

SIMULATED TRANSPORT OF POLYCYCLIC AROMATIC HYDROCARBONS IN ARTIFICIAL STREAMS¹

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Abstract:—A model was constructed to predict transport of polycyclic aromatic hydrocarbons (PAH) in artificial streams. Model processes included volatilization, photolysis, sorption to sediments and particulates, and net accumulation by biota. Simulations of anthracene and benzo(a)pyrene were compared to results of an experiment conducted in the field. The model realistically predicted the concentration of diuron and the rate of degradation in space. Photolytic degradation appeared to be a major pathway of anthracene flux from the streams.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are potentially hazardous by-products of the synthetic industry and the generation of electricity by fossil fuels. Toxic mutagenic (Larbro et al. 1979), carcinogenic (Worren et al. 1977) characteristics of PAH require estimation of human health risks posed by introduction of these chemicals into the environment.

Assessment of health risks associated with introduction of PAH into the environment depends in part upon quantification of environmental transport and subsequent dose (Crawford and Landrum 1980). Thousands of different species of PAHs (Crosby et al. 1979) are known. Therefore, application of elaborate procedures (Landrum et al. 1977) to identify major processes of PAH transport, accumulation, and degradation of specific PAH is impractical for purposes of risk assessment.

This paper reports an attempt to predict the pattern of flow and accumulation of three PAH (anthracene, naphthalene, and benzo(a)pyrene) in artificial streams located on the Savannah River plant near Aiken, South Carolina. Predictions were based upon the premise that the fundamental chemistry of individual PAH contains useful information for predictive purposes.

Predictions of transport of PAH were made for streams because energy input, rate of production or cooling purposes. Thus, they are often located near streams and rivers where the probability of accidental or chronic addition of PAH to adjacent waters might be relatively high.

MODEL DESCRIPTION

Simulation of PAH transport in lotic systems requires an understanding of the basic structure and function of streams. The physical, chemical, and biological processes as well as of that determine transport of PAH compounds are ecologically information concerning species composition, standing crop, nutrients, and energy flow has accumulated for a variety of lotic systems (Coffman et al. 1971, Fisher and Likens 1972, McIntire and Pridney 1965, Minshall 1978, Odom 1957, Teal 1957, Tilly 1968). Yet streams and rivers have not received the attention from ecologists and modelers that other aquatic systems have. Recently (Landrum 1980), models of lotic systems have been developed from the point of view of environmental engineers. Six models of stream transport included dissolved oxygen, biological oxygen demand, and total solids. Model structures represented a stream or river as a series of segments (reaches), which can be individually very different in dimensions and hydraulic characteristics, but which are assumed internally homogeneous.

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Recently, some ecologists have begun to simulate energy and material flow through lotic systems, borrowing the reach-model approach (Shen and Wells 1976, Knowles and Wakeford 1978, McIntire and Gibly 1978, Sandoval et al. 1976, Zedler 1978). Our strategy was to adopt this approach.

Specific processes believed to influence PAH flux included photolytic degradation, volatilization, sorption to suspended particulates, sediments, and uptake and deposition by stream biota. These processes were incorporated into a Fate of Aromatic Model (FOM). Figure 1 illustrates model pathways of PAH flux through a single reach.

An overall mass balance approach was taken to model the change in PAH concentration through time and space:

$$\frac{\partial P_i(t, j)}{\partial t} = \frac{\partial P_i(t, j)}{\partial t} + U_i(t, j) - \frac{\partial P_i(t, j)}{\partial j} \quad (1)$$

where

P_i = PAH concentration in reach j at time t ,
 j = distance downstream (m), and
 U_i = current velocity (m/c).

Equation (1) was solved by numerical approximation after conversion to difference equations (Sandoval et al. 1976). The sum of time dependent change, $\frac{\partial P_i(t, j)}{\partial t}$, is change. Dispersion was not considered in the model. The time step (Δt) was determined by necessary relationship between reach length and current velocity: $U_i \Delta t = \Delta j$ (Bellie and Dobbin 1968).

