Water Resources Research Center
Annual Technical Report
FY 2001

Introduction

As noted in the 2000 annual report, the Maryland Water Resources Research Center was about to undergo a major administrative change. The two 2001 research projects and three summer student assistantships were selected prior to the change in Directors. Dr. Allen P. Davis. Professor, Department of Civil and Environmental Engineering, was appointed the new Center Director in August 2001. The Center moved from the Department of Chemistry to the Glenn L. Martin Engineering Hall in mid August. Dr. Philip Kearney, Associate Director of the Center now is now located in Room 1147, in the Engineering Building.

In 2001, two research projects were completed: "Sustainable Oil and Grease Removal from Stormwater Runoff Hotspots using Bioretention" and "Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay Watersheds." The Center also funded three summer Fellowships for 2001. These projects, as well as the students and advisors participating in this program were: "Evaluating the Influence of Diverse Riparian Leaf Litter of Stream Food Webs," Christopher M. Swan, Advisor - Dr. Margaret Palmer, Department of Biology; "A Status Report on the Ability of Maryland’s Total Maximum Daily Load (TMDL) Program to Reduce Nonpoint Source Pollution to Meet the States Water Quality Standards," Michelle Perez, Advisor - Advisor - Matthias Ruth, School of Public Affairs; and "The Impact of Management Intensive Grazing on Nutrient Losses to Ground and Surface Waters," Rachel E. Gilker, Advisor - Ray R. Weil, Department of Natural Resources and Landscape Architecture.

Several new initiatives were begun by Director Davis. One of the goals of the Maryland Water Resources Research Center has been to identify the water science expertise at the College Park campus of the University of Maryland. The objects of this survey were: (1) to foster greater interaction between water research scientists (2) to be better prepared to compete for large interdisciplinary grants (3) to serve as a focal point for better communication between State and Federal Agencies and campus scientists. A list of about 45 campus scientists was developed, based primarily on their current research or their past interactions with the Center. The Director send out an e-mail to these scientists requesting their cooperation in this survey. The request asked each scientist whether they wanted to participate in the survey, whether they would identify 3-4 areas of their expertise from a list of 18 focus categories (shown below), and whether they could recommend other scientists that should participate in the survey. The survey now contains about 50 scientists whose areas of expertise can be found on our website at http://www.cee.umd.edu/water_resources/home.html.

FOCUS CATEGORIES -1 Agriculture, 2 Aquatic Ecology, 3 Climatological Processes, 4 Environmental Chemistry/Geochemistry, 5 Environmental Toxicology, 6 Groundwater, 7 Hydrology and Hydrogeology, 8 Models/Computer Data Management, 9 Non-Point Source Pollution Measurement and Control, 10 Nutrients, 11 Remote Sensing/GIS/Spatial Analysis, 12 Stream and Riparian Zone Biology/Wetlands, 13 Toxic Substances, 14 Water Quality Management/Monitoring, 15 Water Resources Economics, 16 Water Resources Policy, Regulation, and Education, 17 Water Supply and Conservation, 18 Water and Waste Water Treatment/Environmental Engineering

The survey revealed a broad base of expertise at the University, ranging from public policy , biology, economics, chemistry, engineering, agriculture, and related disciplines.

Research Program

Maryland TMDLs and Nonpoint Source Pollution - Summer Student Project -

Basic Information

Title:	Maryland TMDLs and Nonpoint Source Pollution - Summer Student Project -
Project Number:	2001MD1201B
Start Date:	5/1/2001
End Date:	9/1/2001
Funding Source:	104B
Congressional District:	5th District Maryland
Research Category:	Social Sciences
Focus Category:	Law, Institutions, and Policy, Management and Planning, Non Point Pollution
Descriptors:	TMDL, Nonpoint Pollution, Water Policy, Nitrogen Pollution,
Principal Investigators:	Allen Davis , Philip Kearney

Publication

SEPTEMBER 7, 2001 SUMMER RESEARCH PROGRESS REPORT
WATER RESOURCES RESEARCH CENTER

"Progress and Prognosis: A Status Report on the Ability of Maryland's Total Maximum Daily Load (TMDL) Program to Reduce Nonpoint Source Pollution to meet the State's Water Quality Standards"

By Michelle R. Perez, Candidate for Masters Degree in Environmental Policy
Dr. Matthias Ruth, Advisor
School of Public Affairs, University of Maryland

Introduction

The TMDL Program is an insufficient mechanism for Maryland to employ to reduce nonpoint source pollution. Because Section 303 (d) of the 1972 Clean Water Act (CWA) does not give the federal government authority to regulate nonpoint sources, Maryland's TMDL Program has decided not to regulate nonpoint sources either.

Maryland does address nonpoint source pollution in a variety of ways and the Maryland Office of the Chesapeake Bay Program is presently developing significant policy and programmatic infrastructure to increase their nonpoint source pollution reduction activites. Currently, the state regulates nonpoint sources via the CWA's National Pollutant Discharge Elimination System (NPDES) permits for municipal storm water systems, construction sites, forest areas, and wetlands. Maryland's voluntary agricultural best management practices (BMPs) have been successful at reducing agricultural nutrient pollution and the state's 1998 Water Quality Improvement Act (WQIA) establishes an unprecedented regulatory authority over farmers. Finally, nearly all 66 wastewater treatment plants (WWTPs) with discharge over 0.5 million gallons per day (MGD) have designed or are already operating Biological Nitrogen Reduction (BNR) systems under a 1995 voluntary agreement with the Maryland Department of Environment.

The researcher modified her summer project to focus specifically on nitrogen nonpoint source pollution and to compare the effectiveness of both the TMDL Program and the Chesapeake Bay Program at reducing nitrogen pollution. The conclusion of this report will summarize what she found.

What Was Done

Over the summer, the researcher conducted her investigation by analyzing various hallmark reports, holding interviews, and participating in appropriate meetings. The researcher analyzed the following documents that have helped shape the nitrogen reduction efforts in the state: Maryland's Tributary Strategies for Nutrient Reduction: A Statewide Summary. By MDE, DNR, MDA, MDOSP, Maryland Governor's Office, UMD. March 1995. Maryland's Tributary Teams 1999 Annual Report; Charting out Course. By Maryland's Tributary Teams. December 1999. Maryland's Interim Nutrient Cap Strategy. By Maryland Nutrient Cap Workgroup. March 2001. Status Report on Development and Implementation of Nutrient Management Plans. Office of Resource Conservation, Maryland Department of Agriculture. March 2001. Assessing the TMDL Approach to Water Quality Management. By the National Academy of Sciences Research Council. June 2001. Chesapeake Bay Program Nutrient Subcommittee Meeting Minutes at www.chesapeakebay.net

Interviews with the following persons were conducted to clarify the various nitrogen reduction policies and implementation efforts occurring in Maryland: Chesapeake Bay Foundation: Chuck Fox, Senior Policy Advisor (now MDNR Secretary); Kim Coble, Maryland Senior Scientist; David Anderson, CBF Attorney. Chesapeake Bay Program: Richard Batiuk, Associate Director for Science; Tom Simpson, Nutrient Subcommittee Chair. Maryland Department of Agriculture: Royden Powell, Assistant Secretary, Office of Resource Conservation. Maryland Department of Environment: Rich Eskin, Acting Deputy Director of Technical and Regulatory Services Administration and Steve Luckman, Director of the NPDES Division. Maryland Department of Natural Resources: Sherman Garrison, CWA Section 303(d) Manager. Maryland Tributary Strategies Teams Program: Danielle Lucid, Director; Sean McGuire, Southern Maryland Teams

Coordinator; Ginger Klingelhoefer-Ellis, Lower Western Shore Team Chair and Anne Arundel County: Environmental and Planning Services Administrator. Nutrient Management Plan: Patricia Steinhilber, Coordinator. Wastewater Treatment sector: Cy Jones, Regional and Regulatory Affairs Group Leader, Maryland Association of Municipal Wastewater Agencies (MAMWA); Earl Ludy, Supervisor, Prince Anne Wastewater Treatment Plant. Washington Area Council of Governments: Ted Graham, Water Resources Program Director.

