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Biological Processes Influencing Contaminant Release from Sediments

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Abstract

The influence of biological processes, including bioturbation, on the mobility of contaminants in freshwater sediments is described. Effective mass transfer coefficients are estimated for tubificid oligochaetes as a function of worm behavior and biomass density. The mass transfer coefficients were observed to be inversely proportional to water oxygen content and proportional to the square root of biomass density. The sediment reworking and contaminant release rates are contrasted with those of freshwater amphipods. The implications of these and other biological processes for contaminant release and in-situ remediation of soils and sediments are summarized.

1. INTRODUCTION

The Hazardous Substance Research Center/South and Southwest is a university consortium led by Louisiana State University that also includes Rice University and Georgia Tech University. The primary focus of the research conducted by the Center is the assessment and remediation of contaminated sediments and dredged materials. The Center provides fundamental technical support to the Superfund program, developing the process understanding, tools and technologies that allow the region and the nation to appropriately address contaminated site problems. The Center's activities recognize that assessment, including characterization and evaluation of a contaminated site, evaluation of natural recovery processes, and the identification of appropriate environmental endpoints, are closely linked with remedial technologies and their successful selection and application. As part of that assessment effort, the Center supports research by myself, K.T. Valsaraj and L.J. Thibodeaux into the interaction of biological and physicochemical processes to influence contaminant transport and fate. This paper focuses on recent results of that activity.

Hydrophobic organic and metal contaminants are generally strongly associated with the particulate fraction of soils and sediments and partition only weakly into air and water. This often leads to the retention of these contaminants in the soil and sediments resulting in releases to the air or water long after the original source has been controlled. Assessment of the ecological and human health impact of these contaminants is often difficult because only a portion of the contaminants are available for release or uptake by organisms. Because it is a direct measure of the mobile and available fraction, it is believed that the rate of release of contaminants is a better indicator of contaminant impact than total sediment concentration. The current research is directed toward identification and quantification of key processes influencing the release rate.

For a contaminant that is essentially inert, its ultimate distribution in the environment is controlled by physico-chemical equilibrium. For many organic compounds, this distribution process is dominated by hydrophobic interactions, that is, partitioning to the air is governed by a Henry's Law constant and sorption to the soil is governed by the amount of organic carbon in the soil and the organic carbon based partition coefficient of the compound. For metallic and elemental species this process is much more complicated due to the variety of forms which these species can take. The ultimate distribution remains governed, however, by physico-chemical equilibrium.

Although the ultimate distribution is governed by physico-chemical processes, the rate of movement toward this distribution is often influenced by biological processes. For example, the sediment mixing processes associated with the normal life-cycle activities of benthic organisms, bioturbation, is likely to be the most important mechanism for release of sorbed contaminants from otherwise stable sediments[1,2]. The physico-chemical processes of advection and diffusion only result in the migration of contaminants in the porewater, a very small portion of the total sediment loading of contaminants. Porewater transport of a strongly sorbed contaminant is characterized by retardation by a factor given by the ratio of the total concentration in the sediment to the concentration in the mobile phase. Bioturbation, however, often causes movement of the sediment particles and their associated contaminants. Thus all of the contaminant mass is mobile and the process is not subject to retardation. In addition, the microbial degradation of organic matter leads to colloidal species in the porewater of soils and sediments. For very hydrophobic compounds the presence of this microbially generated organic matter can significantly increase the mass of contaminant associated with the mobile fluid phase, reducing the retardation associated with sorption.

Microbial processes also result in the oxidation and reduction of certain elemental species such as selenium. Selenium is essentially immobile in its reduced form but is soluble and thus more mobile in its oxidized forms. Certain bacteria use selenium as they might sulfur during respiration. As a result, the cycling of selenium may be the result of competition between two biological processes, microbial processes that tend to reduce and thus immobilize selenium, and bioturbation, which through reworking of the upper layers of sediment tends to oxidize that sediment and contribute to the formation of the oxidized mobile forms of selenium.

