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Publisher Taylor & Francis

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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Valerio, F. , Antolini, E. and Lazzarotto, A.(1987) 'A Model to Evaluate Half-Lives of PAHs Naturally Occurring on Airborne Particulate', International Journal of Environmental Analytical Chemistry, 28: 3, 185 – 196

To link to this Article: DOI: 10.1080/03067318708081860

URL: <http://dx.doi.org/10.1080/03067318708081860>

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A Model to Evaluate Half-Lives of PAHs Naturally Occurring on Airborne Particulate†

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(Received May 4, 1986; in final form July 24, 1986)

Constant decay of polycyclic aromatic hydrocarbons (PAHs) adsorbed onto airborne particulate collected in glass fibre filters and exposed to sunlight ranged from 1.8 to 4.4×10^{-3} (min^{-1}), corresponding respectively to a half-life of 100 and 425 min. Half-life of PAHs appeared to be positively correlated with filter loading. Experimental results showed that decay of PAHs adsorbed on airborne particulate was induced by two concomitant reactions; a photochemical reaction involving the outer layers of collected particulate, and a "dark" reaction that may occur in the inner layers.

The constant decays of these two reactions were calculated using a simplified mathematical model.

The authors suggest the use of this model to compare chemical stability of airborne PAHs exposed, during their permanence in the atmosphere, to different physical (light intensity, temperature, humidity) as well as chemical conditions (oxidant concentration, chemical composition of particulate).

KEY WORDS: Polycyclic hydrocarbons, degradation, airborne particulate, half-life estimation.

INTRODUCTION

Chemical and photochemical degradation mechanisms of PAHs require proper studies owing to the possible implications of these

†Presented at the 3rd Workshop on the Chemistry and Analysis of Hydrocarbons, Lausanne, Switzerland, March 20–21, 1986.

phenomena in induction of artifacts during analytical procedures as well as in modification of toxic effects. Many studies have been carried out to establish the photodegradation kinetics of PAH in solution or adsorbed on many solid substrates (silica gel, alumina, glass, fly ash).¹⁻⁷ In these experiments parameters like chemical composition of the adsorbing particulate, amount of adsorbed PAHs and the adsorbing techniques are in many cases very different from those occurring in the environment. To overcome these problems, airborne particulate samples were collected in a residential area by glass fibre filters, and were exposed to sunlight without any modification. The use of high liquid pressure chromatography coupled to a sensitive and selective detection technique (fluorimetry) allowed us to measure the effects of solar radiation on exposed samples and to evaluate the half-life of PAHs present on particulate under these experimental conditions.

In this exposure model the effects of other variables such as temperature (sublimation) and chemical reaction with pollutants (O_3 and NO_x) may also be considered.

Obviously the photodegradation is more effective in outer exposed layers, while the inner layers may be protected from light, because of progressive light intensity fading caused by the absorption properties of particles.

Using data obtained from this experiment and introducing some hypothesis and approximations, it is possible to calculate by extrapolation the half-lives of PAHs with respect to light and to dark reactions.

METHODS

Five samples of airborne particulate with different dust load were collected in a residential area of Genoa (Italy), using glass fibre filters (GELMAN, Type A/E, 20×25 cm) pretreated at 400°C for 60 min to remove organic traces. Using a high volume sampler (Metal Work GMWL 2000) about 2000 cubic metres of air were filtered during 24 hours of sampling time. After collection the filters were dried in an desiccator for 24 hours, weighed and cut into halves. One part of the filter was placed in a refrigerator at 4°C , the other part was exposed flat to solar radiation for 4 hours. The five

samples were exposed contemporaneously from 10am to 2pm during a sunny day in which the mean sun light intensity was $1.07 \text{ cal cm}^{-2} \text{ min}^{-1}$. All the samples (exposed and unexposed) were extracted by sonication with 150 ml of cyclohexane.