Hydrological Submodel

Application of the model was constrained to conditions of constant geometry and constant discharge. For modeling purposes, the 91.4-m long artificial stream channel was conceptually divided into five equal reaches. Reach length was 18.28 m, width was 0.63 m, and depth was 0.20 m. The continuity equation calculated current velocity in relation to constant cross sectional area and discharge:

$$V = Q/A \quad (2)$$

where

V = current velocity (18.28 m/h),
 Q = discharge (4.53 m³/h), and
 A = reach cross sectional area (0.12 m²).

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SIMULATION OF PAH FLUX THROUGH STREAMS

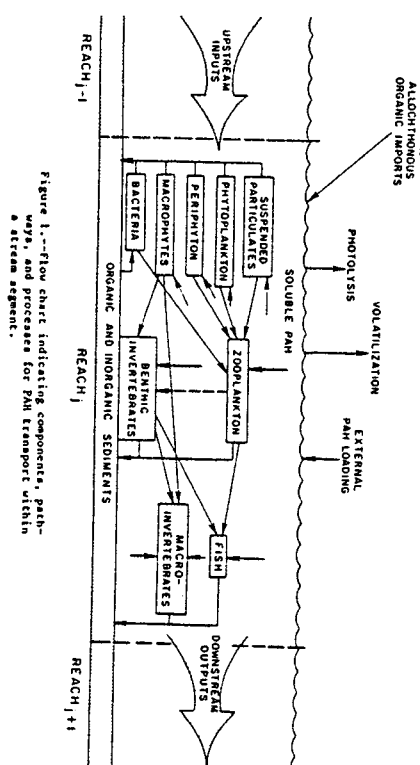


Figure 1.—Flow chart indicating components, pathways, and processes for PAH transport within a stream segment.

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This submodel, while simplistic, was representative of the artificial stream.

Temperature Dependent Processes

In FOMM, water temperature can influence transport of PAH through the foodweb by regulating rates of photosynthesis and respiration according to an empirically derived function (Shugart et al., 1974). Temperature gradients can be simulated using hourly input temperatures for each reach. However, for simulations reported in this study, water temperature was constant, 22°C, for all reaches.

Solar Radiation Submodel

Incident solar radiation drives photolytic degradation of PAH and photosynthesis in FOMM. A modification of Satterlund and Means' (1978) model was incorporated in FOMM to simulate daily moon light intensities used in a 12-h light:dark cycle:

$$I_t = (I_{Da} + I_p) \cdot (1 - C) + (I_{Do} + I_s) C \quad (3)$$

where

I_t = light intensity at reach surface (1y/h),

I_{Da} = slope dependent, direct beam radiation (1y/h),

I_{Do} = scattered clear sky radiation (1y/h),

I_{Ds} = direct radiation on horizontal surface (1y/h),

C = fractional cloud cover,

F = slope correction for scattered radiation, and

d = regression parameter for seasonal cloud effects.

Light intensity at the reach surface was attenuated with water depth. Hypothetical equations generated partial extinction coefficients for suspended particulate matter and phytoplankton.

Photolysis Submodel

Light-dependent degradation of aromatic hydrocarbons in FOMM is based on the photolysis model of Southworth (1979a). Direct photochemical breakdown of dissolved PAH and degradation of photo-oxidized PAH sorbed to suspended particulates both occur; however, Miller and Zopp (1979) concluded that indirect photolytic degradation of

sorbed PAH was minor in comparison to direct photolysis in FOMM only direct photolysis of dissolved PAH was modeled.

In the photolysis submodel, PAH was degraded according to an equation adapted from Zopp and Cline (1977):

$$\frac{dPAH}{dt} = \phi \cdot I \cdot PAH \quad (4)$$

where

ϕ = molar yield coefficient (unitless),

I = light absorbed at wavelength λ , and

PAH_{λ} = concentration of dissolved PAH (moles/L).

Reported yield coefficients ranged between 0.001 and 0.01 for polycyclic aromatic hydrocarbons (Zopp and Schlotzhauer 1979). A linear regression based upon data in Zopp and Schlotzhauer (1979) related molecular weight to yield coefficient:

$$\phi = 0.0235 - 8.36 \times 10^{-5} \cdot MW \quad (5)$$

Light absorbance for specific PAH compounds was summed over 10-nm wavelength increments between 300 and 500 nm, a region of maximum absorbance for PAH. Each λ was calculated as the product of light intensity at λ and the molar extinction coefficient for λ , ϵ_{λ} . Compound-specific values of ϵ_{λ} were supplied as model input.