The effect of biological processes on contaminant release will be illustrated in the present paper by examining the movement of hydrophobic organic compounds in sediments. A series of laboratory experiments with tubificid worms will be used to illustrate the effect of bioturbation. The behavior of the tubificid worms will be contrasted with the behavior of amphipods and the effect of dissolved and suspended organic matter.

2. EXPERIMENTAL PROCEDURE

The laboratory experiments were conducted in small chambers 15 cm long, 5 cm wide and 4.5 cm deep constructed from 0.64 cm thick Plexiglas. The depth of the sediment layer was 3-3.5 cm. Continuous water flow across the sediment bed was provided by a peristaltic pump. In experiments examining the influence of bioturbation, either tubificid oligochaetes (*Limnodrilus hoffmeisteri* and *Tubifex tubifex*) or amphipods

(*Hyallela azteca*) were introduced to the sediment surface. The tubificids were introduced to the sediment after an initial stabilization period at densities of 0, 6700 and 26,700 organisms·m^{-2}. Each organism was 1-3 cm in length and exhibited a dry weight of 200-500 μg. Amphipods were introduced in a similar manner at densities of 0, 4000 and about 9300 organisms·m^{-2}. The amphipods measured 1-2 mm in length and a dry weight of about 100 μg.

In these experiments, the sediments were contaminated with polyaromatic hydrocarbons and the effect of bioturbation was evaluated by monitoring the contaminant flux from the sediments. In experiments evaluating the effect of microbial production of colloidal organic matter, colloidal flux from the sediments was monitored and used to support a model of the influence of colloidal matter migration on contaminant transport. The sediments employed in all experiments were freshwater sediments either contaminated in the field or contaminated by inoculation in the laboratory. The field contaminated samples employed also exhibited a significant oil and grease content of about 4%.

Contaminant flux was determined by analyzing 700-800 mL water samples collected from the effluent of the experimental cells. The sample was either added to 0.5 L of hexane and extracted over 8 hours in a continuous extractor or extracted in a simpler and faster three stage batch procedure. In the three stage extraction procedure, 80 mL of hexane was added to 700 mL of sample and shaken for 45 minutes in the first stage, followed by two extractions with 60 mL of hexane with 15 minutes of shaking each time. Hot water immersion of the sealed sample was used to break any emulsions formed during shaking. After extraction, the hexane was concentrated to 2 mL and exchanged with acetonitrile during evaporation with nitrogen. Analysis was then conducted via UV detection high performance liquid chromatography (Hewlett-Packard Model 1090 HPLC) with a 70/30 acetonitrile/water carrier and 150x4.6 mm column packed with Envirosep-PP (a reversed phase C-18 column). Average recovery of pyrene and phenanthrene by this process was 93.3 and 92.7%, respectively, by continuous extractor, and 77±4.3% for pyrene, 93.70±1.1% for phenanthrene and 83.9±6.5% for dibenzofuran by three stage extraction. Although average recoveries were less by the multi-stage extraction method, it was felt that increased sample frequency was desirable and the method was employed for all but the initial experiments.

3. RESULTS

Bioturbation by Amphipods

The amphipods, *Hyallela azteca,* scavenge the surface of the sediment for food and their influence over particle movement in the sediment extends only to the upper few mm. The organisms are also sensitive to contaminant levels and, as a result, are often used to evaluate sediment toxicity. The combination of limited vertical influence of the organism and toxic response to the sediment contaminants resulted in only a short term influence of the organism on contaminant release rates. Figure 1 shows the flux of pyrene from an inoculated local sediment (Bayou Manchac, Baton Rouge, LA) in the control, low and high amphipod density microcosms. The control microcosm is devoid of animals and therefore contaminant flux is controlled by molecular diffusion. Although some scatter in the experimental data is apparent, the flux in the control chambers decrease with the inverse square root of time. The presence of the amphipods in the other cells gives rise to an increased flux of pyrene.

