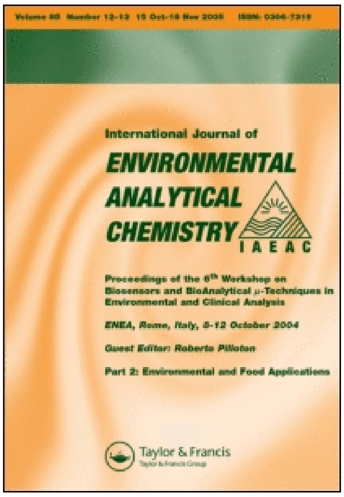

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Desorptivity Versus Chemical Reactivity of Polycyclic Aromatic Hydrocarbons (PAHs) in Atmospheric Aerosols Collected on Quartz Fiber Filters†

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Nine polycyclic aromatic hydrocarbons (PAHs) contained in air samples collected on quartz fiber filters inside an urban tunnel and in a nearby mixed commercial residential area in the city of Rio de Janeiro, Brazil, were exposed to scrubbed air (to measure desorption loss) and to particle-free ambient air (to measure chemical reaction losses in the absence of desorption). The exposures were conducted for 5.5 to 9 hour periods at ambient temperature (22–26°C) at face velocities typical of high volume sampling. Under prevailing atmospheric conditions all nine PAHs experienced filter losses which (for most of them) followed first order kinetics. For the ambient samples, in a 6 hour exposure period, the following five PAHs showed filter losses (%

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in parantheses) attributed exclusively to chemical reaction: benzo(b)fluoranthene (43), benzo(k)fluoranthene (39), benzo(a)pyrene (70), benzo(ghi)perylene (44), and indeno (1,2,3-cd)pyrene (41). The other four showed the following unassigned losses: pyrene (100), fluoranthene (65), crysene (72), and benzo(a)anthracene (71). The results are discussed in the light of possible filter artifacts in PAH sampling and the use of PAH profile signatures for source identification of atmospheric particulate matter in receptor modeling.

KEY WORDS: Polycyclic aromatic hydrocarbons, benzo(a)pyrene, PAH filter losses, PAHs in receptor modeling, atmospheric PAHs.

INTRODUCTION

Thirty two years ago, the atmospheric stability of benzo(a)pyrene was questioned by Kotin *et al.*,[1] in their PAH studies of the Los Angeles atmosphere. Although a substantial body of experimental evidence has been accumulated on chemical reactions and phototransformations of airborne PAHs,[2] relatively few studies have investigated interactions of PAHs with atmospheric pollutants. It has been only in the past eight years, after the elegant work of Pitts and collaborators,[3,4] that the question of atmospheric stability of PAHs has received considerable renewed interest. In general, reported studies dealing with losses of PAHs under atmospheric conditions have not dealt separately the problems of losses due to chemical reactions and of losses due to simple desorption. Assessing the relative importance of these two processes is important (i) for understanding artifact problems associated with PAH sampling, and (ii) for establishing the relative atmospheric stability of PAHs used in receptor modeling.

Profiles of polycyclic aromatic hydrocarbons from various types of combustion processes have the potential of providing signatures for source identification in receptor modeling, provided that their atmospheric reactivity is known.[5] As early as 1962, Sawicki *et al.*,[6] suggested that the ratios of benzo(a)pyrene (BAP) to benzo(ghi)perylene (BGP) and to coronene (COR) could provide possible indicators of air pollution due to automobile exhaust or coal combustion. Chemical element mass balance receptor models employ the characteristic ratio of chemical or elemental constituents emitted from each source to distinguish the relative contributions of each source to the primary aerosol loadings at a downwind receptor site.

In its simplest form, the model assumes that the elements contained in the aerosol at the receptor site are a linear combination of the elements emitted from each source. For nonreactive species the method has been applied with considerable success. However, for reactive species it is necessary to account for the transformations which occur between the source and the receptor sites.

