



Project Summary

Fates and Biological Effects of Polycyclic Aromatic Hydrocarbons in Aquatic Systems

John P. Giesy, Steven M. Bartell, Peter F. Landrum, Gordon J. Leversee, and John W. Bowling

The hypothesis that fates of polycyclic aromatic hydrocarbons (PAH) in ecosystems can be predicted by mechanistic simulation models based on easily measured properties of the compounds in this homologous series was tested. The research involved: 1) development of a mechanistic, predictive simulation model based on kinetic and thermodynamic considerations; 2) development of analytical and quality assurance protocols for the extraction and quantification of PAH associated with biological and geological matrices; 3) determination of the vectors of and rate constants for uptake, depuration and biotransformation of PAH by aquatic organisms and sediments; and 4) comparison of the results of simulation and laboratory scale studies to a large scale ecosystem study. Included were studies of the effect of PAH concentration, temperature, and other exogenous factors on rate constants and efforts to determine whether rate constants were first order.

Laboratory studies indicated that anthracene and benzo(a)pyrene are rapidly biotransformed by fish and dipteran larvae but not by periphyton communities. Biotransformation had a significant effect on the steady state concentrations of parent compound and biotransformation products. These results demonstrated that predictions of steady state concentrations based on ^{14}C -labeled parent compound and the octanol-water partitioning coefficient

of the parent compound would be in error. Thus, the octanol-water partitioning coefficient would not be a good predictor of the behavior of PAH in aquatic organisms. Uptake and depuration rate constants were first order for fish but not dipteran larvae. Induction of biotransformation and changes in biotransformation rate over time means that predictions of long-term disposition in the ecosystem from short term pharmacokinetic studies, using radio-labeled compounds, will be misleading for compounds that are biotransformed.

Anthracene (approximately $12 \mu\text{g/l}$) was acutely toxic to bluegill sunfish dosed in outdoor channel microcosms. This mortality was not observed in laboratory studies and was shown to be caused by a photo-mediated toxic mechanism. Therefore, laboratory toxicity studies on PAH must be conducted under the same lighting conditions if the results of these studies are to be realistic representations of field conditions.

The modeled processes that most influence PAH transport included losses to volatilization, photolytic degradation, sorption to suspended particulate matter and sediments and net uptake by biota. The biota in the model included phytoplankton, periphyton, rooted macrophytes, bacteria, zooplankton, two functionally defined benthic invertebrate components and two functionally defined categories of



fish. Model simulations were compared to results of experiments conducted in artificial streams. A 0.06 μ molar solution of anthracene in ethanol was continuously added into the headwaters for 15 days. The model accurately predicted the dissolved anthracene concentration through time and space. Uptake by periphyton was overestimated by the model; however, the rate of depuration of anthracene by periphyton was reasonably simulated. Photolytic degradation appeared to be the most important pathway of flux with the channels, both experimentally and in the simulations.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Polycyclic (polynuclear) aromatic hydrocarbons (PAH or PNA) are a homologous series of compounds composed of two or more condensed benzene rings with occasional incorporations of cyclopentene rings, such as in the fluorenes, or "heteroatoms" (N, O or S). PAH are derived from natural and man-made sources and are widely distributed in the environment. PAH occur as natural products from plants and microbes and from natural pyrolytic processes such as forest fires and volcanic activities. Man-made sources include industrial processes but the major source is combustion of fuels. Most of the PAH in the environment are due to human activities and freshwater and nearshore marine environments are enriched with PAH. More than 230,000 metric tons of PAH enter the oceans and surface waters each year.

The toxic, mutagenic and carcinogenic properties of PAH have been much studied. Many PAH are carcinogens or procarcinogens in animals and man. Part of the hazard assessment process is to determine the exposure of animals and man. This required an understanding of the fate and transport processes in an ecosystem. Because of their ability to bioconcentrate lipophilic compounds such as PAH, aquatic organisms are an important vector to man. Also, because of their flowing, solvating character and organic sediments, surface waters serve as both a transport mechanism and a sink for PAH.

Because of the vast differences between simple laboratory tests and complex field situations, scientists have formed

conceptual and operational bridges between the two systems. These include mechanistic simulation models and microcosms, which are operational models or simplifications of environments. In this study, both of these types of models were employed to investigate the fate and transport of PAH in aquatic systems.

