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Project Summary

Disposition of Anthracene in the Water and Aufwuchs Matrices of a Large Outdoor Channel Microcosm: A Data Set for Mathematical Simulation Models

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Large-scale, outdoor microcosms were used to study the fate of anthracene, a polycyclic aromatic hydrocarbon, in the aquatic environment. The study provides a data set for describing the disposition of anthracene in the water and aufwuchs of the microcosms for the purposes of comparison with existing laboratory information and as an aid in refining and validating EPA's Exposure Analysis Modeling System (EXAMS) and other computer models. Such models are used to estimate the exposure, fate, and persistence of synthetic organic chemicals in natural waters using easily measured physical and chemical properties of the compounds and the ecosystems.

Anthracene was introduced (~ 14.7 $\mu g \cdot \ell^{-1}$) into a biologically colonized channel microcosm for 36 days. Anthracene concentrations in the water showed significant diel variation. Maximum water concentrations were achieved and maintained during periods of darkness. Concentrations decreased significantly with distance downstream during daylight periods, however. The major loss of anthracene from the channel was due to photolysis, with some loss attributable to volatilization. Anthraquinone concentrations increased as anthracene concentrations dereased during daylight periods. Anthraquinone did not account for all anthracene losses, however, suggesting that other photolytic degradation products may have been formed from anthraquinone. A mass balance accountability of anthracene was not possible because analysis for other breakdown products was not attempted. More than 60% of the nominal anthracene input to the channel was lost by nonadditive processes during periods of light.

Aufwuchs accumulated anthracene and achieved maximum concentrations within 4 days of initiation of input. Aufwuchs did not biodegrade anthracene and losses from the water due to aufwuchs uptake were small (~ 0.02% of total anthracene input). Anthracene concentrations in aufwuchs were similar throughout the length of the channel. Aufwuchs biomass decreased down the length of the channel, thus, anthracene concentrations, expressed on a surface area basis, also decreased with distance downstream. A bioconcentration factor (BCF) for aufwuchs was calculated using the anthracene concentrations measured for aufwuchs and the 24-hour weighted water concentrations. BCFs were not significantly different with distance downstream or through time. The overall BCF for aufwuchs was 1260 ± 96 ($\bar{x}$ ± 95% CI, n = 45).

When anthracene input ended, concentrations in water returned to background levels within 24 hours. Anthracene depuration from aufwuchs was rapid with concentrations returning to background levels within 72 hours.

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

Anthracene is a member of a class of organic chemicals known as polycyclic aromatic hydrocarbons (PAH). PAH are relatively non-polar organic compounds composed of fused benzene rings. PAH occur as natural products in plants and microbes, but most PAH released into the environment result from fossil fuel combustion, oil spills, municipal sewage treatment and industrial processes.

As a class, PAH are of interest environmentally because of their potential health hazard to humans. Numerous high molecular weight PAH have been shown to be carcinogenic, teratogenic, and mutagenic in laboratory mammals and in humans. Assessment of risks associated with the introduction of PAH into the environment depends in part on quantification of environmental transport and subsequent exposure concentrations experienced by biotic components. With recent improvements in analytical techniques and the advent of sophisticated computer models, interest has been directed towards delineating the origin, transport, fate and metabolism of PAH in the environment.

Thousands of different PAH compounds are chemically possible. Therefore, application of elaborate screening protocols to individual PAH in order to estimate major processes of transport, accumulation and degradation would be impractical for purposes of risk assessment. Thus, the importance of developing predictive models of PAH fate in aquatic systems must be emphasized. Large-scale, complex microcosms that incorporate important structural, functional and coupling properties of ecosystems can be important tools for testing mathematical models of pollutant fate. Microcosms of this kind act best as a bridge between noninteractive laboratory tests and complex, highly interactive field experiments and environmental monitoring programs by providing the data sets necessary to facilitate the development of predictive environmental fate models and evaluate their performance.

Anthracene was selected as a model PAH for this study because it is a commercially important PAH produced in large quantities and it is used extensively as a reagent in organic synthesis. Anthracene also has been used frequently as a model PAH for studies of environmental fate in aquatic systems or physiological disposition in aquatic biota, because it is considered noncarcinogenic and relatively nontoxic. This study was designed to provide a data set that would describe the disposition of anthracene in the water and aufwuchs matrices of a large outdoor channel microcosm for the purposes of comparison with existing laboratory information and as an aid in refining and validating EPA's Exposure Analysis Modeling System (EXAMS).

Two biologically colonized channel microcosms were used in this study; one received anthracene input while the other served as a control and received no anthracene. The study was conducted for 40 days, from October 10 to November 18, 1981. This study was designed to collect a variety of environmental, physical and chemical data important in controlling processes believed significant in determining the fate of PAH in the aquatic environment.

