Water Resources Research Center
Annual Technical Report
FY 2002

Introduction

The 2002 annual report reflects initiatives and programs undertaken by the new Director, Dr. Allen P. Davis, Professor, Department of Civil and Environmental Engineering, University of Maryland, College Park, Maryland. This is the first full year that Dr. Davis has served as Director of the Maryland Water Resources Research Center. In FY 2002 the Center supported two new projects and two continuing projects. Also, two Summer graduate fellowships were awarded. Additionally, two internships were sponsored through the USGS office. The range of this research is demonstrated by the fact that these funds went to personnel in four different colleges.

One of the first objectives of the Center was to learn more about the status of water science in the State of Maryland. First, visits were scheduled with leading Federal and State water agencies. Programs were reviewed at the U. S. Geological Survey (USGS), Baltimore Office; the Maryland Department of Natural Resources, Annapolis; and the Maryland Department of the Environment (MDE), Baltimore. Excellent working relationships were established with personnel in these offices. Representatives from these agencies have participated in reviews of submitted proposals, a state-wide water conference on research needs, and have provided informal advice on the Center's proposed programs. Another outgrowth of this collaboration was the establishment of two internships through the Center with the USGS.

A second major outreach initiative was the Center's sponsorship of a Colloquium on "Water Resources Research in Maryland: Highlights and Needs" at College Park. To our knowledge, this is the first Colloquium sponsored by the Center in the last 10-15 years. The colloquium provided an excellent forum for the exchange of information between our University scientists and several Federal/State water agencies. The computerized survey on water science expertise at the College Park campus conducted by the Center in FY 2001 was an ideal source for potential attendees for the colloquium and speakers. The colloquium was well attended and provided opportunities for establishing new contacts with other important water agencies, such as the US Army Corp of Engineers in Baltimore.

Plans for FY 2003 include sponsoring a second conference, this time on Maryland Regional Water Policy. The severe drought in Maryland during the summer of 2002 has prompted interest in what steps can be taken to alleviate any future water shortages and to develop policies governing the distribution of water in the regional infrastructure. We have already contacted an outstanding group of speakers for the October 2003 conference. Our plans also include additional contacts with local agencies with expertise in water research including NASA's Goddard Space Flight Center at Greenbelt, MD and the Agricultural Research Center at Beltsville, MD. Both of these Centers have extensive water science programs. The Maryland Water Center is ideally located to establish working partnerships with these groups.

Research Program

Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay Watersheds.

Basic Information

Title:	Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay Watersheds.
Project Number:	2002MD3B
Start Date:	3/1/2002
End Date:	6/28/2003
Funding Source:	104B
Congressional District:	5th District of Maryland
Research Category:	Water Quality
Focus Category:	Water Quantity, Non Point Pollution, Agriculture
Descriptors:	
Principal Investigators:	Alba Torrents, Laura McConnell

Publication

1. Kuang, Z., McConnell, L. L., Torrrents, A., Merritt, D., Tobash, S. (2003) Atmospheric deposition of currently used pesticides to the Choptank River watershed J. of Environmental Quality (in press).

Annual Report for the period 3/01/02 through 2/28/03

Project Title: Atmospheric Deposition of Currently Used Pesticides Chesapeake Bay Watersheds

Principal Investigator(s): Alba Torrents and Laura McConnell

Problem and Research Objectives

The Delmarva Peninsula, a region within the Chesapeake Bay watershed, is dominated by agricultural land use, which makes the streams and tributaries in this area highly vulnerable to agricultural runoff. This area also contains some of the most important aquatic habitat areas for the living resources of the Bay. The extent of local or regional atmospheric transport and deposition of pesticides to this area is poorly understood and may be an important contributor to the overall pesticide budget for the region. Baseline measurements of atmospheric concentrations and deposition fluxes of pesticides in different parts of the Chesapeake Bay watershed are a fundamental part of determining the importance of atmospheric processes to the overall loading of pesticides to the Bay.

As part of the Maryland's Targeted Watershed Project a number of government organizations and environmental groups are monitoring these watersheds in order to quantify the impacts of land use and non-point pollution control practices on water quality and aquatic life habitat and to determine long-term trends in water quality and aquatic life communities. While the potential for runoff of pesticides as a source of non-point pollution into surface waters is high, atmospheric deposition of pesticides that have been volatilized from local and regional agricultural activity may also play a significant role in water quality deterioration. The Delmarva Peninsula is poorly characterized with respect to the presence of pesticides in its atmosphere. This has hindered our ability to assess the importance of atmospheric loadings to the concentrations of these compounds in the Chesapeake Bay.

The general objective of this research is to characterize the Delmarva Peninsula with respect to the presence of pesticides in its atmosphere with a view to estimating aerial pesticide loadings to the Bay arising from agricultural activity in the Peninsula. In the previous report we presented in detail the sampling and analytical methodology. While sampling and analytical analysis has continued during this reporting period, during this reporting period we have increased our efforts on data analysis with respect to temporal trends in aerial concentrations/atmospheric depositions.

Methodology

As stated, the methodology was mostly developed during the previous reporting period and it has now been accepted for publication (Kuang et al. 2003).

Assessing temporal/spatial trends in the aerial concentration of pesticides

The pesticides being analyzed for in the samples from the Peninsula include those that have been banned and those that are currently being used in the region. In the air samples from 2000, chlorothalonil, metolachlor and a-endosulfan were above the limit of quantification in all samples (n = 31). Atrazine, HCHs, chlordanes, chlorpyrifos and b-endosulfan also occurred frequently (>80%). Chlorothalonil is the most frequently detected pesticide in rainfall. Atrazine degradation products, CIAT and CEAT seen in rainfall, were below the level of quantification in air samples.

In the past few decades awareness about the harmful ecological effects of organochlorine pesticides has led to their limited use or completely phase out. DDTs, chlordanes, HCHs are some pesticides in question. DDT is no longer registered for use in the U.S. Owing to concerns about the risk of cancer; the use of chlordane was banned by the USEPA in 1988. The insecticide is no longer distributed in the U.S. Similarly, Lindane (g-HCH) is no longer manufactured in the U.S. and hence its use is severely restricted (it is still being used in small amounts in the Delmarva). Heptachlor is another pesticide the use of which has been cancelled in the U.S. since 1988. It follows that since these pesticides are no longer being used in agriculture in this country, their concentrations in the environmental compartments should go down with time. For the pesticides currently being used, the concentrations in the atmosphere should be a function of usage, time and temperature.

Chlordanes are present in quantifiable amounts in the air in the Delmarva Peninsula although the concentrations are usually below the limit of quantification in rainfall (data not shown) and water bodies (Choptank river). DDT and its metabolites (DDEs) are below the level of quantification in both air and rainfall. Dieldrin has been sporadically detected in rainfall, which suggests that it might be present in quantifiable amounts in air. Heptachlor and its metabolite were sporadically seen in very small concentrations in precipitation at Horn Point.

Pesticides in precipitation over the Peninsula

Chlorothalonil is by far the most abundant pesticide in precipitation, forming 35-46% of the total flux (Table. 1). Atrazine and metolachlor are the second and third most abundant compounds. There appears to be a decrease in the wet deposition of herbicides atrazine and the fungicide chlorothalonil while the deposition of trifluralin and chlorpyrifos seems to be on the rise. Also the overall deposition of the pesticides seems to be on the decline. These observations suggest that the pesticide usage patterns in the region are changing and the changes are being reflected in the concentrations in precipitation. As more data for the 2002-2003 season becomes available, we will compare the rainfall fluxes data with the usage of pesticides over the years to ascertain if indeed the changes in fluxes are caused by changes in usage patterns. The spatial trends in wet fluxes for the Upper Delmarva Peninsula shall be examined by comparing the trends from the two sites two sites on the opposite ends of the Peninsula (Horn Point and Lewes).

Table 1. Pesticides in rainfall (Horn Point)

Yearly flux (total ng.m^{-2}/total rainfall)			
	2000	**2001**	**2002**
Volume, mL	128714	95637	156267
Rainfall (cm)	64	48	78
trifluralin	0.0	0.8	2.3
diazinon	1.7	1.9	27.7
g-HCH	4.1	5.6	2.6
chlorothalonil	627.5	430.3	252.0
chlorpyrifos	4.7	7.0	14.0
malathion	7.3	0.7	0.5
chlrpyrfs oxon	22.6	38.8	23.3
a-endosulfan	4.1	5.7	1.1
b-endosulfan	11.5	7.9	1.9
endslfn slft	2.1	2.8	3.0
Atrazine	3.1	2.4	1.8
metolachlor	3.1	2.4	2.4
Total flux	2735	2173	1447

Effect of temperature on ambient concentrations: The Clausius Clapeyron Equation

In the case of atmospheric measurements of semivolatile compounds, the largest source of variability is related to atmospheric temperature (Cortes et al., 1998; Hillery et al., 1997). At elevated temperatures, the air concentrations increase indicating that volatilization from the earth's surface is an important factor in the movement of these chemicals. The effect on temperature on ambient concentrations of PCBs and PAHs is well documented (Simcik et al., 1999; Sofuoglu et al., 2001). Sofuoglu et al. (2001) also found statistically significant temperature dependence for gas phase DDD and trans-nonachlor in Chicago air.

Gas phase partial pressures increase as temperature increases and the functional relationship between these two parameters is given by the Clausius-Clapeyron (CC) equation:
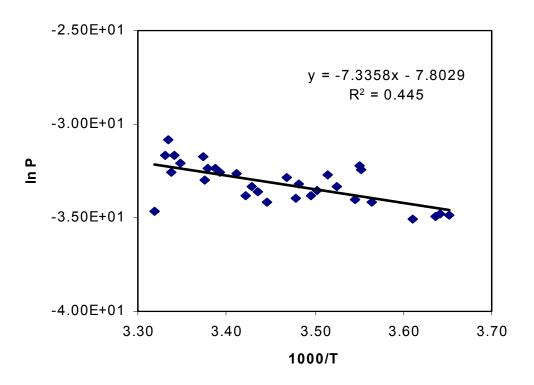
$$Ln\ P = -\Delta H/RT\ + constant$$

Where P is the partial pressure of the compound (atm), ΔH is the characteristic phase-transition energy of the compound (kJ/mol), R is the gas constant and T is the temperature (K). Partial pressures can be obtained from atmospheric concentrations using the ideal gas law. Thus the plot of the natural logarithm of the partial vapor pressure as a

function of the inverse temperature will be a straight line. Thus, the temperature dependence of a phase transition (i.e., surface to air) can be expressed by the Clausius-Clapeyron equation when the system is at equilibrium. In environmental studies these plots have been generated from samples taken at different temperatures (even though a true equilibrium might not exist) and the slopes compared to literature slopes of the vapor pressure (Henry's constant, K_{oa} etc.).