Summary

This program of study tested the overall hypothesis that a dynamic, mechanistic simulation model of the fate of PAH in an aquatic system can be constructed, based on characteristics of the compound of interest and the environment to which it is released. The study tested the ability to predict the fate of anthracene introduced into a channel microcosm using a simulation model, which had been parameterized independently. In addition, the simulation model was used to guide the laboratory investigations. By using a synthesis of microcosm, modeling and laboratory studies, the authors were able to guide their research to answer some of the most pertinent questions related to an understanding of the dynamics of anthracene in aquatic systems.

The fate of aromatics model (FOAM) predicts the concentrations of PAH in water, sediment, phytoplankton, periphyton, macrophytes, zooplankton, two benthic invertebrate components, bacteria, suspended particulate matter and herbivorous and carnivorous fish. The overall simulation model is organized as a main program (MAIN) (Fig. 1), which calls subroutines that calculate solar radiation (SOLAR), movement of water (HYDRO), solubility of PAH, and resuspension and settling of suspended components and graphs the absolute and relative concentrations of PAH in each compartment (Table 1). Other submodels calculate photolysis (PHOTO), volatilization (VOL) and sorption to sediments (SORP). The model is a mass balance, generalized reach model (Fig. 2). The biological components are simulated as a generalized production model with the PAH inputs partitioned into the biotic components (Fig. 3). All of the simulated processes in FOAM are corrected for temperature effects. FOAM, which is programmed in FORTRAN, requires a small number of input variables (relative to many dynamic, mechanistic simulation models) and is easy to use.

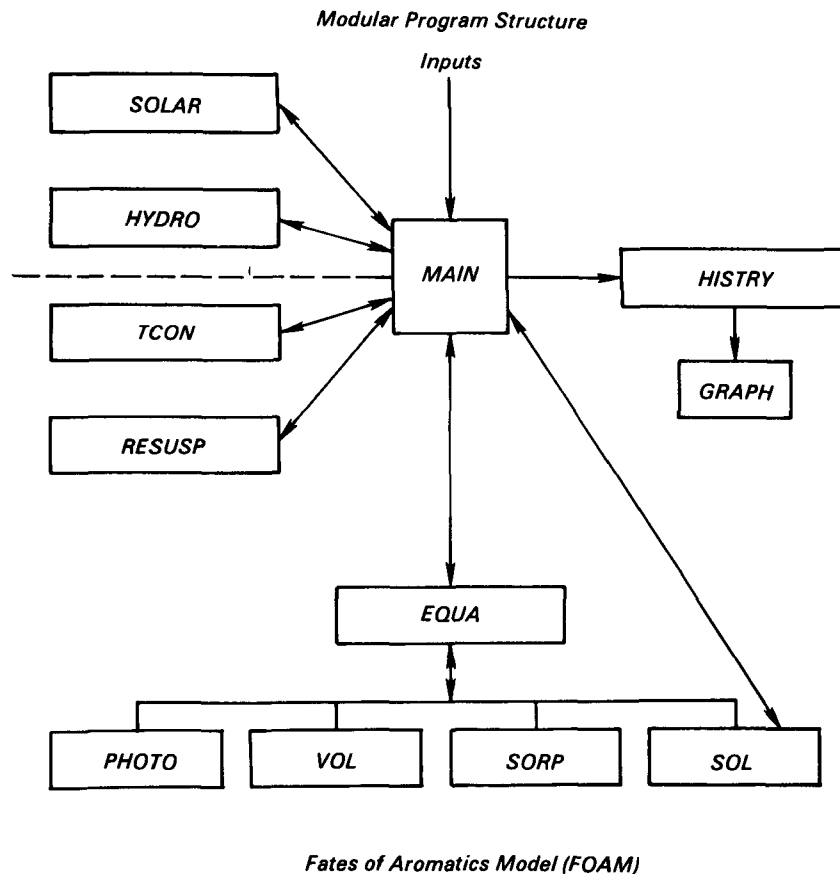


Figure 1. Schematic representation of modular subroutine structure of FOAM.

Each subroutine calculates part of the overall derivative for change in biomass or PAH mass in each state variable. FOAM simulates the dynamics of biological production and PAH dynamics through space

and time. Each state variable value is printed in matrix form where row elements are values at a specific time for each reach. Column elements are temporal values in a particular reach. A complete listing of

FOAM is available from the authors. It should be noted that model development is a dynamic process and FOAM has been undergoing continuous development since it was initially programmed.