Finally, the researcher attended the following meetings to gain an insider's view of the nitrogen reduction policy development and programmatic implementation activities: Nutrient Trading Workshop by Chesapeake Bay Program's Nutrient Trading Committee (6/14/01), Tributary Strategy's Development Workgroup Meeting (7/18/01), Chesapeake Bay's Nutrient Subcommittee Meeting (7/25/01).

Conclusions

Limitations of Maryland's TMDL Program to Reduce Nitrogen Pollution

As Maryland's TMDL Program can only regulate point sources and point sources only contribute about 20% of the state's nitrogen pollution, the TMDL Program cannot effectively address the 80% of nitrogen pollution that comes from nonpoint sources. The TMDL Program for nonpoint sources, thus, can only state that is receiving "reasonable assurance" from the activities of the Bay Program and the WQIA for implementing the nonpoint source load allocations. Unfortunately, no formal communication or collaboration is occurring between the three programs to ensure that nitrogen reductions from the Bay Program and the WQIA activities are reducing nitrogen by the amount specified in the TMDL or even occurring in the TMDL plan sub-watershed area. The researcher concludes that employing only a regulatory approach will not help solve the nitrogen problem in Maryland's portion of the Bay because the TMDL regulatory approach, to date, has fostered a negative professional atmosphere and results in only minimal reduction efforts.

Strengths of Maryland's TMDL Program to Reduce Nitrogen Pollution

After four years of existence, Maryland's TMDL program is a step closer towards fulfilling the CWA's 303(d) program. NPDES permits for four WWTPs have expired and the TMDL Program has successfully rewritten three of those four NPDES permits to include, for the first time in the state, load limits on nitrogen to reflect the TMDL waste load allocation. Only one plant (Princess Anne, Somerset County) is suing MDE to prevent them from including a nitrogen limit in their NPDES permit. Additionally, MDE's TMDL Program is finally starting to work cooperatively with the Bay Program on point source TMDLs. In August, MDE notified the 66 WWTPs discharging over 0.5 MGD of the Department's intention to write NPDES permits, in the future, that reflect the Bay Program's Tributary Strategy Goals for Nitrogen Loads. Finally, the TMDL Program did help pass a strong Chesapeake Bay Agreement. The threat of a Bay-wide TMDL was sufficient for the four states and the District of Columbia to take the Agreement very seriously. The TMDL threat fostered tremendous political collaboration and technical thoughtfulness in designing an Agreement that would warrant removal of the Bay from the Impaired Waters List in ten years.

Limitations of Maryland's Involvement in the Chesapeake Bay Program to Reduce Nitrogen Pollution

The primary limitation of the Maryland Office of the Chesapeake Bay Program is the lack of sufficient funds to carry out the existing nitrogen reduction programs to accomplish the present goals. Furthermore, significantly more funds will be needed in ten years to reduce nitrogen pollution beyond the current goals as even larger nitrogen loads are expected from a growing Bay population. The attempts by the Chesapeake Bay Foundation to put an $8.5 million price tag on the Bay's clean-up efforts is noteworthy but the Bay Program has missed several opportunities to procure that funding. As the Program finalizes their new water quality standards and divides the nutrient reduction loads amongst tributaries and sources, progress may be slowed by lawsuits seeking to maintain the loads as voluntary options rather than enforceable requirements.

Strengths of Maryland’s Involvement in the Chesapeake Bay Program to Reduce Nitrogen Pollution

The Maryland Office of the Chesapeake Bay Program is by far the most progressive and well-established program to carry out the 2000 Bay Agreement. Maryland’s 10 Tributary Teams established a stakeholder approach to the development and implementation of the Agreement. Additionally, the blended approach of employing both voluntary and regulatory programs to carry out the Bay Agreement allows each state’s environmental, natural resource and planning agencies to work together in a positive atmosphere and encourages them to put aside political, geo-physical and cultural differences to solve the excessive nitrogen problem. The result of this unprecedented level of cooperation is a massive overhaul of existing inadequate and inaccurate water quality standards of each state. The Bay Program is currently adopting three “living resources” criteria (dissolved oxygen, chlorophyll a, and water clarity) that will be used to establish bay-wide water quality standards, from which tributary loads will be developed and then divided by sector and, finally, by source. This thoughtful and slow and steady approach is the best mechanism to helping waterbodies in Maryland and the rest of the Chesapeake Bay become significantly less nitrogen polluted.

Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay WatershedsWatershed

Basic Information

Title:	Atmospheric Deposition of Currently Used Pesticides to Chesapeake Bay WatershedsWatershed
Project Number:	2001MD5B
Start Date:	3/1/2001
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	5 MD
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Toxic Substances, Water Quality
Descriptors:	Atmospheric Processes, Contaminat Transport, Trace Organics
Principal Investigators:	Alba Torrents , Laura McConnell

Publication

1. Kuang, Z., McConnell, L. L., Torrents, A., Merritt, D., Tobash, S. Atmospheric deposition of currently used pesticides to the Choptank River watershed Journal of Environmental Quality (in press).
2. Zhihua Kuang (2001) Deposition of Currently used Pesticides in the Cheseapeake Bay MS-Dissertation, Department of Civil and Environmental Engineering, University of Maryland, College Park.
3. Z. Kuang, L. L. McConnell, A. Torrents Atmospheric transport and deposition of currently used pesticides to Choptank River watershed Proc. 22nd Soc. Envron. Tox. Chem. Abstract #214, Page 47., 2001.
4. Z. Kuang, A. Goel, A. Torrents, L. L. McConnell Atmospheric transport and deposition of currently used pesticides to Choptank River Watershed Proc. Chesapeake Bay watershed restoration conference: riparian and wetland stewardship, 2001.

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

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. For example, some studies have estimated that atmospheric deposition counts for more than 25% of the total nitrogen entering the Chesapeake Bay. Very little is known regarding the atmospheric loading of pesticides, particularly on the Eastern Shore where land use is predominately agricultural. The goal of the Chesapeake Bay Basin wide Reduction Strategy is to have a Bay free of Toxics by reducing or eliminating toxics from all controllable sources. 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.