The CC equation has been used by several researchers to explain the concentrations of various SVOCs (mainly PCBs and organochlorines) in the atmosphere (Hillery et al., 1997; Hoff et al., 1998; Simcik et al., 1999; Cortes et al., 1998). It has however, been found that the plots are often nonlinear and there is considerable scatter in some cases (Hoff et al., 1998, Cortes et al., 1999, Wania et al., 1998, Simcik et al., 1999). Some researchers (Wania et al., 1998; Hoff et al., 1998) have suggested that such behavior can be expected from the combination of exchange and transport processes that affect the air concentration at a remote site. Hoff et al. (1998) further suggest that the slopes of the CC plots (and hence the H values) can be interpreted in terms of relative importance of short- vs long-range transport. Their hypothesis is that lower slopes indicate that long-range transport controls atmospheric concentrations and that higher slope values (stronger temperature dependence) indicate that volatilization from local sources dominates atmospheric concentration. This means that the farther we move away from the source, the slopes become shallower (or temperature effect is less significant). Further, local exchange processes could control the atmospheric processes during the warmer months, and long-range transport processes could control the concentrations during the colder months. They support their conclusion by pointing out the fact that for North America it seems that there is a clear decline in slope with increasing distance from suspected PCB sources. However, it is now being suggested (Cortes et al., 1999) that for areas close to regions of current pesticide use, non-linearities and scatter in the CC plots may also result from pesticide usage.

Pesticides in air over the Peninsula

From the 2000 air data from Horn Point (data not shown), it is seen that most organochlorine pesticides (endosulfans, chlordanes etc.) are seen in the air throughout the year. Some compounds are more persistent than others. One way to ascertain the persistence of a compound in the atmosphere is to determine the half-life of the compound of interest. Half-lives can vary widely even for sites situated relatively close and can reflect the difference in the removal mechanisms. The atmospheric half-lives of the g-HCH have been found to range from 2.2 yr at Lake Michigan to 7.3 yr at Lake Ontario. The half-life of g-chlordane was 3.2 yr at Lake Michigan and that of trans-nonachlor was 9.2 yr at Lake Ontario (Cortes et al., 1998). Owing to the higher temperatures in the Delmarva Peninsula (as compared to the Great Lakes region), the half-lives of pesticides no longer in use (e.g. chlordanes) should be smaller than that observed in the Great Lakes region.

Figigure 1. Clausius Clapeyron plot for a-endosulfan

For most pesticides currently in use (atrazine, endosulfans etc.) the concentrations peak during the application periods and are considerably lower during the rest of the year. The concentration pattern suggests that temperature is not the only factor governing the atmospheric concentrations. There is considerable non-linearity and scatter in the Clausius Clapeyron plot for a-endosulfan (Fig. 1) and temperature only explains about 40 % variation in the concentration. As has been suggested (Cortes et al., 1999) the atmospheric concentration for pesticides currently in use is highly dependent on the agricultural cycle.

We are currently determining the half-lives of the pesticides frequently detected in the air the Peninsula, taking into account the agricultural usage in the region. We use the equation suggested by Cortes et al. (1999):

$$\ln P = a_0 + a_1\left(\frac{1}{T}\right) + a_2 t + \frac{a_3}{1 + \left(\dfrac{tMODa_4 - a_5}{a_6}\right)^2}$$

Where, 'a' symbols are constants, T is the temperature; t is the time when the sample was taken (in Julian days). The last term on the right is an expression for the agricultural cycle modeled as a Lorentzian (can also be Gaussian) function. The authors contend that the curvature in the CC plot can be attributed to agricultural usage. For pesticides no longer in use, the agricultural source term shall be removed and the equation reduces to (Cortes et al., 1998)

$$\ln P = a_0 + a_1\left(\frac{1}{T}\right) + a_2 t$$

The half-life of the compound shall be ascertained from the value of the parameter a_2.as

$$t_{1/2} = \frac{\ln 2}{a_2}$$

We are using the aerial concentration data from Horn Point site as it will the largest data set available. The pesticide concentrations available after initial analyses (ng/m^3) shall be converted to partial pressures using the ideal gas law. The parameters shall be determined using multiple linear regressions.

Determination of the atmospheric half-lives is the first step in quantifying the effect that agricultural usage has on atmospheric concentrations. Cortes et al. (1999) have reported that the estimated half-life for a-HCH went up by 50% when recent agricultural usage was accounted for. Incorrect half-lives jeopardize realistic risk assessment. For pesticides no longer in use, the half-lives help us in estimating the rate at which the concentrations are reducing. It is also possible that no plausible decrease for such compounds will be observed. This could point to the fact that the system is still not at equilibrium and the contaminated soils/water bodies are acting as sources of these compounds to the atmosphere. The correlation between aerial concentrations and usage is expected to be high. In the reverse case, that is, if the agricultural function does not greatly affect concentrations, other effects such as long-range transport from other areas might be examined.

Comparison of V/P partitioning of pesticides and PAHs

For the 2000 air data from Horn Point it is seen that the Junge-Pankow model under predicts the vapor particle partitioning of metolachlor and atrazine (Figure 2). It was seen that the model greatly under predicted the particle phase concentration in most cases. This is in contrast to the results of Bidleman et al. (1999) where they found that the model over predicted the distribution of organochlorines. There could be several reasons for the discrepancy. The fact that the deviations were more pronounced for the samples taken during the heavy agricultural activity, suggests that probably equilibrium was not reached. Sampling artifacts such as sorption of gaseous compounds onto the particles on the filter and onto the filter itself (Bidleman and Harner, 2000) could bias the results towards the particulate concentration. Such a possibility is being remedied by using two filters in subsequent sampling periods. Model limitations could also account for these observations (2001 onwards).
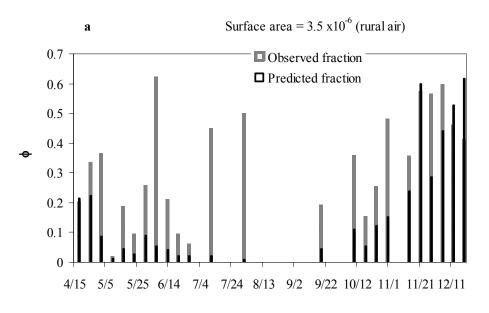
Surface area = 3.5 x10^{-6} (rural air)

Figure 2. Vapor/Particle distribution of atrazine (Horn Point, 2000)

One of the major limitations of the model is that it fails to consider the humidity effects (Cotham and Bidleman, 1995), which might be quite significant in case of the modern polar pesticides: the greater the humidity, the greater would be the amount of water present on the particulates and consequently the greater would be the partitioning of the compound into the water phase on the particle. For PAHs, Pankow et al., (1993) found that PAH particulate fraction is inversely related to relative humidity, although the correlations were low. Delmarva Peninsula is a region with high relative humidity the year round. At the Horn Point site for April-September, 2000, the average relative humidity was 83.58% and the minimum value was 30.66%. Hence, a combination of compound properties and the climate might make humidity an important variable in predicting the V/P partitioning.

In a recent study, Arzayus et al., (2001) found that fractional concentrations of PAHs in the Chesapeake Bay sediment were positively correlated with their atmospheric dry deposition fluxes to the Bay. The authors concluded that atmospheric deposition of aerosol-bound PAHs to the watershed controls their influx to the Bay sediments. The fate of PAHs input to the Bay from gas deposition was determined to be uptake and metabolism within the aquatic food web rather than deposition to sediments. The results from this underline the importance of greater understanding of vapor/particle partitioning of PAHs.

For comparison, we have added PAH's to the toxic chemcials to be analyzed. The Delmarva Peninsula is largely agricultural; the industrial activity is limited at best. It is well established that the sources of PAHs in the environment are predominantly urban (Dachs et al., 2002, Simcik et al., 1997). Hence, it is reasonable to assume that, for most part, the PAH source to the Peninsula would be from the across the Bay (Washington and

Baltimore metropolitan areas) and from the west (the Atlantic ocean on the east largely rules out sources from that end). In contrast, the source of agricultural pesticides is local. The very location of the region sets it apart from the other studies, most of which have been conducted in urban areas with local sources of PAHs and distant pesticide sources. In the case of this study the region is rural with known sources of pesticides and distant PAH sources. The purpose is to compare the effectiveness of the Junge-Pankow model in predicting V/P partitioning of PAHs and pesticides in this region.

Significance

The data obtained as part of this project represents the largest data set available for pesticides in rain and air in the Delmarva Peninsula.   The determination of atmospheric half-lives and effect of relative humidity on partitioning would help in better assessing the fate of these compounds in the environment as well as discriminate between regional and non-regional sources.   While this project is near completion, another project (funded from CICEET) is underway with the addition of a third site.   We plan to continue the analysis with the data from the 3-sites.   We plan to use LandSat imagery to estimate. It is an indirect method of estimating emissions but is well suited in cases where sufficient pesticide usage data is not available. Estimates of amount of pesticides volatilized can be further used to determine the importance of runoff and aerial depositions in pesticide loadings to the Chesapeake Bay.

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Dachs, J., Glenn IV, T.R., Gigliotti, C.L., Brunciak, P., Totten, L.A., Nelson, E.D., Franz, T.P. and Eisenreich, S.J. **2002**, Processes driving the short-term variability of polycyclic aromatic hydrocarbons in the Baltimore and northern Chesapeake Bay atmosphere, USA. *Atmos. Environ.*, 37(2002), 2281-2295.

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Sustainable Oil and Grease Removal from Stormwater Runoff Hotspots using Bioretention

Basic Information

Title:	Sustainable Oil and Grease Removal from Stormwater Runoff Hotspots using Bioretention
Project Number:	2002MD4B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	5th Congressional District Maryland
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Toxic Substances, Water Quality
Descriptors:	storm water management, oil and grease, runoff, water quality
Principal Investigators:	Eric A. Seagren, Allen Davis

Publication

1. Hong, Eunyoung, 2002, Sustainable Oil and Grease Removal from Stormwater Runoff Hotspots using Bioretention, "MS Dissertation, Department of Civil and Environmental Engineering, A.J. Clark School of Engineering, University of Maryland, College Park, Maryland, 167 pages.
2. Hong, Eunyoung, Eric A. Seagren, and Allen P. Davis, 2002, Sustainable oil and grease removal from stormwater runoff hotspots using bioretention, "presented at" PennTec 2002, the 74th Annual Conference and Exhibition of the Pennsylvania Water Environment Association, State College, Pennsylvania, June 23-26, 2002.

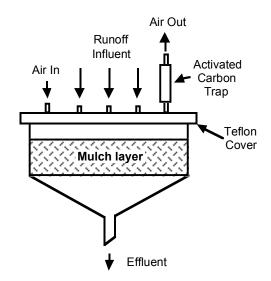## Problem and Research Objectives

Urban stormwater runoff affects the quality of receiving water bodies by carrying a significant load of contaminants that have accumulated on urban surfaces (Vogt, 1995; Line et al., 1996; Wu et al., 1998). One of the important components of this contaminant load is oil and grease (O&G) pollution, which represents a significant source of hydrocarbons to the environment (Stenstrom et al., 1984). The hydrocarbons from urban runoff may later be found in aquatic sediments (Wakeham, 1977) and open water, and ultimately may accumulate in the tissues of aquatic life. Thus, these hydrocarbons may result in a variety of negative environmental effects.

A major input of this O&G is from vehicle emissions, mostly from crankcase oils (Stenstrom et al., 1984). Thus, controlling O&G discharges from impervious areas in automotive-intensive "hotspots", such as roadways, parking areas and commercial properties, can reduce the amount of O&G transported in urban stormwater runoff to receiving water bodies. In this research, it was hypothesized that the removal of O&G from urban runoff could be accomplished via sorption, filtration and subsequent biodegradation in the stormwater best management practice of bioretention, by using a thin surface mulch layer as a contaminant trap.

The objectives of this research were to: (1) evaluate the capacity of the mulch layer to capture dissolved and particulate-associated O&G contaminants via physical and chemical mechanisms during a simulated storm event, and (2) evaluate the rate and extent of O&G biodegradation in the mulch layer in between storm events. A mass balance approach was employed to evaluate the fate of hydrocarbon contaminants during the simulated storm events and to quantify the amount of contaminant biodegraded after the storm events.

