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TRANSPORT AND TRANSFORMATIONS OF ANTHRACENE IN NATURAL WATERS: PROCESS RATE STUDIES[1,2]

G. R. Southworth

Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

Polcyclic aromatic hydrocarbons (PAH) commonly occur in wastes from pyrolysis of biogenic fuels. Because some PAH are known carcinogens, understanding of their environmental behavior and persistence is critical to determining their potential hazard to man. While many processes may remove or transform PAH in aquatic ecosystems, several may be particularly important in determining the fate of PAH in most systems. Laboratory measurement of the rates of various processes under controlled conditions are identifing those critical parameters of environmental transport where more detailed research is necessary.

Anthracene was selected as a representative PAH due to its intermediate molecular and its lack of carcinogenicity. Rates of photolysis, hydrolysis, volatilization, and microbial degradation of anthracene were measured under different environmental conditions using fluorimetric and radiotracer techniques. Equilibrium constants for processes such as sorption and bioaccumulation were also determined.

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DISCLAIMER

Results of the study indicated that photolysis and microbial degradation within the water column are likely to be the dominant pathways of anthracene removal from aquatic systems. More research is needed to ascertain the degree to which microbial degradation rates observed in this study are representative of other PAH contaminated systems. Further study of the role of microbial degradation in bedded sediments in removing PAH's from the water column is also necessary.

Key Words: Anthracene, Polycyclic Aromatic Hydrocarbons, Transformation, Persistence, Degradation, Transport, Volatilization, Photolysis, Microbial Degradation, Bioaccumulation.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are important constituents of effluents and products of synthetic fuels production and are also released to the environment from many other sources, such as combustion of organic fuels and petroleum refining, storage, and transportation (1). Numerous PAH have been shown to be potent skin carcinogens in mammals, while lower molecular weight PAH have demonstrated high toxicity to aquatic life (1). In view of the potential hazard of this class of compounds to inhabitants and users of aquatic resources, an understanding of the processes which determine the persistence, compartmentalization, and transport of PAH in aquatic environments is needed for assessing and minimizing the environmental impact of synthetic fuels technology.

Processes which could act to reduce PAH concentrations in receiving waters include volatilization, photolysis, hydrolysis, microbial degradation, adsorption and subsequent sedimentation, and adsorption by bedded sediments. Processes which could act to concentrate PAH's in certain compartments of aquatic ecosystems are adsorption and bioaccumulation.

This paper represents a first attempt to coallesce the process rate data for a single PAH compound, anthracene, into a framework in which the relative importance of the various processes could be evaluated in several hypothetical environments. The objective is to identify areas where research emphasis should be placed. Much of the data used here is of a preliminary nature and, thus, is not intended to be used to predict the fate of anthracene or other PAH in aquatic environments. Actual

field site measurements of PAH persistence and transport are needed to test the assumptions and methodologies utilized in this study before the information will have predictive utility.

METHODS

It was assumed that each process could be described in such a way that its effect on the total concentration of anthracene in the water column (irrespective of dissolved or adsorbed state) could be expressed as a simple first order decay with an overall removal rate being given by the sum of the decay constants (k_Σ) for all the various processes.

All experimental determinations were carried out at aqueous anthracene concentrations well below the published solubility limit of anthracene of 42 µg/ℓ (2).

Adsorption

The adsorption of anthracene by suspended particulate matter was investigated by adding varying amounts of particulate matter to anthracene solutions, centrifuging to remove the particulates, and monitoring the resultant change in anthracene concentration in the supernatant by ^{14}C techniques or fluorescence. Distribution coefficients were calculated using the following expression:

$$K_d = \frac{[A]_{\text{particulate}}}{[A]_{\text{dissolved}}} , \qquad (1)$$

where:

K_d is distribution coefficient,

$[A]_{particulate}$ is the equilibrium anthracene concentration on particulates, (μg anthracene/g particulates), and

$[A]_{dissolved}$ is the equilibrium dissolved anthracene concentration in water (μg anthracene/g water).

Absorbents investigated were autoclaved yeast cells, wastewater treatment effluent (particulate organics), clay and silt size fractions of natural sediment, and a reference clay mineral. All studies were done at 25°C. For further details, see Herbes (3).

A key assumption was that only dissolved anthracene was available for removal by processes such as volatilization, photolysis, etc., and that adsorption was readily reversible. Thus, in the presence of particulate matter, which causes a fraction of the total anthracene to be adsorbed, the rate of removal by any of these processes is reduced by the fraction adsorbed. The first order decay expression is thus given by:

$$\frac{d[A]_{H_2O}}{dt} = k_{\Sigma}[A]_{H_2O} f_{dis} , \qquad (2)$$

where:

$[A]_{H_2O}$ is the total anthracene concentration in the water column (includes dissolved and particulate),

f_{dis} is fraction of $[A]_{H_2O}$ that is dissolved, given by $\frac{1}{K_d[part] + 1}$ with [part] being the concentration of particulates, in g particulate/g water.

k is the sum of first order rate constants of all removal processes.

Volatilization

Volatilization of anthracene from aquatic systems was described using the mass transfer equations previously used to describe the transfer of gases across an air-water interface (4,5). The rate of the process under a given set of conditions is described as a simple first order exponential decay, $\frac{d[A]_{H_2O}}{dt} = \frac{-K_L}{D} [A]_{H_2O} f_{dis}$

where:

D is the depth of the water column, and

K_L is the overall mass transfer coefficient.

K_L has units of distance time^{-1} (such as cm hr^{-1}) and has three components: k_g, k_l and H, related by the expression

$$K_L = \frac{Hk_g k_l}{Hk_g + k_l}, \qquad (3)$$

where:

H, the Henry's Law constant, is a distribution coefficient representing the equilibrium distribution of a material between

gaseous and liquid phases. Units used for H in this paper are

$$\frac{\text{molar concentration anthracene}_{(air)}}{\text{molar concentration anthracene}_{(water)}}$$

k_g, the gas phase exchange constant, is a measure of the rate of transport of the material away from the interface in the air.

k_l, the liquid phase exchange constant, is a measure of the rate of transport of the material to the interface in the water.

Both k_g and k_l are influenced by mixing within their respective phases and, to a lesser extent, by mixing within the adjoining phase (4). The rate of volatilization of a substance from a given water body will be determined by properties of the substance (H) and the environment (wind, water turbulence, and temperature). Temperature acts to influence H, while k_l and k_g are functions of wind and water turbulence.

The Henry's Law constant at 25°C was estimated using the method of Mackay (6), which consists of sparging a column of water containing PAH with a measured flow of nitrogen. Preliminary experiments indicated that the PAH concentration within the nitrogen attained 95% of the equilibrium value in passing through a 38 cm column, 6 cm in diameter. Anthracene concentration was analyzed directly using fluorescence spectrophotometry (7). Henry's Law constant was calculated directly as the rate constant for the exponential decay of aqueous PAH concentration vs volume of nitrogen.

The gas phase mass transfer coefficients (k_g) were calculated at various wind velocities by multiplying the data of (4) for water by

$\left(\frac{\text{Mol. wt } H_2O}{\text{Mol. wt anthracene}}\right)^{1/2}$. Liquid phase mass transfer coefficients were calculated for various current velocities from stream reaeration coefficients (k_2) using the expression derived by Churchill et al. converted to metric units (8).

$$k_2\ (25°C) = 0.2351\ \frac{V^{0.969}}{D^{1.673}}\ hr^{-1}\ , \qquad (4)$$

where:

V is current velocity (m/sec), and D is mean depth (m).