The main goal of this study is to determine weather atmospheric deposition can represent a significant source of pesticides in some Delmarva Peninsula watersheds due to the intensive nature of corn and soybean production in the area. Herbicides and their breakdown products are likely to be the dominant components released to the atmosphere as they are used in the highest amounts. Specific Objectives for the project are:

1. Directly determine the vapor and particle-phase concentrations, and wet deposition flux of selected pesticides and degradation products over a two-year period at two sites.
2. Determine pesticide concentrations in surface waters and soils at representative sites within the Choptank watershed to use in gas exchange calculations and to

estimate the reservoir of pesticides in watershed at different times of the year.

3. Measured atmospheric deposition fluxes of atrazine and metolachlor in the Choptank River and compare them to the predictions from the Regional Atmospheric Transport Model.
4. Analyzed the hypothesis and simplifications included on the Regional Atmospheric Transport Model and recommend modifications, if needed, to better reflect real data .

Specific Tasks for the reporting period were to:

1. Laboratory development and validation of automated rain sample collection method for currently used pesticides.

2. Collection of weekly air samples and daily precipitation samples from the two collection sites. January and February months were omitted due to equipment limitations in cold weather.

3. Collection of water and sediment samples.

Methodology

Rain samples were collected on an event basis using a modified commercially available MIC-B rain collector (Meteorological Instrument Center, Ontario, Canada) at one site on the campus of The Center for Environmental Studies, University of Maryland, Horn Point Laboratory, close to the shore of the Choptank River in Cambridge, MD (38^{o} 36′04″ N, 76^{0} 07′47″ W). The range of sample volumes was from 0.05 to 13.6 L, and the median value was 1.1 L.

The sampler was equipped with a 0.2 m^2 stainless steel funnel that was covered with a lid until the rain sensor activated the lid to open (Figure 1). A Teflon column (12 cm length × 14 mm diameter), which was attached to the bottom of the funnel, was connected to a Teflon filter head containing a 45-mm diameter glass fiber filter (Whatman GF/F, 0.75 μm nominal pore size). The filter was designed to trap the operationally defined particle-phase pesticide residues in the rainwater. Attached to the filter head was a solid phase extraction (SPE) cartridge containing 200 mg of a hyper cross-linked styrene-divinylbenzene copolymer (Jones Chromatography, IST Isolute ENV+, 6 ml reservoir) to capture the operationally defined dissolved-phase residues. A peristaltic pump (Cole - Parmer, Model 7518-00) was connected to the cartridge to pull rainwater through the filter cartridge assembly at a flow rate of 20 to 50 mL/min, and the extracted water was collected in a 20-L bottle for volume measurement. The pump was activated while the funnel was open.

After a rain event, the site operator removed the cartridge and filter, and shipped the samples on ice packs via overnight mail to the Environmental Quality Laboratory in Beltsville, MD for analysis. Each rain event was any rain that fell during a 24-hr period from 10 AM to 10 AM (± 1 hour) the following day. Samples of less than 50 ml were not analyzed, and cartridges and filters were discarded by the site operators. Three samples had volumes of <50 ml, so they were not analyzed. Between rain events, the funnel, column and the filter holder assembly were cleaned by wiping with lint-free paper and rinsing with 4 to 6 L of distilled water followed by approximately 0.5 L chromatographic grade acetone (Burdick & Jackson, High Purity Solvent). The collection and extraction of field blanks involved pouring 4-L distilled water into the precleaned rain sampler once a month and treating it in an identical fashion to field samples.

The SPE cartridge was dried upon receipt using clean nitrogen gas. The absorbed analytes were eluted and concentrated using the same method as described for surface water samples (Liu et al., 2002).

Figure 1 illustrates the deployment of the rain and air samplers in the field. The automatic sample collection method has been validated in the laboratory before deployment. Experiments were conducted using pesticide spiked distilled water passed through the funnel and sampling train. The extraction method efficiency is speed dependency, with the best speed ranging from 30-50 mL/min. (Figure-2). Sample volume did not have a significant effect on overall recoveries (see Figure-3). Spike recovery experiments for selected pesticides resulted in average recoveries of 68- 104 % with a standard deviation 3-21.5 % up to a sample volume of 10 L or the equivalent of 5 cm of precipitation. Minimum detection limits range from 0.22 ng/L for β-endosulfan to 2.7 ng/L for diazinon.

Figure 1: Air and Rain Sampling Apparatus

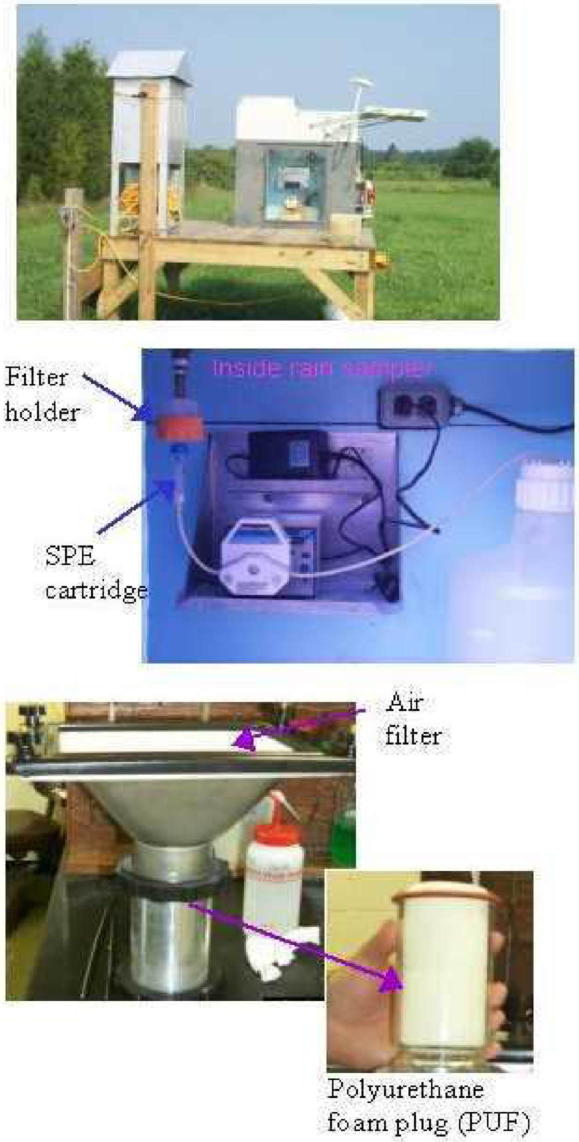


Figure 2: Recoveries of spiked water samples at different flow rates. Total Volume 6 L.