Methodology

Stormwater runoff simulation experiments were performed using a bench-scale bioretention reactor (Figure 1), made using a porcelain Büchner funnel (253-mm I.D., 110-mm bowl depth), and containing a 3-cm thick layer of leaf mulch (mulch source: Department of Public Works, College Park, MD). The only microorganisms supplied to the system were the native microbes present in the mulch. The contaminants selected for the bench-scale stormwater runoff simulation experiments included naphthalene, toluene, and commercial automobile motor oil (Shell, SAE Grade 10W-40), which were added to simulated runoff (Davis et al., 2001). The naphthalene, toluene, and motor oil were added in dissolved (all three) or particulate-associated (naphthalene only) form to the simulated runoff with influent concentrations of ~1.6, 2.7, and 30.8 mg/L,

Figure 1. Schematic illustration of the mulch-based bioretention reactor

1

respectively. For the particulate-associated naphthalene experiments, Berryland Oe soil (Levin, 1994) was added to a naphthalene-water solution to allow sufficient sorption, after which the soil was then removed from the suspension by centrifugation, and subsequently added to synthetic runoff, resulting in total influent naphthalene concentrations of 1.5~1.6 mg/L and total suspended solid (TSS) concentrations of 270~340 mg/L.

All experiments had two phases: Phase 1, which simulated a 6-hour runoff event (4 cm/hr), followed by Phase 2, simulating the time between storm events. During Phase 1, the influent simulated runoff and the reactor effluent were sampled and extracted with hexane, and the hexane was analyzed for the naphthalene or toluene concentration by gas chromatography (GC). This allowed for calculation of the trapped contaminant mass in the mulch. Motor oil concentrations in aqueous samples during Phase 1 were determined by using a solid phase extraction method (Lau and Stenstrom, 1997). Then, a mass balance approach, incorporating monitoring of contaminant levels in the aqueous, gaseous and solid phases, was used to quantify the contaminant mass removal via biodegradation during Phase 2. Specifically, to monitor contaminant loss by degradation, mulch samples were taken everyday for inhibited-control runs and twice per day for biotic runs, and analyzed for the contaminant concentration using hexane extraction and GC. To provide additional evidence supporting that the contaminant removal was due to biodegradation, enumeration of total heterotrophic plate counts (HPC) and naphthalene- and toluene-degrader plate counts (NDPC and TDPC, respectively) and oil-degrader counts was performed using mulch samples during Phase 2. In addition, the activated carbon from the trap (Figure 1) was also extracted with hexane for GC analysis to account for losses by volatilization.

The results of inhibited-control and biotic experiments were compared to distinguish the impact of biodegradation. Mulch for the inhibited-control experiments was amended directly with mercuric chloride ($HgCl_2$) at a rate of 1.84 mmol/kg and soaked in 1000 ppm $HgCl_2$ solution for 48 hours. In the same manner, mulch for biotic runs was soaked in 1000 ppm calcium chloride ($CaCl_2$) solution. The mulch was drained after soaking and packed in the reactor up to a height of 3 cm. $HgCl_2$ was also introduced to the influent solution for the inhibited-control experiments at a level of 400 mg/L. In the toluene experiments, autoclaved mulch was also used to run another control to better inhibit the microbial activity.

All the samples were taken and analyzed in duplicate. In the figures presented below, the average values are plotted and the standard deviations are shown as error bars; however, in many cases the magnitude of the standard deviations is even smaller than the symbols and, thus not visible in the figures.

Principal Findings and Significance

Experiments performed with ~1.6 mg/L (~3.2 mg/hr surface loading) dissolved naphthalene in the influent simulated runoff demonstrated approximately 90% removal from the aqueous phase via sorption to the mulch layer during the simulated storm event (Figure 2). Subsequently, about 92% naphthalene removal from the solid phase occurred in the mulch layer within 62 hours following the end of the stormwater addition, which was about twice as fast as in the inhibited-control (Figure 3 (a)). In particular, removal of naphthalene in the biotic run proceeded rapidly during the first 48 hours. It was found from analysis of the carbon trap that losses due to volatilization were negligible in experiments with naphthalene, indicating that the fast removal of naphthalene occurred due to microbial activity.

To provide additional evidence confirming that the naphthalene removal was due to biodegradation, the populations of total heterotrophic bacteria and naphthalene-degrading bacteria in the mulch were counted periodically after the stimulated storm event (Figure 3 (b)). From the corresponding results of the microbial plate counts, it was found that the population of the microorganisms in the mulch increased with time, and that the sterilization method inhibited some microbial growth, especially the naphthalene-degraders, causing an approximately four orders of magnitude decrease in the population at 24 hours after Phase 1. Nonetheless, even though the control inhibited the microbial activities, naphthalene-degraders were still present. Thus, the slow decrease of naphthalene with time in the inhibited-control mulch might be explained as being due to biodegradation by the remaining bacteria. The observation of microbial growth in the reactor after introducing the naphthalene supports the hypothesis that the rapid degradation of naphthalene is mainly because of the microbial activities.
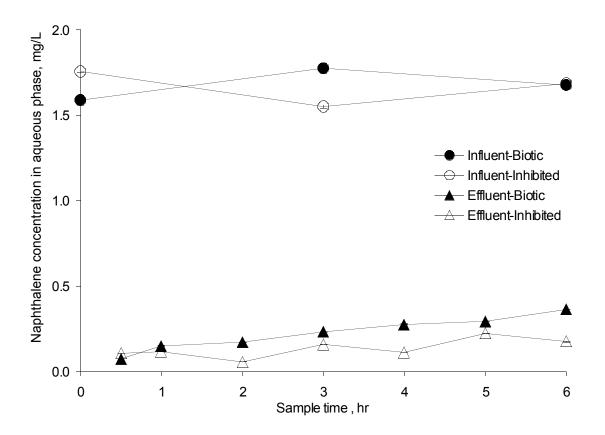

Figure 2. Naphthalene removal from the aqueous phase through the bioretention mulch layer during the simulated storm event. Error bars represent ± one standard deviation.
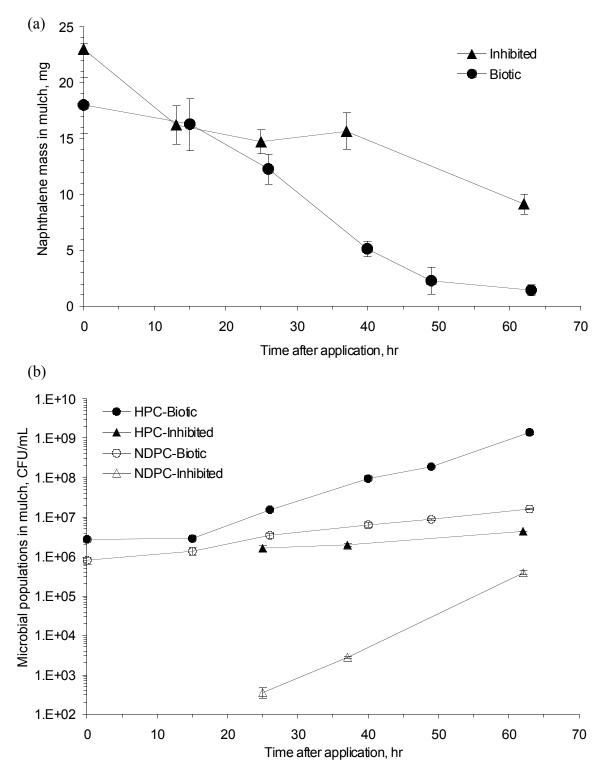
Figure 3. Biodegradation of naphthalene captured on bioretention mulch: (a) Reduction of naphthalene in the mulch, and (b) Microbial growth based on total heterotrophic plate counts (HPC) and naphthalene-degrader plate counts (NDPC) in the mulch. Error bars represent ± one standard deviation.

Experiments using simulated stormwater runoff contaminated with about 2.7 mg/L dissolved toluene (~5.4 mg/hr surface loading) showed similar results. In this case, biotic and two inhibited control (HgCl$_2$ amended and autoclaved) experiments were performed. The influent aqueous phase concentration was reduced by approximately 86% during Phase 1 in both the biotic reactor and the control run amended with HgCl$_2$. However, a lower removal efficiency (~56%) was observed in the autoclaved control experiment (Figure 4). A greater portion of toluene in all experiments (about 8~15% of toluene introduced) was volatilized during storm events compared to the negligible volatilization in the naphthalene experiments. After completion of Phase 1, about 90% removal of toluene from the mulch occurred in the biotic experiments within around 4 days (101 hours) (Figure 5 (a)). Even though the difference between the biotic run and the control run is not very obvious in this case, the more rapid drop in the toluene concentration suggests greater biological activity in the biotic experiment.

Similar to the naphthalene results, corresponding trends between the cumulative amounts of toluene biodegraded from the mulch, and the microbial plate counts provide strong evidence that biodegradation played a major role in the toluene removal from the mulch (Figure 5 (b)). The population of the microorganisms in the mulch appeared to increase gradually with time based on both the HPC and the TDPC.
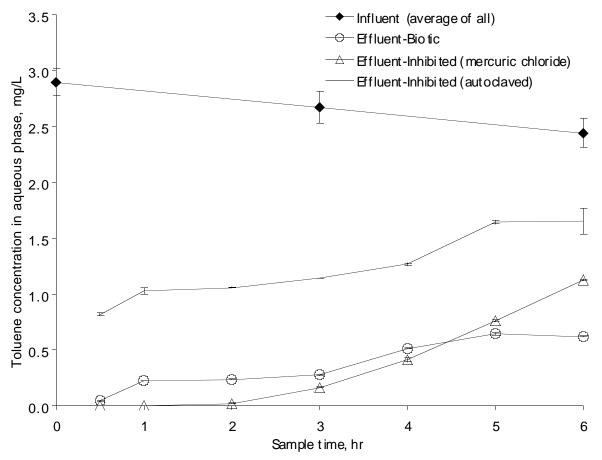

Figure 4. Toluene removal from the aqueous phase through the bioretention mulch layer during the simulated storm event. Error bars represent ± one standard deviation.
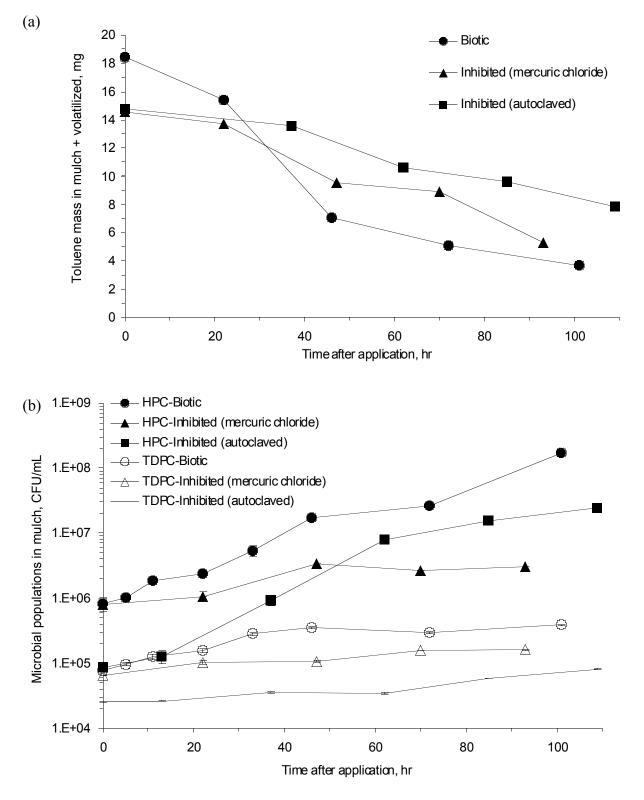
Figure 5. Biodegradation of toluene captured on bioretention mulch: (a) Reduction of toluene in the mulch, and (b) Microbial growth based on total heterotrophic plate counts (HPC) and toluene-degrader plate counts (TDPC) in the mulch. Error bars represent ± one standard deviation.