The information required in a chemical mass balance is not the source profile at the point of emission, but rather the source profile as it appears at the downwind receptor site. Whereas elemental profiles are generally conserved during transport in the atmosphere, the polycyclic aromatic hydrocarbons can undergo both chemical reactions and physical transformations. Although PAH profiles can be measured at a source, these profiles can change between the source and receptor sites. To use the PAH source profiles in a mass balance model, it is necessary to assess how the profiles are altered during transport. Specifically, one must determine the relative atmospheric stability of the different polycyclic aromatic hydrocarbons.

In our earlier studies,[7-9] the relative atmospheric stability of PAHs were assessed by exposure of both source and ambient samples to particle-free ambient air. The experimental set up used then did not permit the distinction between chemical reaction and physical desorption losses. The present study was designed specifically to distinguish between these two types of loss mechanisms. The chemical and physical losses experienced in filter sampling may be greater than those which occur in the atmosphere. The mass transfer is enhanced by flow through the filter. Thus, to estabilish the atmospheric stability of the PAH compounds from filtration experiments, it is necessary to distinguish between reactivity and desorption losses.

EXPERIMENTAL SECTION

Experimental design

The objective of this work was to separately determine the contributions of physical desorption and chemical reaction to the loss of polycyclic aromatic hydrocarbons in atmospheric aerosols collected on quartz fiber filters. Aerosol samples were collected on quartz filters, and then subjected to two types of exposure tests, as follows:

1) Samples were exposed to filtered ambient air, from which particles, but not reactive gases had been removed (Figure 1a). The decrease in PAH loadings on the sample filter upon exposure is attributed to chemical reaction if no physical desorption occurs (verified in test 2 below).

2) Samples were exposed to scrubbed filtered ambient air from which both particles and reactive gases had been removed (Figure 1b). The observed PAH losses from the sample filter are attributed to physical desorption alone.

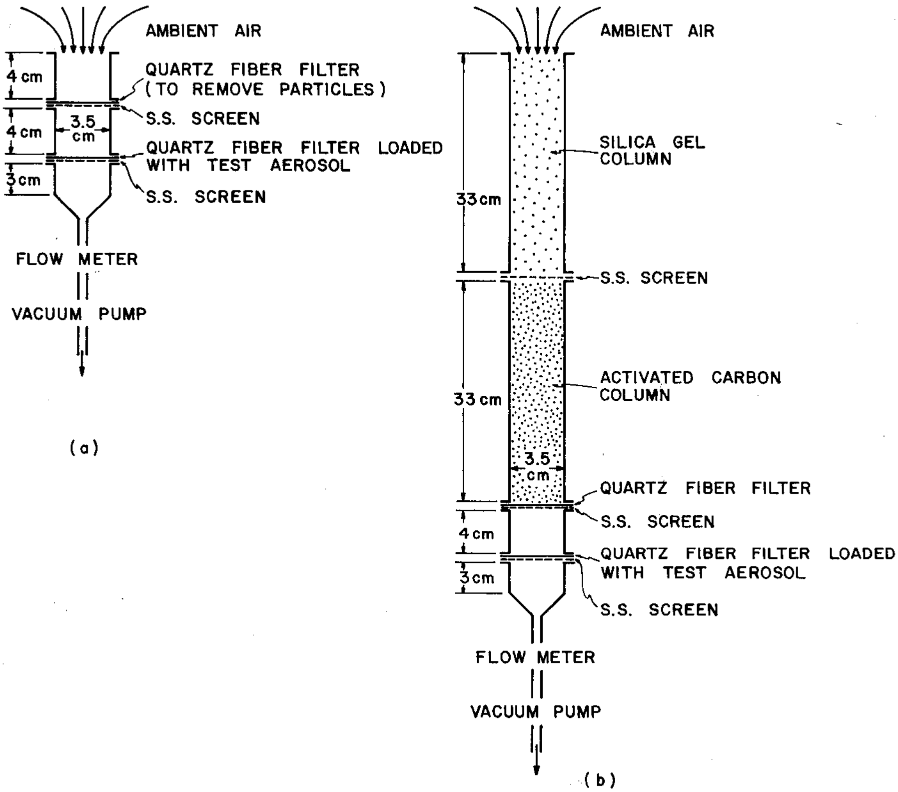

FIGURE 1 Reactor systems utilised in the PAH exposure experiments: (a) for losses due to chemical reaction if no desorption takes place; (b) for desorption only. The systems were built of borosilicate glass. Both the silica gel and the activated carbon were reactivated prior to exposure. Exposures were conducted at ambient temperatures in the range of 25–30°C.