Results

Anthracene concentrations in the water column showed significant diel variation. Concentrations were greatest prior to measured solar irradiation exposure at 0800h. Statistical comparison showed that only samples collected farthest downstream from the anthracene input had concentrations that were significantly less than the nominal anthracene input concentration (HSD, $\alpha \leq 0.05$). This suggests that the overall anthracene loss rate resulting from all loss processes (e.g., volatilization, hydrolysis, sorption, photolysis, and biological degradation) is quite slow during periods of darkness. The slow anthracene loss rate during darkness resulted in an anthracene half-life in the channel microcosm that exceeded the 2.5-h water retention time of the system. Approximately 79% of the anthracene introduced into the channel was being transported out of the system as anthracene at 0800h.

Anthracene concentrations in the water at 1230h decreased significantly as a function of distance downstream. Mean anthracene concentrations in the water were statistically different (HSD, $\alpha = 0.05$) from the nominal input concentration for all sampling stations downstream from reach 1. Nearly 90% of this decrease occurred in the first half of the channel; only 10% occurred in the remaining 46 meters. As a result of this downstream loss of anthracene from the water, only 30% of the total input to the channel was transported out of the system as anthracene at 1230h.

Anthraquinone was not detected in water samples from upstream stations and was near the analytical detection limit of ($36.6 \pm 5.3 \times 10^{-2}$ nmoles ℓ^{-1}, $\bar{x} \pm$ 95% CI, n = 6) in all mid and downstream stations at 0800h. The amounts of anthraquinone present at 0800h accounted for only a small portion of the anthracene loss detected at downstream stations at 0800h. Anthraquinone concentrations in the water increased with distance downstream at 1230h. The sum of anthracene plus anthraquinone at downstream stations, however, accounted for only 50% of the total mass of anthracene input to the channel. Therefore, processes other than direct conversion of anthracene to anthraquinone were occurring and were responsible for the majority of anthracene loss observed at 1230h.

The overall mean rate constant for anthracene loss from the channel resulting from all loss processes at 1230h was calculated by fitting the data to a first order exponential decay function ($Y_t = Y_0 e^{-kt}$). The calculated rate constant (k) was $9.8 \times 10^{-3} \pm 1.9 \times 10^{-3}$ min^{-1} ($\bar{x} \pm$ 95% CI, n = 5, $r^2 = 0.869$), which results in a calculated half-life for anthracene in the channel at 1230h of 74.8 ± 20.5 min, approximately 50% of the water retention time for the system.

The response of anthracene and anthraquinone concentrations in the water column to solar irradiation intensity and exposure is shown in the full report. The water retention times (thus, exposure time) from the point of anthracene input to the midpoint of reaches 1, 3 and 5 were 15, 75 and 135 min, respectively. The exposure times at all stations remained constant; however, solar irradiation intensity increased from 0800h to 1230h. Anthracene concentrations in the water decreased in proportion to the increased exposure times and increasing intensity of solar irradiation. Anthraquinone concentration in the water increased as anthracene concentration decreased. The increasing inability to calculate a mass balance for anthracene inputs based only on the sum of the masses of anthracene and anthraquinone in the water as exposure time increases or as solar irradiation intensity increases is very apparent. The decrease in anthracene concentrations and the concomitant increase in anthraquinone concentrations in the water column as solar exposure and/or intensity of solar irradiation increases suggests that photolysis is a major loss process for anthracene in aquatic systems.

The aufwuchs community of the channel microcosm accumulated anthracene and achieved an apparent steady state concentration (97.0 ± 7.42 nmoles g^{-1} dry wt; $\bar{x} \pm$

95% CI, n = 87) within 96h of the initiation of the anthracene input. Aufwuchs did not accumulate anthraquinone or appear to biodegrade anthracene during the experimental period. Anthracene losses from the water column due to aufwuchs uptake were small (0.02% of the total anthracene input). Anthracene concentrations in aufwuchs, based on surface area of channel sampled, decreased with the distance downstream. The biomass of aufwuchs per unit surface area of channel sampled also decreased with distance downstream, however, at nearly the same rate. Thus, when anthracene concentrations in aufwuchs were expressed on a gram dry weight basis, there was no significant difference through time or with distance downstream. This result is somewhat misleading because aufwuchs were always sampled early in the day when anthracene concentrations in the water were most stable in order to meet requirements for application of data to EXAMS. Recent laboratory data suggest that anthracene concentration in this same aufwuchs may, in fact, respond quite rapidly to changes in anthracene concentrations in the water.

Anthracene bioconcentration factors (BCF) for aufwuchs were calculated for all reaches of the channel and for every sampling date (Table 1). No significant differences ($p \leq 0.05$) were found among these values. Thus, aufwuchs concentrated anthracene to the same extent irrespective of exposure time and distance from input and regardless of the fact that anthracene concentrations in the water column changed significantly on a diel basis at downstream stations. This observation may in part be an artifact of the manner in which BCF were calculated using a weighted 24-h anthracene concentration in water as an estimation for the actual dose to aufwuchs prior to sampling. The manner by which one chooses to calculate the exposure dose in a dynamic system has always posed a problem that needs more research.