The reaeration coefficient (a first order rate constant) was converted to the mass transfer coefficient by multiplying it by the depth (D). While the most direct effect of varying wind velocity is upon k_g and current velocity upon k_l, each also affects the mass transfer coefficient of the adjoining phase. In order to take this interaction into account, wind and water velocities were summed before determining k_g, and the observed relationship between wind and k_l was incorporated into the estimation of k_l by fitting an exponential curve to the data of (4) (for values of wind velocity < 1.9 m/sec, k_l was assumed to be unaffected by wind). The equations used to generate k_g and k_l as functions of wind and current velocity were

$$k_g = 1137.5\ (V_{wind} + V_{current}) \left(\frac{18}{\text{Mol. wt anthracene}}\right)^{1/2}\ , \qquad (5)$$

and

$$k_l = 23.51 \frac{V_{current}^{0.969}}{D^{0.673}} \left(\frac{32}{\text{Mol. wt anthracene}}\right)^{1/2}, \quad (6)$$

for $V_{wind} \leq 1.9$ m/sec, and

$$k_l = 23.51 \frac{V_{current}^{0.969}}{D^{0.673}} \left(\frac{32}{\text{Mol. wt anthracene}}\right)^{1/2} (e^{0.526(V_{wind}-1.9)}, \quad (7)$$

for $V_{wind} > 1.9$ m/sec.

where:

V_{wind} is wind velocity (m/sec),

$V_{current}$ is current velocity (m/sec),

D is stream depth (m), and

Units of k_l and k_g are cm hr^{-1}.

The estimations of $H_{25°C}$, k_g, and k_l were used to calculate the volatilization rate of anthracene in a hypothetical river 1.0 m in depth, at current velocities ranging from 0.1-1.0 m/sec and wind velocities ranging from 0.25-4.0 m/sec. A critical assumption in this estimation was that of thorough and instantaneous mixing throughout the water column; thus a concentration gradient exists only at the surface.

Photolysis

The rate of photolysis of anthracene in aqueous solution was measured by exposing solutions of anthracene (∿ 10 ppb) in distilled water to midsummer, midday sunlight at Oak Ridge (∿ 35°N latitude). Solutions 2 cm in depth were maintained in shallow pyrex vessels enclosed by a pyrex cover to eliminate volatilization and exposed to

direct sunlight for 30 minutes at midday. Pyrex does not absorb wavelengths of sunlight absorbed by anthracene; no correction was made for decreased incident radiation or increased pathlength due to reflection--these processes would tend to counteract each other. The change in anthracene concentration was monitored by fluorescence spectrophotometry, and the first order rate constant calculated. A sample containing ^{14}C labeled anthracene was exposed to sunlight, acidified, extracted into hexane and then chromatographed with benzene on a silica gel-G TLC plate. The TLC plate was scanned with a ^{14}C counting TLC scanner. The presence of a large portion of the ^{14}C near the origin in the sunlight exposed sample while nearly all ^{14}C was near the solvent front in a dark control sample indicated that in the presence of sunlight anthracene was converted to more polar (probably hydroxylated) compounds.

In natural waters, the rate of photolysis of a substance is affected a great deal by the attenuation of incident solar radiation by substances dissolved and suspended in the water column (9). Such attenuation of incident is described by the expression

$$I_d = I_o \, 10^{-\alpha D} \quad , \qquad (8)$$

where:

I_o is the intensity of incident radiation at surface,

I_d is intensity of radiation at depth D (in cm), and

α is the decadic light extinction coefficient (in cm^{-1}) at 350 nm (approximate midpoint of the anthracene absorption spectrum.

The ratio of the rate constant for photolysis of a substance in distilled water (k_{DW}), ($\alpha = \alpha_{DW}$, depth = D_{DW} (cm) to the rate constant in natural water (k_N) of depth (D_N) (cm) and α_N is given by:

$$\frac{K_N}{K_D} = \frac{\alpha_{DW} D_{DW}}{\alpha_N D_N} \frac{[(1-10^{-\alpha_N D_N}) + 1.1\ (1-10^{-1.2\ \alpha_N D_N})]}{[(1-10^{-\alpha_{DW} D_{DW}}) + 1.1\ (1-10^{-1.2\ \alpha_{DW} D_{DW}})]}, \qquad (9)$$

for solar declination < 20° at midday, from (9).

Thus, the estimated rate constant for the midday photolysis of anthracene in a body of water of transparency characterized by α_N and depth D_N at 35° N latitude, midsummer, is given by the experimentally observed rate constant in distilled water multiplied by $\frac{k_N}{k_{DW}}$ calculated from equation (9), using $\alpha_{DW} = -0.002\ cm^{-1}$ and $D_{DW} = 2$ cm.

The expression for the midday midsummer photolysis of anthracene is thus given by:

$$\frac{d\ [A]_{H_2O}}{dt} = -k_{DW}\ \frac{k_N}{k_{DW}}\ [A]_{H_2O}\ f_{dis} = -k_p\ [A]_{H_2O}\ f_{dis} \qquad (10)$$

Microbial degradation

The rate of degradation of anthracene by microorganisms suspended in the water column was estimated by adding 10 µl of anthracene stock solution in methanol (10 mg/l) to 100 ml of natural water in a 200 ml glass bottle. The sample was incubated overnight (18 hr) at 25°C on a wrist action shaker. Incubation was terminated by adding 50 ml of

methanol and 0.1 g of NaOH, followed by 50 ml of distilled water. The sample was extracted with 5 ml of hexane, and a 1 ml aliquot of the hexane extract evaporated to dryness. A small amount of nonvolatile lipid was added to the hexane extract prior to evaporation to prevent volatilization losses in this step. The sample was redissolved in 5 ml of methanol, and anthracene content determined by fluorescence spectrophotometry. The sample procedure was carried out with samples inoculated with ^{14}C labeled anthracene in addition to untagged anthracene. In this experiment, a KOH CO_2 trap was placed in the sample bottle at the end of the incubation period, and the water acidified to pH 2. After two hours, the CO_2 trap, hexane extract, and remaining aqueous phase were analyzed for ^{14}C using liquid scintillation counting.

Water samples were obtained from Third Creek, in Knox County, Tennessee, a small stream receiving chronic PAH inputs from a refined oil storage facility, and a small woodland stream on the Oak Ridge reservation in Anderson County, Tennessee. The latter originated from a spring about 400 m upstream, and was considered a pristine environment. Autoclaved Third Creek samples and distilled water were used as controls. Anthracene concentration in all water samples prior to additions was < 0.05 ppb lower case in all cases.

Microbial degradation rate was assumed to be first order with respect to anthracene concentration, and was described by:

$$\frac{d\ [A]_{H_2O}}{dt} = -k_b\ [A]_{H_2O}\ f_{dis} \quad . \qquad (11)$$

Microbial degradation rates of anthracene in sediments were determined by adding ^{14}C labeled anthracene to mixed sediment samples, which were incubated at 25°C for up to 48 hours. $^{14}CO_2$ was trapped in KOH as in water samples, and the sediment extracted overnight with acetone in a micro-soxhlet apparatus. Residual cellular ^{14}C in the sediment was determined by liquid scintillation counting following combustion (Tri-carb Sample Oxidizer, Packard Instruments). The acetone extract was chromatographed on a silica gel-G column, using benzene to initially elute anthracene, followed by 19:1 v/v butanol-acetic acid to remove polar metabolites. Quantitation of ^{14}C was carried out using liquid scintillation counting, and the degradation rate constant was calculated from the rate of change of $[^{14}C\text{-anthracene}]_{sediment}$ (10).

