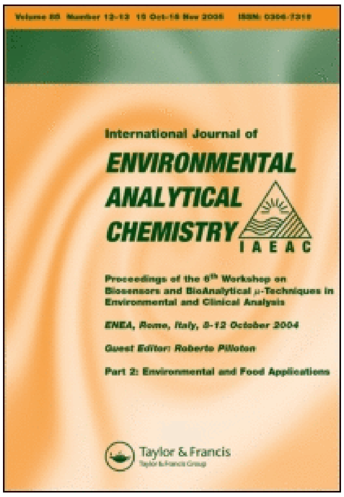

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Photochemical Degradation of Polycyclic Aromatic Hydrocarbons (PAH) in Real and Laboratory Conditions†

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Studies were carried out on the effects induced by the main components of airborne particulate matter (APM) as soot, inorganic and cyclohexane soluble substances and by glass fiber filters on photodegradation of pyrene, benz(a)anthracene and benzo(a)pyrene exposed to UV and solar radiation. In both experimental models tested hydrocarbons showed a higher photochemical stability when absorbed on APM. Inorganic components of APM slightly enhance UV photodegradation. In real condition (outdoor exposure to solar radiation) PAH half lives generally showed a good linear correlation with mean solar radiation intensity; only degradation rate of benzo(a)pyrene on APM, exposed to sunlight was practically constant. Pyrene, in particular, showed a higher degradation rate when high ozone concentrations (0.2 ppm) occurred.

KEY WORDS: Photodegradation, pyrene, benz(a)anthracene, benzo(a)pyrene, absorbing substrates.

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INTRODUCTION

Polycyclic aromatic hydrocarbons are compounds produced by pyrolysis of organic substances present in urban atmosphere, where they are mainly absorbed on airborne particulate matter (APM).

The last few years registered a growing interest about the degradation mechanism of PAH that may occur in the atmosphere, because some degradation products may be more mutagenic and therefore potentially more dangerous for human health than parent PAH.[1,2]

Recent reviews[3-6] emphasised the complex mechanisms involved.

According to experimental results, PAH degradation appears to depend on several physical and chemical parameters such as, spectral composition and intensity of light, composition and physical characteristics of adsorbing matter (specific surface, particle size, humidity content) and also on the presence and concentration of reactive gases (NO_x, O_3). Degradation studies of PAH were carried out using various adsorbing matrices (silica gel, alumina, glass fiber, soot, fly ash etc.). PAH appear to be more stable when adsorbed on soot and particularly on fly-ash; in this case the suppression of photochemical photodegradation of PAH has been tentatively explained by the role of transition metal ions at the surface in quenching excited states formed upon irradiation.[7]

By using a simple experimental model that approaches real conditions (APM as absorbing substrate, irradiation by sunlight, amounts of spiked PAH on adsorbing matrix comparable to those found in heavily polluted areas) we obtained preliminary informations about the role of some components of APM, as soot, inorganic and cyclohexane soluble matter, in the photodegradation of pyrene (PY), benz(a)anthracene (BA) and benz(a)pyrene (BaP) exposed to UV radiation and directly to sunlight in a real urban atmosphere.

METHODS

Particulate sampling

Two samples of APM were collected in an urban area by a high volume sampler on glass fiber filters (Gelman type A/E), fired at 400°C for 1 hour before use. Sampling was carried out for 72 hours to have a high filter loading in order to minimize interferences induced by glass fibers. About 6000 m^3 of air were filtered and filter loading resulted in 0.95 and 0.99 mg/cm^2.

The first filter was used for UV exposure, the second one for solar radiation exposure.

Preparation of absorbing substrates

Using a hollow punch, disks (2 cm in diameter) were cut from the dust-loaded filters and from a clean one.

Disks with APM were divided into three groups:

1) untreated;
2) fired at 400°C for 1 hour;
3) extracted with cyclohexane by soxhelet for 12 hours.

These samples and those obtained from the clean filter were spiked (under N_2 and operating with a red light) with 50 μl of benzene containing 0.9 μg of PY, 0.5 μg of BA and 0.7 μg of BaP in UV exposure experiment. In solar radiation exposure the used quantity of PAH was 2.1, 2.0 and 2.2 μg, respectively.

Exposure to UV radiation

After solvent evaporation, spiked filters (two filters for each sample type) were exposed to UV rays produced by a 15-watt unfiltered quartz lamp. After 80 and 160 min of exposure, samples were removed and extracted. A set of unexposed spiked samples was used as control.

Exposure to solar radiation

A set of each substrates spiked with PAH was placed on an horizontal surface on the roof of our Institute. Exposure occurred from 10 a.m. to 1 p.m. During this period, solar radiation intensity was monitored using a Kipp and Zonen solarimeter connected to a Sigma 10 integrator. Mean solar radiation intensity was expressed as counts of area per minute. In the first exposure hour, ozone concentration was monitored using the colorimetric alkaline KI method suggested by NIOSH (method *n*: P & CAM 154). For every exposure a set of unexposed spiked samples was used as control.

Eleven measure sets were carried out from September to October 1984 in different meteorological conditions.

