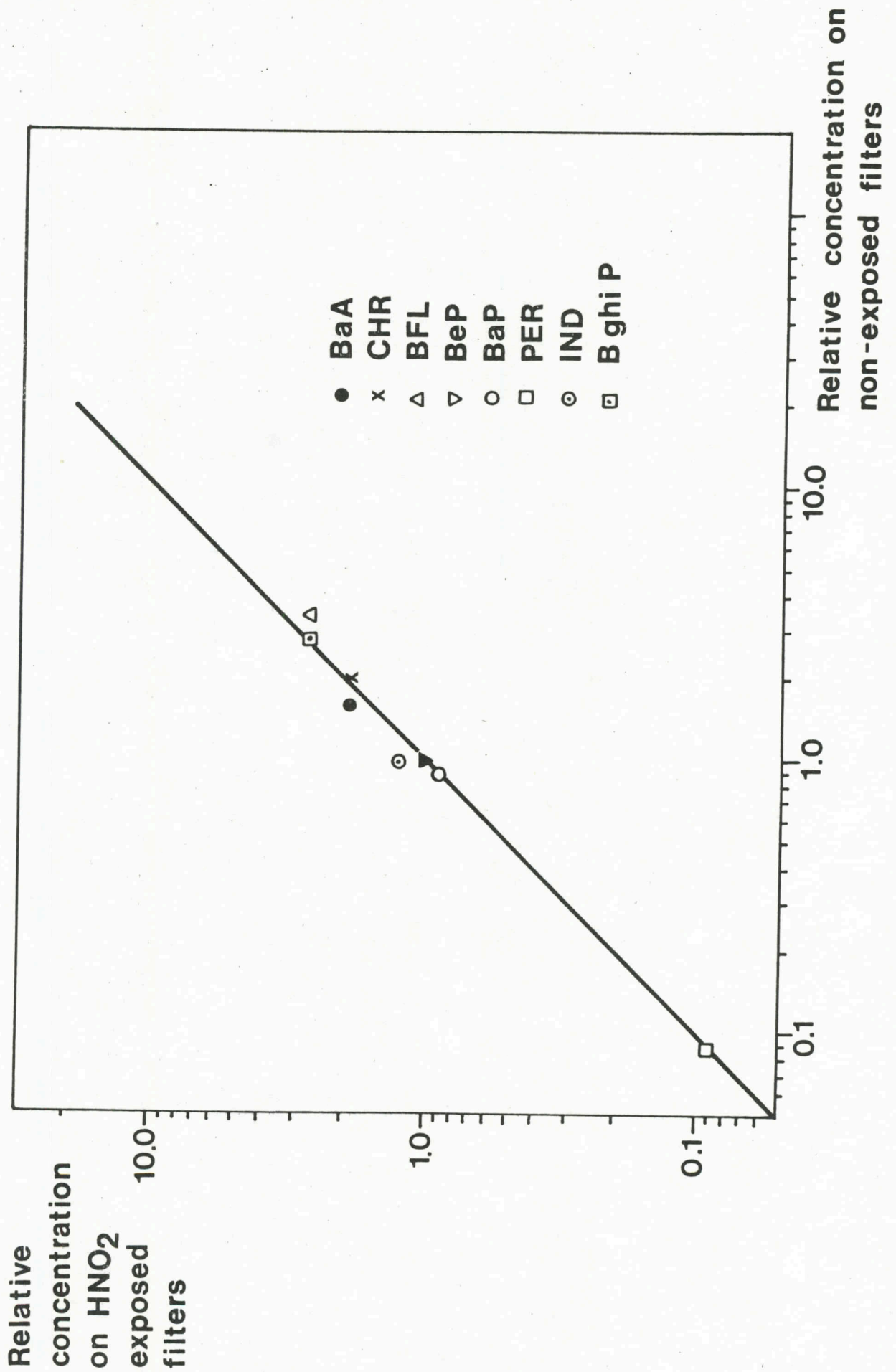


FIGURE 4.