Experiments also were carried out to compare the rate of degradation of anthracene added only to the surface of intact sediment cores with that observed in mixed sediments. Rate of degradation in sediments was described by:

$$\frac{d\ [A]_{sed}}{dt} = -k_m\ [A]_{sed} \qquad (12)$$

Sedimentation

Sedimentation of particulate materials containing adsorbed anthracene can act as a removal process, transporting anthracene from the water column to the sediments. The rate of removal of anthracene by this process in quiescent water for a given type and size of particulate matter is given by the expression:

$$\frac{d[A]_{H_2O}}{dt} = -k_s\,[ant]_{H_2O} \quad , \qquad (13)$$

with,

$$k_s = \left(\frac{V_f}{D}\right) f_{ads} \quad ; \qquad (14)$$

where:

V_f is the settling velocity of the particulates cm hr^{-1} (calculated from Stoke's Law),

D is the depth of the water column cm, and

f_{ads} is the fraction of the total anthracene in the water column adsorbed to particulates:

$$f_{ads} = \frac{K_d\,[part]}{K_d\,[part] + 1} \quad . \qquad (15)$$

An estimation of the rate of removal of anthracene from typical river systems was obtained by using a sedimentation rate typical of the highest values observed in tributary reservoirs in the Ohio River system (6 cm/yr, or $\sim 1 \times 10^{-3}$ g/cm^2hr) (11) to calculate the suspended sediment load [part] of a given sediment type producing such a sedimentation rate,

$$[part] = \frac{1 \times 10^{-3}}{V_f}\ g/cm^3 \quad . \qquad (16)$$

The value of [part] was used in equation (15) to determine f_{ads}.

Resuspension forces generated by water turbulence in flowing water systems act to make k_s far smaller in flowing systems. There will be no net movement of suspended particles from the water to the sediment unless the [part] exceeds the amount of suspended load the stream is capable of carrying in suspension. The suspended load capacity given by (12) is:

$$\frac{J_s}{Q} = 0.016\ \rho\ \frac{\mu}{V_f} \sin \beta, \qquad (17)$$

where:

ρ is the density of water (g/cm^3),

μ is the mean current velocity,

β is the slope of the stream in degrees from horizontal,

J_s is the suspended load wet mass transport rate

Q is the hydrologic flow rate

$\frac{J_s}{Q}$ was calculated for 2 μm clay and 10 m silt for a current velocity of 0.1 m/sec and $\beta = 5.7 \times 10^{-4}$ (1 cm drop per 1000 m of stream).

Adsorption to bedded sediments

In the absence of some mechanism for removal of anthracene from sediments along the water-sediment interface, an adsorption equilibrium condition would be rapidly established in this layer and net movement of anthracene from water to sediments would tend to zero. The action of microorganisms in removing anthracene from surface sediments to promote an adsorption disequilibrium can act to cause a net movement of anthracene from water into the sediments.

The rate of adsorption of anthracene by sediments was described in a way analagous to mass transfer across an air-water interface, yielding the expression:

$$\frac{d\ [A]_{H_2O}}{dt} = \frac{-k_1}{D}\left(1 - \frac{[A]_{sed}}{K_d\ [A]_{H_2O}\ f_{dis}}\right)[A]_{H_2O}\ f_{dis} \quad , \qquad (18)$$

where:

$[A]_{sed}$ is the concentration of anthracene in sediment (g anthracene/g sediment dry weight).

k_1 is the liquid phase mass transfer coefficient used previously.

D is depth of the water column.

Under steady state conditions, the flux of anthracene across a given surface area of sediment (adsorption) is equal to the rate of degradation of anthracene in a depth of sediment (d) in which the concentration of anthracene can influence the rate of adsorption. Thus, the rate of degradation of anthracene under 1 cm^2 of interface, given by:

$$\text{degradation } (\mu g/cm^2\ hr) = -k_m\ [A]_{sed}\ \rho_s\ d \quad , \qquad (19)$$

where:

ρ_s is the mass of dry sediment/cm^3 bedded sediment

d is the depth of adsorption,

ρ is the density of water (g/cm^3),

is equal to the rate of adsorption, given by:

$$\text{adsorption } (\mu g/cm^2\ hr) = k_1\left(1 - \frac{[A]_{sed}}{K_d\ [A]_{H_2O}\ f_{dis}}\right)[A]_{H_2O}\ \rho\ f_{dis}. \qquad (20)$$

Setting equation (17) equal to (18) and solving for $[ant]_{sed}$ yields:

$$[A]_{sed} = \frac{K_d k_1 [A]_{H_2O} f_{dis}}{K_d k_m^d \rho_s + k_1} \quad . \qquad (21)$$

Finally, substituting equation (21) into equation (18) gives an expression describing the effect of adsorption by bedded sediments-microbial degradation on aqueous anthracene concentration:

$$\frac{d[A]_{H_2O}}{dt} = \frac{-k_1}{D}\left(1 - \frac{k_1}{k_1 + k_d k_m^d \rho_s}\right) [A]_{H_2O} f_{dis} \quad . \qquad (22)$$

Removal rates were calculated using parameters representative of Third Creek, $K_d = 1000$, $\rho_s = 1.7$ g/cm^3, and measured k_m values. The depth of sediment actively adsorbing anthracene directly from the water was estimated to be 0.1 cm. While this estimate is somewhat arbitrary, it seems reasonable for clay type sediments, where the anaerobic zone is likely to be less than 0.5 cm from the interface (13).

Bioaccumulation:

The bioaccumulation potential of anthracene was investigated using the zooplankter, Daphnia pulex, and fathead minnow, Pimephales promelas. Each species was exposed to dissolved anthracene in water ($\sim$ 6 ppb for Daphnia, 0.25 ppm for Pimephales) at 25°C for varying periods of time, and analyzed for anthracene content by fluorescence spectrophotometry following digestion-extraction. Daphnia could be analyzed by direct extraction into methanol, while minnows required

homogenization (Tekmar Tissuemizer) and NaOH digestion (5 ml 1 N NaOH, ~ 0.2 g fish, 70 °C for 30 min) followed by hexane extraction (14), evaporation and dissolution in methanol.

Bioaccumulation data were analyzed as a first order approach to equilibrium in a two compartment model (water and organisms). Uptake was assumed to be a first order process with respect to aqueous anthracene concentration, and the elimination rate first order with respect to anthracene concentration in the organism. These assumptions lead to the following differential equation as our model:

$$\frac{d\ [A]_{ORG\ (t)}}{dt} = C\ [A]_{H_2O\ (t)} - k_e\ [A]_{ORG} \quad , \qquad (23)$$

where:

$[A]_{ORG}$ is the anthracene concentration in the organism, (μg anthracene/g tissue wet weight)

k_e is the elimination rate constant in the organism, (hr^{-1})

aC is the uptake rate constant, (ml mg^{-1} hr^{-1}).