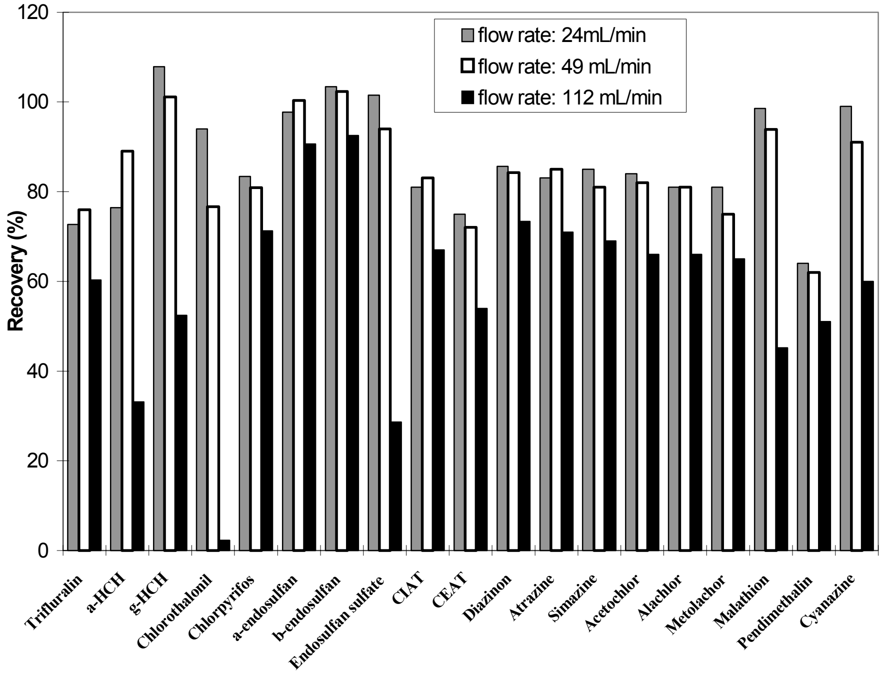
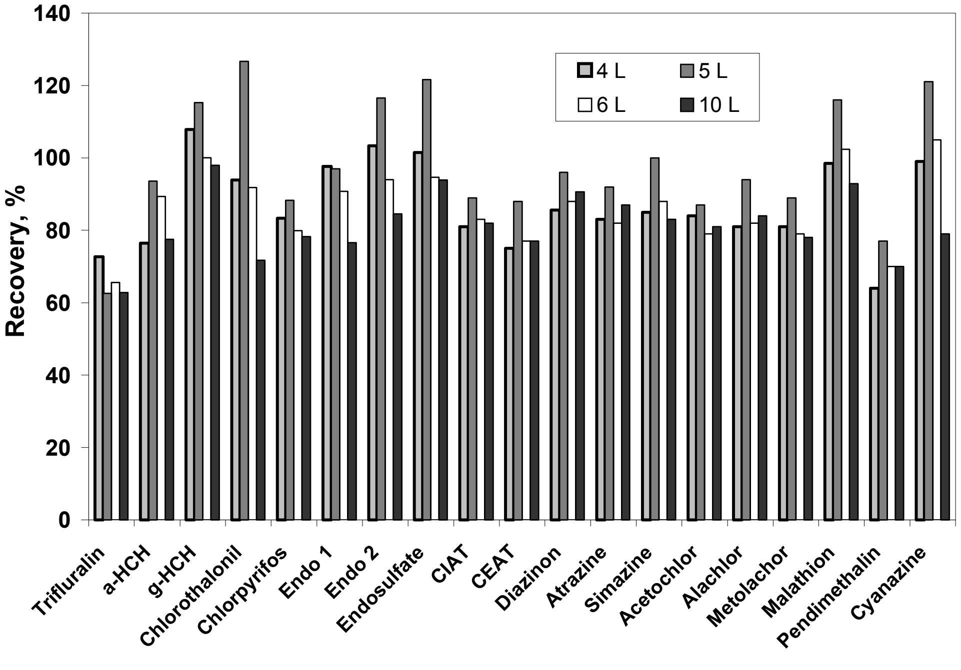


Figure 3 Spike recoveries for different volumes



Air samples were collected over a 24-h period once a week using a high-volume sampler (Model GPNY 1123, Thermo Anderson, Smyrna, GA) at the same site where rain samples were collected. Air was pulled at a flow rate ranging from 0.29 to 0.54 m^3 min^{-1} through a 20.3 × 25.4 cm rectangular glass fiber filters (Gelman, type A/E) followed by two cylindrical 7.6 cm diameter × 7.6 cm length polyurethane foam plugs (PUF) held within a glass sleeve. PUF plugs were precleaned using tap water, distilled water, and Soxhlet extraction with pesticide grade acetone (12 h) followed by ethylacetate (12 h) (Burdick and Jackson, High Purity Solvent). Filters were pre-cleaned by baking at 400 ^{o}C (4 h) and were individually wrapped with aluminum foil prior to use.

At the end of each sampling period the air filter was folded with particles inside and placed back into the clean foil pocket, and PUF plugs were returned to clean jars. The PUF plugs and filters were kept frozen (-20 ^{o}C) until extraction. PUF plugs were extracted separately in batches of 11 using a Soxhlet extraction apparatus with ethylacetate for 12 h. One clean PUF plug was extracted along with samples for each batch to observe any matrix interference or any contamination from laboratory procedures. Another clean foam plug in each batch was spiked with a mixture of target analytes shown in Table 2 to determine extraction efficiency. All samples were spiked with 25 µL of diazinon-d_{10} (concentration 41.4 mg L^{-1}) as an extraction efficiency surrogate. Extracts were reduced to 5-10 mL by rotary evaporation and further reduced to 1 mL using a gentle stream of chromatographic grade (99.9%) N_2 gas.

Principal Findings

Pesticide Use

Because of heavy agricultural land usage in the Choptank River watershed, volatile losses from local pesticide application are the most likely source of these residues to our collection sites. Pesticide usage may vary year-to-year depending on local farming practices and weather conditions. No pesticide use data exists specifically for the Choptank River watershed. A rough estimate of pesticide use within the watershed was made based on the fractions of the surrounding four counties (Caroline, Dorchester, Queen Anne's and Talbot) that are within the watershed and the most recent county-specific pesticide usage data from 1997 (Maryland Dept. of Agriculture, 1999). The resulting annual pesticide use estimates for the entire watershed are listed in Table 1.

Table 1. Pesticide physical properties and air and rain concentration data above quantification

		Physical properties†			Dissolved-phase Rain Water‡			Gas-phase Air§		
Pesticide	Usage¶	P_L#	HLC ††	Solubility#	Freq‡‡	conc.	avg.	Freq	conc.	median
	kg/yr	mPa	Pa m^3/mol	mg/L	%	ng/L		%	pg/m^3	
Acetochlor	8800	5.9	2.0×10^{-3}	230	9.9	14-165	59	9.7	81-490	99
Alachlor	6200	4.1	3.2×10^{-3}	342§§	24	9.5-450	99	29	130-350	190
Atrazine	19000	1.29	2.9×10^{-3}	970	32	22-1100	245	94	55-1600	190
CIAT	na ¶¶	na	na	438000##	14	21-270	75	13	nd†††	nd
CEAT	na	na	na	56700##	nd	nd	nd	nd	nd	nd
Cyanazine	2900	$5.2 \text{ x } 10^{-3}$	2.8×10^{-7}	4400	nd	nd	nd	nd	nd	nd
Diazinon	830	8.0	0.072‡‡‡	38	1.4	13	13	48	16-220	74
Malathion	150	5.3§§	1.1×10^{-3}‡‡‡	130‡‡‡	7.0	1.9-360	89	3.2	95	95
Metolachlor	38000	1.73	7.9×10^{-3}§§§	530	55	4.3-1000	190	100	63-10200	520
Pendimethalin	2900	7.8§§	3.75	0.7§§	13	20-83	39	nd	nd	nd
Simazine	9500	0.860	9.8×10^{-5}‡‡‡	500.00	18	18-870	200	9.7	130-310	260
Chlorothalonil	1100	13§§	0.022‡‡‡	101‡‡‡	89	7.7-2010	160	100	36-2500	230
Chlorpyrifos	2300	3.6§§	0.32§§§	2.9§§	14	0.97-29	4.8	87	15-670	110
□-Endosulfan¶¶¶	□	6.2††††	6.6§§§	3.7††††	13	1.3-31	5.1	100	11-680	68
□-Endosulfan¶¶¶	□	3.2††††	0.88§§§	21††††	28	0.27-81	7.2	87	5.3-120	26
Endosulfate###	na	na	na	na	8.5	0.98-14	4.1	58	5.6-230	15
□-HCH	na	64.7	0.68‡‡‡‡	22	1.4	0.44	0.4	97	17-140	62
□-HCH	□□	22	0.34‡‡‡‡	48	15	0.48-22	5.2	97	7.2-150	43
Trifluralin	82	9.8	10.3§§§	0.82	nd	nd	nd	29	5.9-94	11

† Values were determined at 20-25 °C and compiled by Majewski et al. (1995) unless otherwise cited.