FOAM was parameterized to simulate anthracene dynamics in the channel microcosms facility located at the Department of Energy's (DOE) Savannah River Plant (SRP). The channel microcosms facility is a pass-through system consisting of six separate cinder-block-lined channels each 91.5 m long, 0.61 m wide, and 0.31 m deep. Located at the upper end of each channel is a pool 3.1 m long, 1.5 m wide and 0.9 m deep. At the lower end of the facility is a single large pool 10.2 m long, 3.1 m wide and 1.0 m deep. For these studies, the channels and headpools were lined with a 0.05 cm thick black polyvinyl chloride film and the bottom covered with 0.05 m of washed quartz sand.

Water was pumped from a deep well and treated so that the inorganic water quality was similar to that of surface waters in the upper coastal plain. Water flows were monitored by V-notch weirs on each headpool. Flow rates of 75.7 l/min were maintained by input valves. This resulted in a current velocity of 1.0×10^{-2} m/sec and a retention time of 2.5 h. The water depth in the channels was maintained at 20 cm. The channels were naturally colonized with algae, bacteria, fungi and aquatic invertebrates. Clams and fish were held in the channels in cages for the validation study.

Laboratory studies demonstrated that benzo(a)pyrene (BaP) and anthracene were rapidly biotransformed by bluegill sunfish and chironomid larvae but not unionid clams or periphyton assemblages. Biotransformation rates were dependent on temperature and time of exposure. The rates of biotransformation also influenced the bioconcentration factors predicted from short-term pharmacokinetic studies. Temperature and food ration also influenced the rates of uptake and depuration. Uptake and depuration were adequately described by first-order relationships. Depuration was generally multiphasic with some biotransformation products bound to tissues, such that they were very slowly depurated.

Recovery of anthracene from sediments was inversely proportional to the time of exposure. Internal standards, added at the time of extraction, did not allow accurate determination of extraction efficiencies. Drying of sediments resulted in reduced recovery from sediments. A benzene-acetonitrile (1:2; V/V) extract resulted in the best recovery of anthracene from sedi-

Table 1. Output from FOAM. Each Variable is Simulated Hourly

Parameter	Units
Irradiance	langleys · h ⁻¹
Allochthonous organic matter	g · dry weight · m ⁻²
External PAH loading	g PAH · m ⁻²
Periphyton biomass	g · m ⁻²
Macrophyte biomass	g · m ⁻²
Benthic invertebrate biomass	g · m ⁻²
Clam Biomass	g · m ⁻²
Bacterial biomass	g · m ⁻²
Fish biomass	g · m ⁻²
Suspended particulate organics	g · m ⁻²
Dissolved organics	g · m ⁻²
Bottom sediments	g · m ⁻²
Suspended inorganic particulates	g · m ⁻²
Settled detritus	g · m ⁻²
PAH in periphyton	μ.mol PAH · g ⁻¹ , dry weight
PAH in macrophytes	μ.mol PAH · g ⁻¹ , dry weight
PAH in benthic insects	μ.mol PAH · g ⁻¹ , dry weight
PAH in bacteria	μ.mol PAH · g ⁻¹ , dry weight
PAH in fish	
predaceous	μ.mol PAH · g ⁻¹ , dry weight
herbivorous	μ.mol PAH · g ⁻¹ , dry weight
Suspended organic particulates	μ.mol PAH · g ⁻¹ , dry weight
PAH in dissolved organic matter	μ.mol PAH · g ⁻¹ , dry weight
PAH in bottom sediments	μ.mol PAH · g ⁻¹ , dry weight
PAH in suspended inorganic particulates	μ.mol PAH · g ⁻¹ , dry weight
PAH in settled detritus	μ.mol PAH · g ⁻¹ , dry weight
PAH dissolved in water	μ.mol PAH · l ⁻¹
PAH which has been transferred	μ.mol PAH · l ⁻¹