Since aqueous anthracene concentration tended to decrease with time at very low concentrations due to uncharacterized removal and degradation processes, $[A]_{H_2O}$ (t) was empirically approximated by the function

$$[A]_{H_2O\ (t)} = a + be^{-\lambda t} \qquad (24)$$

to give a description of the behavior of the aqueous concentration over time. Substitution of equation (24) into equation (23) and integrating

this differential equation yields the expression

$$[A]_{ORG\ (t)} = \frac{Cb}{\lambda - k_e} - \frac{Ca}{k_e} e^{-k_e t} - \frac{Cb}{(\lambda - k_e)} e^{-\lambda t} + \frac{C}{K} a \quad . \qquad (25)$$

For an unchanging aqueous concentration, i.e. the expression takes the form:

$$[A]_{ORG\ (t)} = \frac{C\ [A]_{H_2O}}{k_e} (1 - e^{-k_e t}) \quad . \qquad (26)$$

The estimates of the parameters C and k_e were obtained using a two stage iterative least squares technique. The first stage used the observed $(t, [A]_{H_2O}\ (t))$ values to obtain estimates of a, b, and λ or $[A]_{H_2O}\ (o)$ for the unchanging aqueous concentration case. (The estimate of $[A]_{H_2O}\ (o)$ was equal to the sample average of the observed $[A]_{H_2O}\ (t)$ values). By substitituting the parameter estimates from the first stage into equation (25) or equation (26), a non-linear iterative least squares procedure was used to determine the estimates of C and k_e (15). The bioaccumulation curve (concentration factor vs time) was derived from the ratio of equation (25) to (24), and approached C/k_e as a limit with increasing time.

RESULTS

Volatilization

Despite its low vapor pressure at 25°C, anthracene in aqueous solution is appreciably more volatile than water, (H = 0.0027 ± 0.0001)* and

*In these and all further cases, the number to the right of ± is the standard error of the estimated quantity.

thus volatilization would tend to reduce aqueous concentrations of anthracene. Mixing of both aqueous and gaseous phases acts to increase the rate of volatilization. Thus, under quiescent conditions, anthracene has a predicted volatilization half life of about 300 hours in a body of water 1 m deep, while in a system with current velocity of 1 m/sec and wind of 4 m/sec, the predicted half life is reduced to about 18 hours (Fig. 1).

Photolysis

Anthracene in distilled water was observed to be rapidly degraded under exposure to natural sunlight, with a photolysis half life of about 35 minutes under a midday sunlight in midsummer at 35°N latitude ($k_p = 1.19 \pm 0.10\ hr^{-1}$). A 24-hour photolysis rate for anthracene in midsummer would be about 0.36 times the summer midday photolysis rate, while a winter 24-hour photolysis rate would be roughly 0.12 times the summer midday rate (9). Thus, in pure water at shallow depths, anthracene would exhibit 24-hour photolytic half lives of about 1.6 hours in summer and 4.8 hours in winter at $\sim$ 35°N latitude.

In most natural waters, the absorption of light by dissolved and suspended matter would act to reduce photolysis rates considerably. Thus, for a decadic light absorption coefficient of 0.020 at 350 nm (a value observed in Third Creek water), the photolysis half life in a 100 cm deep body of water is increased by about 4 fold (Fig. 2). In a more turbid system ($\alpha = 0.100$, typical of $\sim$ 50 mg/l clay suspension), the half life is increased about 19 fold. Photolytic activity in most natural waters is thus limited to the uppermost 100 cm or less except for

waters of exceptional clarity (which would not be likely recipients of wastes containing PAH).

Hydrolysis:

No degradation was observed in controls for photolysis and microbial degradation experiments, indicating that the rate constant for non photolytic abiotic processes that degrade anthracene was < 0.001 hr^{-1} at 25°C. This process was assumed to be unimportant with respect to other, more rapid removal processes.

Microbial degradation

The rate constant of microbial degradation of anthracene in Third Creek water incubated 18 hours at 25°C was 0.061 ± 0.007 hr^{-1}. No degradation was observed in autoclaved Third Creek water, distilled water, or water from Walker Branch over the same time period. Anthracene concentration in the Third Creek water prior to addition of 1 ppb anthracene was below the limit of detection by fluorescence (< 0.05 ppb). Analysis of ^{14}C fractions in this experiment indicated that about 5% of the ^{14}C in the degraded anthracene (labeled at C-9 position) was converted to CO_2, with the remainder present in 1 N NaOH soluble metabolites. Fluorescence and ^{14}C techniques agreed well in estimating anthracene degradation rates.

Adsorption

Anthracene was sorbed by inorganic sediments and suspended organic particulates. The organic particulates (autoclaved yeast) exhibited a high affinity for anthracene, with K_d being approximately 25,000 at

25 C (3). As a result of such a high K_d, a 40 mg/l suspension would remove 50% of the anthracene from solution. Sorption by inorganic particulates was considerably less, with a 2.0-0.1 μ clay fraction exhibiting a K_d value of about 1600. Larger particles (5-10 mm silt) had appreciably less sorptive affinity, with $K_d \sim 100$. In the effluent from a biological waste water treatment plant, only 4.4% of anthracene added was adsorbed by 18.8 mg/l (dry weight) of solids, for a $K_d \sim 2500$.

Sedimentation

The rate of removal of anthracene by adsorption and subsequent sedimentation of particulates is determined by the extent of adsorption and rate of sedimentation. Calculated removal rate constants for anthracene (assuming no forces act to maintain particulates in suspension - a clearly incorrect assumption) range from 7.2×10^{-3} hr^{-1} ($T_{1/2}$ = 96 hr) for depth 1 m, 1 g/ℓ, 2 μ clay sediment to 1.44×10^{-3} hr^{-1} ($T_{1/2}$ = 481 hr) for depth 1 m, 40 mg/l 10 μ silt sediment. (Both sediment concentrations produce sedimentation rates of 8.4 cm/yr, a value higher than that found in most reservoirs of the Ohio River system).

The sedimentation rate constant for removal of anthracene by organic detritus was calculated for particles 10 μ in diameter of specific gravity 1.02, using k_d = 25000 and [part] of 20 mg/l. The resulting rate constant was 0.0012 hr^{-1} for a depth of 1.0 meters.

Sedimentation rates calculated in this way are unrealistically large due to neglecting suspension forces (resulting from the kinetic energy of flowing water), but the removal rates are nevertheless considerably slower than those predicted for volatilization, photolysis, and microbial degradation. In the presence of water current, sedimentation rates are likely to be far slower than these; hence adsorption-sedimentation is not likely to be a significant process for the net removal of anthracene from the water column. Sediment concentrations calculated in Equation (14) for a sedimentation rate of 8.4 cm/yr would be maintained in suspension (Equation (15)) by 0.1 m/sec current if composed of either 2 μ or 10 μ particles.

Adsorption to bedded sediments

The rate of adsorption of anthracene by bedded sediments is determined by mixing in the aqueous phase (k_ℓ from volatility determinations) and the degree to which the uppermost layer of bedded sediment is not in equilibrium with respect to adsorption of anthracene from the water. In the absence of some process which removes anthracene from the uppermost sediment layer, anthracene in the sediment would attain an equilibrium concentration ($K_d\ [A]_{H_2O}\ f_{dis}$) and net adsorption would approach zero. Degradation of anthracene in the sediments by microorganisms provides the driving force for the removal process. Thus, the rate of removal of anthracene by this process is determined by the rate of microbial degradation unless microbial degradation is so rapid that delivery of anthracene to the sediment-water interface (k_1) becomes limiting.