All extracts were collected and concentrated by rotating evaporator till 0.5 ml. Concentrated solutions were developed on a precoated TLC preparative plate (Silica gel 60 Merck). Developing mixture was hexane:benzene (1:1 in vol). Using a UV lamp the fluorescent band containing PAH was evidenced, scraped and eluted with 12 ml of tetrahydrofuran.

The solvent was evaporated under nitrogen and the residue was dissolved in methanol (400 μl).

Reversed-phase HPLC separation and analysis of the PAHs in the extracts were performed with a Perkin-Elmer, Liquid Chromatograph Series 4, using a model 7125 Rheodyne injector valve with a 20 μl loop, and a model LS 1 fluorescent detector. The output from the detector was recorded on a LCI 100 (Perkin-Elmer). A Supelco LC-PAH C18 5 μm Supercosil column was used to separate individual PAHs. The analytical column was protected with a Supelco LC 18 pellicular packing guard. Mobil phase: water and methanol. Flow rate: 1 ml/min.

Gradient program: hold at 80% methanol for 2 min, from 80 to 100% of methanol in 10 min, hold at 100% of methanol for 35 min. Fluorescence excitation and emission wavelengths were 340 nm and 425 nm respectively.

RESULTS

Chromatograms of the analyzed mixture evidenced the presence of about 25 major components. Among them, the following PAHs were tentatively identified according to their retention times: Pyrene (PY), Fluoranthene (FLA), Benzo(a)anthracene (BaA), Benzo(a)pyrene (BaP), Benzo(k)fluoranthene (BkF). The total area of the chromatogram was taken as a measure of the total amount of PAHs in the sample.

Degradation occurred in all exposed samples even if at different rate. Half-lives obtained for each sample appeared to correlate with filter loading (Table I), being half-lives higher in samples extracted from filters in which a greater amount of particulate was collected.

TABLE I
PAH half-lives (min)

Filter load (mg/cm ²)	<i>PY</i>	<i>FLA</i>	<i>BaA</i>	<i>BaP</i>	<i>BkF</i>	PAH tot
0.337	161	248	161	198	154	158
0.412	301	347	224	267	347	266
0.415	248	301	204	289	347	300
0.436	385	—	173	257	385	288
0.586	408	365	301	301	433	385

A possible explanation of these results was that photodegradation occurs only in the outer layers of particulate, which are more exposed to radiation. The filtering effect produced by outer layers of particulate protects the inner layers from light so that the internally adsorbed PAHs are not degraded. Therefore the half-life of light-exposed PAHs is apparently greater in samples where much more protective layers of particulate are present.

However PAHs collected on filters with higher particulate loads showed half-lives shorter than expected. We postulated that this effect might be due to the simultaneous occurrence of two degradation mechanisms involving PAHs adsorbed onto the particulate.

The first one, with shorter half-lives, depends on light intensity and involves outer layers of particulate, the second one characterized by slower rates, occurs in the inner layers. According to this hypothesis we propose the following model: in the particulate stratified on the filter, two different layers may be identified (Figure 1). Photochemical reactions may occur in the first one and its extension is a function of light intensity. The second layer is not reached by light.

To describe the kinetics of reactions occurring in these two layers we made the following hypothesis.

For each PAH adsorbed on the particulate:

- a) Photochemical reactions occur only in the layer 1.
- b) The constant decay of photoreactions is the same in all the layer 1.