Extraction and analysis (UV)

1 + 1 ml of methanol were added to samples, which were shaken by vortex for 2 minutes. Solution was filtered by a Teflon filter (millipore, Type FH, 0.5 μ pore diameter) and PAH concentration was evaluated by High Liquid Pressure Chromatography (Table I). This method was repeated twice for each sample type.

TABLE I
Characteristics of HPLC analysis

Instrument	Gynkotec Mod. 600 (Hoechst, Italy)
Column	Glass, length: 30 cm
Packing	Silica gel 60, C 18, diam. 10μ
Solvent	CH_3—OH, H_2O (95:5)
Flow	1 ml/min
Detector	Fluorescence Spectromonitor Shimazu-RF-530 (Hoechst, Italy) Ex: 292 nm Em: 389 nm

Samples of untreated airborne particulate matter showed no appreciable amount of naturally occurring PAH both in HPLC and GLC analysis.

Extraction and analysis (Solar radiation)

Each sample was placed into a conical vial, added with 1.5 ml of cyclohexane and with 1 μg of tryphenyl benzene as internal standard. Samples were sonicated in a water bath for 5 minutes. The solvent was transferred to another vial. The extraction by sonication was repeated twice using 1 ml of cyclohexane. The collected fractions were evaporated to dryness with N_2. Residues were solved with 50 μl of benzene and analysed by Gas Liquid Chromatography (Table II).

RESULTS

UV exposure

PAH concentration decreased at different rates in all samples after

TABLE II

Characteristics of GLC analysis

Instrument	Perkin Elmer 990
Column	Glass, i.d. 2 mm, length 1.82 m
Liquid phase	2.5% SP-301 on 100–120 mesh Supelcoport
Temperatures	Column 270°C, injector 280°C, detector 280°C
Carrier	Helium, 20 ml/min
Detector	FID
Integrator	Perkin Elmer Sigma 10

TABLE III

Half-life of PAH adsorbed on different surfaces and exposed to UV lamp

	Half-life (min)[e] (absorbing surface)			
	GF[a]	FIRED[b]	EXTR[c]	APM[d]
Pyrene	364 ± 82	203 ± 21	321 ± 33	716 ± 191
Benz(a)anthracene	454 ± 49	315 ± 43	693 ± 103	866 ± 80
Benzo(a)pyrene	535 ± 46	233 ± 62	533 ± 96	697 ± 109

[a] GF = Glass fiber filter.
[b] FIRED = Airborne particulate collected by filtration and fired at 400°C.
[c] EXTR = Airborne particulate collected by filtration and extracted with cyclohexane.
[d] APM = Airborne particulate collected by filtration.
[e] Mean of Two analysis.

exposure to UV rays. Experimental data fitted fairly well the equation:

$$\ln Q = \ln Q_x - kt$$

where Q_x = initial amount of PAH; Q = amount of PAH present on the filter at time (t); k = decay constant.

Half-life for each tested PAH, according to adsorbing surface was evaluated by the equation:

$$t_{1/2} = \ln 2/k$$

and reported on Table III.

In Table IV half-lives measured in reference to the different substrates are statistically compared.

TABLE IV

Comparison of PAH half-life according surface characteristics. Statistical significance

	Half-life (min)							
	GF[a]	FIRED[b]	EXTR[c]	APM[d]	FIRED[b]	APM[d]	GF[a]	APM[d]
Pyrene	364	203	321	716	203	716	364	716
	($p < 0.20$)		($p < 0.1$)		($p < 0.05$)		($p < 0.2$)	
Benz(a)anthracene	454	315	693	866	315	866	454	866
	n.s.		n.s.		($p = 0.05$)		($p < 0.2$)	
Benzo(a)pyrene	535	233	533	697	233	697	535	697
	($p < 0.1$)		n.s.		($p < 0.05$)		n.s.	

[a] GF = Glass fiber filter.

[b] FIRED = Airborne particulate collected by filtration and fired at 400°C.

[c] EXTR = Airborne particulate collected by filtration and extracted with cyclohexane.

[d] APM = Airborne particulate collected by filtration.

PY and BA were more stable when adsorbed on APM rather than when directly on glass fibers. On the contrary, BaP showed similar half-lives. Thermic treatment of APM enhanced photodegradation of all tested PAH; half-lives of PAH adsorbed on fired samples were significantly different from those obtained on APM.

After treatment at 400°C, particulate colour changed from dark grey to pale grey and optical microscopic analysis confirmed strong reduction of soot particles.

Naturally in fired samples a higher interaction between PAH and glass fiber was also possible. Comparison between half-lives obtained with clean fiber glass samples and those with fired particulate showed that the presence, on glass fiber filters, of inorganic salt or oxides may effectively reduce half-lives of PY and BaP.

Differences did not reach a significative level for BA.

Extraction of particulate with cyclohexane did not modify half-lives of BA and BaP; on the contrary after this treatment PY adsorbed on this substrate was more photodegradable.

Solar radiation exposure

The mean reproducibility of analytical method used for sunlight exposure (evaluated from results obtained from different spiked samples not exposed to solar radiation) ranged from 5% to 13% according to the studied substrates.

Pyrene adsorbed on glass fiber filters showed the lowest recovery (62%) while the recovery of BaP was practically quantitative (100%) in all substrates.