The predicted rate of adsorption to bedded sediments vs microbial degradation rate is depicted in Fig. 3 for a system 1 m deep flowing at 1 m/sec. At microbial degradation rates observed in Third Creek sediments (k_m = 1 x 10^{-3} - 1 x 10^{-2} hr^{-1}), (10) the adsorption of anthracene by bedded sediments would reduce the concentration of anthracene in the overlying water with a half life of 65-500 hr. If the depth of sediment actively participating in the adsorption process is greater than that used in these estimations (1 mm), the rate of adsorption would be increased equivalent to a proportional increase in k_m, with d remaining 1 mm. Similarly, increasing K_d of the sediments would act to increase the rate of adsorption (assuming microbial degradation rates in sediments do not vary with adsorptive potential of the sediments).

Bioaccumulation:

Bioaccumulation of anthracene by both Daphnia and Pimephales was rapid, with Daphnia attaining apparent equilibrium concentrations within several hours, while the minnows attained apparent equilibrium within 2-3 days. Uptake and elimination kinetics of the minnows were roughly an order of magnitude less rapid than those of the zooplankter. Uptake (C) and elimination (k_e) rate constants of 0.702 ± 0.077 ml mg^{-1} hr^{-1} and 0.589 ± 0.077 hr^{-1} were observed for Daphnia, and 0.031 ± 0.025 ml mg^{-1} hr^{-1} and 0.064 ± 0.059 ml mg^{-1} hr^{-1} were noted for Pimephales. Equilibrium concentration factors, $(\frac{[A]_{organism}}{[A]_{H_2O}})$, were similar, being 1192 ± 52 for Daphnia and 480 ± 96 for Pimephales.

In order to assess the importance of possible food chain bioaccumulation, the uptake rate for minnows ingesting 10% of their live weight per day in Daphnia equilibrated with the ambient aqueous anthracene concentration was calculated using the observed Daphnia concentration factor and compared to the anthracene uptake rate (C) for Pimephales. In a 1 µg/l anthracene solution, a 200 mg minnow would take up an estimated 6.2×10^{-3} µg anthracene/hr through direct uptake, while uptake from ingesting Daphnia would be 1.0×10^{-3} µg anthracene/hr. Since the rapid bioaccumulation kinetics of Daphnia indicate that zooplankton populations would maintain body burdens of anthracene nearly in equilibrium with ambient water concentrations, fish would require ingestion of more than 60% of their weight per day to take in an amount of anthracene equivalent to that taken up directly.

DISCUSSION

The persistence of anthracene in natural waters under summer conditions of temperature and illumination appears to be primarily determined by the processes of photolysis and degradation by microorganisms suspended in the water column (Table 1). In a large, deep (5 m), slow moving (0.1 m/sec) river such as the upper Ohio (Table 1A), depth and turbidity would act to reduce the importance of photolysis, making microbial activity the major removal process. In highly turbid waters (Table 1B), photolysis is reduced further, while the removal of anthracene from solution by adsorption to suspended particles acts to reduce the rate of microbial degradation and volatilization. In a relatively

transparent deep water body (Table 1C), microbial degradation of anthracene is still dominant, accounting for 74% of the estimated degradation rate, with photolysis accounting for 18%. In shallower systems, interface related phenomena become of increased importance. Thus, for a system 1 m in depth, relatively clear (Table 1D), the abiotic processes, photolysis and volatilization account for 63% of the estimated removal rate. Microbial degradation still plays an important role. For a very shallow (0.25 m), clear stream (Table 1E), photolysis and volatilization dominate even more, and anthracene is estimated to be removed with a half life of only 1.5 hr (mean daily photolysis rate).

The process of adsorption-sedimentation and adsorption to bedded sediments-microbial degradation in sediments do not appear to be of major significance in determining the persistence of anthracene in the hypothetical systems considered. This does not indicate, however, that anthracene will not accumulate in sediments, in fact, the coupling of rates of adsorption to bedded sediments and microbial degradation rates within the sediments predicts sediment concentrations of > 80% of equilibrium values (K_d [A] $_{H_2O}$ f_{dis}).

CONCLUSIONS

(1) Anthracene chronically introduced to aquatic environments will be rapidly removed by the action of suspended microorganisms, sunlight, and volatilization. Half lives of substantially less than one day are anticipated in many systems.

(2) Microbial degradation by suspended organisms is likely to be the most significant of these processes under a variety of conditions,

but under situations of shallow depth and clear water photolytic degradation and volatilization may be more rapid.

(3) Bioaccumulation kinetics of anthracene in small fish and zooplankton are rapid, and equilibrium concentration factors attained are comparable. Food chain magnification at this step (zooplankton → fish) is not likely to be great due to the rapid direct uptake of anthracene from water by fish. Rapid bioaccumulation kinetics suggest that body burdens of anthracene in zooplankton will respond rapidly to changing aqueous anthracene concentrations, while body burdens in fish would follow a similar, but somewhat damped, pattern.

We have identified the following areas where greater research emphasis is needed.

(1) Since microbial degradation rates used in these estimations were measured in a single contaminated aquatic ecosystem, further research needs to be done in other contaminated systems to determine more representative rates and factors affecting them, such as aqueous concentrations of anthracene and other PAH's.

(2) Estimation of the rate of the process of adsorption to bedded sediments--microbial degradation requires a knowledge of chemical, physical, and biological characteristics of a thin surface layer at the sediment-water interface, specifically the thickness (d), adsorptivity (K_d), and microbial activity (k_m). While k_m estimations made in mixed sediments vs intact sediment surfaces did not differ greatly, the the values of d and K_d assumed are somewhat arbitrary. Further attempts to experimentally determine these parameters seem warranted.

(3) Data on bioaccumulation by filter feeding invertebrates such as clams is needed. Such organism may be consumed by humans, and may exhibit higher concentration factors than fish due to their less complex physiological detoxification capability.

(4) Experimental determination of volatility and microbial degradation of anthracene at low temperatures is needed.