Atmospheric aerosol samples for the exposure studies were collected from an automotive tunnel and from an urban site in the city of Rio de Janeiro. Nine different polycyclic aromatic hydrocarbons were analysed by high pressure liquid chromatography with fluorescence detection. Analyses of small portions of the filter sample taken from different sections of the filter showed that the initial loadings for all nine PAHs on the filter were homogeneous within 9%. This figure also includes analytical uncertainties.

The initial filter samples were split into several smaller sample sections. Half of these were exposed to particle-free ambient air; the other half were exposed to scrubbed ambient air, from which both particles and reactive gases had been removed. Desorptivity exposures of all samples and filtered air exposure of ambient samples were conducted on the 5th floor of the Chemistry Department Building at PCU, located in a residential area of Gavea in the city of Rio de Janeiro, approximately 2 Km to the north of the Atlantic Ocean. For the tunnel sample, exposure to particle-free air was conducted approximately 3 m above the ground on a busy intersection of a mixed residential-commercial section of São Cristovão, typical of many in the city of Rio de Janeiro. Every few hours during the exposure, one of the sample sections was removed for analysis while the other sections continued to be exposed. In this way the loss of PAHs from the filter sample was determined as a function of time for exposure to both particle-free and scrubbed ambient air.

Sample collection

All samples were collected with a General Metal Works Hi-Vol sampler, at a flow rate of 1.12 m 3/min (40 CFM), using 8″ × 10″ quartz fiber filters (type 2500QA0W/D2) from Pallflex (Putnan, CT). The mass of collected aerosol was determined gravimetrically. Immediately after collection, the filters were wrapped in aluminum foil, equilibrated, weighed and stored in a freezer.

An automotive TSP source sample was collected inside the Santa Barbara Tunnel, in the city of Rio de Janeiro. The tunnel is 1.3 Km long, and carries four lanes of traffic, two in each direction. The sampler was located about 340 m from the south exit of the tunnel, approximately 1 m above the ground. Sample collection time was 75 min. The temperature during collection was 31 ± 1°C.

An ambient TSP sample was collected during the day from 7.00 hrs to 19.00 hrs at the mixed residential-commercial site described above. During the collection period the temperature varied between 19°C and 22°C.

PAH analysis

An aliquot of 10.6 cm^2 of the filter was extracted ultrasonically in a 25 mL erlenmeyer with approximately 8 ml of HPLC grade acetonitrile (McCN) for 10 min. The extract was filtered using a double sheet of Whatman No. 40 filter paper. The sample filter, which remained in the erlenmeyer, was washed twice with new portions of MeCN. The extracts were combined and evaporated to about 7 mL by passage of a gentle stream of nitrogen gas at room temperature. The extract was then transferred to a 10 mL volumetric flask and the volume adjusted with MeCN for direct analysis by HPLC. The separation was done using a 15 cm × 4.6 mm Supelcosil LC-PAH C18 (5 μm) column using MeCN and water (40% to 100% MeCN in 20 min, held at 100% MeCN for another 5 min), at 0.9 mL/min. Fluorescence excitation and emission wavelengths were 250 and 370 nm, respectively. NBS Standard Reference Material No. 1647 was used for instrument calibration and No. 1649 was used as a positive control. Ten PAHs determined in SRM No. 1649 using this method were, on average, within ±5% of NBS values. Full details of the HPLC procedure and results of SRM and ambient samples are in preparation.[10]

RESULTS AND DISCUSSION

The results from the exposure studies are presented in Figures 2–4. The PAH losses from exposure to filtered, scrubbed ambient air are presented by the solid circles. The losses from exposure to ambient air which had only been filtered are shown by the open circles. The data are presented in terms of the mass of PAH left on the filter, divided by the volume of air sampled during the original collection. The values are the apparent PAH loadings after filter exposure.