Stormwater runoff simulation experiments using motor oil were performed in order to ensure that a bioretention mulch layer could capture and degrade not only a single target compound, but also a complex mixture of hydrocarbons. Experiments performed with an influent concentration of about 27 mg/L dissolved motor-oil hydrocarbons (55 mg/hr surface loading) demonstrated approximately 85% removal from the aqueous phase via sorption to the mulch during the Phase 1 (data not shown). This is comparable to the results in the single contaminant studies with naphthalene and toluene.

Gas chromatograms of the mulch sample hexane extracts can be used to compare the change in the oil content with time during Phase 2 (Figure 6). The heights of the peaks clearly decreased with time in the biotic chromatograms, especially during first two to three days, whereas no significant change in the chromatograms was observed in the inhibited-control experiment throughout Phase 2. Quantitatively, the total mass decrease of oil during Phase 2 was observed by monitoring the total area in the chromatograms (Figure 7 (a)). Although a significant amount of experimental variability is noted, about 92% removal of oil from the mulch occurred in the biotic reactor within around 10 days after the end of Phase 1, whereas only approximately 20% removal of oil was observed in the control reactor after 9 days. Removal of most oil in the biotic reactor was found to occur during the first few days, with more than half of the oil degraded within three days. An increase in the population of the oil-degrading and heterotrophic bacteria in the biotic reactor in the first two to three days correlates well with the initial loss of the majority of oil in that reactor, suggesting microbial activity as a primary removal mechanism (Figure 7(b)).

The time to reach approximately 90% removal of oil (~8 days) in the biotic reactor was much longer than that for naphthalene (~3 days) and toluene (~4 days). This is not unreasonable given that oil is a complex mixture of hydrocarbons, some of which require more time for biodegradation (Yerushalmi and Guiot, 1998). In addition, it is also possible that the longer time needed for degradation is due to the higher concentration of dissolved oil hydrocarbons that was introduced in this experiment compared to the concentrations of the individual target compounds.

Particulate-associated experiments were performed with a total influent concentration of about 1.6 mg/L naphthalene (3.2 mg/hr surface loading). The amount of sorbed naphthalene on the soil particulates in the influent and effluent was determined by the difference between the hexane-extracted naphthalene concentrations of total and centrifuged aqueous samples. The results of biotic and inhibited-control experiments demonstrated approximately 98% removal of total and dissolved naphthalene during Phase 1 (Figure 8 (a)). In both experiments, the influent TSS concentrations increased with time because not all the solids were homogeneously distributed in the influent bottle, even though mixing was provided, causing an accumulation of solids as time elapsed (Figure 8 (b)). All the effluent TSS concentrations, including the control without the input of particulates, demonstrated similar trends, decreasing to very low levels at the end. Even though most particulates appeared to be accumulated on the surface of the mulch, there was almost no water head buildup observed on the mulch during Phase 1. From a practical perspective, this provides a real benefit of using mulch as a top layer material on a bioretention system.

The results for naphthalene loss due to volatilization, naphthalene removal in the mulch, and microbial growth during Phase 2 were very similar to those for the dissolved naphthalene experiments. This indicates that the fast removal of naphthalene observed in Phase 2 of the biotic experiment with particles occurred due to biodegradation (data not shown).
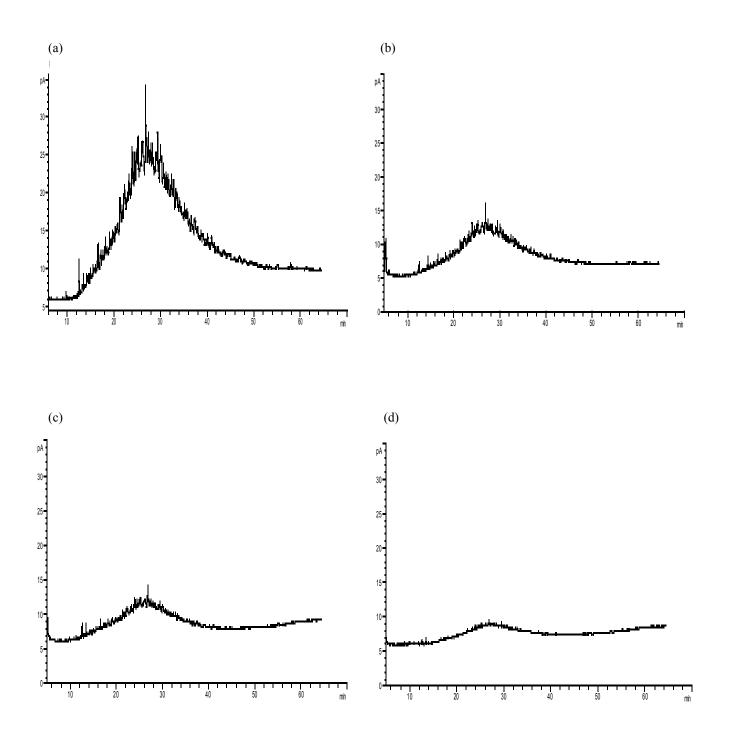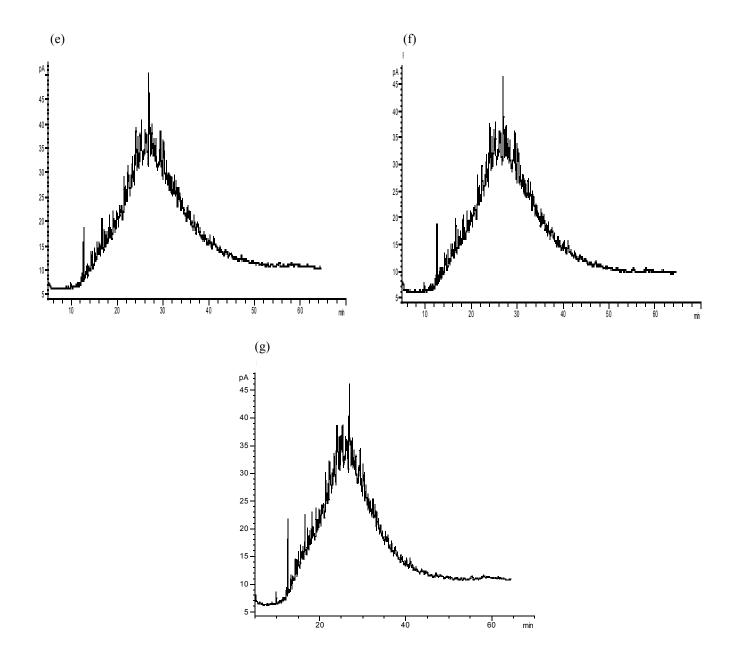
Figure 6. Representative gas chromatograms of oil extracted from the mulch in the biotic
experiment at times (a) 0, (b) 2, (c) 3, and (d) 10 days, and in the inhibited-
control experiment at times (e) 0, (f) 5, and (g) 11 days
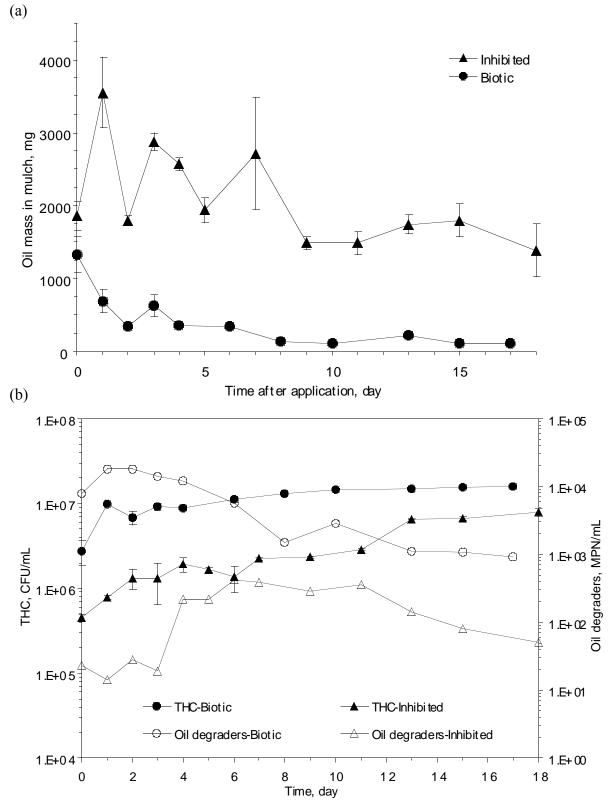
(e)

(f)

(g)

9

Figure 7. Biodegradation of oil captured on bioretention mulch: (a) Reduction of oil in the mulch, and (b) Microbial growth based on total heterotrophic plate counts (HPC) and oil-degrader counts in the mulch. Error bars represent ± one standard deviation.
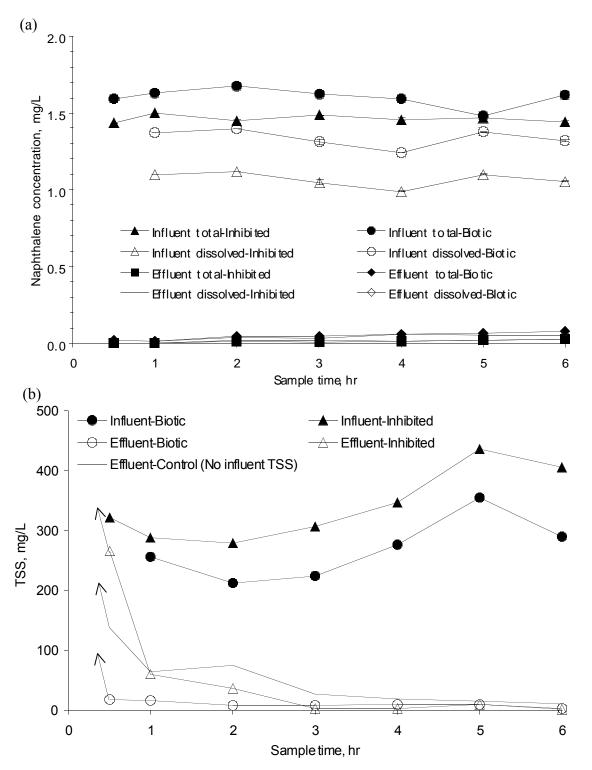
Figure 8. Removal of naphthalene and total suspended solid (TSS) from influent through the bioretention mulch layer during the simulated storm events in particulate-associated naphthalene experiments: (a) Removal of total and dissolved naphthalene, and (b) Removal of TSS. Initial effluent values (at t≈0) exceeded 1000 mg/L and are not shown. Error bars represent ± one standard deviation.