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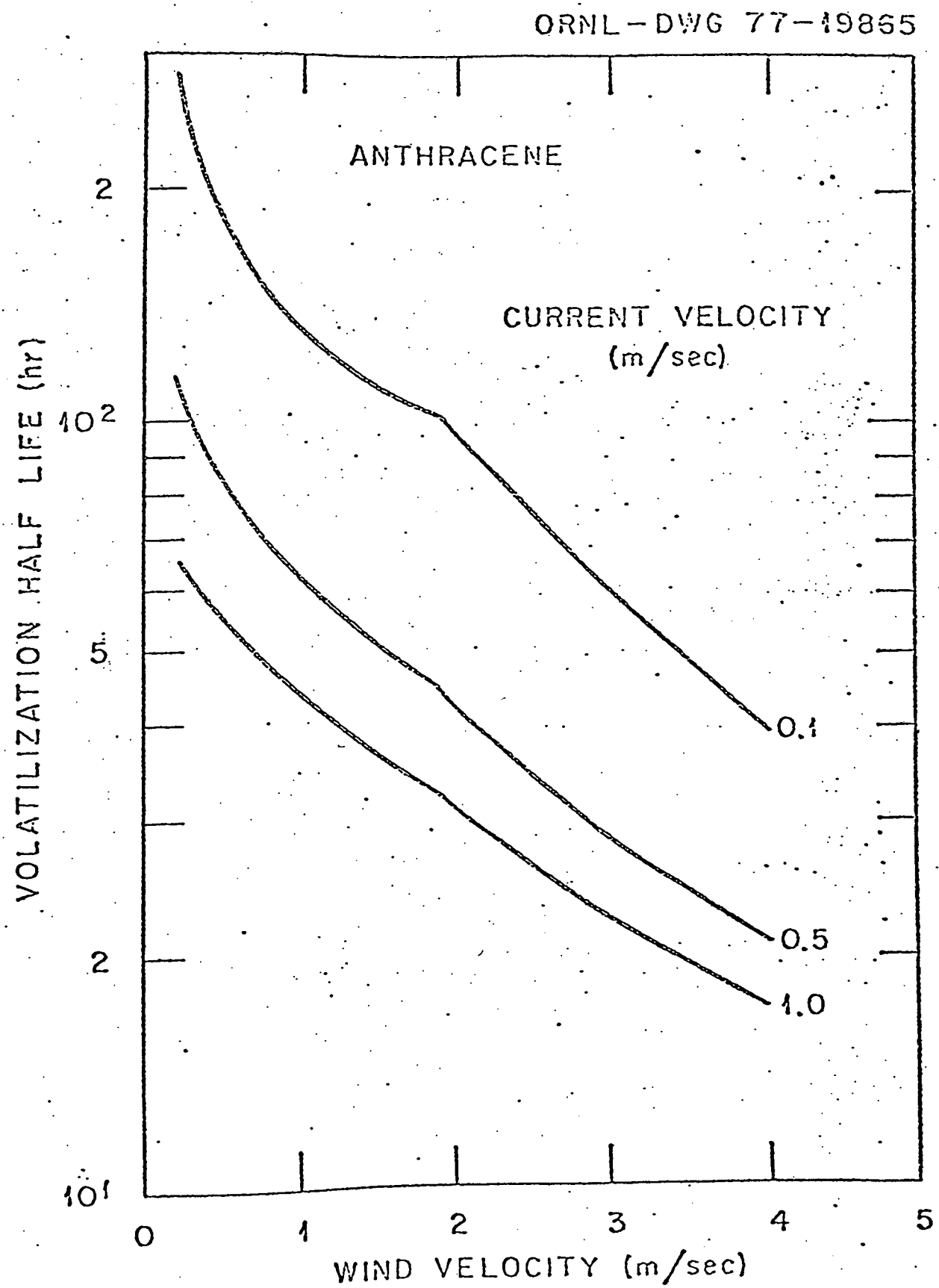
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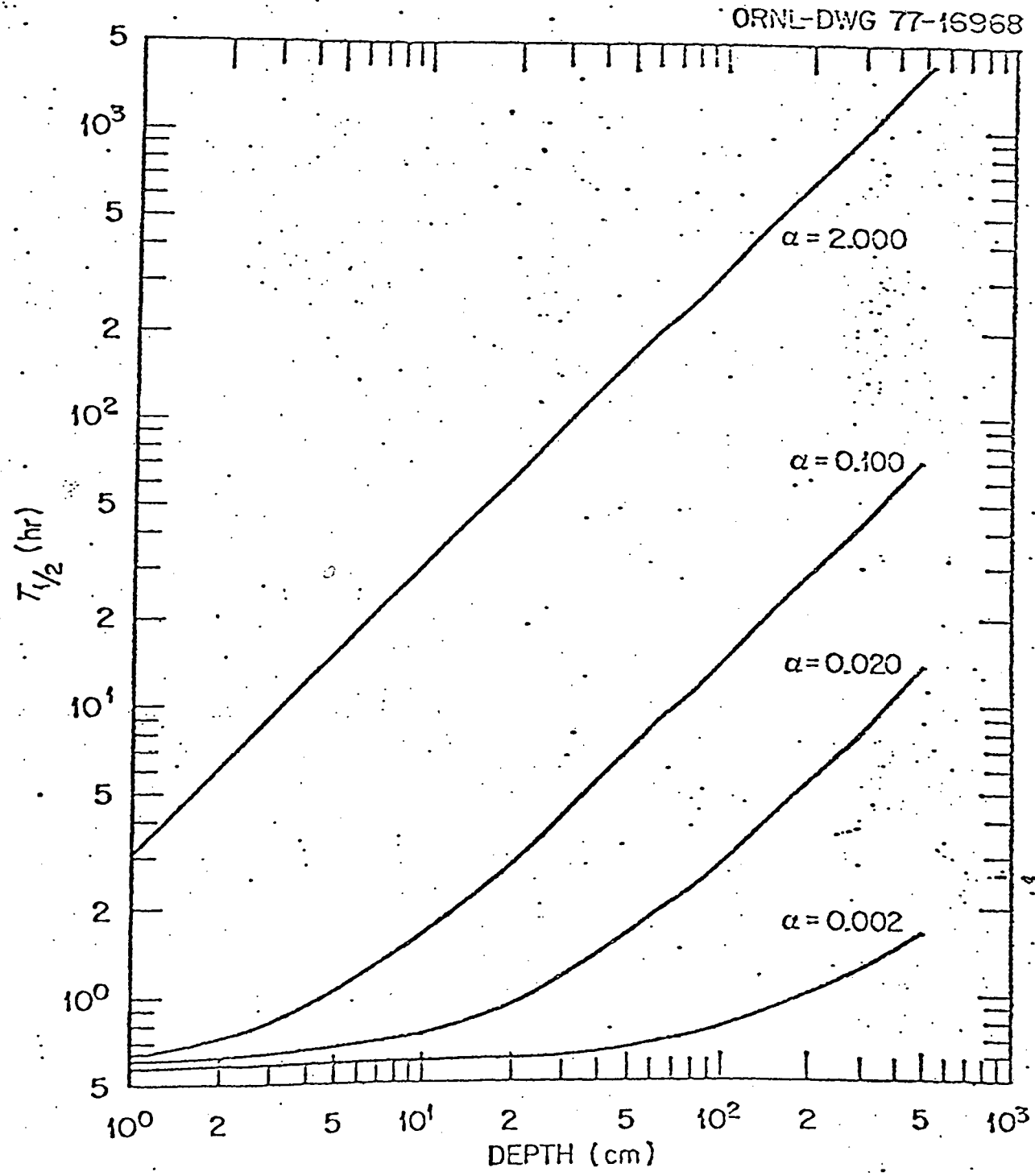
CURRENT VELOCITY
(m/sec)
0.1
0.5
1.0
VOLATILIZATION HALF LIFE (hr)
2
10²
5
2
10¹
0
1
2
3
4
5
WIND VELOCITY (m/sec)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DEPTH (cm)
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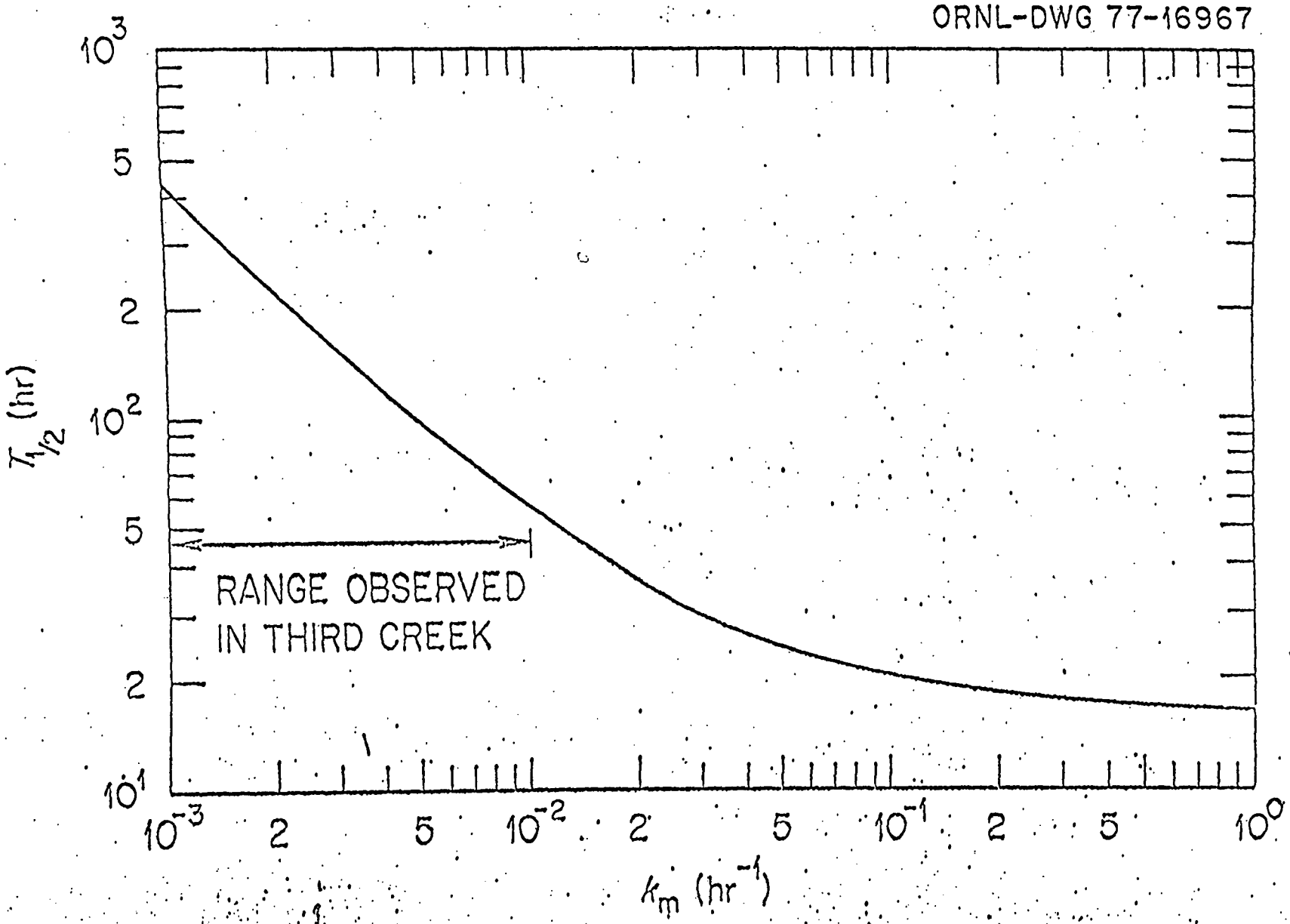
α = 0.100
α = 0.020
α = 0.002
5
10^3
5
2
10^2
5
2
10^1
5
2
10^0
5
10^0
2
5
10^1
2
5