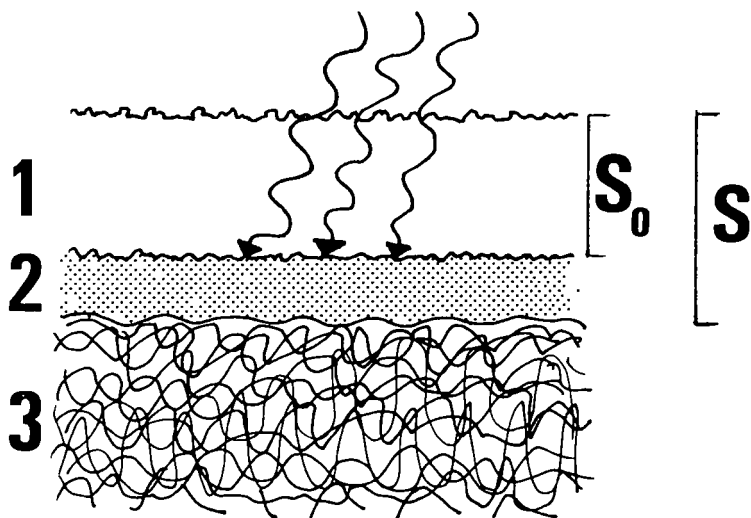


FIGURE 1 Schematic representation of exposure model. (1) Layer of particulate where photochemical reactions occur. (2) Layer of particulate not reached by light. (3) Glass fibre filter. S_0 = thickness of layer 1; S = thickness of layers 1 and 2.

c) PAHs may degrade at the same rate, owing to “dark” reactions occurring both in layer 1 and layer 2.

d) Kinetic of photoreactions and “dark” reactions is of first order.

e) The concentrations of PAHs on the particulate, particulate density and granulometry is the same in layers 1 and 2.

f) Glass fibres have no effect on chemical stability of PAHs.

By the term “dark” reactions we mean all the reactions not induced by light modifying the concentration of PAHs on the particulate (degradation due to reaction with ozone, nitrogen oxides, or other oxidant present in polluted atmosphere and losses by sublimation or desorption).

According to all the above hypothesis, after exposure to sunlight, the amount of each PAH at the time t will be:

$$Qt = QL \exp -t(Kd + Kl) + QD \exp -tKd \quad (1)$$

where:

Q_t = total amount of PAH at time t (layer 1 + layer 2)

Q_L = amount of PAH at $t=0$ in layer 1

Q_D = amount of PAH at $t=0$ in layer 2

K_l = constant decay of photoreaction

K_d = constant decay of dark reaction.

Dividing Eq. (1) by Q_T (Q_T = total amount of PAH at time $t=0$) results:

$$Q_t/Q_T = Q_L/Q_T \exp -t(K_d + K_l) + Q_D/Q_T \exp -tK_d \quad (1a)$$

being

$$Q_t = Q_T \exp -KT \cdot t \Rightarrow Q_t/Q_T \exp -KT \cdot t \quad (a)$$

where KT = Total constant decay (experimental).

Q_t/Q_T is substituted in Eq. (1a) that becomes:

$$\exp -KT \cdot t = Q_L/Q_T \exp -t(K_d + K_l) + Q_D/Q_T \exp -tK_d. \quad (1b)$$

We know that:

$$K = \ln 2/T_x \quad (b)$$

where T_x = half life time

$$Q_D = Q_T - Q_L. \quad (c)$$

Each constant decay in (1b) is substituted with respective expression (b).

$$\begin{aligned} \exp -\ln 2 \cdot t/T &= Q_L/Q_T \exp -t(\ln 2/T_d + \ln 2/T_l) \\ &+ Q_D/Q_T \exp -t \ln 2/T_d \end{aligned} \quad (1c)$$

where:

T = experimental half-life

T_d = half-life of "dark" reaction

T_l = half-life of photoreactions.

QD is substituted with (c) in Eq. (1c).

$$\begin{aligned} \exp(-\ln 2 \cdot t/T) &= QL/QT \exp(-t(\ln 2/T_d + \ln 2/T_l)) \\ &+ (QT - QL)/QT \exp(-t(\ln 2/T_d)). \end{aligned} \quad (1d)$$

QL/QT are collected in (1d).

$$\begin{aligned} \exp(-\ln 2 \cdot t/T) &= \exp(-\ln 2 \cdot t/T_d) \\ &+ QL/QT \exp(-\ln 2 \cdot t/T_d) \cdot (\exp(-\ln 2 \cdot t/T_l) - 1). \end{aligned}$$

In Eq. (2) the ratio QL/QT , may be substituted by the ratio S°/S where:

S° is the filter load due to the particulate exposed to light, expressed in mg/cm^2 .