Light intensity, I_0 , incident on each reach surface was attenuated by equation (3). Light intensity at each wavelength was attenuated as a function of depth according to a regression derived for 12 southeastern United States rivers (Zopp and Cline 1977):

$$I_{\lambda} = 0.42e^{(-0.004d - \lambda)} \quad (6)$$

where I_{λ} has units of 1/c.

A depth-specific rate of photolysis was calculated for 1.0-m intervals until: (1) the depth of the reach had been equaled or (2) the depth specific rate was less than 10% of the rate calculated for the 0 to 1.0 cm depth interval. Depth-specific rates were integrated over the water column and converted to units of $gPAH/m^2$. The mass of degraded PAH was added to the dissolved metabolite pool.

Modeled differences in rate of photolysis of specific PAHs from differences in molar extinction coefficients (eq. 5), and from differences in absorbance spectra.

Sorption Submodel

Karickhoff et al. (1979) modeled sorption as a first-order relationship between the concentration of dissolved PAH and an equilibrium-partition coefficient, K_p . The partition coefficient increased linearly as a function of the organic content of the sorbent material. The partition coefficient also correlated with the octanol/water sorption coefficient (K_{ow}) of the PAH.

Depending upon available data, rates of sorption were calculated in one of three ways. First, if K_p and the organic fraction of the sorbent were known, R_p was calculated from:

$$LOO(R_p) = LOO(K_p) \cdot 0.21 \quad (7)$$

and

$$R_p = K_p \cdot oc \quad (8)$$

where

oc = fractional organic content of the sorbent, and

K_p = coefficient for partitioning into organic fraction of sorbent.

Second, if K_{ow} was not known, K_p was estimated from the solubility of the particular PAH:

$$LOO(K_p) = -0.34 + LOO(S) - 0.46 \quad (9)$$

where

S = solubility of the PAH, as a mole fraction, and R_p was estimated from (8).

Third, if neither K_{ow} nor the organic fraction of the sorbent was known, a partition coefficient was estimated directly from:

$$LOO(R_p) = 4.16 - 0.51 \cdot LOO(S) \quad (10)$$

where

S = solubility of the PAH, (ppm).

Equation (10) resulted from analysis of data in Karickhoff et al. (1979).

As a first approximation, R_p values were divided by the duration of the Karickhoff et al. (1979) experiments to convert to units of first-order rate constants. We assumed that these rates of sorption per unit mass of sorbent, S_{norm} , were constant over the duration of the model. Specific rates of sorption were calculated for suspended particulate matter and sediments according to:

$$S = S_{norm} \cdot SBMT \cdot SBMT \cdot oc / SBMT \cdot (SBMT \cdot oc) \quad (11)$$

where

S = rate of sorption ($gPAH \cdot m^{-2} \cdot h^{-1}$),

S_{norm} = maximum sorption rate ($gPAH \cdot g^{-1} \cdot h^{-1}$),

$SBMT$ = soluble PAH (g/m^3), and

$SBMT$ = sorbent (g/m^2).

With (11), the rate of sorption was proportional to the concentration of dissolved PAH when the concentration of the sorbent was constant. From (11), sorption was primarily reflected the concentration of the sorbent.

Description of PAH from sorbent material was not included in the sorption submodel. Net sedimentation of suspended particulate matter and sediments provided pathways for advective loss of sorbed PAH from each reach in the modeled stream.

Volatilization Submodel

The submodel that simulated losses of PAH from the artificial streams as a result of volatilization was taken directly from Southworth (1979b). The rate of volatilization was modeled as a function of current velocity, wind velocity, reach depth, and molecular weight of the PAH according to a hyperbolic equation involving Henry's law:

$$R_L = H \cdot K_g \cdot K_L / (H + K_g) \cdot K_L \quad (12)$$

where

H = molar concentration of PAH in air divided by molar concentration of PAH in water,

K_g = gas phase exchange coefficient (cm/h), and

K_L = overall transfer coefficient (cm/h).