As indicated above, however, amphipod morbidity combined with depletion of the contaminant in their limited region of influence caused a rapid decrease in the flux after three days. The measured fluxes in the control and populated cells were essentially identical after that time. In order to determine if contaminant depletion or reduced organism activity or mortality was the cause of the decrease, additional amphipods were introduced to the microcosm at Day 20 of the experiment. A significant increase was observed in the flux was observed indicating that at least some of the initial reduction was the result of the loss of organism activity. The enhancement, especially in the high population density cells, however, was less than originally observed and of shorter duration. This suggests that surface depletion of the contaminants was also a significant factor in the initial rapid decrease in flux. Thus, bioturbation by amphipods would not be expected to have long-term significance without continuous replenishment of the contaminant at the sediment surface.

Bioturbation by Tubificids

The behaviour of the amphipods is much different than that of the tubificid worms which can penetrate far more deeply into the sediments and can burrow to continually expose fresh contaminated sediment. A comparison of the experimentally measured flux from a local sediment (Bayou Manchac, LA) in control and animal populated cells is shown in Figure 2. 200 organisms in the 75 cm^2 area cell implies an organism density of 26,700 organisms·m^{-2}. The flux from the control cell follows the expected inverse square root of time dependence and can be predicted with high accuracy purely on the basis of the physico-chemical characteristics of the sediment and the contaminant. The flux from the bioturbated cell is clearly significantly different, however, and that difference is essentially constant at 50-70 ng·cm^{-2}·day^{-1}. Because of the ability for the tubificid worms to continuously expose fresh sediment, the bioturbation flux would be expected to continue until the entire upper layers of sediment were depleted of contaminants, while the diffusion flux would rapidly decrease to negligible levels.

This is clearly seen in experiments with aged Rouge River, Michigan sediments in Figures 3 and 4. In these experiments, the diffusive flux from the sediment is essentially negligible while the bioturbation flux remains at 50-70 ng·cm^{-2}·day^{-1} in the high population density microcosms. The contaminant and biomass loadings is approximately the same as in the inoculated Bayou Manchac sediments. The effect of bioturbation can be easily quantified by estimation of effective mass transfer coefficients from the experimental data. The effective mass transfer coefficient is given by

$$k_{bio} = \frac{\{Flux\}}{\{Sediment\ concentration\}} = \frac{F}{W_s \rho_b} = \frac{\left\{\frac{\mu g}{cm^2 \cdot yr}\right\}}{\left\{\frac{\mu g}{g}\right\}\left\{\frac{g}{cm^3}\right\}} = \left\{\frac{cm}{yr}\right\}$$

Table 1 summarizes a variety of experiments that indicate the effect of population density, water oxygen content, contaminant hydrophobicity and sediment type on flux enhancement by bioturbation. The effect of hydrophobicity was illustrated

Table 1 Effective Mass Transfer Coefficients - Tubificid Bioturbation

Bayou Sediments	k_{bio} - cm/yr (Tubificid worms - 26,700 #·m^{-2})			Biomass Exponent[2]
	Low O_2 ~2 mg/L	Med O_2 ~5 mg/L[1]	High O_2 ~8 mg/L	
Pyrene	1.7	0.63	0.15	0.46
Phenanthrene	7.5	1.4	0.42	0.32
Rouge River Sediments				
Pyrene	4.0	0.58	-	0.55
Phenanthrene	3.1	2.2	-	0.49

1 Inadequate control of oxygen level during this experiment- oxygen level estimated on the basis of limited measurements

2 Biomass exponent is defined as α in k_{bio} ~(Biomass)$^{\alpha}$ based on difference between low and high biomass loading experiments

by use of the two tracers, pyrene and phenanthrene, which exhibit water solubilities of about 0.135 and 1.15 mg/L, respectively. As shown by the table, the rate of bioturbation is essentially the same between the inoculated and aged sediments but varies significantly with oxygen content, the hydrophobicity of the compound and the biomass density.