The PAHs are classified into three groups on the basis of their desorption characteristics (solid circles). We find significant desorp-

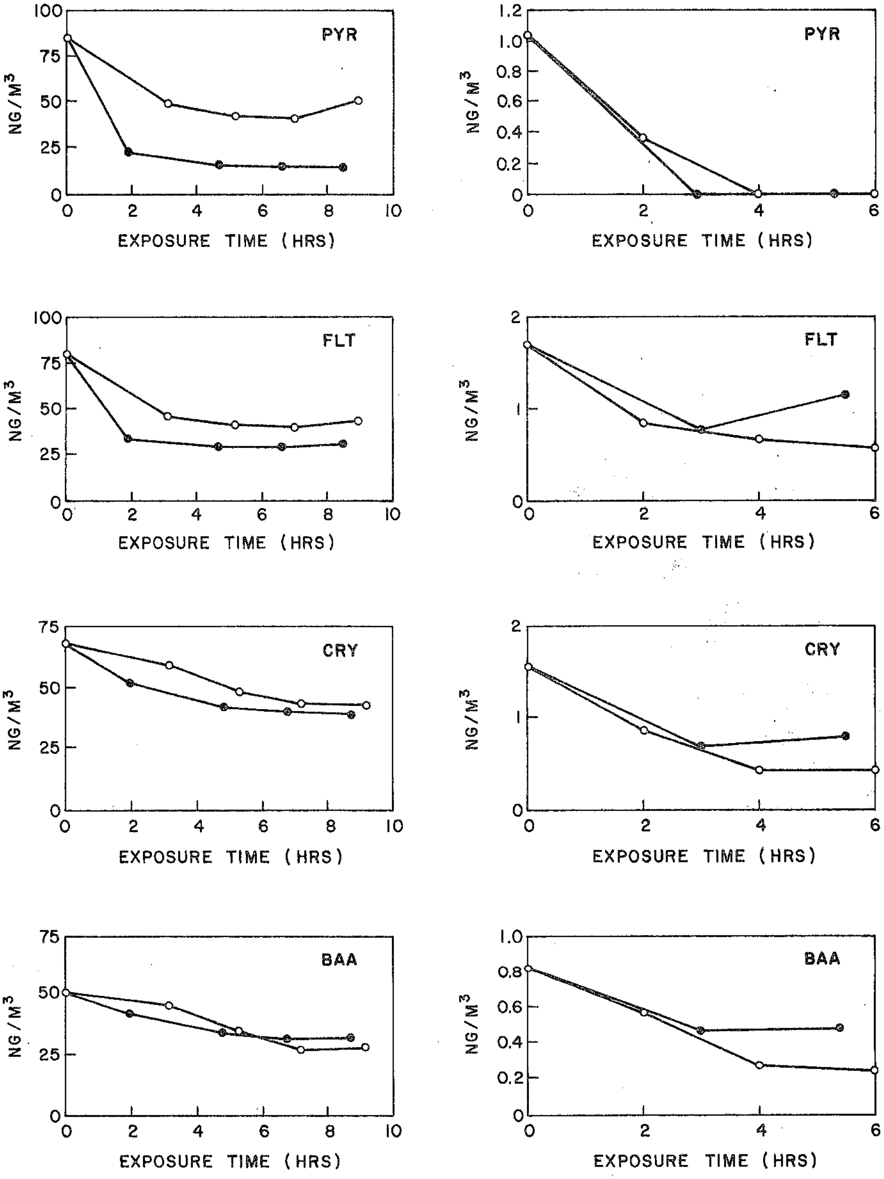

FIGURE 2 Dependence of initial PYR, FLT, CRY and BAA concentration on exposure time. Open circles denote losses due to chemical reaction and desorption. Closed circles denote losses due to desorption alone. Results obtained with the tunnel and the ambient sample are on the left and right columns, respectively.