The logarithms of H , K_g , and K_L were entered into regressions defined in Southworth (1979b). Current velocities required by the regression equations were calculated by the hydrological submodel. Wind velocity was specified as an input parameter and was a constant 1.0 m/s in all simulations.

Biological Production Submodel

Rates of biomass change were determined by first-order equations for production and mortality. The equations for production, phytoplankton, phytoplankton, macrophytes) in reach j at time t was:

$$\frac{dP_j}{dt} = (F_{Ij} - F_{Oj}) + P_j (P_j - R_j - U_j - S_j) - C_j \quad (13)$$

where

P_i = biomass of producer i (g dry wt/m²),

$F_{i,j}$ = inflow of P_i from reach $j-1$ (g m⁻² h⁻¹),

PQ_i = outflow of P_i to reach $j+1$ (g m⁻² h⁻¹),

PS_i = rate of gross photosynthesis of P_i (g g⁻¹ h⁻¹),

R_i = respiration rate (g g⁻¹ h⁻¹),

M_i = non-grazing mortality rate (1/h),

U_i = secretion-excretion rate (1/h),

S_i = sinking rate (1/h), and

Q_i = loss of P_i to grazing (g m² h⁻¹).

The mass balance equation for changes in consumer biomass (invertebrates, bacteria, benthic invertebrates, fish) was:

$$\frac{dN_i}{dt} = (F_{i,j} - PQ_i) + C_{i,j} - N_i (R_i + S_i + U_i + M_i) - Q_i \quad (14)$$

where

N_i = biomass of consumer i in reach j at time t (g dry wt/m²),

$C_{i,j}$ = consumption of prey j by consumer i (g m⁻² h⁻¹),

$F_{i,j}, PQ_i$ = same as in equation (13), but for consumer i ,

R_i = respiration rate of consumer i , (g g⁻¹ h⁻¹),

S_i = fraction of consumption that was egested (1/h),

U_i = excretion rate for consumer i (1/h),

M_i = non-predatory mortality rate for consumer i (1/h),

Q_i = predatory losses of consumer i (g m⁻² h⁻¹).

Photosynthesis.--Gross photosynthesis was modeled after Smith (1976):

$$PS_i(t) = (IT) \cdot P_{max} \cdot I \cdot (1 + I/I_0)^{-1/2} \quad (15)$$

where

PS_i = gross photosynthesized per gram producer at time t in reach j by producer i ,

P_{max} = light saturated photosynthetic rate for i (g g⁻¹ h⁻¹),

I = light intensity from solar submodel (1/h),

I_0 = light saturation constant for producer i (1/h), and

(IT) = temperature dependence of photosynthesis.

Respiration.--For producers, a fraction of gross photosynthesis of for consumers, a fraction of consumption, was lost through respiration.

Consumption.--PAM moved through the foodweb by the feeding activities of the consumer components. Consumption was modeled as a function of predator and prey biomass (DeAngelis et al. 1975):

$$C_{i,j} = (fT) \cdot \frac{C_{max,i} \cdot N_i \cdot U_j \cdot N_j}{N_i + U_j + N_j} \quad (16)$$

where

$C_{i,j}$ = biomass of prey j consumed by consumer i (g m⁻² h⁻¹),

$C_{max,i}$ = maximum feeding rate of consumer i , (g m⁻² h⁻¹),

N_i = biomass of consumer i (g/m²),

N_j = biomass of prey j (g/m²),

U_j = Bayesian preference of consumer i for prey j (unitless),

(fT) = temperature dependence of predation (eq. 4), and

j = PAM concentration of prey j (gPAM/g dry wt).

This equation has been usefully applied to models of feeding, zooplankton, benthic invertebrates and fish (Kilham et al. 1974, O'Neill 1976, and Smith et al. 1975).

Excretion.--At each iteration a fraction of biomass and its PAM content were excreted from its primary producer and consumer component. It was assumed that 23% of the excretory products was a metabolite product that was shunted to the metabolite pool. The remainder was excreted into the dissolved PAM pool.