The possible presence of degradation products in the samples exposed to UV and sunlight didn't affect our results. In HPLC analyses these compounds were retained in the column, being eluted only by a more polar solvent mixture.

In the experiment carried out with GLC, the low solubility in cyclohexane of oxigenated compounds eventually formed from PAH and their relative lower volatility in the gas chromatographic system[8] rendered a preliminary clean-up unnecessary.

Figure 4 shows an example of the gaschromatographic separation of PAH extracted from spiked APM unexposed to sunlight and from a similar sample after four hours of exposure to sunlight and to atmospheric pollutants; only a minor well-resolved peak appeared in the sample exposed to sunlight.

With the previously described method half-lives and decay constants of PAH were evaluated according to mean sunlight intensity and adsorbing surfaces after solar radiation exposure.

All samples degraded after exposure to solar radiation even if at different rates. Minimum and maximum half-lives for each tested PAH are reported in Table V.

A) Excluding BA (Figure 2(a)) and BAP (Figures 3(a)–(b)) adsorbed on APM, the time constant of all the other samples showed a good linear correlation with mean solar radiation intensity (Figures 1, 2 and 3).

BaP and BA were more stable when absorbed on APM, particularly after solvent extraction (Figures 3(b) and 2(b)). Inorganic components of APM did not show significant effect in respect to samples absorbed on glass fibres (Figures 1(c), 2(c), 3(c)). Also in this experiment glass fiber surface demonstrated to be particularly active in inducing PAH degradation (Figures 1(d), 2(d) and 3(d)).

Our results suggested that also O_3 concentration should be taken into account. When similar radiation intensities were measured, degradation rates were higher in the two days where high O_3 level were registered. This was particularly evident for PY absorbed on all tested substrates (Figure 1), and for BA and BaP absorbed on glass fibers (Figures 2(d) and 3(d)).

TABLE V

Minimum and maximum half-life of PAH exposed to sunlight adsorbed on different matrices

	Half-life (min)	
	Min	Max
Pyrene	65 (EXTR)	413 (APM)
Benz(a)anthracene	107 (GF)	504 (FIRED)
Benzo(a)pyrene	123 (FIRED)	1716 (EXTR)

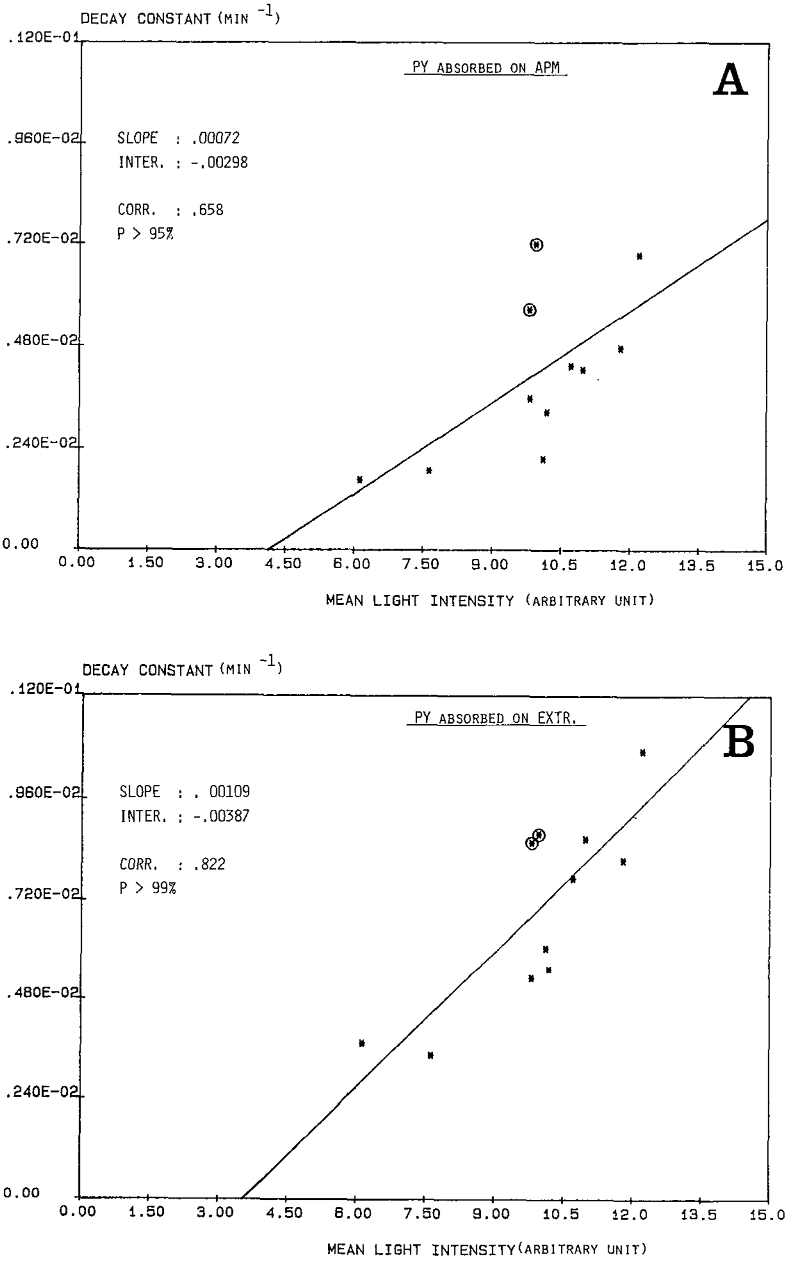
In brackets the corresponding adsorbing surfaces:

APM = Airborne particulate collected by filtration.