Overall, it can be concluded that there are several advantages to placing a surface mulch layer on a bioretention system for O&G removal. First, it appears that high contaminant removal efficiency can be achieved by the placement of a thin (~3 cm) layer of mulch to treat both dissolved and particulate-associated hydrocarbon contaminants. Second, because it only takes a relatively short time (3 to 4 days with single contaminants, and a maximum 10 days with the higher contamination of oil) to degrade the trapped contaminants after the storm event, no accumulation of hydrocarbons occurs, demonstrating that this as a sustainable process. Third, there is no need to inoculate the mulch with specific microorganisms to degrade the O&G contaminants because the native microbial population in the mulch tested has been found to have an appropriate biodegradation capacity. In addition, after exposure of the mulch microorganisms to the contaminants, an increased population of contaminant-degrading microbes is available for biodegradation during a subsequent re-exposure. Fourth, the moisture content of the mulch layer did not decrease drastically after the storm event under an air stream, which will be beneficial for microorganisms in the mulch as well as in the soil below. Fifth, the mulch layer has high permeability; therefore, it should not cause significant head build-up on the surface of bioretention system during the storm event, so that the runoff can readily infiltrate to the soil layer below. Finally, the mulch layer is low cost and is convenient to maintain.

The O&G removal demonstrated in this research, coupled with the pollutant removals shown in previous studies (Davis et al., 2001; 2003), suggests the great potential for water quality improvement via conventional bioretention systems and the possibility for greater pollutant removal through re-engineering.

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The Effects of the Removal of Herbaceous Vegetation Along the Stream Edge on Aquatic Invertebrate Community Structure and Ecosystem Function, Summer Research Assistantship - Holly Menninger

Basic Information

Title:	The Effects of the Removal of Herbaceous Vegetation Along the Stream Edge on Aquatic Invertebrate Community Structure and Ecosystem Function, Summer Research Assistantship - Holly Menninger
Project Number:	2002MD10B
Start Date:	6/1/2002
End Date:	9/1/2002
Funding Source:	104B
Congressional District:	5thCongressional District Maryland
Research Category:	Biological Sciences
Focus Category:	, Ecology, Conservation
Descriptors:	
Principal Investigators:	Allen Davis, Philip Kearney

Publication

THE EFFECTS OF THE REMOVAL OF HERBACEOUS VEGETATION ALONG THE STREAM EDGE ON AQUATIC INVERTEBRATE COMMUNITY STRUCTURE AND ECOSYSTEM FUNCTION - PROGRESS REPORT TO THE WRRC -
Holly Menninger

In Maryland, farmers are encouraged to employ best management practices to minimize soil erosion and improve stream water quality (MD Dept. of Agriculture, Office of Resource Conservation 1996). Practices like the planting of vegetative filter strips, the exclusion of livestock, and stream bank stabilization are thought to maintain the riparian buffer zone, which is important for filtering nutrient-enriched run-off and protecting stream integrity (MD Dept. of Agriculture, Office of Resource Conservation 1996). There has been significant debate in the primary literature as to whether land managers should plant grasses or trees in these riparian buffers (Lyons et al. 2000, Montgomery 1997). Research has focused primarily on riparian forest buffers and their large-scale effects, but few have examined how grasses and other herbaceous vegetation growing along stream edges specifically affect invertebrate community structure and stream ecosystem processes at a reach scale. This summer, I examined how the removal of herbaceous vegetation from stream edges 1.) affects the diversity and abundance of aquatic insects in the stream channel and 2.) alters the rates of key ecosystem processes that fuel aquatic food webs (primary production, organic matter decomposition, nutrient uptake). I predicted that removing the dense herbaceous vegetation from stream edges would eliminate a detrital resource base and important habitat structure for the aquatic insect community, thereby causing a decrease in insect diversity and abundance. The removal of herbaceous vegetation may also change the local biotic and physical environment in which stream ecosystem processes occur. I therefore predicted that streams where vegetation was removed would experience higher primary production by algae and lower decomposition rates of organic matter than streams with intact edge vegetation.

With the assistance of the Howard County Soil Conservation District, I identified eight paired headwater stream sites for my study. Sites were selected based on the following criteria: 1.) spring-fed first-order streams, 2.) open canopy with grassy/herbaceous edges, 3.) livestock prohibited from grazing on streams banks, 4.) gravel/cobble substrate in the Piedmont physiographic province. In each pair, one stream was designated the experimental stream in which herbaceous vegetation would be removed and the other designated a reference stream. Unfortunately, the severe drought and subsequent drying of stream channels forced me to drop one pair of streams from the study. I decided to use a before-after-control-impact design in order to measure changes in invertebrate community structure and ecosystem processes before and after vegetation removal as well as to account for natural variability over time during the course of the experiment.

I assayed rates of decomposition in all stream sites before vegetation removal using leaf packs of dried reed canary grass (*Phalaris arundinacea*), a common grass that I had collected and dried in early June. Six leaf packs were attached to each stream bottom on day 0. I collected one pack per stream on days 4, 11, 18, 25, and 32, and then dried and weighed the remaining leaf material to determine mass loss. I calculated decomposition rates using the negative exponential decay model (Webster & Benfield 1986). Decomposition rates ranged from 0.0287 to 0.0649 day^{-1}, breakdown rates considered fast as compared to those known for other non-woody plants (Webster & Benfield 1986). More importantly, the decomposition rates for reed canary grass were not significantly different within each paired stream. I expect this pattern to change when I assay rates of decomposition using the same grass following the removal of vegetation from the three experimental sites.

I used the accrual of algal biomass on unglazed ceramic tiles over a period of two weeks to estimate primary productivity by algae. I set out 3 tiles transects across the width of each stream to capture spatial variation in algal productivity. In addition, I measured photosynthetically active radiation and stream velocity above each tile as covariates that may affect algal growth. After two weeks, I collected the tile substrates, scraped off the algae (appeared to be mostly diatoms), and determined algal biomass using the ash-free dry mass and chlorophyll *a* extraction techniques. Although I have not yet statistically analyzed the data, I can say qualitatively that there was variation in algal growth within single

transects of streams. Algae seemed to grow in discrete patches where light passed through the vegetation, analogous to the growth of understory plants in forest light gaps.

In addition to decomposition and primary production, I also measured another important ecosystem function at the six stream sites: the uptake of essential nutrients, specifically ammonium and phosphate, by benthic organisms. Using short-term nutrient injections of ammonium, phosphate, and a conservative bromide tracer, we were able to calculate an uptake length, or the average distance a molecule travels in the water column before being removed, for each nutrient in each stream. Uptake length provides a useful measurement for how efficiently a stream can retain nutrients (Marti and Sabater 1996). Uptake lengths for ammonium ranged between 50 and 500 m, somewhat surprising for such small densely vegetated streams. I am currently investigating the possibility of nitrogen saturation in my study sites by performing water quality analyses. If the streams are in fact nitrogen-saturated, a definite possibility in agricultural streams, we could have unknowingly violated a major assumption of the stream solute dynamics model for calculating uptake lengths, resulting in inaccurate estimates of uptake length (Stream Solute Workshop 1990).

I randomly sampled benthic invertebrates with a Surber sampler at three locations in each stream site. I preserved the samples and will process them following the conclusion of my field season. I also collected and sorted the invertebrates from the leaf packs for the decomposition study. I found a diverse community including aquatic insect larvae (e.g., caddisflies, mayflies, stoneflies, dragonflies, damselflies, beetles, black flies, and midges) and freshwater crustaceans (e.g., amphipods, isopods, copepods).

Following the pre-treatment sampling, a field crew and I used weed trimmers to cut all herbaceous vegetation within 1 m of the stream channel along the 45 m study reach in the three experimental streams. We carefully removed the clipped vegetation from the channel to avoid major inputs of detritus to the stream. Because this removal resulted in some disturbance to the stream bottom, I walked and disturbed the substrate of the reaches of the three reference streams as a control for effects due to disturbance and not the removal of vegetation. Following a 3-week recovery period, I have just begun my post-treatment sampling in all streams and recently deployed temperature loggers at all sites. While I have not officially collected post-treatment data, I can report that the growth of algae in the experimental streams is astounding. I look forward to officially documenting changes in community structure and ecosystem processes in the forthcoming weeks. Ultimately, the results from this study will enable me to develop and test hypotheses about proximate mechanisms for these changes and the specific role herbaceous plants play at the stream edge.

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Effect of Wetland Plant Rhizosphere Aeration Capacity on the Biodegradation of a Model Contaminant, CIS-1,2-Dichloroethene, Summer Research Assistant - Nagoda

Basic Information

Title:	Effect of Wetland Plant Rhizosphere Aeration Capacity on the Biodegradation of a Model Contaminant, CIS-1,2-Dichloroethene, Summer Research Assistant - Nagoda
Project Number:	2002MD9B
Start Date:	6/1/2002
End Date:	9/1/2002
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Congressional District:	5thCongressional District
Research Category:	Biological Sciences
Focus Category:	, Water Quality, Ecology
Descriptors:	
Principal Investigators:	Allen Davis

Publication

EFFECT OF WETLAND PLANT RHIZOSPHERE AERATION CAPACITY ON THE BIODEGRADATION OF A MODEL CONTAMINANT, CIS-1,2-DICHLOROETHENE
-Progress Report to the WRRC-
Cary Nagoda

INTRODUCTION

The overall goal of my M.S. research, which I am conducting under the direction of Dr. Jennifer Becker in the Department of Biological Resources Engineering, is to gain insight into the relationships between wetland plant characteristics and microbial transformations of anthropogenic contaminants in the rhizosphere. Specifically, funding from the Water Resources Research Center enabled me to focus my efforts this summer on investigations of the effect of wetland plant rhizosphere aeration capacity on the biodegradation of a model contaminant, *cis*-1,2-dichloroethene (*cis*-DCE).

COMPLETED RESEARCH

The first objective of my research was to quantify and compare the amounts of oxygen released into the rhizospheres of several wetland macrophyte species that have different morphologies and are commonly used in constructed wetlands. Most of my effort this summer was devoted to accomplishing this goal, because, as discussed below, I discovered a fundamental problem with the colorimetric method for assaying dissolved oxygen losses from plant roots that is reported in the literature (Chabbi et al., 2000; Kludze et al., 1994; and Wu et al., 2000). While troubleshooting this method and developing a modified approach for measuring O_2 losses took a significant amount of time, it provided a valuable learning experience. Further, I plan to highlight the need to use the modified colorimetric method when I write a paper, based in part on the results I obtained this summer, for publication in a peer-reviewed journal. This way, other researchers working in the areas of wetland ecology and water quality will benefit from my efforts.