The influence of oxygen content was unexpected and is apparently the result of a change in behavior of the in-dwelling tubificids. The tubificid worms move sediment to the surface during tube building and as a result of deposit feeding. Tubificid worms have been shown to ingest and defecate several times their body weight daily. Under our experimental conditions an average defecation rate of about 2.3 $mg \cdot worm^{-1} \cdot day^{-1}$ was measured by collection of the fecal matter. With an organism density of 26,700 $worms \cdot m^{-2}$ and a sediment bulk density of 1 g/cm^3, this suggests that the sediment reworking rate is governed by a mass transfer coefficient of about 2.2 cm/yr. This is consistent with the observed mass transfer coefficient for pyrene under hypoxic or low oxygen conditions as shown in Table 1. Under low oxygen conditions the worms employ the motion of their tails to assist in oxygen exchange from the water. More time must be spent at the surface where fecal matter that represents contaminated material at depth can be deposited directly on the surface. Under higher oxygen conditions, the need for interaction at the sediment surface is diminished and direct contaminant transport to the surface is reduced. This result implies that the contaminant release associated with bioturbation is strongly dependent upon temperature as a result of both increased metabolic activity and the decreased oxygen solubility at higher temperatures. Sediments that exhibit high sediment oxygen demands may also increase the effect of bioturbation as a result of the low oxygen conditions.

The effect of hydrophobicity is to influence the relative importance of particle movement vs. water movement in transporting contaminants. Phenanthrene is less sorbing than pyrene and the fact that the effective mass transfer coefficient is greater than expected by the defecation rate suggests that water-borne phenanthrene may be a significant fraction of the mass released via bioturbation. In addition, release at the surface is likely more rapid for the less sorbing phenanthrene.

Significant secondary porosity is also developed within the sediment as a result of the tubificid bioturbation. Advective processes driven by porewater motion would likely be considerably enhanced by the presence of this secondary porosity. The experiments, however, were conducted such that advective transport normal to the sediment-water interface was minimal.

Despite the differences in flux noted with different organisms and under different experimental conditions, a surprisingly good correlation has been observed between biomass density and effective bioturbation rates. Reible et al. (1996) compares measured bioturbation transport coefficients to a correlation with biomass density using data presented by Matisoff (1981)[3]. The correlation suggests that the effective bioturbation transport (diffusion) coefficient varies with the square root of the biomass density, that is, a doubling of the biomass density increases the effective diffusion coefficient by about 40%. This is consistent with the data shown in Table 1.

Other Biologically-Mediated Transport Processes

In addition to bioturbation, other biological processes also influence contaminant transport and fate. Microbial processes are normally of interest as a result of their potential for the degradation of contaminants. These processes also result in the breakdown of natural organic matter, however, which results in the formation of fine particulate and dissolved organic matter in the porewaters of the sediment. Hydrophobic organic contaminants tend to sorb to this organic matter and effectively increase the proportion of these contaminants that are suspended or dissolved in the mobile water phase. The flux of contaminants by porewater diffusion or advection is in direct proportion to the total mass suspended in that phase. At dissolved organic carbon concentrations of 10 mg/L or less this is expected to cause no effects on the phenanthrene in the porewater and a slight effect on pyrene. At 100mg/L disssolved organic matter, the pyrene loading in the pore water may increase by a factor or 10.

Microbial systems also drive oxidation-reduction reactions in sediments. The resulting oxidation state of metals and elemental species can significantly influence the mobility of these species. The solubility of oxidized forms of selenium, for example, is much greater than that of the reduced or elemental form. Again, reduced water capacity for the contaminant translates directly into reduced mobility and release rate. Since the microbial reactions involving selenium are very similar to those of sulfur, bacteria tend to produce the less mobile reduced form. Bioturbating organisms compete directly with this process by promoting the introduction of oxygen into the sediments. The balance between these two competing processes and the implications for selenium mobility and fate is currently under study.