Figure 5. Comparison of the concentration of individual PAH relative to the concentration of benzo(e)pyrene on NO₂ exposed filters and non-exposed filters.

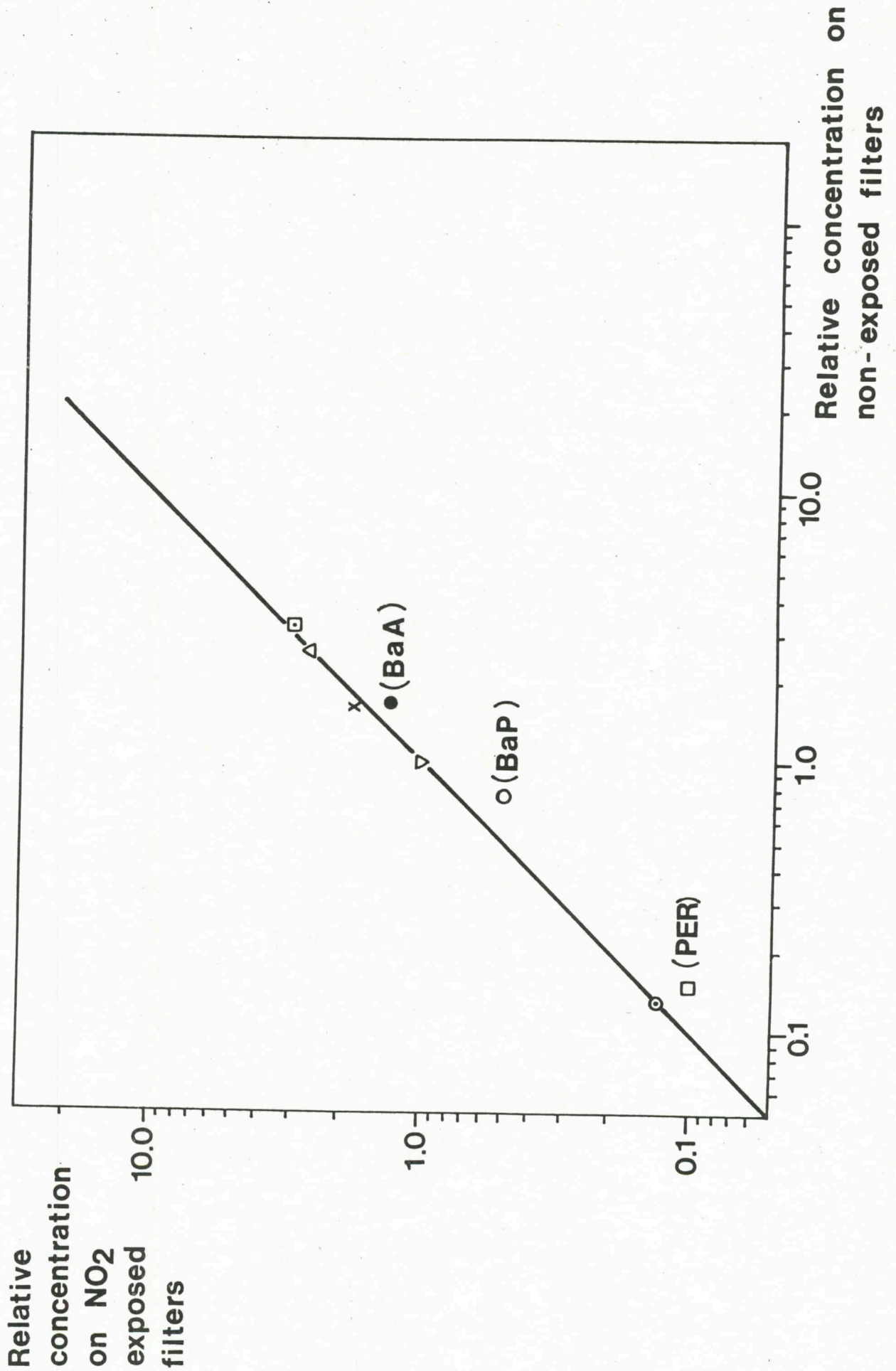


FIGURE 5.