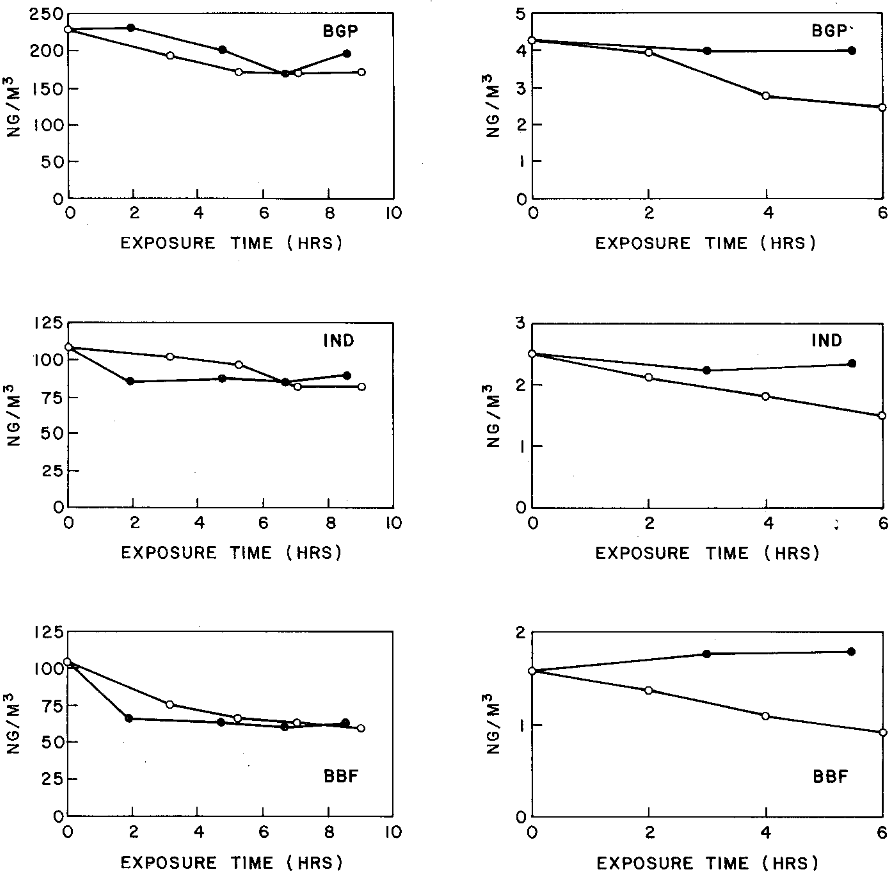

FIGURE 3 Dependence of initial BGP, IND and BBF concentration on exposure time. Open circles denote losses due to chemical reaction and desorption. Closed circles denote losses due to desorption alone. Results obtained with the tunnel and the ambient sample are on the left and right columns, respectively.

tion losses for pyrene, fluoranthene, crysene and benzo(a)anthracene (Figure 2). Losses are 32% to 100% after 5.5–8.6 hours of exposure (Table I). Greatest losses are seen for pyrene. The second group, which includes (benzo(ghi)perylene, indeno(1, 2, 3-cd)pyrene, and benzo(b)fluoranthene, show desorption losses for the tunnel sample, but not for the ambient sample (Figure 3). Losses for this group are up to 39% after the maximum exposure period. For