S is the total particulate load on the filter (mg/cm^2).

Therefore, Eq. (2) becomes:

$$\begin{aligned} \exp(-\ln 2 \cdot t/T) &= \exp(-\ln 2 \cdot t/T_d) \\ &+ S^\circ/S \exp(-\ln 2 \cdot t/T_d) \\ &\times (\exp(-\ln 2 \cdot t/T_l) - 1). \end{aligned} \quad (2a)$$

Eq. (2a) is a straight line equation where

$$y = \exp(-\ln 2 \cdot t/T)$$

and

$$x = 1/S.$$

Introducing experimental data (t, T, S) for each tested sample a good linear correlation of $\exp(-\ln 2 \cdot t/T)$ versus $1/S$ was found. In Table II coefficient correlations for identified PAHs and total PAH are shown and in Figure 2 an example of the obtained result is

TABLE II
Linear correlation coefficient and intercept
of $\exp(t \cdot \ln 2/T)$ vs $1/S$

	<i>R</i>	Intercept
<i>FlA</i>	-0.980	0.800
<i>PY</i>	-0.903	1.135
<i>BaA</i>	-0.887	0.836
<i>BkF</i>	-0.884	1.201
<i>BaP</i>	-0.811	0.779
PAH tot	-0.918	1.081

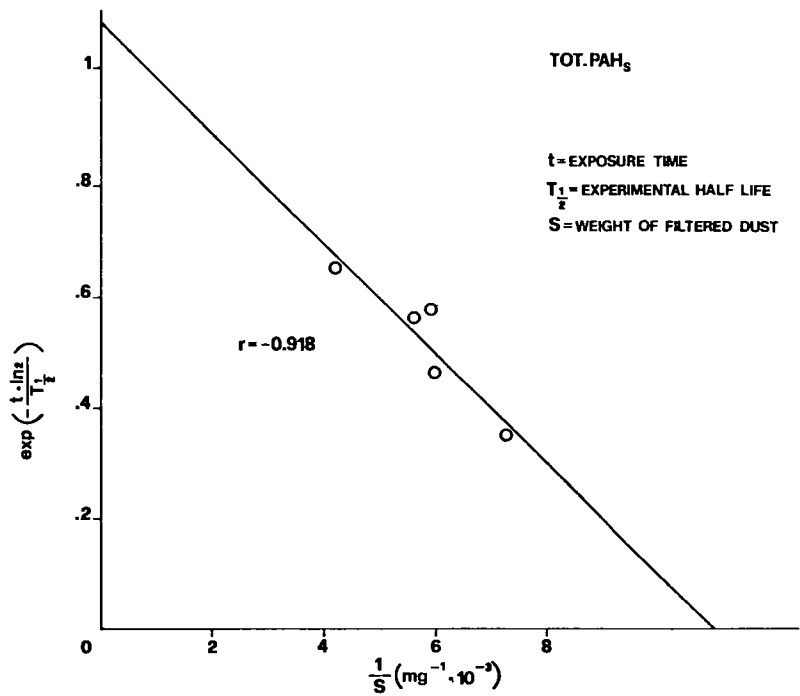


FIGURE 2 According to experimental data a good linear correlation exists between $\exp(t \cdot \ln 2/T)$ and $1/S$. This is in agreement with our exposure model and Eq. (2a).

reported. This is a confirmation of acceptability of our model and the value of the intercept allowed the calculation of the value of Td . Therefore to solve Eq. (2a) the values of two other variables must be known, namely S° and Tl .

To do this a more simplified equation (Eq. (3)) was introduced to calculate experimental half-life.