Mortality.--Nonpredatory mortality was modeled in a temperature-dependent manner. Biomass of dead plankton, benthic invertebrates and fish was added to the suspended detritus pool. Nonpiscivorous PAM from biota was the product of biomass lost to mortality and the PAM concentration of the biomass.

Sinking losses.--Losses of PAM from the water column due to sinking phytoplankton was modeled in a linear fashion. In FOM the sinking rate was not coupled to the current velocity.

Egestion losses.--A fraction of ingested food was egested by the consumer components of the model. Losses due to egestion were added to the suspended particulate pool. Egested PAM was modeled as the product of egestion rate and the PAM concentration of the food item egested.

Direct PAM uptake.--Uptake of dissolved PAM by the primary producers in FOM was modeled as a second-order process:

$$PU_i = P_i \cdot U_{P_i} / (K_{P_i} + P_{M_d}) \quad (17)$$

where

PU_i = uptake by producer i (gPAM m⁻² h⁻¹),

P_i = biomass of producer i (g dry wt/m²),

U_{P_i} = maximum uptake rate (gPAM g⁻¹ h⁻¹),

K_{P_i} = dissolved PAM concentrations (gPAM/m³), and

P_{M_d} = dissolved PAM concentrations constant (gPAM/m³).

R_{P_i} is analogous to half the saturation constant (gPAM/m³).

Direct uptake was assumed independent of rates of photosynthesis or respiration.

Direct uptake of PAM by consumers was coupled to the rate of respiration, assuming that uptake occurred across respiratory membranes and was an active process:

$$CU_j = N_j \cdot UC_j \cdot R_j \cdot P_{M_d} / (K_{C_j} + P_{M_d}) \quad (18)$$

where

CU_j = uptake of dissolved PAM (gPAM m⁻² h⁻¹),

NC_j = biomass of consumer j (g dry wt/m²),

UC_j = maximum uptake per unit respiration,

R_j = g dry wt respired per g dry wt,

P_{M_d} = dissolved PAM (gPAM m³), and

K_{C_j} is constant (gPAM m³).

As an initial assumption, values of R_{P_i} and K_{C_j} were all defined as half of the maximum solubility of the particular PAM.

Degradation of PAM.--Metabolic degradation of assimilated PAM was modeled as a function of respiration rate and was therefore indirectly affected by water temperature.

$$D_i = R_i \cdot P_i \cdot h_i \cdot D_{max,i} \quad (19)$$

where

$D_{max,i}$ = gPAM degraded h⁻¹ g dry wt⁻¹ respired by component i

P_i = g dry wt/m² of component i , and

h_i = fractional PAM content of P_i .

Metabolically degraded PAM was added to the metabolite pool.

External loading of PAM and Solubility

Polycyclic aromatic hydrocarbons were added to the headwaters of the artificial stream. FOM structure reflects this practice: dissolved PAM entered the first reach in the modeled stream as the product of a predefined discharge regime (m³/h) and the PAM concentration of the influent (gPAM/m³).

A relationship between PAM molecular weight and solubility of specific compounds was derived from data in Strawn et al. (1977):

$$\text{LOC}(P_{M_d}) = 6.50 - 0.06 \cdot MW \quad (20)$$

where

P_{M_d} = dissolved PAM (mg/l), and

MW = molecular weight.

This regression was used to estimate solubility for 1000s PAM compounds and to ensure that solubility was not exceeded during the course of a simulation. PAM in excess of solubility was added to the sediments.

Model Parameters

Parameters for physical/chemical processes of PAM flux were estimated from data presented in papers referenced in sections that describe physical/chemical submodels.

Parameters for biological pathways of uptake and deposition result from laboratory and field microcosm with 14C-PAM tracers and various components of the stream biota (Laversee et al. 1981).