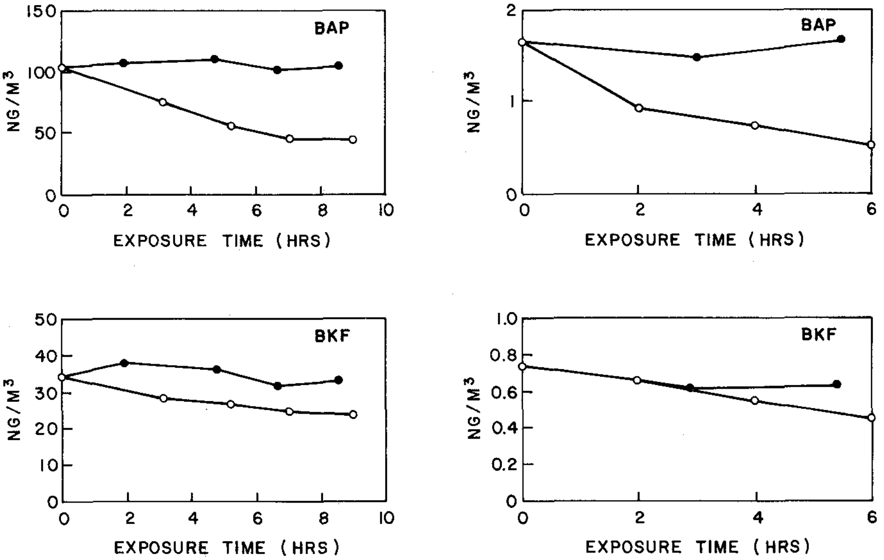

FIGURE 4 Dependence of initial BAP and BKF concentration on exposure time. Open circles denote losses due to chemical reaction and desorption. Closed circles denote losses due to desorption alone. Results obtained with the tunnel and the ambient sample are on the left and right columns, respectively.

benzo(b)fluoranthene a net gain of 13% was actually observed (Table II). Considering the overall 9% accuracy in these experiments, it is reasonable to assume that no loss was observed for this PAH under the experimental conditions employed. The polycyclics from the third group, benzo(a)pyrene and benzo(k)fluoranthene show no significant desorption.

The chemical reactivity is most pronounced for benzo(a)pyrene (BAP). For the tunnel and ambient samples, the BAP losses due to chemical reactivity after 5.5 and 8.6 hours of exposure were, respectively, 57% and 70% (Table I). The losses follow first order reaction kinetics as shown in Figure 5. The "apparent" half-life times for both the tunnel and ambient samples are 5.7 hrs and 3.6 hrs, respectively. These half-life differences may result from (i) differences in the initial PAH loadings of the sample filters and, especially (ii) differences in the reactivity and temperature of the ambient air used to expose the filters. For example, in separate exposure experiments (not reported

TABLE I

PAH losses observed upon exposure to scrubbed and to filtered ambient air (%). Average sampling flow rate: 1.1 m^3/min. Temperature range during exposure: 24 ± 2°C.

	Tunnel sample		Ambient sample	
	Scrubbed air	Filtered air	Scrubbed air	Filtered Air
	(Desorption)	(Reaction and desorption)	(Desorption)	(Reaction and desorption)
PAH				
FLT	−61	−45	−32	−65
PYR	−83	−41	−100	−100
BAA	−37	−45	−42	−71
CRY	−44	−39	−50	−72
BBF	−39	−43	+13	−43
BKF	−2	−30	−15	−39
BAP	+1	−57	+1	−70
BGP	−15	−25	−27	−44
IND	−18	−25	−6	−41
E.P.	8.6	9	5.5	6

Plus signs represent apparent gains.
E.P. = exposure period in hours.
FLT = fluoranthene; PYR = pyrene; BAA = benzo(a)anthracene; CRY = crysene; BBF = benzo(b)fluoranthene; BKF = benzo(k)fluoranthene; BaP = benzo(a)pyrene; BGP = benzo(ghi)perylene; IND-indeno(1, 2, 3-cd)pyrene.

TABLE II

Apparent half-life times (τ) and correlation coefficients (r^2) obtained from first order kinetic plots

	Tunnel sample			Ambient sample			E.V.C.[a]
PAH	τ (hrs)	r^2	comments	τ (hrs)	r^2	comments	(ng/m^3)
FLT	7.1	0.86	R & D			m.o.k.	
PYR	6.5	0.89	R & D			m.o.k.	74,000
BAA	7.8	0.92	R & D	3.1	0.94	R & D	1,050
CRY	10	0.97	R & D	2.1	0.99	R & D	
BBF	9.5	0.94	R & D	7.3	0.99	R only	
BKF	15	0.97	R only	8.2	0.98	R only	16
BAP	5.7	0.99	R only	3.6	0.97	R only	85
BGP	16	0.96	R only	6.7	0.95	R only	1.6
IND	19	0.87	R only	8.1	0.99	R only	

[a] R = reaction; D = desorption; m.o.k. = mixed order kinetics.
[a] E.V.C. = equilibrium vapor concentration at 25°C (Ref. 15).