Quantification of O_2 released to the rhizosphere is achieved colorimetrically, using a Ti^{3+}-citrate solution, which changes from a purple-blue color to colorless as Ti^{3+} is oxidized to Ti^{4+} (Kludze et al., 1994). Thus, the first step was to determine the relationship between absorbance and the amount of O_2 added or released to the solution, which was measured using a spectrophotometer. For the initial attempt to create a calibration curve, standards containing known amounts of O_2 were prepared under N_2 using deoxygenated Ti^{3+}-citrate and Hoagland's nutrient solution in anaerobic culture tubes. Hoagland's nutrient solution is a common growth medium, which consists of macro-nutrient, micro-nutrient and iron solutions, and was used in previous rhizosphere oxidation studies (Chabbi et al., 2000, Kludze et al., 1994, Wu et al., 2000). Pure oxygen was added to the anoxic medium in the sealed tubes using a gastight syringe. However, absorbance measurements made periodically over 24 hours, showed a gradual decrease in absorbance and, therefore, oxidation of the Ti^{3+} over time. Because the experiments involving plants were designed to last for 24 hours, this was unacceptable, so I began systematically evaluating and ruling out potential causes of the change in color over time. I verified that inadequate mixing and photodegradation were not to blame. A major concern was that oxygen was somehow leaking into the standards over time. However, similar results were observed when oxygen-impermeable tape was wrapped around septa and tubes, or when the tubes were stored inside an anaerobic chamber. I next considered the possibility that one or more constituents of the nutrient solution were reacting with the Ti^{3+}. To test this theory, standards were prepared as described above, except that deoxygenated, deionized water replaced the nutrient solution. The absorbance of standards prepared with deionized water was monitored and did not change significantly within 24 hours. Because plants must, at a minimum, be supplied with macro-nutrients in order to survive the duration of the experiment, I endeavored to make a simple solution that met these needs and did not react with Ti^{3+}. A new growth solution containing diammonium phosphate $((NH_4)_2HPO_4)$ was prepared and tested for use in the experiment.
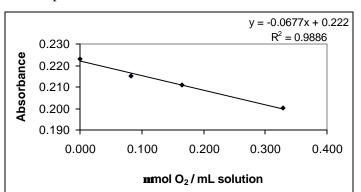
$$y = -0.0677x + 0.222$$
$$R^2 = 0.9886$$

Figure 1. Standard curve relating oxygen concentration and absorbance.

As shown in Fig. 1, a standard curve was successfully created using the $(NH_4)_2HPO_4$ growth solution. The interference caused by nutrient solution was apparently overlooked in previous studies using the colorimetric method because standards were either prepared with deionized water (Kludze et al., 1994) or measured only at a single point in time (Wu et al., 2000).

The amount of oxygen released by the roots of several wetland plants: softstem bulrush (*Schoenoplectus tabernaemontani*), Pennsylvania smartweed (*Polygonum pennsylvanicum*), and soft rush (*Juncus effuses*) was measured using an experimental system that I developed for this purpose. For each experiment, a single plant was mounted in the cap of a Nephelo culture flask and sealed with Teflon tape covered with non-toxic RTV sealant. The plant was situated so that its roots were suspended in the $(NH_4)_2HPO_4/Ti^{3+}$-citrate solution in the flask. The stem and/or leaves were positioned above the cap so that the plant could provide the roots with O_2. Assembly of the plants and flasks was done inside an anaerobic chamber. A plant/flask assembly is shown in Fig. 2. The plant was exposed to 12h of light and 12h of dark, and the absorbance of the solution in each flask was measured at regular intervals. Duplicate planted flasks and a root control, which had no leaves/stems, were monitored during this time period. Similar trends were observed for all of the plants tested. As shown for *S. tabernaemontani* in Fig. 3,
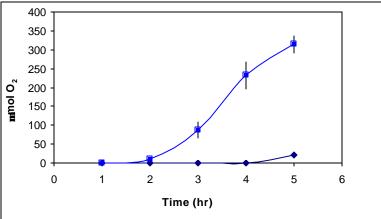

Figure 2. Experimental system used to quantify O_2 released from wetland plant roots (*P. pennsylvanicm* shown).

no significant oxidation was observed in the root only controls; however, significant oxidation of the rhizosphere was observed in the flasks containing intact plants. Based on the maximum water depths tolerated by the wetland plants listed above, I predicted that the following trend in rhizosphere oxidation capacity would be observed: *Typha latifolia* > *S. tabernaemontani* > *J. effuses* > *Sagittaria latifolia* > *P. pennsylvanicum.* The rhizosphere oxidation capacities of the plants tested to date are consistent with this prediction. Rhizosphere oxidation experiments have not yet been completed

Figure 3. Oxygen released to rhizosphere by root only control and intact plants of *S. tabernaemontani* over time. Diamonds represent the amount of O_2 in the control. Squares represent the average amount of O_2 in duplicate plant reactors with error bars showing 1 standard deviation.

using *T. latifolia* and *S. latifolia* due to unexpected stresses introduced to the plants while transplanting and slow growth, respectively. New growth methods are currently being tested to prevent transplant shock of *T. latifolia* during experiment preparation.

WORK IN PROGRESS

Working on the second objective of my research, which is to construct and test a prototype plant bioreactor to study the impact of wetland plant characteristics on microbial processes, is actively ongoing. In addition, I am currently preparing to perform a series of experiments to quantify the phytotoxicity of a model contaminant, *cis*-DCE, on each of the plants evaluated in the Objective 1 experiments. Ultimately, the wetland plant that demonstrates the best combination of rhizosphere oxidation and resistance to DCE will be used along with the prototype plant bioreactor to characterize the fate of *cis*-DCE added to the rhizosphere. It is expected

that the results of these investigations will ultimately lead to more efficient use of natural and constructed wetlands for contaminant removal.

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Investigation of Isotopic Methods for Identifying Atmospheric Deposition of Nitrate to the Chesapeake Bay Watershed

Basic Information

Title:	Investigation of Isotopic Methods for Identifying Atmospheric Deposition of Nitrate to the Chesapeake Bay Watershed
Project Number:	2002MD12B
Start Date:	3/1/2002
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Congressional District:	5th district Maryland
Research Category:	Not Applicable
Focus Category:	Non Point Pollution, Geochemical Processes, Acid Deposition
Descriptors:	nitrate isotopes
Principal Investigators:	James Farquhar

Publication

Investigation of Isotopic Methods for Identifying Atmospheric Deposition of Nitrate to the Chesapeake Bay Watershed.

Research Objectives:

We have been developing methods to analyze $\Delta^{17}O$ of nitrate and are assessing whether these methods can be used to place limits on the amounts of nitrate that are derived from non-point atmospheric sources. The work builds upon that of G. Michalski and coworkers (2002) who have shown that a unique isotopic signature is present in atmospheric nitrate that is derived from NO_x - Ozone chemistry. This signature has the potential to be used as a tracer of atmospheric nitrate and also to place constraints on the magnitude of this source in a watershed. Our work has three goals: (1) to establish the capabilities for analyzing $\Delta^{17}O$ in nitrate at the University of Maryland, (2) to test whether this approach can be used to place constraints on the contribution of non-point atmospheric sources, and (3) to apply these methods to studies of the Chesapeake Bay Watershed. This work is the Ph.D. research of Katherine Cooney.

The research conducted to date has focused on developing and testing the techniques that will be required to measure the $\Delta^{17}O$ of nitrate in precipitation that falls to the Chesapeake Bay Watershed. The project has been divided into three parts: (1) sample collection, (2) nitrate extraction, and (3) isotopic analysis of extracted nitrate.

Sample Collection:

Precipitation samples are collected in HDPE bins that have been rinsed with 10% hydrochloric acid followed by numerous rinses of Millipore water. Due to relatively low concentrations of nitrate in precipitation, a minimum of 12-18 liters of rainwater or melted snow are needed in order to recover an adequate amount of nitrate for analysis. Collection bins are placed outside immediately before and collected at the end of rain events. Bins are also placed outside to catch falling snow, and at the end of the storm more snow is scooped into the bins using clean HDPE lids. Snow samples have also been collected in regular intervals following snow events. These snow samples have been collected in a time series so we could look for changes in concentrations and isotopic compositions in the snow packs. Whenever possible, the precipitation samples have been immediately frozen and kept in a frozen state until they are thawed and filtered prior to nitrate extraction.

Thus far, precipitation samples have been collected from five locations within the Chesapeake Bay Watershed, including College Park, Kensington, Laurel, Tacoma Park, and Urbana, MD. These samples will be used to collect a preliminary data set. Further sampling strategies will be devised after we evaluate this groundwork data.

Nitrate Extraction:

We carefully considered the techniques discussed in Silva et al. (2000) and Chang et al. (1999), and we consulted with Janet Hannon about the methods being used to extract nitrate at the USGS in Reston, Virginia. The preparation scheme detailed below utilizes aspects of all of these procedures. R. Carmody has processed test samples that are being used to verify various steps to

the method. K. Cooney is in the process of applying the technique to the natural precipitation samples.

Approximately 15 L of each natural precipitation sample is filtered through 0.4 μm polycarbonate membrane filters and poured or pumped into a clean container. Approximately 20mL of the each sample is syringe filtered through a 0.2 μm polycarbonate filter into acid soaked and Millipore water rinsed glass bottles with polyseal caps. This portion of the sample is used for ion chromatography.

The sample gravity drips through a series of two columns. The first is a cation exchange column loaded with AG50WX8 resin, in hydrogen form. This column is intended to protonate the DOC in the sample. The second column contains anion exchange resin (AG2X8 resin, in chloride form) onto which nitrate and other anions from the sample are collected. In order to determine the amount of anion exchange resin needed to accommodate the anions in the precipitation samples, concentration data on chloride, sulfate, and nitrate are obtained using ion chromatography. We are very thankful to Dr. Allen Davis for his willingness to let us use the Dionex DX100 Ion Chromatograph, housed in the Civil and Environmental Engineering Environmental Lab, and to Hunho Kim for training us to operate the instrument.

Once the nitrate is absorbed onto the anion exchange resin, nitrate and other ions are eluted from the column using a 0.25M KCl solution. We are able to track the elution of the nitrate peak using nitrate reducing solution and nitrite coloring solution. We learned to make and use these solutions from Janet Hannon at USGS. The nitrate is eluted using 5- or 10-mL aliquots of 0.25M KCL, and each "cut" is collected in a separate, clean test tube. Only the "cuts" containing nitrate are saved for continued processing. Other anions (e.g. sulfate), are removed by adding $BaCl_2$ to the solution. The precipitate (e.g. $BaSO_4$) is then separated from the KCl/KNO_3 solution by filtering and the precipitate is saved and dried.

The next step is to eliminate the chloride from the KCl/KNO_3 soultion. This is accomplished by combining the nitrate-bearing eluant with AG MP-50 cation exchange resin in silver form. Potassium exchanges for silver on the resin's exchange sites, and the silver introduced to solution allows chloride to precipitate as $AgCl_{(s)}$. After stirring this mixture for one hour, and then allowing it to stand overnight, the resin and $AgCl_{(s)}$ is separated from the chloride-free solution by pouring the mixture into a large column. The solution is allowed to drain out into a clean graduated cylinder. After the resin and precipitate in the column have been rinsed and the rinse-water has been checked with the colorimetric test solutions to confirm that it is nitrate-free, the solution goes through a final clean-up column to insure that a pure precipitate will form when the sample solution is freeze-dried prior to isotopic analysis. At this stage, one must decide whether the final solid form of the sample should be $AgNO_3$ or KNO_3. If $AgNO_3$ is desired, the solution is run through a 5-mL AG MP-50 resin (in silver form) column. If KNO_3 is desired, the sample solution is run through a 5-mL AG50WX8 resin (in potassium form) column. At this point the solutions are ready to be freeze-dried.

We are still working to establish freeze-drying techniques. Six freeze-dryer experiments have been undertaken. The most successful freeze-dryer experiments have involved two steps. First, 100mL of nitrate solution ($KNO_{3(aq)}$ or $AgNO_{3(aq)}$ was distributed among five 50-mL plastic

centrifuge tubes so that each tube contained approximately 20mL of solution. These tubes were placed in the freezer at an angle to produce greater surface area on the ice. After freezing, the caps on the tubes were removed. Each of the tubes was then covered with a Kimwipe secured with a rubber band. Then, the tubes with frozen nitrate solution were placed in a 900-mL freeze-dryer flask and freeze-dried. The second freeze-drying stage involved transferring the KNO_3 or $AgNO_3$ from the plastic centrifuge tubes to a pre-weighed glass vial by pipetting a few milliliters of Millipore water into each tube to dissolve the nitrate, and then pipetting this solution into the glass vial. This vial containing more concentrated nitrate solution was then frozen, placed in the freeze-dryer flask, and freeze-dried.