Aufwuchs depurated anthracene rapidly upon cessation of input. Anthracene concentrations in aufwuchs on day 39, 72h after termination of input, were highly variable. In every case the 95% CI for each reach sampled overlapped the analytical detection limit for anthracene, indicating that mean anthracene levels in the aufwuchs had returned to near baseline in 72h.

Conclusions

Anthracene concentrations in the water exhibited similar responses for the entire 36-day experimental period. Anthracene concentrations in the water showed significant diel variation. Maximum water concentrations were achieved and maintained throughout the channel during periods of darkness. Anthracene concentrations decreased significantly, however, with distance downstream during daylight hours. The major loss of anthracene from the channel was due to photolysis, with some loss attributable to volatilization. Other loss processes such as sorption and metabolism by aufwuchs were insignificant. Anthraquinone concentrations in water increased as anthracene concentrations decreased during daylight hours. Anthraquinone did not account entirely for the observed anthracene losses, however, suggesting that other photolytic degradation products were formed. Upon termination of anthracene input, concentrations in the water returned to background levels within 24h.

Aufwuchs accumulated anthracene and achieved maximum concentrations within 4 days of initiation of input. Anthracene concentrations in aufwuchs were similar throughout the length of the channel. Anthracene loss from the water due to aufwuchs uptake was small (~ 0.02% of total anthracene input). Aufwuchs did not accumulate anthraquinone from the water or as a result of metabolism of anthracene. The BCF calculated for aufwuchs was not significantly different with distance downstream or through time (36 days). Anthracene depuration from aufwuchs was rapid with concentrations returning to background levels within 72h, after termination of anthracene input.

Microcosms of the size and complexity studied here can provide data useful in verifying or validating results obtained in laboratory and modeling studies. Microcosms of this nature are most effective and efficient, however, when used as a research tool incorporated into an integrated program involving rigorous laboratory experimentation as well as conceptual model development. With this type of interactive research, all aspects of the program can gain insight from one another, providing the opportunity to acquire information and/or understanding that has meaningful application. Lack of such an interactive approach, on the other hand, severely diminishes the usefulness of large microcosms.

Recommendations

Future studies of the disposition of photolabile compounds in aquatic systems should be designed to investigate the magnitude of diel variations in dissolved compound concentrations resulting from daily changes in the natural light intensity. Such studies should include close interval (hourly) sampling of major components within the test system to determine how these components track water concentrations on a diel cycle. Close interval sampling is most important for those components of the test system for which laboratory or literature data indicate rapid uptake and depuration rate constants or short half-lives. Future studies should address the potential for toxic effects on biota that could alter the structure and/or function of the test system. Such alterations could affect the dynamics and/or disposition of the compound of interest within a test system.

In the future, if large-scale microcosms are used as tools to verify or validate independently developed predictive models, there needs to be a conscious and concerted effort to establish the needed communication between both the modeling experts and those with a knowledge of the design and operational constraints of the test facility. This communication is required to insure an appropriate experimental design and to provide the best possible test of the model. Large-scale microcosms can never be effective tools for verification and/or validation of laboratory studies or predictive models if the wrong questions are asked or inadequate and inappropriate data are collected. If large-scale, complex microcosms are perceived as relevant and valuable research tools for testing hypotheses about environmental

Table 1. Aufwuchs Bioconcentration Factor (BCF)

	Mean BCF by Channel Reach		
Sampling Date	*Reach Number 1*	*Reach Number 3*	*Reach Number 5*
10/14/81	*1620 ± 562*[a]	*1370 ± 534*	*1150 ± 1140*
10/21/81	*959 ± 437*	*1120 ± 1250*	*1490 ± 714*
10/28/81	*1250 ± 680*	*1440 ± 874*	*1280 ± 501*
11/4/81	*1080 ± 358*	*1020 ± 130*	*1070 ± 413*
11/11/81	*973 ± 727*	*1590 ± 645*	*1510 ± 181*
Overall Mean by Reach	*1180 ± 228*[b]	*1310 ± 190*	*1300 ± 164*
Overall Mean for Channel		*1260 ± 96*[c]	

[a] $\bar{x}$ ± 95% CI, n = 3
[b] $\bar{x}$ ± 95% CI, n = 15
[c] $\bar{x}$ ± 95% CI, n = 45

functioning, serious consideration should be given by funding agencies to establish a facility with the necessary funding structure to support and maintain the facility and expertise on a long-term basis. Large-scale, complex microcosms are too expensive to construct upon demand and too complex to understand during one or two years of operation.

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The complete report, entitled "Disposition of Anthracene in the Water and Aufwuchs Matrices of a Large Outdoor Channel Microcosm: A Data Set for Mathematical Simulation Models," (Order No. PB 84-158 344; Cost: $10.00, subject to change) will be available only from:

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