10^2
2
5
10^3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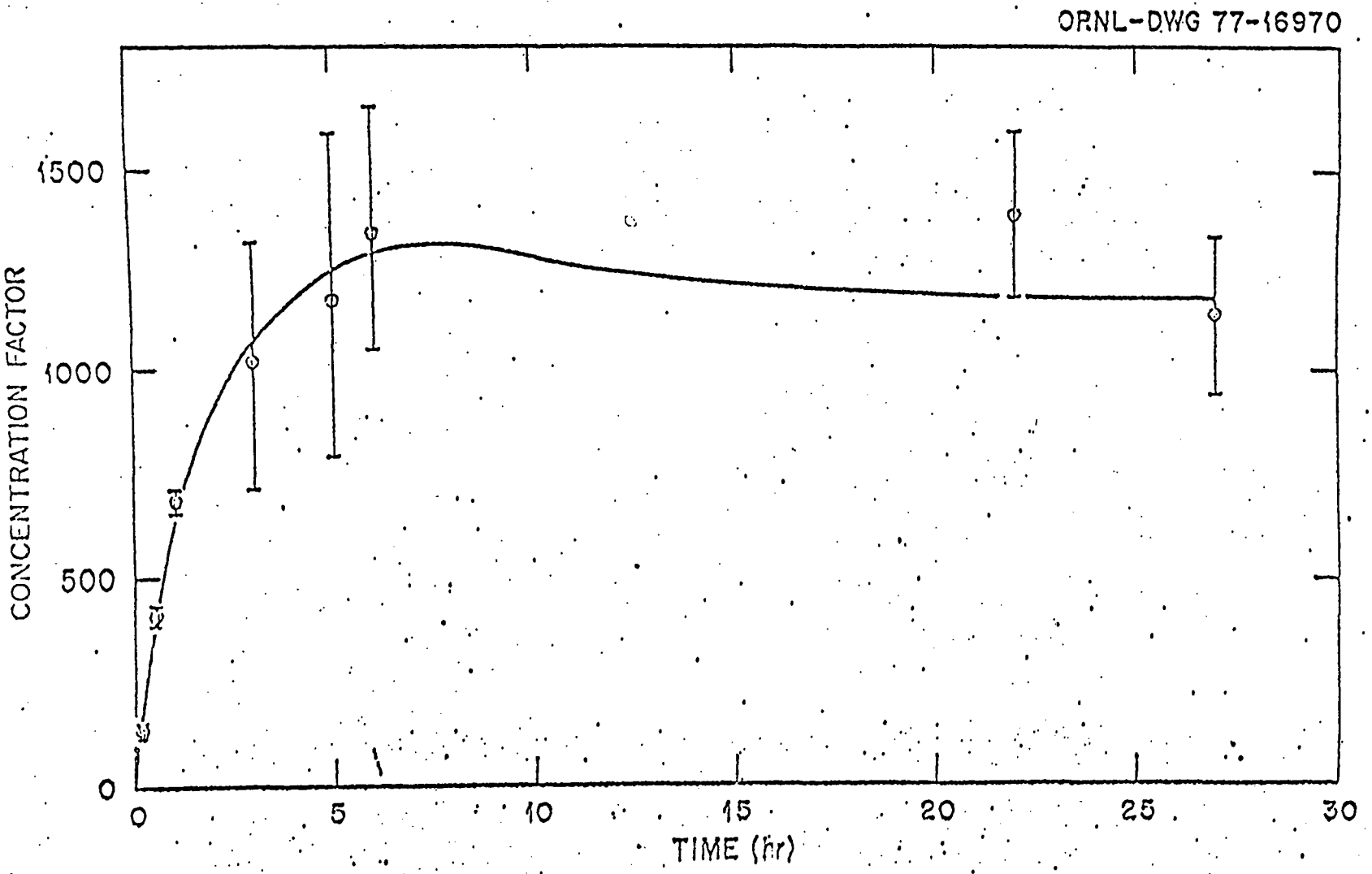
10^3
5
2
10^2
5
2
10^1
$T_{1/2}$ (hr)
RANGE OBSERVED
IN THIRD CREEK
10^{-3}
2
5
10^{-2}
2
5
10^{-1}
2
5
10^0
k_m (hr^{-1})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CONCENTRATION FACTOR
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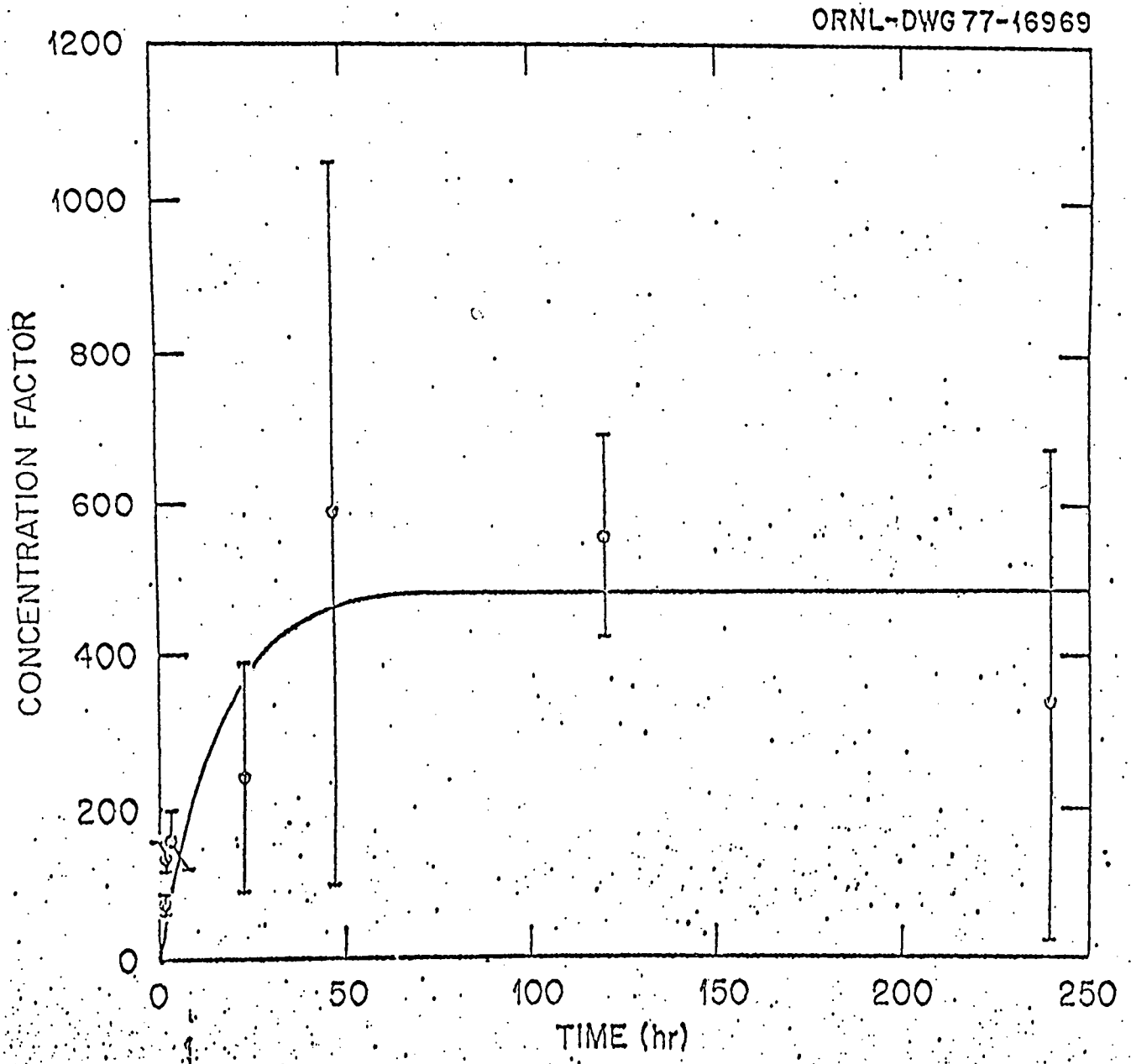
1000
500
0
0
5
10
15
20
25
30
TIME (hr)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1000
800
600
400
200
0
0
50
100
150
200
250
TIME (hr)