4. SUMMARY AND CONCLUSIONS

Laboratory experiments were used to identify the rate and characteristics of the release of hydrophobic contaminants from sediments during bioturbation. Common freshwater tubificid oligochaetes were shown to have a dramatic impact on the rate of contaminant release and the structure of the sediments. The effect of tubificid bioturbation on contaminant release rate was especially dramatic in aged oil and grease contaminated sediments in which the contaminants were largely immobile without bioturbation. The measured rate of bioturbation-induced contaminant release correlated well with the defecation rate of the organisms and a square root dependence on biomass density. By comparison, amphipods influence only the upper few mm of sediment and the increase in contaminant release rate was minimal and of short duration. Bioturbation and other biological processes exhibit significant influences over the rate of release of contaminants from stable (i.e. non-eroding) sediments.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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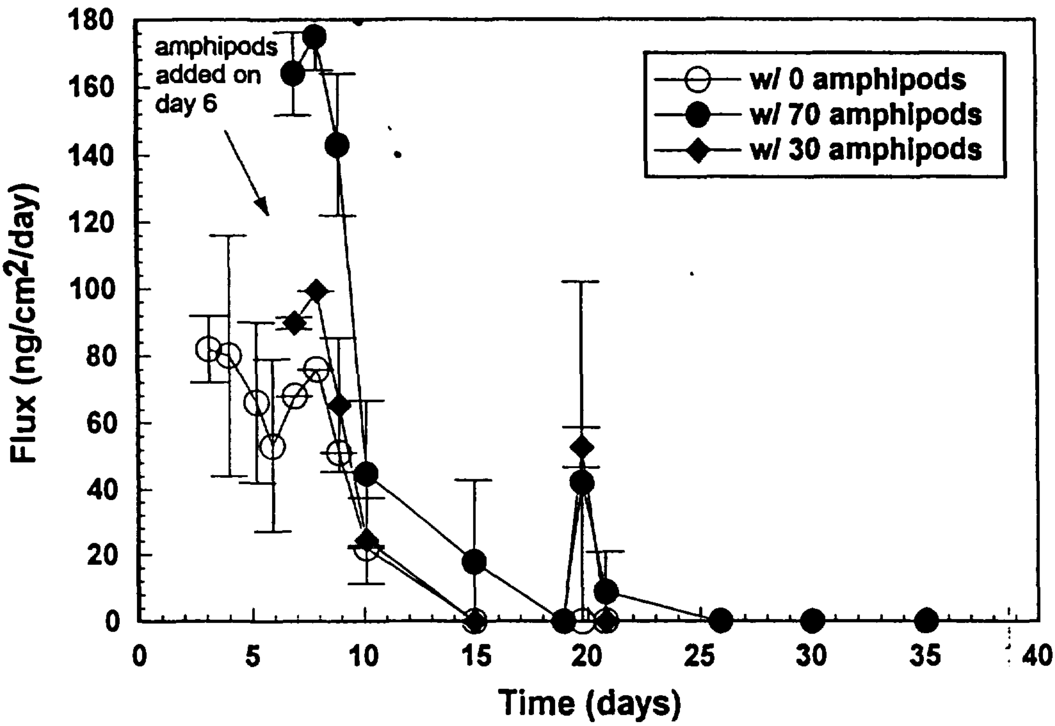

Figure 5.16 Pyrene Flux with Amphipods

Figure 1.