Figure 6. A comparison of the concentration of individual PAH relative to the concentration of benzo(e)pyrene on HNO₃ exposed filters and non-exposed filters.

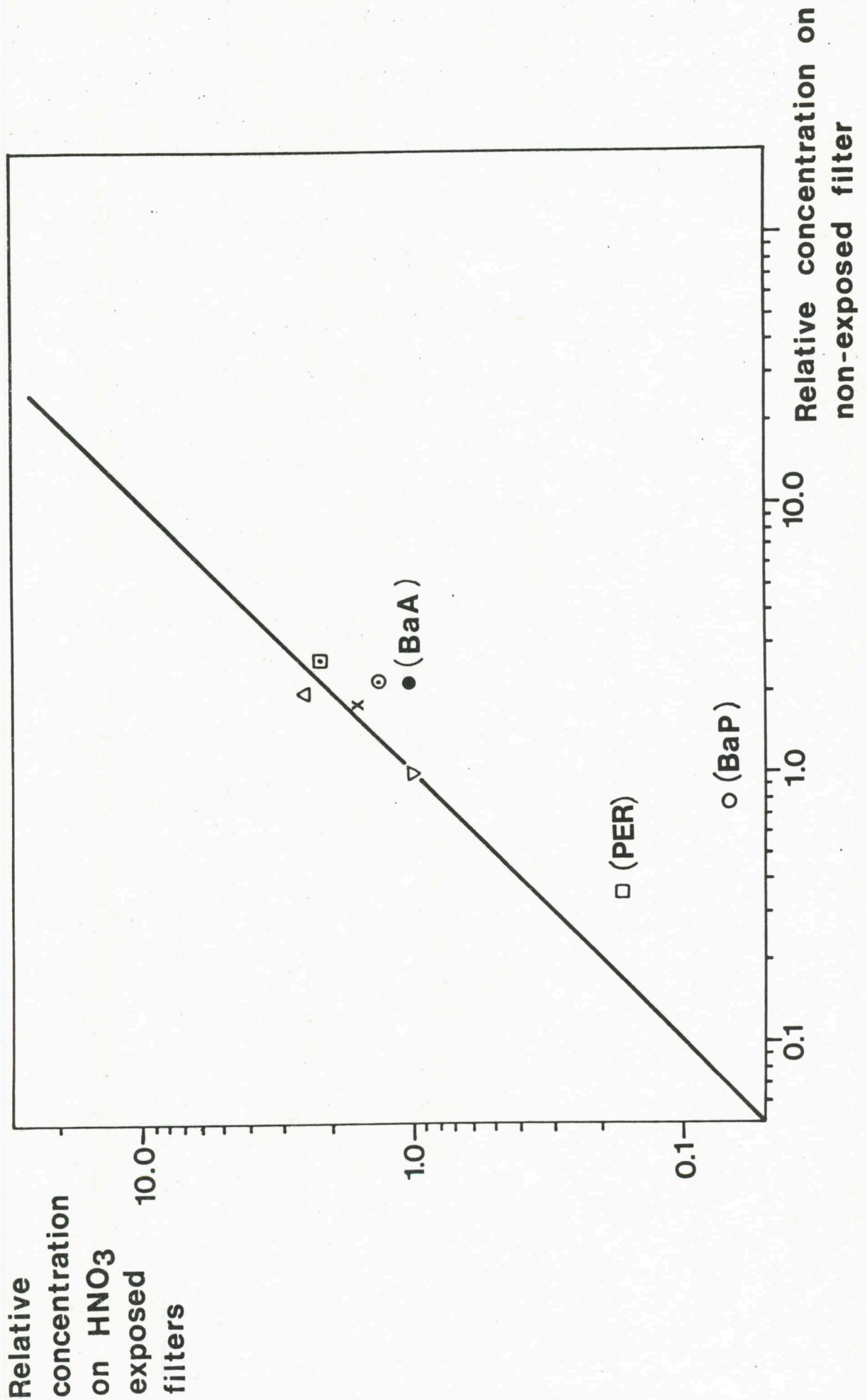