‡ Dissolved-phase rain water concentrations are operationally defined as solid-phase extraction cartridge results.

§ Gas-phase air represents results from polyurethane foam plug extracts.

¶ Values given represents estimated annual usage in the watershed caluculated from county-based data (MDA, 1999).

\# Listed vapor pressure(P_L) and water solubility values are adjusted from their solid phase values to their sub-cooled liquid values using the method described by Majewski and Capel, 1995.

†† HLC = Henry's law constant.

‡‡ freq = Detection frequency.

§§ Kidd, et al.(1991), determined at 20-25 °C.

¶¶ na = not available

\## Solubility and melting point values used to calculate Psl values from Mills and Thurman, 1994.

††† nd = not detected.

‡‡‡ USDA-ARS pesticide properties database [Online].

§§§ Rice et al. (1997), measured at 20 °C.

¶¶¶ Endosulfan is assumed to be applied in a technical mixture containing alpha/beta isomer ratio of 7:3.

\### Endosulfate = Endosulfan sulfate

†††† Cotham and Bidleman (1989), determined at 25 °C.

‡‡‡‡ Kucklick, et al. (1991), measured at 23 °C.

Pesticide Concentration Data

Air and Rain

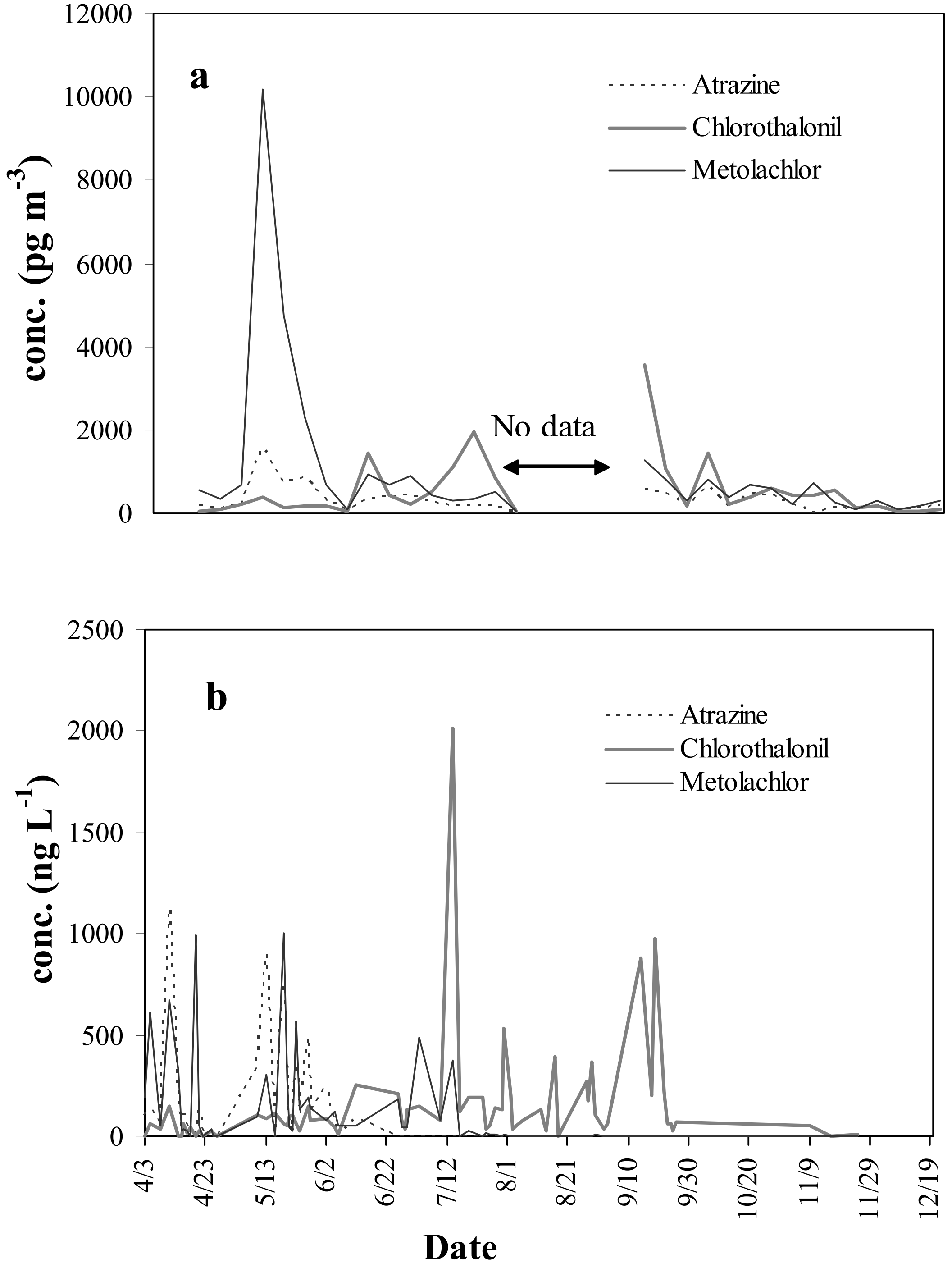
Thirty-one air samples and seventy-one rain events were collected during the study covering the prior year and the reporting period. Concentrations and detection frequency is presented in Table 1. Currently-used pesticides like metolachlor, atrazine, simazine, chlorothalonil, endosulfan and chlorpyrifos were detected in the air and rain with relatively high frequency. Results from analysis of a representative portion of the rain filter samples (50% randomly selected) revealed that none of the target analytes were present in the particulate phase at concentrations above quantification limits. Therefore all rain sample results are operationally defined dissolved phase concentrations.

Metolachlor and atrazine were detected frequently on the air filter extracts and trends in particle phase concentrations follow the same pattern as gas phase samples. A complete examination and discussion of the vapor particle partitioning behavior of these chemicals is currently underway (Kuang et al., in prep).