Preliminary tests using the continuous flow isotope ratio mass spectrometer (CF-IRMS) and elemental analyzer overseen by Jay Kaufman show that the measured $\delta^{18}O$ of the freeze-dried KNO_3 is within error of the $\delta^{18}O$ of the reagent KNO_3 that had been dissolved and freeze-dried.

Nitrate Pyrolysis and Isotopic Analyses:

The final step in our analytical protocol is the conversion of nitrate to molecular oxygen for isotopic analysis. Potassium nitrate and silver nitrate are converted to molecular oxygen for isotopic analysis using methods that are modified from techniques used at the University of California, San Diego. The manifold that we use for the vacuum pyrolisis of silver and potassium nitrate is described in Figure 1. This system consists of a Platinum resistance furnace in a vacuum chamber that is heated by a 10 volt 15 amp DC current. KNO_3 and $AgNO_3$ decompose to O_2 and NO_2 when heated in vacuum. The O_2 is purified by condensing the NO_2 in a liquid nitrogen-cooled trap. O_2 is then separated from the frozen NO_2 by freezing it onto a molecular sieve substrate that is kept at liquid nitrogen temperature. The purified O_2 is then introduced to a gas-source mass spectrometer for isotopic analysis.
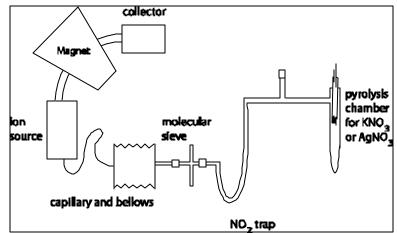

Figure 1. Schematic diagram of nitrate pyrolysis manifold and mass spectrometer. Nitrate samples are wrapped in silver foil and placed in the pyrolysis chamber which is evacuated overnight. The sample is heated using a platinum resistance furnace to generate NO_2 and O_2. O_2 is purified by condensing NO_2 in a liquid nitrogen-cooled trap and then by transferring the O_2 onto a liquid nitrogen-cooled molecular sieve trap. This purified O_2 is then introduced to the Delta plus gas-source mass spectrometer for determination of its oxygen isotopic composition. The gas is introduced through the capillary to the ion source where it is ionized and accelerated by a voltage potential. The ion beams are separated according to mass by the magnet and the intensities of the ion beams are measured by an array of Faraday collectors. The isotopic abundances of the gas are measured by isotope ratio measurement relative to a standard.

Figure 2 presents the results of our $\Delta^{17}O$ analyses of nitrate standard materials that have been previously analyzed at UCSD by Greg Michalski and coworkers (2002). We have good agreement between our methods and theirs and have better reproducibility for $\Delta^{17}O$ than reported by Michalski et al. (2002) which we attribute to the design of our pyrolysis cell which is internally heated.
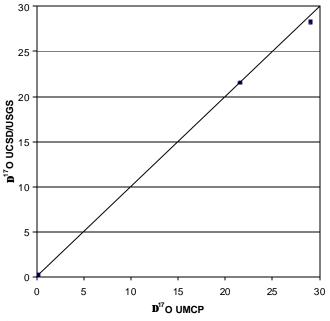

Figure 2 illustrates the $\Delta^{17}O$ values that we have measured for thermal decomposition of two nitrate standards that are reported in Michalski et al (2002) and one nitrate sample that Michalski sent to us. The standards fall within error of a slope 1 line indicating a good correspondence between labs. The third sample yielded higher $\Delta^{17}O$ at UMCP that is outside of analytical uncertainty and thought to reflect a blank contribution in the UCSD/USGS data that is not present in the UMCP preparation procedure.

Planned work:
In the next year, we will (1) verify the nitrate extraction procedures by analyzing the resulting KNO_3 or $AgNO_3$ from the test experiments on the CF-IRMS. From the isotopic measurements of these test experiments, we will be able to identify any fractionation that is occurring in the nitrate extraction process and any blank contribution. We will (2) continue to evaluate our techniques for measuring $\delta^{15}N$ and $\delta^{18}O$ on the CF-IRMS and $\Delta^{17}O$ using the dual-inlet isotope ratio mass spectrometer. In addition, we will (3) continue to collect precipitation samples using more guided sampling strategies and (4) proceed to apply nitrate extraction and analysis procedures to the collected precipitation samples. We can then (5) further assess how to apply these isotopic tools to studies on the atmospheric deposition of nitrate to the Chesapeake Bay Watershed.

References cited:

Chang, C.C.Y., J. Langston, M. Riggs, D.H. Campbell, S. Silva, and C. Kendall. 1999. A method for nitrate collection for $\delta^{15}N$ and $\delta^{18}O$ analysis from waters with low nitrate concentrations. Can. J. Fish. Aquat. Sci. 56: 1856-1864.

Michalski, G., J. Savarino., J.K. Böhlke, and M. Thiemens. 2002. Determination of total oxygen isotopic composition of nitrate and the calibration of a Δ^{17}O nitrate reference material. Analytical Chemistry. 74: 4989-4993.

Silva, S. R., C. Kendall, D.H. Wilkison, A.C. Ziegler, C.C.Y. Chang, and R.J. Avanzino. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. Journal of Hydrology. 228: 22-36.

Advancement of Electron Beam Methodologies for Remediation of PCB Containments in Patuxent River and Chesapeake Bay Sediments

Basic Information

Title:	Advancement of Electron Beam Methodologies for Remediation of PCB Containments in Patuxent River and Chesapeake Bay Sediments
Project Number:	2002MD13S
Start Date:	3/15/2002
End Date:	3/14/2005
Funding Source:	Supplemental
Congressional District:	5th
Research Category:	Water Quality
Focus Category:	Treatment, None, None
Descriptors:	electron beam treatmenet of sediment
Principal Investigators:	Mohamad Al-Sheikhly

Publication

1. No publication
2. No publication
3. Dainne L. Poster, Mahanaz Chaychian, Pedatsur Neta, Robert E. Huie, Joseph Silverman and Mohamad Al-Shiekhly, 2003, Degradation of PCBs in a Marine Sediment Treated with Ionizing and UV Radiation, Journal of Environment Science and Technology, in press.

PI: Mohamad Al-Sheikhly

Electron beam radiolysis. PCB-laden sediment samples were mixed with an aqueous alcohol solution and irradiated with an electron beam under continuous stirring in the absence of oxygen. During this process, some PCB congeners are extracted into the liquid phase and undergo dechlorination within that phase; the rest remain within the sediment and undergo dechlorination either within the solid phase or at the interface. After the irradiation, solvent extracts of PCBs from both media were combined and analyzed. It is not possible to determine the increase in chloride ion concentration in the liquid phase because the sediment is rich in chloride and the fractional change in Cl- concentration upon PCB dechlorination is negligible. Therefore, only the change in PCB concentration was determined. The results for individual PCB congeners indicate that the concentrations of PCBs in electron-irradiated sediment samples decrease as a function of dose (Figure 1). To estimate the initial radiolytic efficiency we calculated the decrease in concentration of each congener after irradiation with 10 kGy, the lowest dose. By assuming that each congener underwent a single dechlorination step, and taking the total dechlorination yield as if all the PCBs were in the liquid phase, we calculate a radiolytic yield (G-value) of 1.3×10^{-11} mol J^{-1}. By comparison with the radiolytic yield of e_{aq}^- in aqueous alcohol solutions (Spinks and Woods, 1990), 2.7×10^{-7} mol J^{-1}, our observed dechlorination yield is lower by four orders of magnitude. One reason is the fact that some of the PCBs remain within the solid phase and do not react with e_{aq}^- formed in the liquid phase. Reaction at the interface is likely not significant with the SRM 1944 sediment particles where the median diameter (dry) is on the order of 135 μm (Certificate of Analysis *SRM 1944*, 1999). Small amounts of water penetrate the channels within the particles and e_{aq}^- produced within these channels probably reacts with PCBs that may be present within the same channels. The lifetime of the e_{aq}^- in our system under electron beam irradiation is several microseconds or less. Therefore, if PCBs are not available in the immediate vicinity of hydrated electrons, the electrons decay by reacting with other compounds or other radicals, including self-reaction. Scavenging of e_{aq}^- by the protons formed upon radiolysis is prevented by the use of the carbonate buffer, which keeps the solution at pH > 7. Other compounds present in the sediment, which may react with e_{aq}^-, are metal ions. If we assume that all metal ions in the sediment, based on the concentration values reported for SRM 1944

(Certificate of Analysis *SRM 1944, 1999*), are extracted into the aqueous phase, we estimate the concentrations of the most abundant ions as follows: $[Zn^{2+}] = 1.5$ mmol L^{-1}, $[Pb^{2+}] = 0.24$ mmol L^{-1}, $[Cr^{3+}] = 0.77$ mmol L^{-1}, and $[Mn^{2+}] = 1.4$ mmol L^{-1}. Since all of these ions react with e_{aq}^- very rapidly (Buxton et al., 1988), and since their concentrations are much higher than the concentrations of PCBs, it is likely that most of the electrons are scavenged by the metal ions. The reduced metal ions formed by these reactions have lower reduction potentials than e_{aq}^- and are less likely to transfer an electron to PCB molecule.
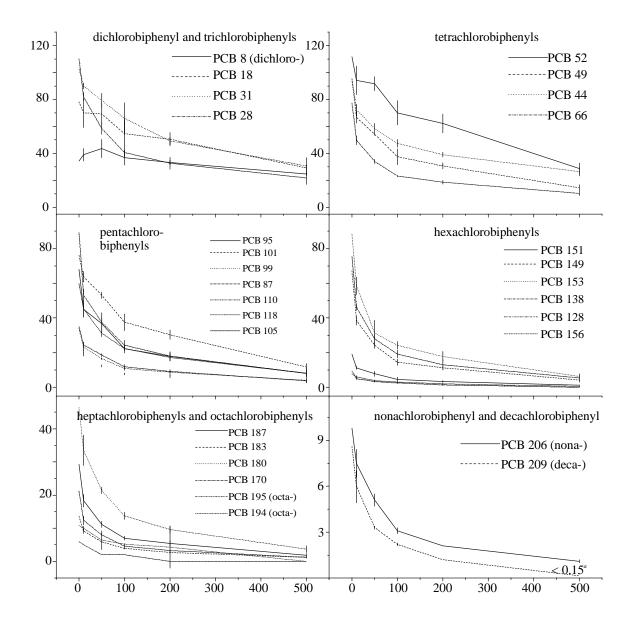
dichlorobiphenyl and trichlorobiphenyls

PCB 8 (dichloro-)
PCB 18
PCB 31
PCB 28

tetrachlorobiphenyls

PCB 52
PCB 49
PCB 44
PCB 66

pentachloro-biphenyls

PCB 95
PCB 101
PCB 99
PCB 87
PCB 110
PCB 118
PCB 105

hexachlorobiphenyls

PCB 151
PCB 149
PCB 153
PCB 138
PCB 128
PCB 156

heptachlorobiphenyls and octachlorobiphenyls

PCB 187
PCB 183
PCB 180
PCB 170
PCB 195 (octa-)
PCB 194 (octa-)

nonachlorobiphenyl and decachlorobiphenyl

PCB 206 (nona-)
PCB 209 (deca-)

< 0.15[a]

Figure 1. Concentrations (ng g^{-1}) of PCB congeners in electron beam irradiated slurries of SRM 1944 (New York/New Jersery Waterway Sediment as a function of dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (n=3, represented by an error bar) was calculated. [a]Value is three times the standard deviation of the baseline noise.