FIRED = Airborne particulate collected on filter and fired at 400°C.

GF = Glass fiber filter.

EXTR = Airborne particulate collected on filter and extracted with cyclohexane.


DECAY CONSTANT (MIN $^{-1}$)
.120E-01
.960E-02
.720E-02
.480E-02
.240E-02
0.00
PY ABSORBED ON APM
A
SLOPE : .00072
INTER. : -.00298
CORR. : .658
P > 95%
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
MEAN LIGHT INTENSITY (ARBITRARY UNIT)
DECAY CONSTANT (MIN $^{-1}$)
.120E-01
.960E-02
.720E-02
.480E-02
.240E-02
0.00
PY ABSORBED ON EXTR.
B
SLOPE : . 00109
INTER. : -.00387
CORR. : .822
P > 99%
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
MEAN LIGHT INTENSITY (ARBITRARY UNIT)

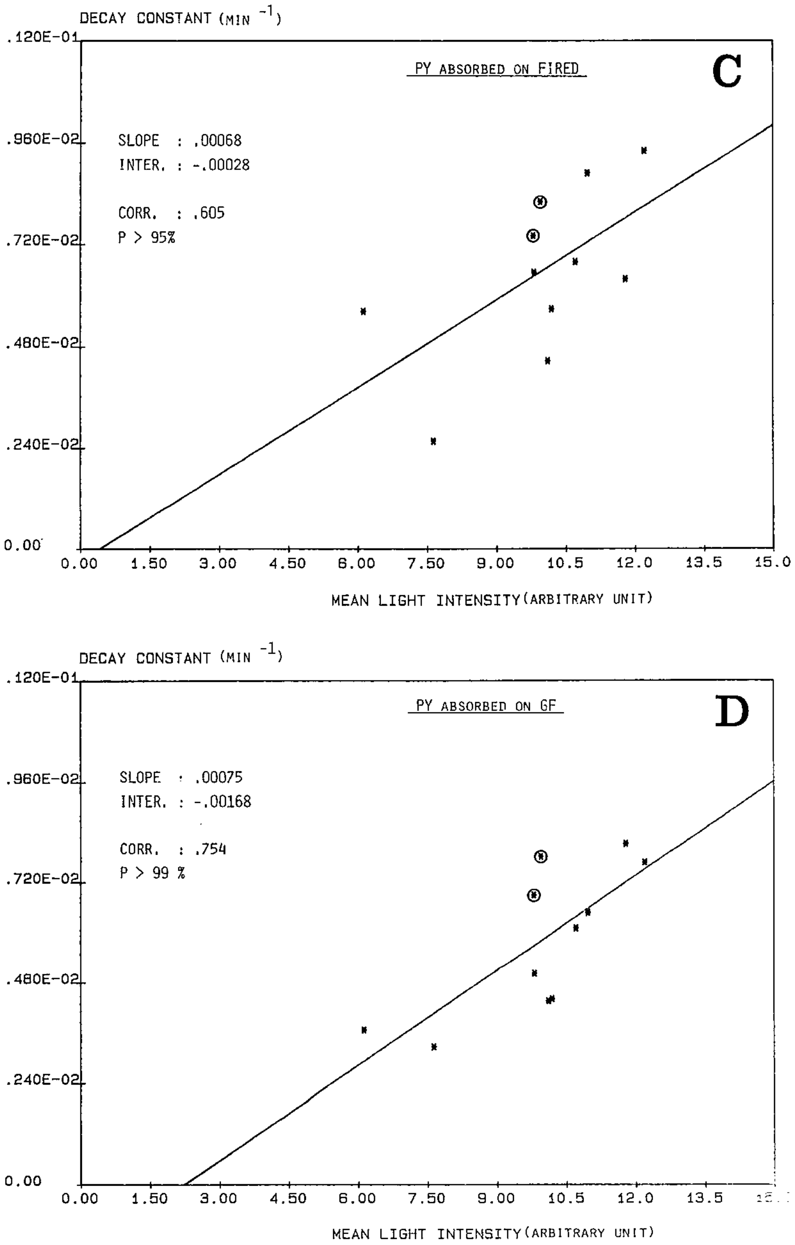
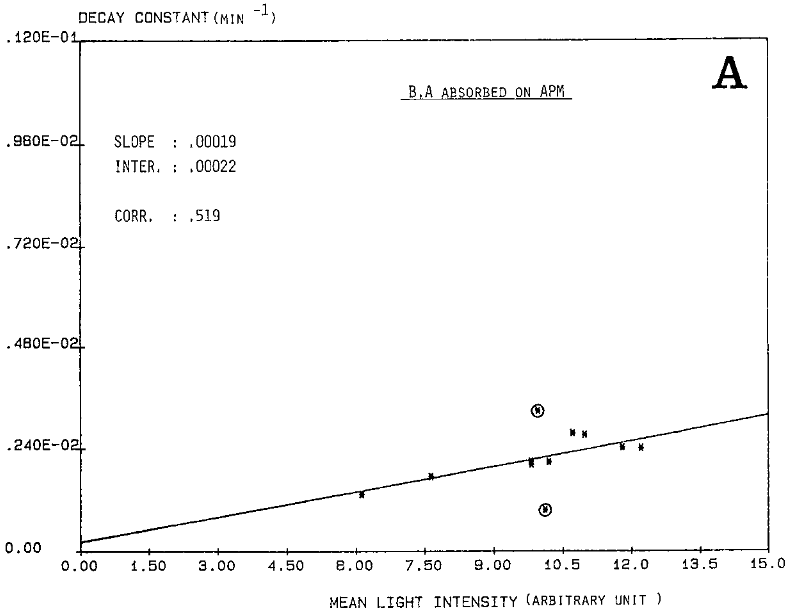
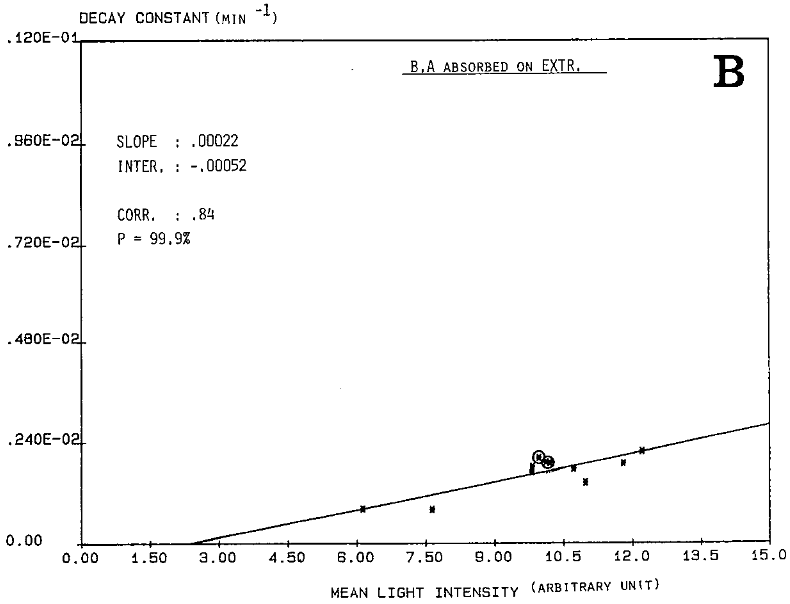