Metolachlor concentration data in gas-phase air were not normally distributed ($P < 0.01$) based on four normality tests (Shapiro-Wilk, Kilmogorov-Smirnov, Craner-von Mises, and Anderson-Darling normality tests). Results are better described as a log-normal distribution ($P = 0.098- 0.14$). Metolachlor concentrations in the gas-phase ranged from 72 pg m^{-3} to a maximum value of 10,000 pg m^{-3} on 9 May 2000 with a median value of 520 pg m^{-3} (Table 1). Concentrations of metolachlor in air were low in April and then increased to maximal values in May before decreasing in June (Fig. 4). The maximum concentration in May coincided with the highest expected application use rate, the overlap of corn and soybean planting seasons. Metolachlor was observed in rainfall frequently between April and July with the highest concentration of 1000 ng L^{-1} on 19 May 2000. Analysis are underway to see if the same trends are observed for the 2001 season. The concentrations then declined to below quantification limit (3.6 ng L^{-1}) in late August.

Temporal trends in atrazine gas-phase concentration were similar to metolachlor but concentrations were 1 to 6 times lower, consistent with lower use rates and lower vapor pressure (Table 1). Concentrations were low in April (91-180 pg m^{-3}) and jumped to maximal concentrations in May (230-1600 pg m^{-3}) before declining again in June. The highest atrazine gas-phase concentration was observed on May, corresponding to corn planting activity. Atrazine was only detected from April to June in rainfall with a maximum concentration of 1100 ng L^{-1} occurring on 11 April 2000. Although the maximum atrazine concentration in rain occurred in April, atrazine concentrations were also elevated in May, coinciding with the high concentrations of atrazine in the air. The maximum atrazine concentration observed on 11 April may be due to the very small volume of rain received (110 mL). Large rain events in May (70-2600 mL) may have diluted atrazine concentrations in rain. These results illustrate the need to view rain results in terms of flux rather than concentration.

Figure 4: Atrazine, metolachlor and chlorothalonil concentrations in (a) gas-phase air (pg/m^3) and in (b) dissolved-phase rain (ng/L).



In contrast to atrazine and metolachlor, simazine was observed in much lower concentrations and less frequently in air. The highest gas-phase concentration was 310 pg m^{-3}, 4 and 30 times lower than that of atrazine and metolachlor, respectively. The very low vapor pressure of simazine and lower application rate (Table 1), may account for the difference. Simazine mirrored the temporal pattern of atrazine in rain except at lower concentrations and for shorter periods.

The other remaining herbicide target analytes such as alachlor and acetochlor were only found in air and rain for short periods during our study. The triazine degradation product CIAT (6-amino-2-chloro-4-isopropylamino-*s*-triazine), sometimes called DEA in the scientific literature, was only detected in air in May when atrazine concentrations in air were high. CIAT mirrored atrazine in rainfall with a mean ratio of CIAT to atrazine of 0.28 ± 0.15 (n =10).

Chlorothalonil is a widely used organochlorine fungicide applied to vegetables, trees, fruits, turf, ornamentals, and other agricultural crops and may be applied on multiple occasions depending on weather conditions (Lehotay et al., 1999). It is highly toxic to fish, aquatic invertebrates, and marine organisms (US EPA, 1999). Chlorothalonil had the second highest maximum concentration in air following metolachlor with a median concentration of 230 pg m^{-3}. Chlorothalonil concentration values in air were low in the spring, increased in the summer, and reached the maximum concentrations of 3500 pg m^{-3} in mid-September before decreasing later in September (Fig. 4). Air data are missing from August to early September due to problems with sampling equipment. It is possible that the highest air concentrations of chlorothalonil were missed during this period.

Chlorothalonil was also frequently detected in rain ranging from 12 to 2000 ng L^{-1}. Chlorothalonil concentration values were low during the spring and then reached a maximum concentration of 2000 ng L^{-1} on 14 July. High rain concentrations of chlorothalonil observed in September corresponded to the high concentrations in the air (Figure 4). The presence of chlorothalonil in rain samples is consistent with its physical properties. The reported Henry's law constant for chlorothalonil is 0.022 Pa m^3 mol^{-1} (Table 1), making it relatively volatile. This compound has also been detected with relatively high frequency in precipitation from the Sierra Nevada Mountains of California (McConnell et al., 1998; Lenoir et al., 1999). This indicates that chlorothalonil is persistent in the air and can be transported a significant distance. Harman-Fetcho et al. (2000) also found high concentrations of chlorothalonil in the Patuxent River watershed (max = 6,800 pg m^{-3}). In a separate study by Lehotay et al. (1999), chlorothalonil was detected in the Patuxent River (2.4-18 ng L^{-1}) at the end of July and in the Choptank River in mid-August.

Endosulfan is an insecticide commonly used on vegetables in the mid-Atlantic region (Lehotay et al., 1999), and is generally applied in a technical mixture containing α/β isomer ratio of 7:3 (Rice et al., 1997). Endosulfan was detected in all air samples with maximum concentration of 680 pg m^{-3} of α-endosulfan found on 18 July, 2000 coinciding with the expected high use rate in summer. Throughout the study, α-endosulfan was always observed at higher concentrations than β-endosulfan, reflecting the composition of the technical mixture and the higher vapor pressure of α-endosulfan (Table 1).

Chlorpyrifos is an organophosphate (OP) insecticide that is used for a broad range of lawn and home insecticide products, for agricultural purpose, and for termite treatment (Racke, 1993). The U.S. EPA recently banned chlorpyrifos for home use as a result of a risk assessment associated with the Food Quality Protection Act (FQPA) (U.S. EPA, 2001). The highest concentrations of chlorpyrifos in air were found in May, July and September with the maximum concentration observed on 23 May at 670 pg m^{-3}. Higher gas-phase concentrations of chlorpyrifos up to 2000 pg m^{-3} have been detected in the Patuxent River watershed (Harman-Fetcho et al., 2000). The lower chlorpyrifos concentrations in air from our study may be due to less residential land use in Choptank River watershed compared with the Patuxent River watershed. Chlorpyrifos was sporadically detected in rain samples with concentrations in the range of 0.70 to 29 ng L^{-1}.

Diazinon is another widely used OP insecticide applied to control grubs in soil and pests of vegetables, fruit, and tobacco (Lehotay et al., 1999). In contrast to chlorpyrifos, diazinon was detected in air less frequently and at a lower concentration. Concentration values fluctuated during the study period but tended to increase in the summer and fall with a maximum gas-phase diazinon concentration of 220 pg m^{-3} on 19 September. The increase in gas-phase diazinon in the summer and fall may be a result of local usage of this insecticide and from increased volatilization rates as air and soil temperatures increase. However diazinon was only detected once in the rainfall with a concentration of 13 ng L^{-1} despite its relatively high vapor pressure and low Henry's law constant (Table 1). Diazinon hydrolysis in water may cause concentrations in rainfall to be below quantification limits.

On-going Determinations and Data Analysis for the 2/2002 – 2/2003 reporting period

Relatively high pesticide concentrations in rainwater can be observed during small rain events (Goolsby et al., 1997; Harman-Fetcho et al., 2000), while concentrations may decrease during large rain events due to dilution, despite higher overall pesticide mass. Consequently, in order to normalize the magnitude of pesticide mass deposited, results of wet deposition here are presented in ng m^{-2} $event^{-1}$, called wet flux.

In the next progress report we will illustrate our determinations of wet deposition fluxes. We are also combining event-based fluxes to determine cumulative amounts of pesticides deposited.