In this case two hypothesis are made:

- a) $T = Tl$ when $S \leq S^\circ$,
- b) $T \rightarrow Td$ when $S \rightarrow \infty$

$$1/T = 1/Td + S^\circ / S(1/Tl - 1/Td). \quad (3)$$

Also in this case Eq. (3) is an equation of a straight line and it is possible to calculate a relationship between Tl and S° . Inserting such a relationship in Eq. (2a) it is possible to calculate Tl and S° . In Table III the values of Tl , Td , and S° calculated by this model are shown. *BkF* appeared to be the compound more degraded by light together with *PY*. *FLA* and *BaP* result more stable to photodegradation.

Degradation due to "dark" reactions occurs to significantly lower rate and the half-lives of *PY* and *BkF* are particularly high.

It is interesting to observe that the value of S° calculated for each PAH is about the same; this means that, as expected, the thickness of the layer of particulate involved in photoreactions is not dependent on chemical characteristics of each PAH but only on the chemical composition and physical properties of the particulate that

TABLE III
Calculated half-lives (min)

	photo reaction	dark reaction	$S^\circ(\text{mg/cm}^2)$
<i>FLA</i>	273	745	266
<i>PY</i>	94	∞	258
<i>BaA</i>	133	923	285
<i>BkF</i>	88	∞	254
<i>BaP</i>	198	667	254
PAH tot	96	∞	261

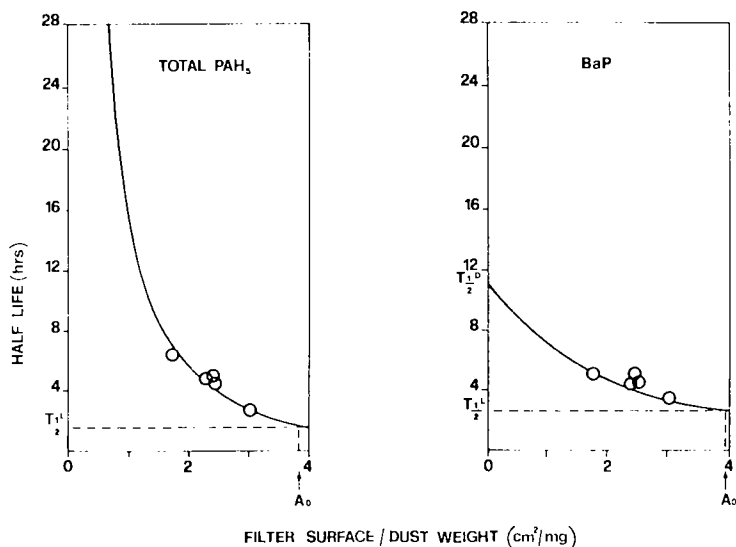


FIGURE 3 Half-life of total PAH and of Benzo(a)pyrene as a function of filter loads, calculated placing in Eq. (2a) the following values: Total PAH: $T_d = \infty$; $T_l = 1.6$ h; $S^\infty = 261$ mg/cm². BaP: $T_d = 11.1$ h; $T_l = 2.6$ h; $S^\infty = 254$ mg/cm². ○: experimental results.

in this case are similar for each sample. In Figures 3–5 the trend of PAHs half-lives as a function of filter loads, are shown. These functions were calculated introducing the calculated values of T_d , T_l and S^∞ in Eq. (2a). In this case T_l is calculated as the half-life resulting from the sum of dark and photoreactions, as it was supposed to occur in layer S^∞ .

It is difficult to compare these data with those found in the literature, as experimental models are very different. However, the order of magnitude of the half-lives found in this experiment is similar to that we obtained in previous research⁸ in which airborne particulate matter collected on filter was spiked with pure PAHs. Particularly, the higher photodegradability of PY respect BaP and BaA is confirmed.

CONCLUSION

The proposed model allows estimation of the value of PAHs half-lives due to photochemical reactions and of “dark” reactions.