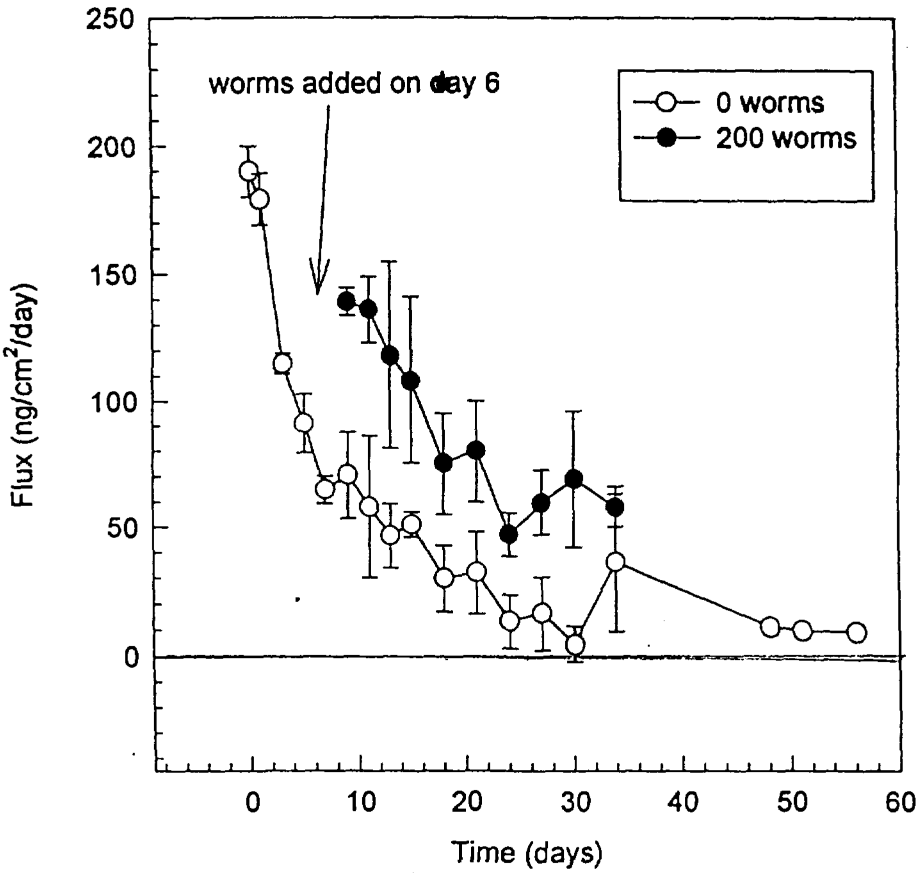

Figure 5.1 Pyrene Flux from Bayou Manchac Sediment with and without Worms

Figure 2.