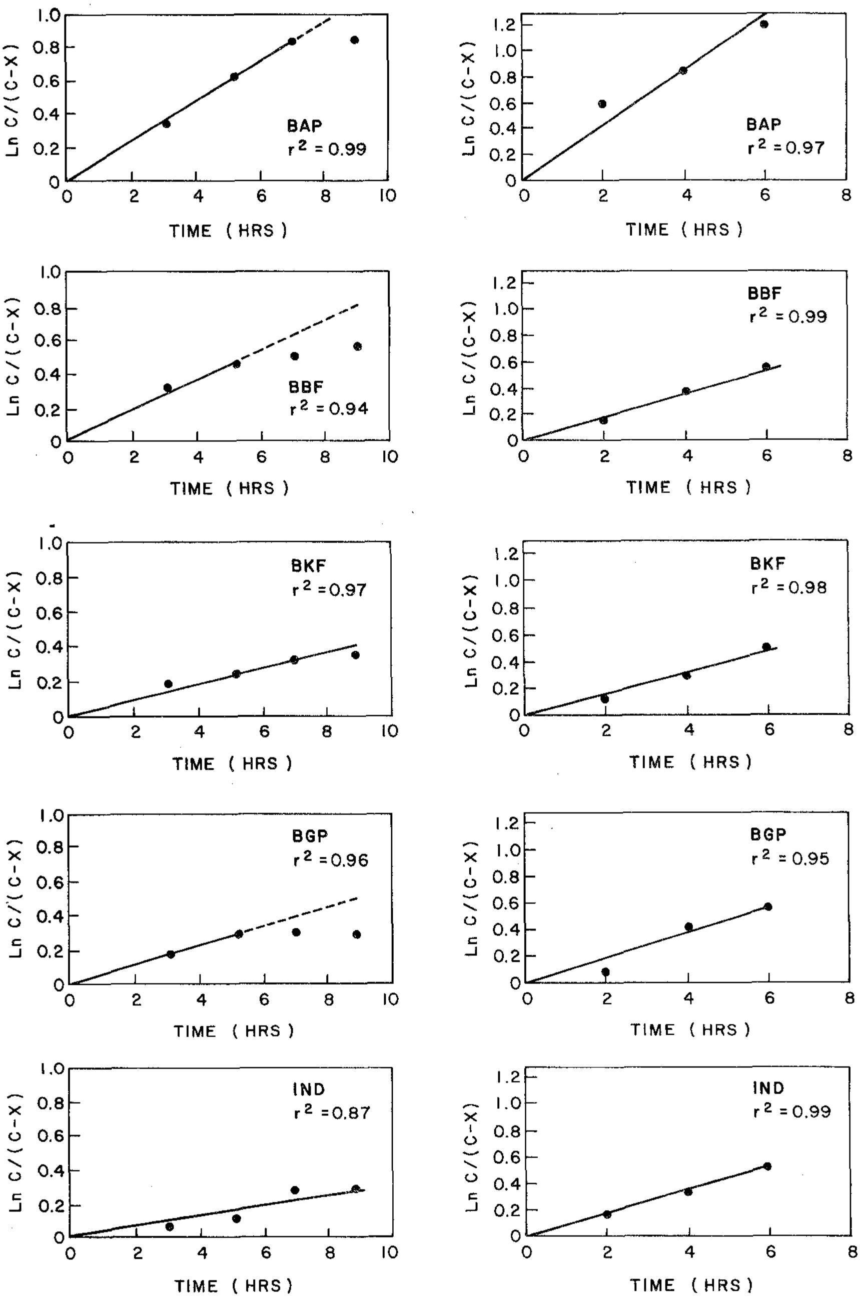

FIGURE 5 First-order tests for the losses of BAP, BBF, BKF, BGP, and IND resulting from the exposure of the tunnel sample (left column) and the ambient sample (right column) to ambient air at room temperature (25–30°C).