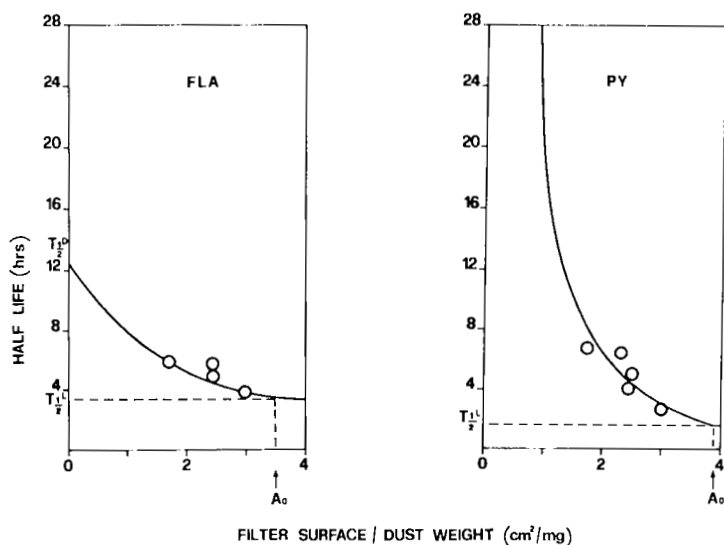


FIGURE 4 Half-life of Fluoranthene and Pyrene as a function of filter loads, calculated placing in Eq. (2a) the following values: *FLA*: $T_d = 12.4$ h; $T_l = 3.3$ h; $S^* = 266$ mg/cm². *PY*: $T_d = \infty$; $T_l = 1.6$ h; $S^* = 258$ mg/cm². ○: experimental results.

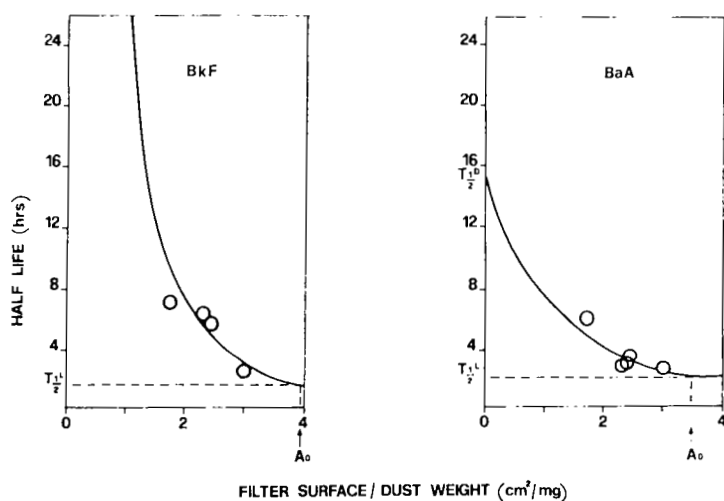


FIGURE 5 Half-life of Benzo(K)fluoranthene and Benzo(a)anthracene as a function of filter loads, placing in Eq. (2a) the following values: *BkF*: $T_d = \infty$; $T_l = 1.5$ hr; $S^* = 254$ mg/cm². *BaA*: $T_d = 15.4$ h; $T_l = 2.0$ hr; $S^* = 285$ mg/cm². ○: experimental results.

Notwithstanding the many approximations, the proposed mathematical model seems to be in good agreement with experimental results. Therefore it is possible to calculate the half-lives due to photochemical reactions and of dark reactions, exposing airborne particulate collected on filters with different loads and controlling the variables that may affect the PAHs stability. The correspondence of these values with those effectively occurring in the atmosphere need confirmation. On the other hand the experiment is easy to perform and requires no complex equipment. Therefore, it may represent a useful method to understand the fate of PAHs in real conditions and particularly to compare the chemical stability of PAHs according to the chemical composition of airborne particulate.

Acknowledgement

This research was supported by a CNR grant no. 84 00782 44.

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