Air-water gas exchange is an important process for the delivery and removal of semivolatile organic pollutants from natural waters (Bidleman, 1988; McConnell et al., 1993; Hornbuckle et al., 1995). We have chosen metolachlor to examine in-depth with respect to this process as it was present in air and water throughout the study and information on the temperature-dependence of its' Henry's Law constant is available. In order to determine the direction and magnitude of air-water gas exchange of pesticides in the Choptank River, the river was divided into seven segments, each of which borders at two neighbors sampling sites and the concentrations in surface water and in air will be to the values of Henry Constant.

Significance

The data presented here and the analysis currently underway would allow us the determination of gas exchange and wet deposition Load to the Choptank River. A similar analysis will be conducted at the other site and for last year sampling. This will allow the determination of upper and lower limits of the total mass of pesticides entering the river via atmospheric processes and determine weather wet deposition is an important source as compared to the total input of pesticides.

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Dairy Farm Management and Water Quality - Summer Student Project

Basic Information

Title:	Dairy Farm Management and Water Quality - Summer Student Project
Project Number:	2001MD6B
Start Date:	5/1/2001
End Date:	9/1/2001
Funding Source:	104B
Congressional District:	5th District -Maryland
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Management and Planning, Water Quality
Descriptors:	Intensive Grazing, Groundwater, Pasture, Dairy, Manure,
Principal Investigators:	Allen Davis , Philip Kearney

Publication

Dairy Farm Management and Water Quality

Rachel Gilker
Advisor: Ray Weil
Natural Resource Sciences and Landscape Architecture

Dairy farmers in the mid-Atlantic have begun to try management intensive grazing (MIG), a radical shift from the conventional confined feed animal operation. Under management intensive grazing, virtually the entire land base of the dairy farm is converted from crop production to grazed permanent grass/legume pastures, an approach that leads to high soil quality and lower soil erosion. However, the environmental impact of the grazing system is not yet understood, and MIG may lead to nutrient losses to ground and surface waters (Stout et al., 1999; Stout et al., 2000).

The goal of this research is to characterize the water quality impacts of MIG in four watersheds on two dairy farms in Maryland and compare this with the impacts on two watersheds on a dairy farm typical of the conventional confinement feeding system. The impacts examined include nutrient concentrations in soil percolation water, groundwater and (for two watersheds) surface water. The research project will also document the economic profitability and the nutrient balances of each system.

During the summer of 2001, arrangements were made for cooperation with the three farm owners and a network of groundwater and percolation water sampling stations were installed. Work done this summer was essential in providing the background for the project as a whole. Two small (2 to 10 ha) watersheds were identified on each of the 3 farms, and transects were defined for well and lysimeter installations. Along each transect, three nests of three wells each were installed inside protective boxes. Additionally, one control well site was installed on each farm, for a total of 57 wells installed in the six watersheds. To enable sampling of soil pore water, a 90-cm and a 120-cm long lysimeter were installed from within each nest, at a 45-degree angle to the surface of the soil, with the tips extending into the pasture or field outside the nest at 60 and 90 cm. The wells within each nest were screened to cover a 3 m range of depths to allow for the collection of the upper meter of groundwater over the leaching season (October to May). Water was available in these wells over much of the summer, so samples were taken to determine the most appropriate method of sampling, including number of times a well should be emptied by bailing and the time to be allowed for the wells to refill. Based on the minimal change in pH in wells that had been emptied 1, 2 or 3 times, it was determined that emptying each well a single time before sampling would be sufficient. Two sets of samples were also taken to compare storage methods. One set of samples was frozen between sampling and lab work, while one was stored in chilled (but not frozen $4^{o}C$) storage. The results of this comparison should indicate whether any cell lysing caused by freezing might lead to higher levels of organic nitrogen in frozen samples.

Since obtaining soil pore water samples from suction lysimeters requires a nearly saturated condition in the soil profile, sampling of the lysimeters will begin with the fall leaching season. Samples of ground and surface water were collected on 15 dates and are currently being tested for pH and electrical conductivity (EC) (Figures 1 and 2). An initial set of 56 samples was sent to the Water Quality Lab at Wye, Md for analysis of nitrate and phosphate by ion chromatography (Figure 3). Measurements for EC (Figure 1) may eventually be correlated with nitrate levels and are included below (Doran and Parkin, 1996). Methods being studied for measurement of total and organic nitrogen and phosphorous include microwave versions of the persulfate and kjeldahl methods. These methods will be applied over the next semester.

Figure 2: Groundwater EC Measurements

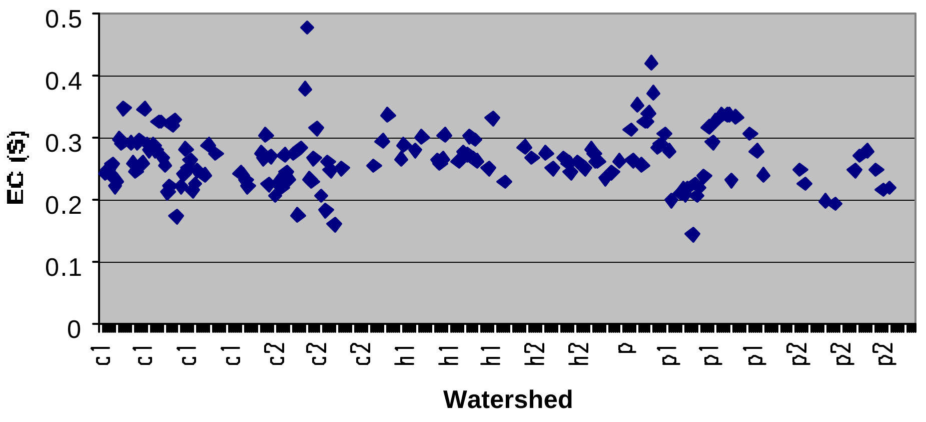
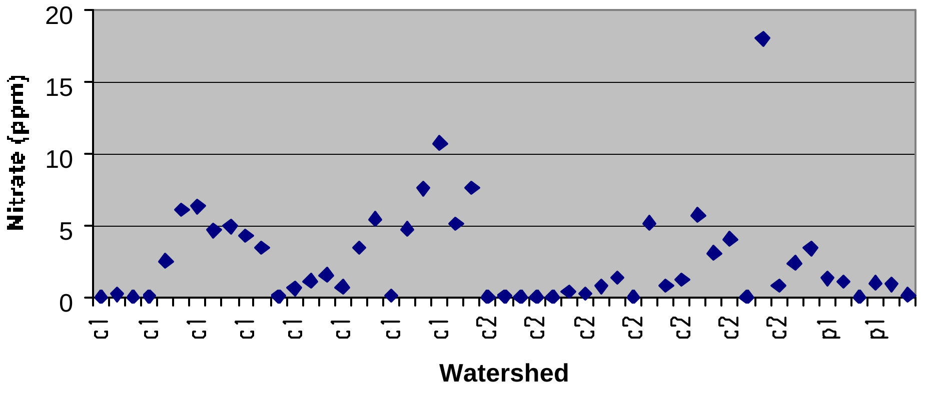


Figure 3: Nitrate Measurements from Initial Set of Groundwater Samples



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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:	2001MD7B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104G
Congressional District:	5th District of Maryland
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Toxic Substances, Water Quality
Descriptors:	Stormwater 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, College 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, and thus 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 is hypothesized that the removal of O&G from urban runoff could be accomplished via sorption, filtration and subsequent biodegradation in a bioretention system, by using a surface mulch layer as a contaminant trap.