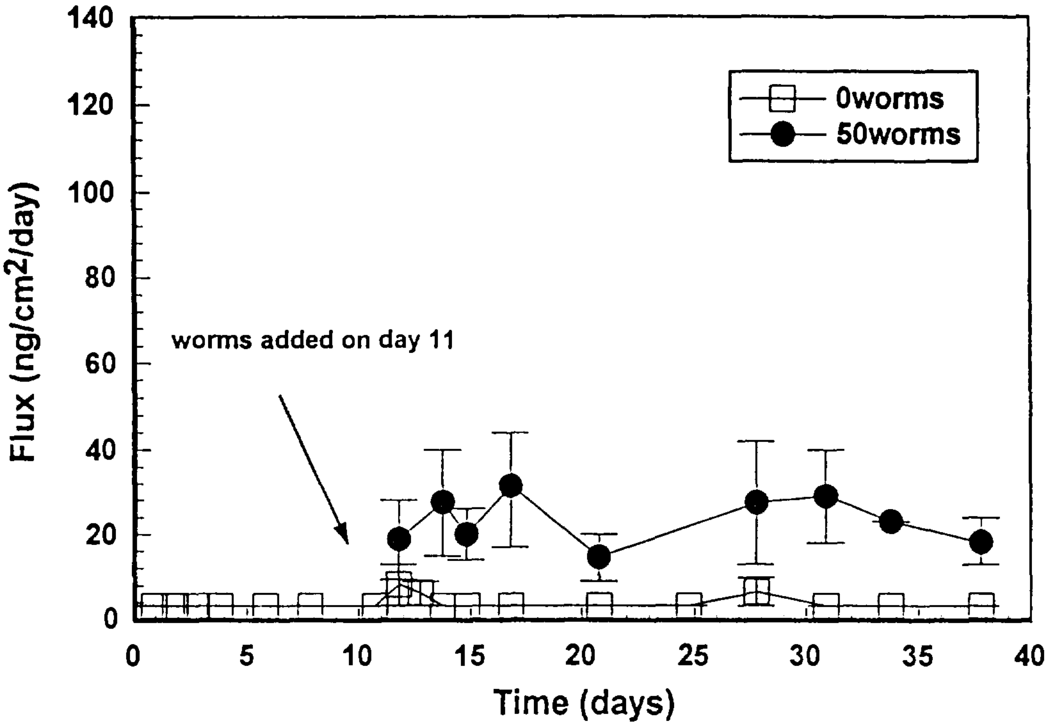

Figure 5.32 Fluoranthene Flux from Rouge River Sediment with 50 Worms-Run 2

Figure 3.

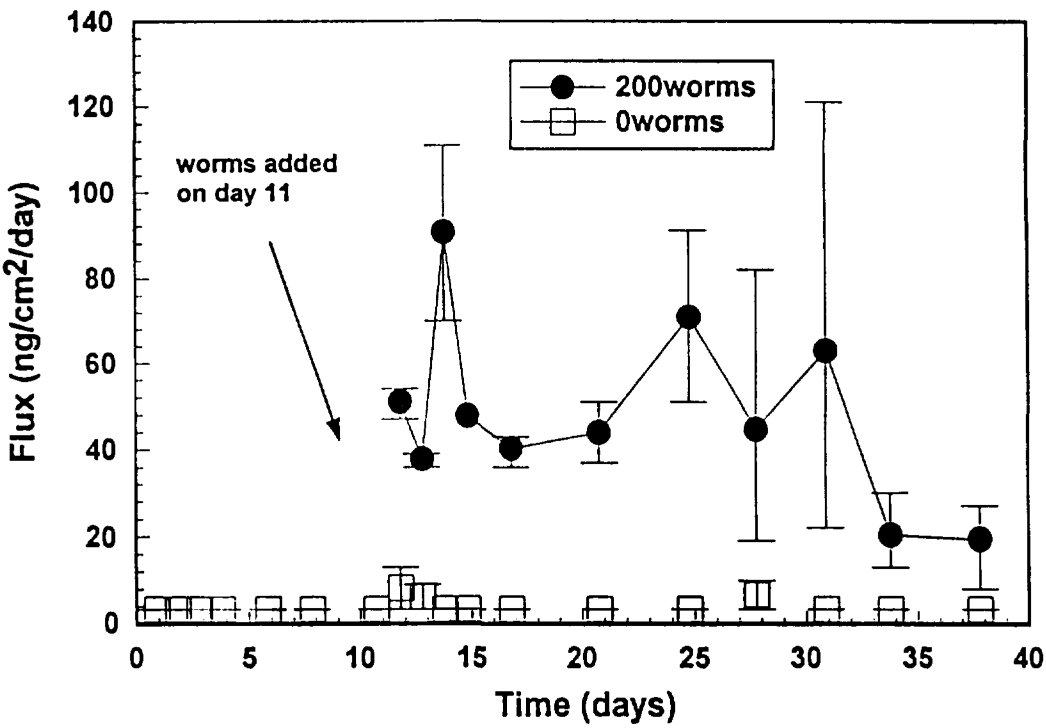

Figure 5.33 Fluoranthene Flux from Rouge River Sediment with 200 Worms

Figure 4.