here) conducted at the same sites, using both tunnel and ambient samples, half-life times between 5.8 hrs and 9.5 hrs were observed for this PAH. Earlier exposure experiments reported for the same site (at PCU/RJ) showed BAP half-life times of 3 days for ambient samples exposed to ambient air.[7] These large variations in half-life times of aerosols collected within the same city at different times indicate high variation in the constitution of reactive gaseous atmospheric pollutants. For example, Grosjean *et al.*,[11] found no evidence of filter loss when PAHs were exposed in the dark to particle-free ambient air in Camarillo, California. Peters and Seifert[12] detected substantial losses for labelled BAP deposited on high volume filters exposed to ambient air in Berlin, Germany. Significant conversion was observed for several diesel exhaust PAHs when exposed to particle-free air containing ppm levels of ozone in Belgium.[13]

For the benzo(k)fluoranthene in the tunnel sample (Figure 4) and the benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene and benzo(ghi)-perylene in the ambient sample (Figure 3) some chemical reactivity is observed, but it is not as significant as for BAP.

The first group of PAHs, shown in Figure 2, are dominated by desorption losses. For a reactive species such as BAP the losses from the filter are less (negligible) when exposed to scrubbed filtered air than when exposed to air which has only been filtered. For the pyrene, fluoranthene, crysene and benzo(a)anthracene in the tunnel sample, the opposite effect is observed. Losses are greater when exposed to filtered, scrubbed air than when exposed to the filtered air. This suggests that a significant fraction of these PAHs exist in the gas phase. At ambient temperature levels, substantial amounts of three- to five-ring PAHs were found in the vapor phase in Japan,[14] whereas six-ring PAHs were found only in the particulate phase. In fact, two of them PYR and BAA have reported equilibrium vapor concentration (E.V.C.)[15] of 74,000 and 1,050 ng/m^3, respectively, at 25°C (Table II). The reported E.V.C. for PAHs included in the remaining PAH groups are between one and four orders of magnitude smaller (Table II). Our desorptivity observations are consistent with these reported E.V.C.

A number of studies have reported on gas-phase concentrations of several PAHs, the most recent one been that of Thrane *et al.*,[16] for samples collected in Norway. The changes in PAH masses on the filter are controlled by a continual adsorption and desorption from the loaded filter. It is important to observe that, for group one PAHs (Figure 2), losses due to desorption were greater than the combined effects of desorption and chemical reaction. This apparent anomaly results from the fact that our desorption experiments were carried out under non-equilibrium conditions, i.e., all of the vapor-phase PAHs were removed from the the ambient air prior to exposure of the filters containing particulate-phase PAHs.

As pointed out in the introduction, the use of PAH profiles as signatures for source identification in receptor modeling requires knowledge of their relative stability. The experimental arrangement described permits the evaluation of choice PAHs for successful source apportionment. Of all nine PAHs studied in the present study, based on filter loss considerations, the following three are suggested for use in receptor modelling: indeno(1, 2, 3-cd)pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene. If PAH ratios are to be used instead of concentrations, care should be exercised to select PAHs which have approximately the same half-life times.

CONCLUSIONS

The experimental protocol described permits a separate evaluation of the extent of PAH desorption and chemical reaction taking place on a filter surface under the conditions of hi-vol sampling. The following PAHs did not show significant desorption from the filter upon exposure to scrubbed ambient air: benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, and indeo(1,2,3-cd)pyrene. For an ambient and a tunnel sample, their chemical reaction half-life times ranged between 3.6 hrs to 19 hrs. For pyrene, fluoranthene, crysene and benzo(a)anthracene, due to their fast desorption from the filter, it was not possible to separately evaluate their chemical reactivity. Benzo(b)fluoranthene showed a mixed behaviour: it did not desorb from the ambient sample, whereas about 38% of its mass was desorbed from the tunnel sample in the first two hours of exposure.

Based on the results obtained in this study we suggest that pyrene, fluoranthene, crysene, benzo(a)anthracene, benzo(a)pyrene and perhaps benzo(b)fluoranthene should be avoided as compounds of choice in source profile signatures for receptor modeling of carbonaceous species. The best choices are: indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene.

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