FIGURE 1 Correlation between decay constant and average solar radiation intensity of Pyrene absorbed on: (A) airborne particulate matter (APM); (B) APM extracted with cyclohexane; (C) APM heated to 400°C; (D) Glass fiber filter ⊛: Decay constant registered in concurrence of high ozone concentrations (0.2 ppm). Mean O conc. and s.d.: 0.075 ± 0.085.


DECAY CONSTANT (MIN $^{-1}$)
.120E-01
.960E-02
.720E-02
.480E-02
.240E-02
0.00
A
B.A ABSORBED ON APM
SLOPE : .00019
INTER. : .00022
CORR. : .519
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
MEAN LIGHT INTENSITY (ARBITRARY UNIT)


DECAY CONSTANT (MIN $^{-1}$)
.120E-01
.960E-02
.720E-02
.480E-02
.240E-02
0.00
B
B.A ABSORBED ON EXTR.
SLOPE : .00022
INTER. : -.00052
CORR. : .84
P = 99.9%
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
MEAN LIGHT INTENSITY (ARBITRARY UNIT)

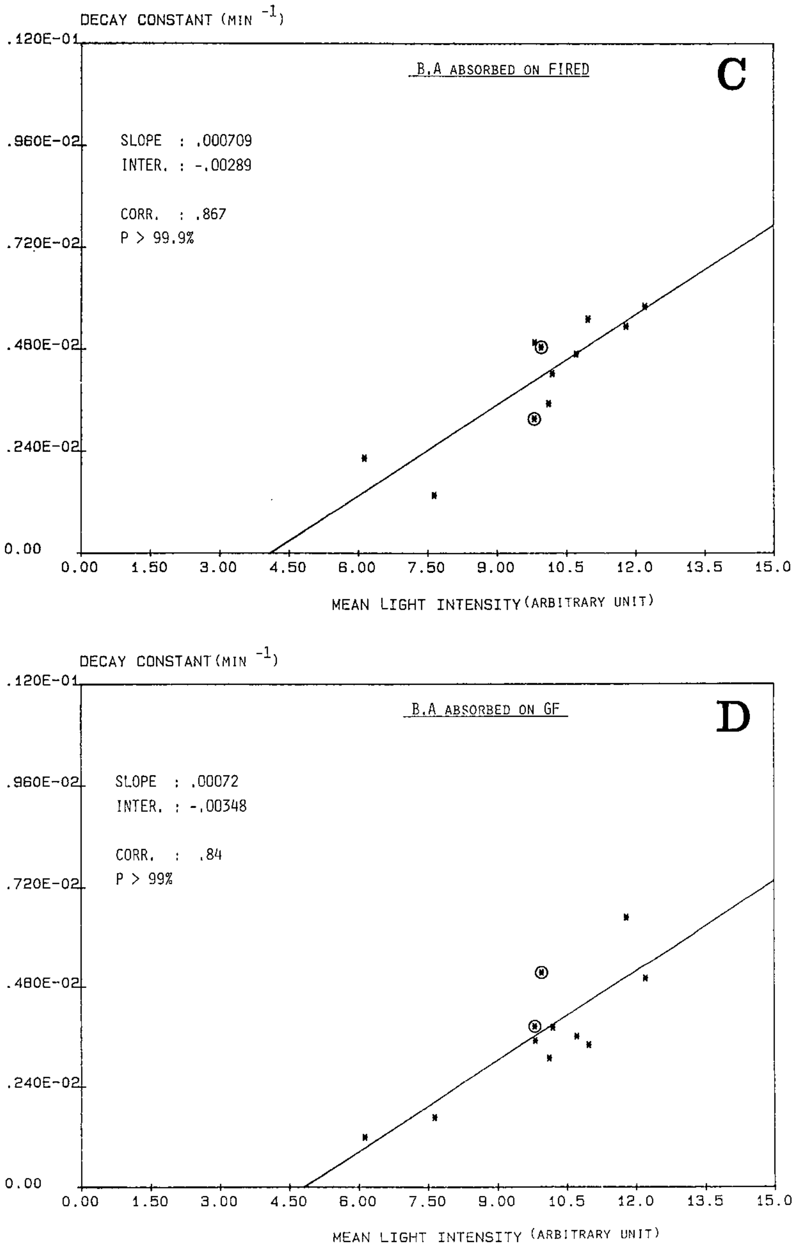
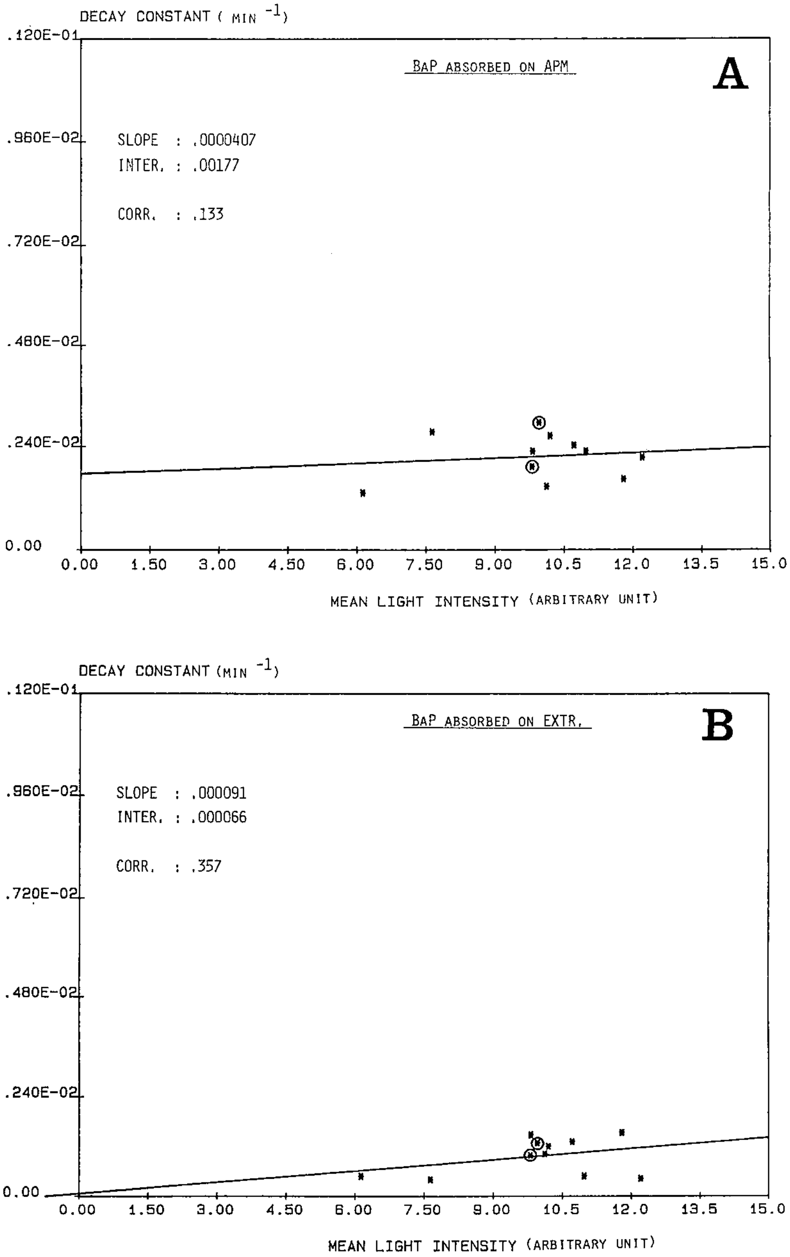


FIGURE 2 Correlation between decay constant and average solar radiation intensity of benz(a) anthracene absorbed on: (A) airborne particulate matter (APM); (B) APM extracted with cyclohexane; (C) APM heated to 400°C; (D) glass fiber filter ⊛: Decay constant registered in concurrence of high ozone concentrations (0.2 ppm). Mean O_3 conc. and s.d.: 0.075 ± 0.085.