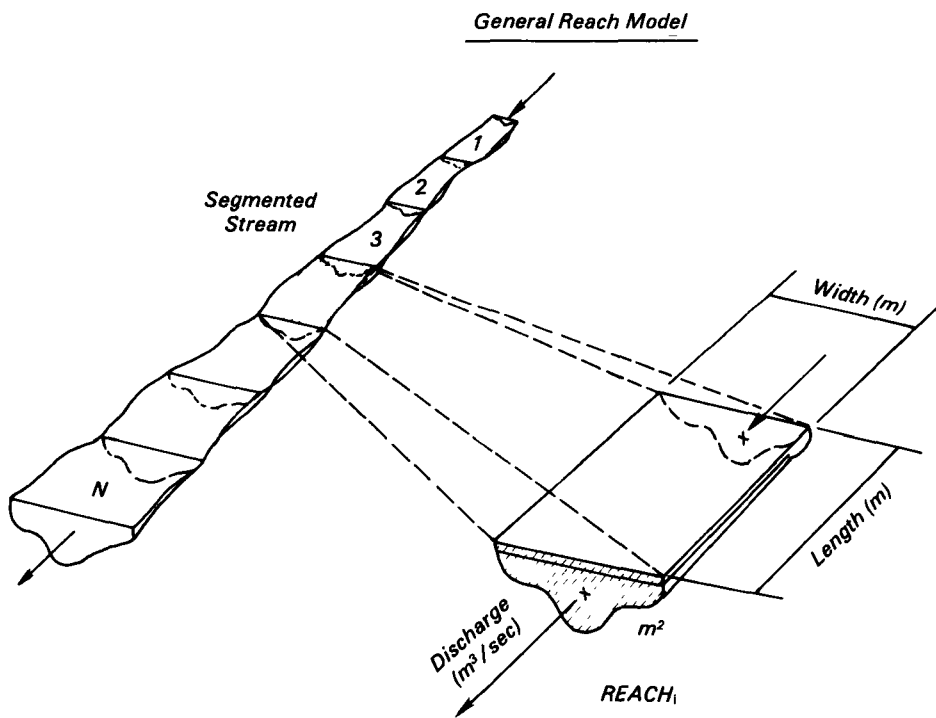


Figure 2. Conceptualization of generalized stream reach transport model.

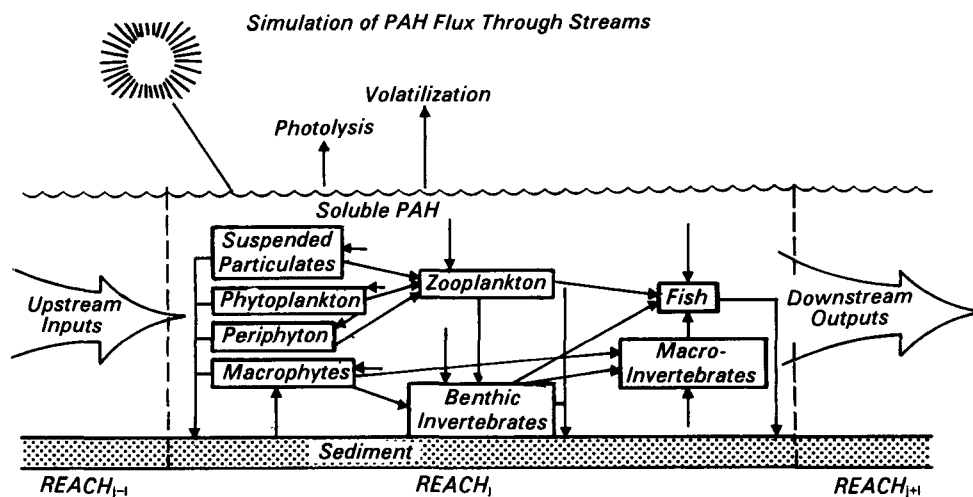


Figure 3. Schematic representation of FOAM model.

ments. Capillary gas-liquid chromatography coupled to mass spectrometry (GC-MS) showed that anthracene could be extracted from sediments and separated from naturally occurring organic compounds but anthraquinone (a transformation product of anthracene) could not.

Dissolved organic carbon (humic substances) interfered with the extraction of anthracene and BaP from water by macroreticular resins. Humic acids also reduced the availability of anthracene, benzo(a)pyrene and dimethylbenzanthracene to *D. magna* but increased the availability of 3-methylcholanthrene and dibenzanthracene. The presence of suspended particulates also reduced the availability of PAH to *D. magna*.

FOAM accurately simulated and predicted the flux along physical-chemical pathways (Table 2). The model, however, was less accurate in predicting the accumulation and biotransformation of PAH by aquatic biota. Future versions of predictive simulation models should be kinetically based, as FOAM is, if accurate information on cycling is to be predicted. This type of model, however, requires a great amount of information. Because of

the scale of the input parameters, models such as FOAM will be useful in describing overall processes and fluxes along different pathways but will not be very useful in simulating the concentrations of PAH and PAH transformation products in individual biotic components. Also, some of the physical processes, which are important in determining the fates of PAH in natural systems, are discontinuous functions or catastrophic events, such as storms, which do not lend themselves to mathematical simulations. Therefore, models of the type developed here will always be limited to relatively gross predictions. Accurate prediction of concentrations in individual types of organisms may not be attainable.