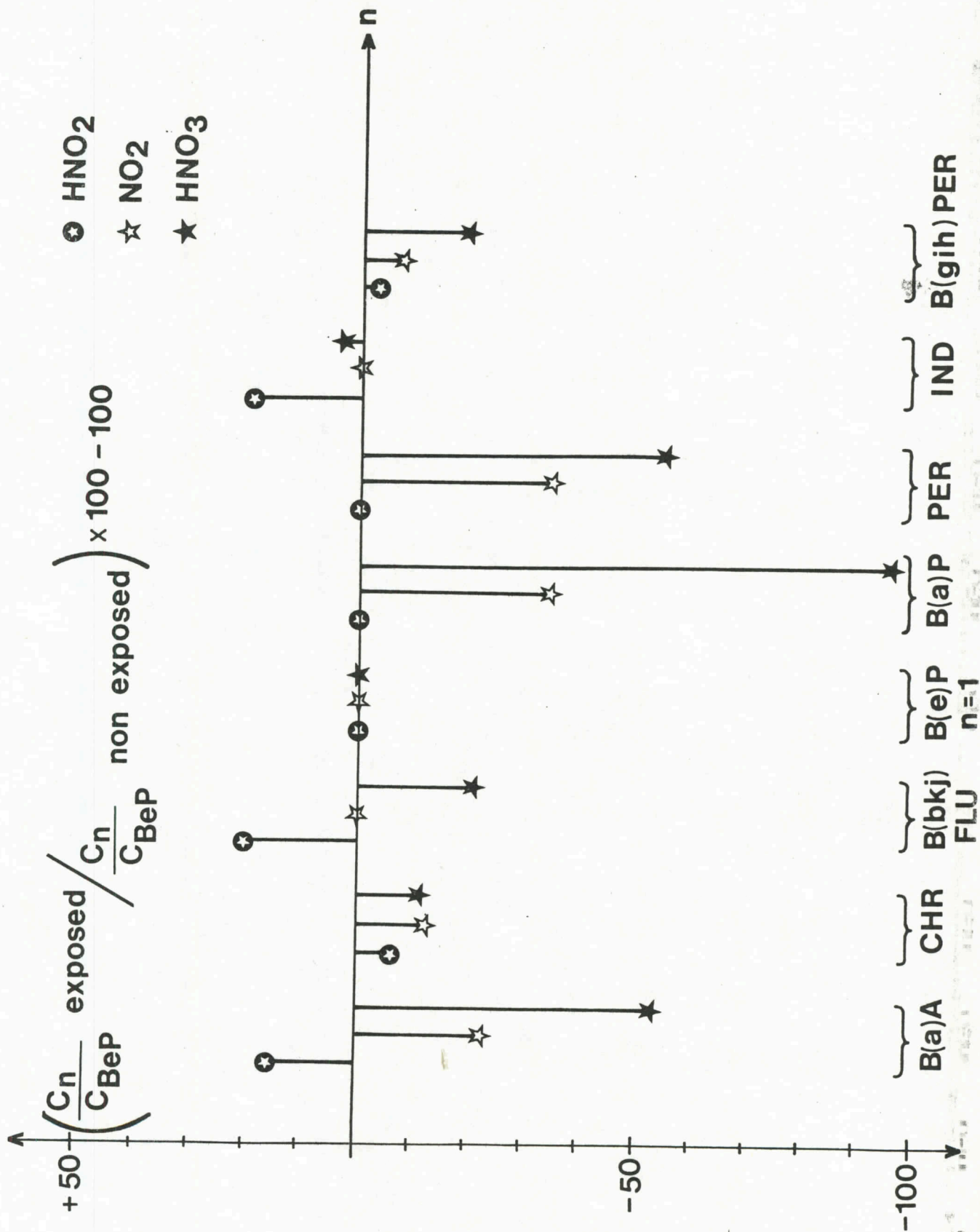


Figure 7. Degradation of individual PAH on exposure to HNO₂, NO₂ and HNO₃



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