Achievements

Our paper "Degradation of PCBs in a Marine Sediment Treated with Ionizing and UV Radiation" was accepted for publication in Environmental Science and Technology on May 21, 03.

Information Transfer Program

Colloquium- Water Resources Research in Maryland: Highlights and Needs

Basic Information

Title:	Colloquium- Water Resources Research in Maryland: Highlights and Needs
Project Number:	2002MD14B
Start Date:	10/25/2002
End Date:	10/25/2002
Funding Source:	104B
Congressional District:	5th District
Research Category:	Water Quality
Focus Category:	Management and Planning, Non Point Pollution, Water Quality
Descriptors:	Water quality, Water Policy, Nonpoint Source Pollution
Principal Investigators:	Allen Davis

Publication

The Maryland Water Resources Research Center sponsored a colloquium on *Water Resources Research in Maryland: Highlights and Needs* on Friday, October 25, 2002. About 65 participants representing a broad spectrum of water expertise attended the meeting. Throughout the day research highlights and needs were shared by State and Federal Agencies and University scientists. The Center hopes to build stronger ties between these major contributors to water science in the State.

Opening remarks were made by Dr. Greg Baecher, Chair, Department of Civil and Environmental Engineering and Dr. Scott Angle, Associate Dean, Maryland Agricultural Experiment Station. Dr. Baecher chaired the morning session.

The morning keynote speaker was Dr. Robert M. Summers, Director, Water Management Administration, Maryland Department of the Environment. Dr. Summers described the duties of his office and addressed some critical water research needs for the state. The Water Management Administration's mission is to restore and protect the quality of Maryland's surface and ground waters in order to protect the public health and the environment. The Administration includes programs for the control of wastewater discharges, protection of the State's water supply, protection of tidal and non-tidal wetlands and waterways, oversight of State and local government sediment and erosion control and storm water management programs, and the regulation and mitigation of mining activities and abandoned mines. The Administration also provides technical assistance and financing through grants and loans to local governments for wastewater, water supply, storm water management and environmental restoration projects.

Our second speaker was Robert J. Shedlock, Associate District Chief & Supervisory Hydrologist, U.S. Geological Survey. Mr. Shedlock described several of the ongoing research projects at the Baltimore USGS office. The USGS water resources of Maryland, Delaware, and the District of Columbia consist of numerous streams, springs, lakes, and aquifer systems. Streamflow, ground-water levels, and water-quality data are collected at numerous locations, and water-use-data are collected throughout the area. These hydrologic data and other data are used in research and hydrologic studies to describe the quantity, quality, and location of the area's water resources. The collection, analysis, and interpretation of these data is done in cooperation with other federal, state and local agencies, universities, and research centers.

Following Mr. Shedlock was Dr. Margaret A. Palmer, Professor, Department of Biology, University of Maryland. Dr. Palmer discussed her research to understand what controls the establishment and survival of stream invertebrates. She specifically focused on the relative importance of geomorphic / hydrodynamic factors in predicting invertebrate colonization of new habitats, post-recruitment survival, biodiversity and restoration of ecological processes. Her work also addresses the role of spatial habitat configuration in invertebrate population and community dynamics. Dr. Palmer has a diverse research group in her lab with broad training in the ecology of freshwater systems, fluid dynamics, and hydrology. The research includes field experimentation and laboratory experiments performed on the main campus as well as in her nearby recirculating flume laboratory. Currently she is involved in a nationwide effort on stream restoration.

The next speaker was Patricia Coury, Team Leader, U.S. Army Corps of Engineers, Baltimore District. Ms. Coury directs a number of important Corp water projects, including: Chesapeake Bay Shoreline Erosion (Sediment Behind Dams), Middle Potomac Watershed (water supply emphasis), Chesapeake Bay Oyster Recovery, and Dredged Material Management Plan for the Chesapeake Bay. She presented information on ongoing Corps projects in the Maryland area.

The final morning speaker was Dr. Alba Torrents, Associate Professor, Department of Civil and Environmental Engineering, University of Maryland. Dr. Torrents spoke on her work and other

water resources research in the College of Engineering. She is interested in chemical transformations of organic pollutants, environmental fate of toxic chemicals, sorption of organic pollutants, applications of spectroscopic techniques to environmental systems, and wet and dry deposition of POP's onto sensitive ecosystems. Her recent research has included studies on the atmospheric distribution of commonly used pesticides in Chesapeake Bay watersheds and the fate of endocrine disrupters in water.

Our afternoon keynote speaker was J. Charles Fox, Secretary, Maryland Department of Natural Resources. Secretary Fox provided an overview of the Chesapeake Bay Program, with a focus on nutrient sources and control. At the state level, Mr. Fox served as Assistant Secretary and Chief Operating Officer of the Maryland Department of the Environment (MDE). As Maryland's principal environmental regulatory agency, he directed budgetary realignments and permit streamlining reforms, and initiated establishment of statewide environmental indicators and goals. With a 15-year career dedicated to protecting the earth's living and natural resources, Mr. Fox worked as a consultant or Board member to a number of non-profits including American Rivers, Friends of the Earth, the Environmental Policy Institute, the Nature Conservancy, the Sierra Club, and Maryland League of Conservation Voters. Most recently, Mr. Fox served as senior policy advisor to the Chesapeake Bay Foundation, where he developed an analysis of the 2000 Chesapeake Bay Agreement, identifying cost projections, policy options and federal opportunities available to support the Agreement's new water quality goals. Secretary Fox spent most of his presentation on the important implications of the Chesapeake Bay Agreement to the State of Maryland.

Our concluding speaker was Dr. Adel Shirmohammadi, Professor, Biological Resources Engineering Department, University of Maryland. Dr. Shirmohammadi covered his research in water resources engineering with interests in hydrographic modeling, nutrient and pesticide leaching, and other nonpoint source pollution efforts. Dr. Shirmohammadi's interests include modeling as a tool to predict movement of pesticides and nutrients from watersheds in response to hydrological events, ground water pollution and how to prevent nutrient movement into the ground and surface water systems. Field and watershed scale monitoring is used to develop and to validate mathematical models for identifying best management practices. His research also involves interfacing nonpoint source pollution models with geographic information systems (GIS) for pollution identification. He also discussed other ongoing water research in the College of Agriculture and Natural Resources.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	2
Masters	1	0	1	0	2
Ph.D.	5	0	1	0	6
Post-Doc.	0	0	0	0	0
Total	8	0	2	0	10

Notable Awards and Achievements

Sponsored a 1-day colloquium on Water Resources Research in Maryland: Highlights and Needs, in October. This event consisted of a series of seven presentations and related discussion. Four presentations were by administrators from State and Federal agencies and three were by UMCP faculty. All of our feedback has indicated that this event was successful in its goal of providing a forum for interactions between faculty and these agencies. Attendance included over 65 faculty, students, and professionals from outside agencies.

Developed two internships through the Center for UMD graduate students to work with USGS personnel (at Reston, VA and at Baltimore).

Visited with several state, federal, and local agencies to create a link between these agencies and the University.

Worked with Ken Paynter of the MEES program at the University of Maryland in submitting an NSF IGERT pre-proposal to provide an integrated graduate program in watershed restoration and management among several colleges and programs.

Upgraded the Center website to include a list of over 50 faculty on campus and their expertise in water resources, to include links to personal pages. The website is at www.cee.umd.edu/water_resources/home.html. Work continues on this site to make it more useful to water researchers in the state and persons needing expertise in water resources.

Made a major effort to enhance our biannual newsletter. With the Fall 2002 issue, we have expanded the content to 8 pages (from previous 4). We have included focus articles on research on campus and a featured scientist. Through various contacts and initiatives, our newsletter mailing list has doubled to over 300.

Continued to work with the National Institutes of Water Resources to advocate increased support for water resources research by Congress and the Administration.

Developed a poster and provided a groundwater demonstration at Maryland Day in April.

Joined the Consortium of Universities for the Advancement of Hydrologic Sciences, Inc.(CUAHSI) (with matching funds from the Provost). Kaye Brubaker of Civil and Environmental Engineering will be the University representative to this group.

Publications from Prior Projects

1. 1997MD2 ("Development Activities of a Systematic Approach for Channel restoration") - Articles in Refereed Scientific Journals - 1. Beighley, R.E., and G.E. Moglen (2003). "Adjusting Measured Peak Discharges from an Urbanizing Watershed to Reflect a Stationary Land Use Signal." Water Resources Research, 39(4), 1093, doi: 10.1029/2002WR001846.
2. 1997MD2 ("Development Activities of a Systematic Approach for Channel restoration") - Conference Proceedings - 1. Moglen, G.E. and J.A. Berger, "Quantifying the Effect of Land Use Change on Channel Hydraulic Geometry in the Maryland Piedmont," Presented at American Geophysical Union, Spring Meeting, Boston, MA. May 1998.
3. 1997MD2 ("Development Activities of a Systematic Approach for Channel restoration") - Conference Proceedings - 2. Moglen, G.E. (invited), "Use of GIS to Quantify the Impacts of Land Use Change on Streamflow and Channel Geometry", Watershed '99 Conference, University of Virginia, Charlottesville, Virginia, April 9, 1999.
4. 1997MD2 ("Development Activities of a Systematic Approach for Channel restoration") - Conference Proceedings - 3. Moglen, G.E. (invited), "Use of GIS to Quantify the Impacts of Land Use Change on Streamflow and Channel Geometry", Presented to ASCE Water Resources Division - Washington, D.C. Chapter, April 20, 1999.
5. 1997MD2 ("Development Activities of a Systematic Approach for Channel restoration") - Dissertations - Seth Brown, "Prediction of Stream Geometry in the Maryland Piedmont Based on Land Use and Urbanization" (1999)
6. 2000MD1B ("Structural and Functional Assessments for Evaluating Elevated Nutrient Levels in Maryland Streams") - Other Publications - Baer, N.A. and W.O. Lamp. 2003. Effects of nutrients and dissolved organic carbon on microbial and macroinvertebrate contributions to leaf litter breakdown. Bulletin of the North American Benthological Society. 20(1): 372 (abstract).
7. 2000MD2B ("Engineered Bioretention for Nitrogen from Urban Stormwater Runoff") - Articles in Refereed Scientific Journals - Kim, H., Seagren, E.A., and Davis, A.P. "Engineered Bioretention for Removal of Nitrate from Stormwater Runoff," Water Environ. Res., in press, March 2003.
8. 2000MD4B ("Multi-faceted Investigation of Arsenic Biogeochemistry") - Articles in Refereed Scientific Journals - Kim, J.-Y., Davis, A.P. and Kim, K.-W. "Stabilization of Available Arsenic in Highly Contaminated Mine Tailings using Iron," Environ. Sci. Technol., 37(1), 189-195 (2003).
9. 2000MD2B ("Engineered Bioretention for Nitrogen from Urban Stormwater Runoff") - Articles in Refereed Scientific Journals - Davis, A.P., Shokouhian, M., Sharma, H., Minami, C., and Winogradoff, D. "Water Quality Improvement through Bioretention: Lead, Copper, and Zinc," Water Environ. Res., 75(1), 73-82 (2003).