DECAY CONSTANT (MIN $^{-1}$)
BaP ABSORBED ON APM
A
SLOPE : .0000407
INTER. : .00177
CORR. : .133
.120E-01
.960E-02
.720E-02
.480E-02
.240E-02
0.00
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
MEAN LIGHT INTENSITY (ARBITRARY UNIT)
DECAY CONSTANT (MIN $^{-1}$)
BaP ABSORBED ON EXTR.
B
SLOPE : .000091
INTER. : .000066
CORR. : .357
.120E-01
.960E-02
.720E-02
.480E-02
.240E-02
0.00
0.00
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
MEAN LIGHT INTENSITY (ARBITRARY UNIT)

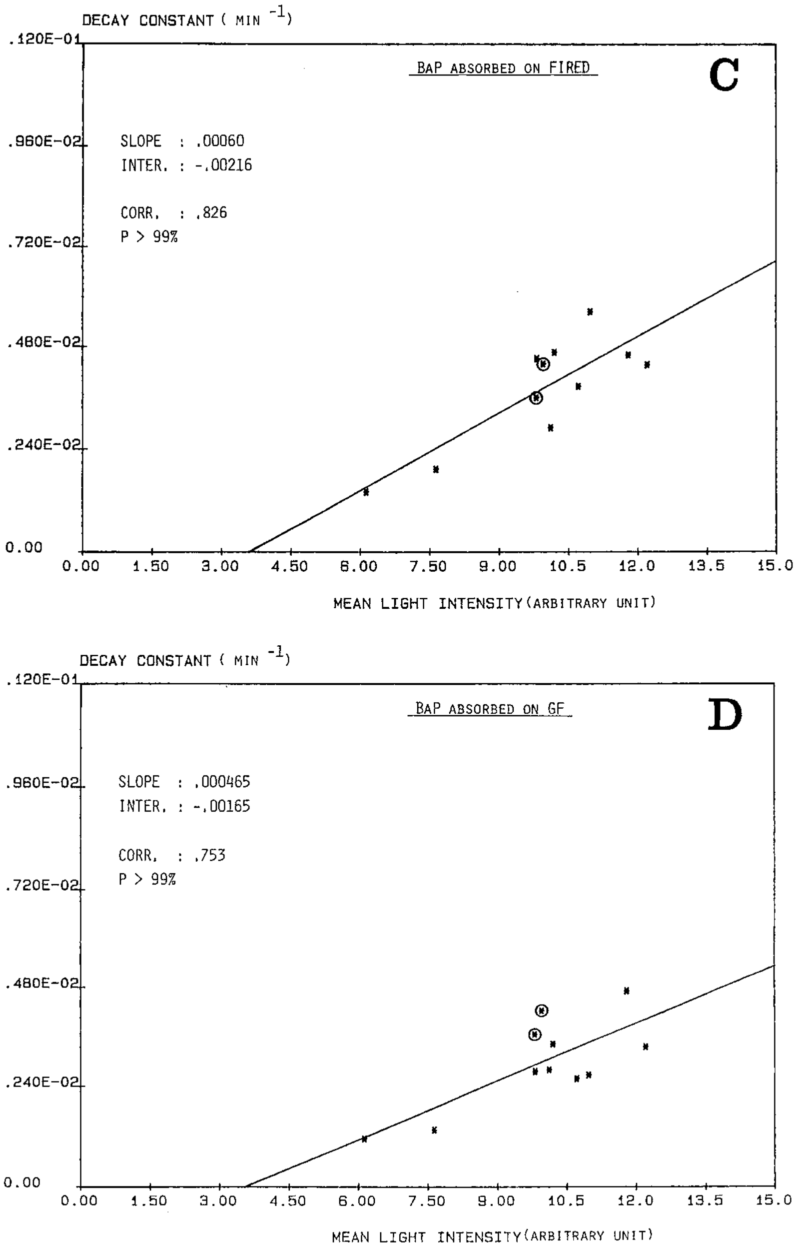


FIGURE 3 Correlation between decay constant and average solar radiation intensity of benzo(a)pyrene absorbed on: (A) airborne particulate matter (APM): (B) APM extracted with cyclohexane: (C) APM heated to 400°C; (D) glass fiber filter ⊛: Decay constant registered in concurrence of high ozone concentrations (0.2 ppm). Mean O_3 conc. and s.d.:0.075±0.085.