The channel microcosms were useful for testing the reliability of FOAM to simulate the behavior of PAH in a complex ecosystem. The greatest utility of the channel microcosms, however, was in allowing studies to be conducted under more natural conditions than allowed by laboratory systems. From these studies we learned that exposure to sunlight caused acute mortality due to anthracene. Thus, laboratory studies of anthracene

toxicity to aquatic organisms do not accurately predict toxicity observed under more natural conditions. Although microcosms may not be used as a screening tool for individual compounds, they are useful in studies of classes of compounds and to verify laboratory and simulation conclusions. Because of their scale, however, microcosms will never be useful in validation of long-term or global simulation models. The test of the benchmark hypothesis was only partly supported by our studies.

Future simulations will need to consider more complex measures of chemical behavior. The proposed use of octanol/water partitioning coefficients shows promise for predicting uptake by organisms but not biotransformation. Thus, the benchmark approach will probably not give adequate predictions of the dynamics of organic compounds in complex environments.

A coordinated synthesis of information on ecosystem structure and function is required to assess environmental impacts of any technology that must ultimately be interfaced with the environment. While this research was on PAH compounds (anthracene and benzo(a)pyrene specifically) it supports the hypothesis that valid generalizations about the behavior of general classes of organic compounds in complex environments can be made from knowledge about the compounds obtained in relatively simple laboratory studies and the environments to which these compounds are released. Knowledge of this type can be transferred to other organic compounds and has broad applicability.

Recommendations

Future studies of the fates and effects of trace contaminants should be conducted in laboratory, field, and simulation modes concurrently. All three modes of investigation added to the overall understanding of the dynamics of PAH in aquatic ecosystems.

Simulation models should be developed to predict general behavior of PAH in aquatic systems. That is, to determine when the greatest mass of PAH accumulates and where the most sensitive ecosystem components are. Where physical and chemical processes dominate, simulation models will be able to accurately predict the overall dynamics of PAH, but rare events of large magnitude will reduce the accuracy of predictions on a short-term basis. Optimization of time step duration relative to system level variability needs to be further investigated to increase the accuracy of predictive models.

Table 2. Predicted and Observed Concentrations of Dissolved Anthracene in Channels Microcosms

Time	Reach 1 (Head)	mol anthracene ⁻¹ Reach 3 (Middle)	Reach 5 (Tail)
Dawn			
observed	0.066	0.065	0.063
predicted	0.056	0.056	0.055
Noon			
observed	0.067	0.045	0.028
predicted	0.056	0.045	0.036

The current state of predictive simulation models will not allow the accurate prediction of concentrations of single PAH in individual species but can be useful in simulating overall processes in a gross manner. Future simulation should be kinetic in nature but the relationships used to predict rate constants need to be based on structure-activity relationships.

The channel microcosms used in this study were sufficient to test some simulation processes, and the authors recommend the use of this type of a system in future studies. Microcosms of this type, however, will not be useful as screening tools. The utility of the realism of such systems was demonstrated by the photo-mediated toxicity of anthracene effect observed in the microcosm, which was not observed under laboratory conditions. This type of system needs to be used to validate processes that are indicated by laboratory and/or simulations because they allow testing in a more complex and more natural system than that of the laboratory, while not releasing trace contaminants to the biosphere.

J. P. Giesy is with Michigan State University, East Lansing, MI 48824; S. M. Bartell is with Oak Ridge National Laboratory, Oak Ridge, TN; P. F. Landrum is with the National Oceanographic and Atmospheric Administration, Ann Arbor, MI 48104; G. J. Leversee is with Keene State College, Keene, NH 03431, and J. W. Bowling is with the University of Georgia, Savannah River Ecology Laboratory, Aiken, SC 29801.

H. W. Holm is the EPA Project Officer (see below).

The complete report, entitled "Fates and Biological Effects of Polycyclic Aromatic Hydrocarbons in Aquatic Systems," (Order No. PB 83-250 191; Cost: \$20.50, subject to change) will be available only from:

*National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650*

The EPA Project Officer can be contacted at:

*Environmental Research Laboratory
U.S. Environmental Protection Agency
College Station Road
Athens, GA 30613*

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

BULK RATE
U.S. POSTAGE
PAID
Cincinnati, OH
Permit No. C

Official Business
Penalty for Private Use \$300