Initial Conditions

Initial biomass conditions for the simulation were estimated from samples collected from the artificial stream or measured directly from organisms used in stream. Pre-physion biomass was estimated as 0.1 g dry wt/m² in all reaches. Biomass of invertebrate in reach 6 (macroinvertebrates) was 9.31 g dry wt/m² in reach 6 and 8.80 in reach 5. Clams were added only to

Without data for comparison with FOMM simulations, discussion of the dynamics of individual state variables becomes rather meaningless. However, it is reasonable to examine the relative importance of the various processes of transport in light of available information on observed or experimental systems. The simulated flux of naphthalene was similar to that of anthracene with respect to the relative importance of physical/chemical versus biological processes. Figure 4b shows that physical/chemical processes accounted for more than 90% of naphthalene flux through the model system. However, the absence of periodic behavior corresponding to the light-dark cycle indicated that, unlike anthracene, naphthalene was not dominated by the circadian inspection of the data presented in Figure 4b revealed that volatilization was the dominant local/chemical pathway of naphthalene loss from the simulated stream. Lee et al. (1978) concluded that evaporation was an important process in the overall loss of naphthalene from large aquatic enclosures. Similar to the anthracene situation, the processes of consumer egestion and defecation assumed importance in the overall flux of naphthalene following the termination of naphthalene infusion to the simulated stream.

The transport of benzo(a)pyrene (BaP) was dominated by biological processes and naphthalene the lighter weight anthracene and naphthalene to (Figure 4c). Following an initial BaP period of infusion where photolytic degradation was important, uptake by primary producers, movement through the foodweb, and consumer processes of egestion and defecation played the determining role in the non-advective transport and fate of BaP in the modeled stream. Lee et al. (1977) observed biotransformation of BaP by biota in a simple aquatic microcosm that contained algae, zooplankton, and fish. Lee et al. (1978) from *in situ* studies on marine pelagic enclosures in samples of sediment. The physical/chemical processes simulated, sorption to suspended particulates and settled sediments was the most important vector simulated for BaP by FOMM.

DISCUSSION

The modeling effort attempted to evaluate the relative importance of various processes of transport of individual PAH compounds. Molecular weight was correlated with water-solubility, K_{ow} (30), photolytic molar yield coefficient, q_{ph} (4), rate of sorption (inversely), q_{s} (10), and gas-phase exchange coefficient in volatilization, q_{v} (12) (Southworth 1979).

The absence of rate coefficients for biological transport processes in relation to molecular weight or other fundamental chemical properties of PAH reflected the limited amount of available data. The model depended on extrapolation of rate constants measured in the

Laboratory or published in the literature. A number of necessary rate parameters that must be directly measured in the systems of interest increases, specific application of transport models become more difficult (e.g., Baughman and Lassiter 1978).

Results of initial simulations indicated that FOMM predicted the observed spatial-temporal dynamic behavior of the system with reasonable accuracy (Table 1). This agreement may reflect the comparative simplification of the photolytic submodel and the ascription of anthracene to photolytic degradation (Zepf and Schlotzauer 1979, Southworth 1979a).

Lack of close agreement between simulated and measured concentrations of anthracene in periphyton, algae, and sediment indicates the difficulty in extrapolating laboratory determined rate constants to the stream. For example, the rate of absorption of anthracene was overestimated. The cultures of algae periphyton did not vary in their ability to determine uptake did not vary in the species composition of the flora that was growing in the experimental stream.

While data from the stream were not available for comparison, simulations of naphthalene and BaP transport demonstrated that the model was sensitive to changes in parameters that determined PAH transport in relation to molecular weight and light absorbance. Furthermore, the general patterns of flux predicted by the model were reproduced and agreed qualitatively with observations made in aquatic systems (Lee et al. 1978, Lee et al. 1977).

Results of this initial modeling effort suggest that:

- (1) rate of physical/chemical processes of PAH transport in lotic systems can be predicted from molecular weight of individual compounds.
- (2) Light absorbance spectra between 300 and 500 nm contain information predicting rates of photolytic degradation of PAH and parameter for biological transport and accumulation of PAH can be extrapolated to artificial streams with limited success.
- (3) The modeling effort suggested that future work is required in the following areas:
 - (1) collection of data to examine possible relationships between PAH compound structure and rates of biological uptake, degradation, and depuration, and
 - (2) collection of data in additional monitoring experiments for comparison with model predictions.

Results of this suggested research will increase our ability to predict exposure and dose in an

overall assessment of risk associated with introduction of PAH into aquatic systems.

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