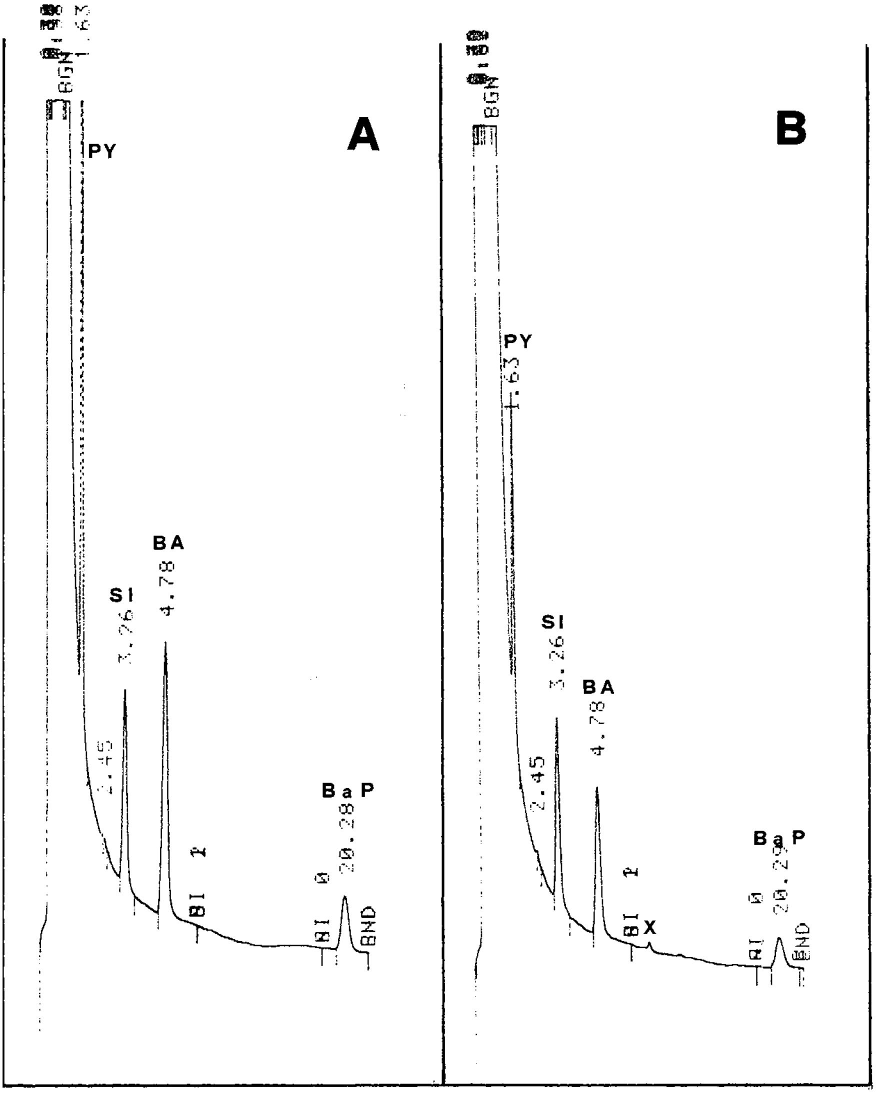


FIGURE 4 Gaschromatographic separation of pyrene (PY), benz(a)anthracene (BA), benzo(a)pyrene (BaP) spiked on airborne particulate matter and extracted by sonication with cyclohexane. For analytical condition see Table II. (A) unexposed sample; (B) after four hours of exposure to sunlight. (X) probable photodegradation product. (SI) triphenyl benzene (Internal Standard).

DISCUSSION

The prediction of chemical stability of PAH in real conditions is difficult to achieve owing to a difficult simulation of all involved variables.

The "ideal" photoreactor to carry out this research could have these characteristics:

— Light intensity and emission spectra similar to sun radiation;
— Temperature and humidity control;
— Air composition similar to the one existing in polluted atmosphere;
— Tridimensional exposure of particulate to radiation with continuous mixing;
— Use of real airborne particulate matter, whose dimension distribution, specific surface, chemical composition, must be well known.

This last point appears to be the most critical as chemical and physical characteristics of particulate may change according to the emitting source and during the permanence in the atmosphere; moreover these parameters may modify another critical factor, i.e. the nature of binding of PAH to the substrate.

Our experimental model was far from ideal but the main advantage was the use of real sunlight and atmosphere as well as of real airborne particulate matter.

The main drawbacks were: the spiking method, simple to be applied but unsuitable to supply uniform distribution of PAH on particulate, the steady-state of exposure that allowed interaction with light only in the outer layers of particulate deposited on filter and possible interaction of spiked PAH with glass filter, even if heavy loaded filters were used to minimize this interference.

Notwithstanding this limitation a quantification of effects induced by light intensity on PAH adsorbed on different substrates was possible in relative terms.

Our results confirmed the importance of chemical composition of adsorbing substrate for PAH photodegradation and in particular the great surface reactivity of glass fibers.

According to this, the possibility that artefacts may be produced during particulate sampling with glass fiber filters must not be underestimated.

Sunlight intensity seems to be one of the main factors involved in PAH degradation while organic and inorganic components of particulate probably play a minor role.

We have also confirmed the protective effect, with regard to BaP and BA, of particulates containing high levels of soot.

In some cases, regression curves of decay constant versus mean sunlight intensities gave negative intercepts.

This may be a mathematical artefact simply due to a casual dispersion of measured values owing to the occurrence of casual variables with different statistical weight as O_3 and nitrogen oxides concentration or air humidity. It is noteworthy that the two lowest mean light intensities were registered during cloudy weather when humidity of air was particularly high. On the other hand a limited number of experiments with low sunlight intensity made it more difficult to estimate the decay constant and particularly its extrapolation to zero radiation.

Notwithstanding these limitations we think that our experimental model can give useful information to clarify the mechanisms of PAH degradation in a real world if applied to a higher number of samples exposed to different, well documented, meteorological and environmental situations.

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