Table 1. Removal of anthracene from the water column at 25°C, midsummer sunlight in various environments

(A) Deep, slow, somewhat turbid

depth - 5 m
current - 0.1 m/sec
wind - 4 m/sec

suspended solids - 50 mg/l, 2 μ clay
$k_d = 1000$, $f_{ads} = 0.05$
$\alpha = 0.100$

Process	Rate constant (hr^{-1})	Fractional contribution
Volatilization	0.002	0.03
Adsorption to bed	< 0.001	-
Photolysis	0.004	0.06
Microbial degradation	0.060	0.91
Sedimentation	< 0.001	-
Combined	0.066	

$T_{1/2}$ = 10.5 hr

(B) Deep, slow, muddy

depth - 5 m
current - 0.1 m/sec
wind - 4 m/sec

suspended solids - 1 g/l, 2 μ clay
$k_d = 1000$, $f_{ads} = 0.5$
$\alpha = 2.00$

Process	Rate constant (hr^{-1})	Fractional contribution
Volatilization	0.001	0.03
Adsorption to bed	< 0.001	-
Photolysis	< 0.001	-
Microbial degradation	0.030	0.79
Sedimentation	0.001	0.18
Combined	0.032	

$T_{1/2}$ = 21.6 hr

Table 1. (continued)

(C) Deep, slow, clear

depth - 5 m
current - 0.1 m/sec
wind - 4 m/sec

suspended solids - low, $f_{ads} < 0.01$
$k_d = 1000$
$\alpha = 0.020$

Process	Rate constant (hr^{-1})	Fractional contribution
Volatilization	0.002	0.02
Adsorption to bed	0.001	0.01
Photolysis	0.018	0.22
Microbial degradation	0.061	0.74
Sedimentation	< 0.001	-
Combined	0.082	

$T_{1/2}$ = 8.5 hr

(D) Shallow, fast, clear

depth - 1 m
current - 1 m/sec
wind - 4 m/sec

suspended solids - low, $f_{ads} < 0.01$
$k_d = 1000$
$\alpha = 0.020$

Process	Rate constant (hr^{-1})	Fractional contribution
Volatilization	0.042	0.21
Adsorption to bed	0.008	0.04
Photolysis	0.086	0.44
Microbial degradation	0.061	0.31
Sedimentation	< 0.001	-
Combined	0.197	

$T_{1/2}$ = 3.5 hr

Table 1. (continued)

Very shallow, clear, fast

depth - 0.25 m
current - 1 m/sec
wind - 4 m/sec

suspended solids - low, $f_{ads} < 0.01$
$k_d = 1000$

$\alpha = 0.020$

Process	Rate constant (hr^{-1})	Fractional contribution
Volatilization	0.179	0.35
Adsorption to bed	0.032	0.06
Photolysis	0.238	0.47
Microbial degradation	0.061	0.12
Sedimentation	< 0.001	-
Combined	0.510	

$T_{1/2} = 1.4$ hr