The objectives of this research are 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 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 is 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

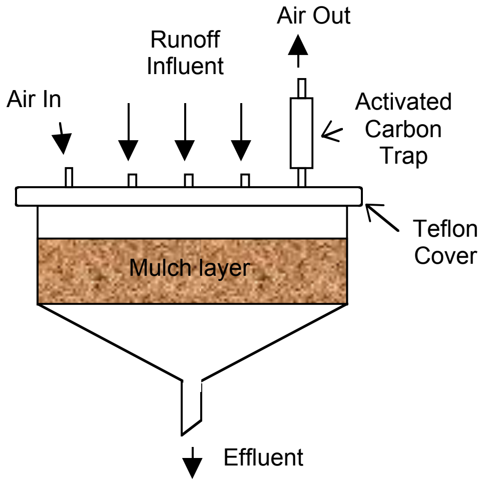

Figure 1. Bioretention reactor

Stormwater runoff simulation experiments are being performed using a bench-scale bioretention reactor (Figure 1), made using a porcelain Buchner 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 are the native microbes present in the mulch. The contaminants selected for the bench-scale stormwater runoff simulation experiments include naphthalene, toluene, and motor oil, which are added in dissolved and/or particulate-associated form to simulated runoff (Davis et al., 2001). During a simulated storm event, the influent simulated runoff and the reactor effluent are sampled and extracted with hexane, and the hexane is analyzed for the contaminant concentration by gas chromatography (GC). This allows calculation of the trapped contaminant mass in the mulch. Then a mass balance approach, incorporating monitoring of contaminant levels in the aqueous, gaseous and solid phases, is used to quantify the contaminant mass removal via biodegradation during the period between storm events. Specifically, to monitor contaminant loss by degradation, mulch samples are taken everyday for abiotic runs and twice per day for biotic runs, and analyzed for the contaminant concentration using hexane extraction and GC. The mulch samples are also analyzed for microbial population counts. In addition, the activated carbon from the trap (Figure 1) is also extracted with hexane for GC analysis to account for losses by volatilization.

By comparing the results of the abiotic and biotic experiments, it is possible to distinguish the impact of the biodegradation. Mulch for the killed-control reactor used in the abiotic experiments is 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 is soaked in 1000 ppm calcium chloride ($CaCl_2$) solution for 48 hours. The mulch is drained after soaking and packed in the reactor up to the 3 cm height. $HgCl_2$ is also introduced to the influent solution for the abiotic experiments at a level of 400 mg/L. In the toluene experiments, autoclaved mulch is also used to run another abiotic control to better inhibit the microbial activity.

All the samples are 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 ranges of standard deviations are even smaller than the symbols and, thus not visible in the figures.

Principal Findings and Significance

Experiments performed to date with ~1.6 mg/L (~3.2 mg/hr surface loading) dissolved naphthalene in the influent simulated runoff have demonstrated approximately 90% removal from the aqueous phase via sorption to the mulch layer during the simulated storm event (Figure 2). Subsequently, about 95% naphthalene removal from the solid phase occurred via biodegradation in the mulch layer within three days (74 hours) following the end of the stormwater addition (Figure 3 (a)). Removal from the mulch in the biotic run was about twice as fast as that in the abiotic run. In particular, degradation of naphthalene in the biotic run proceeds rapidly during the first two days. 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 occurs due to microbial activity.

To provide additional evidence confirming that the naphthalene removed was due to biodegradation, microbial populations of total heterotrophic bacteria and naphthalene-degrading bacteria in the mulch were counted periodically after the simulated 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 increases with time, and that the sterilization method inhibited some microbial growth, especially naphthalene-degraders, causing an approximately four orders of magnitude decrease in the population at 24 hours after the experiment. However, even though the killed-control inhibited the microbial activities, naphthalene-degrading bacteria were still present. Thus, the slow decrease of naphthalene with time in killed-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, which is shown by the plate count method, supports the hypothesis that the rapid degradation of naphthalene is mainly because of the microbial activities.

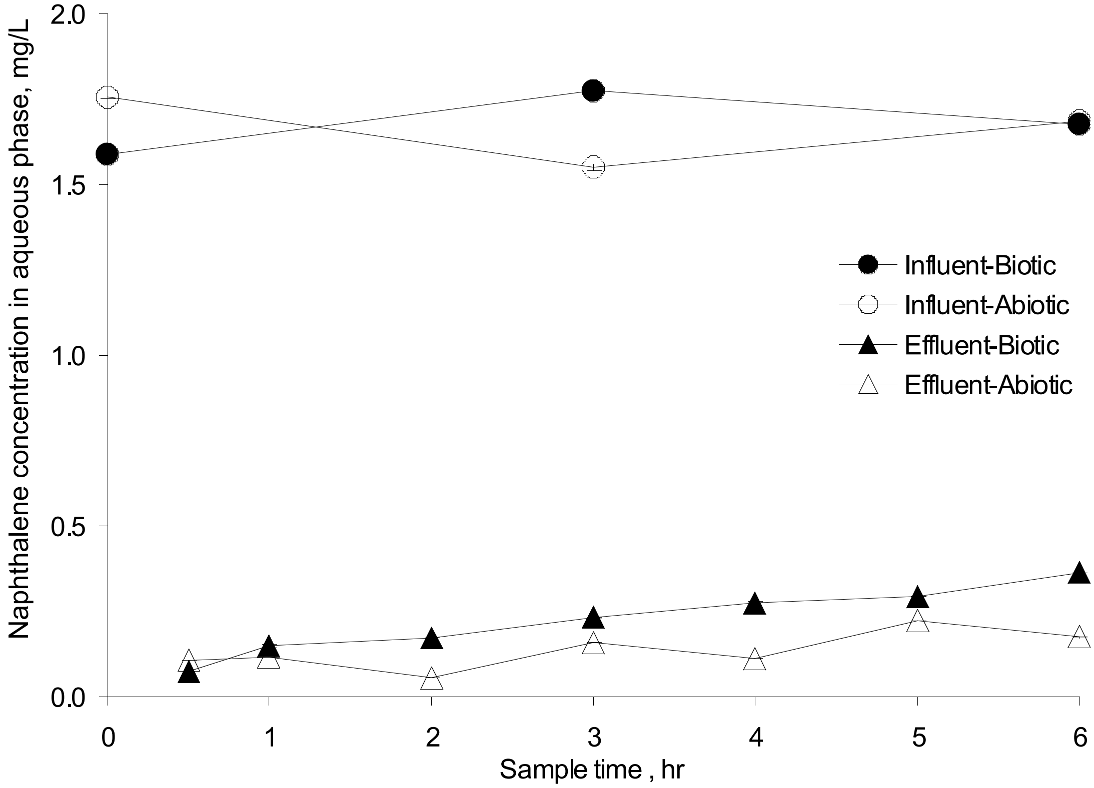

Figure 2. Naphthalene removal from the aqueous phase through the bioretention mulch layer during the simulated storm event. Error bars represent the standard deviations.

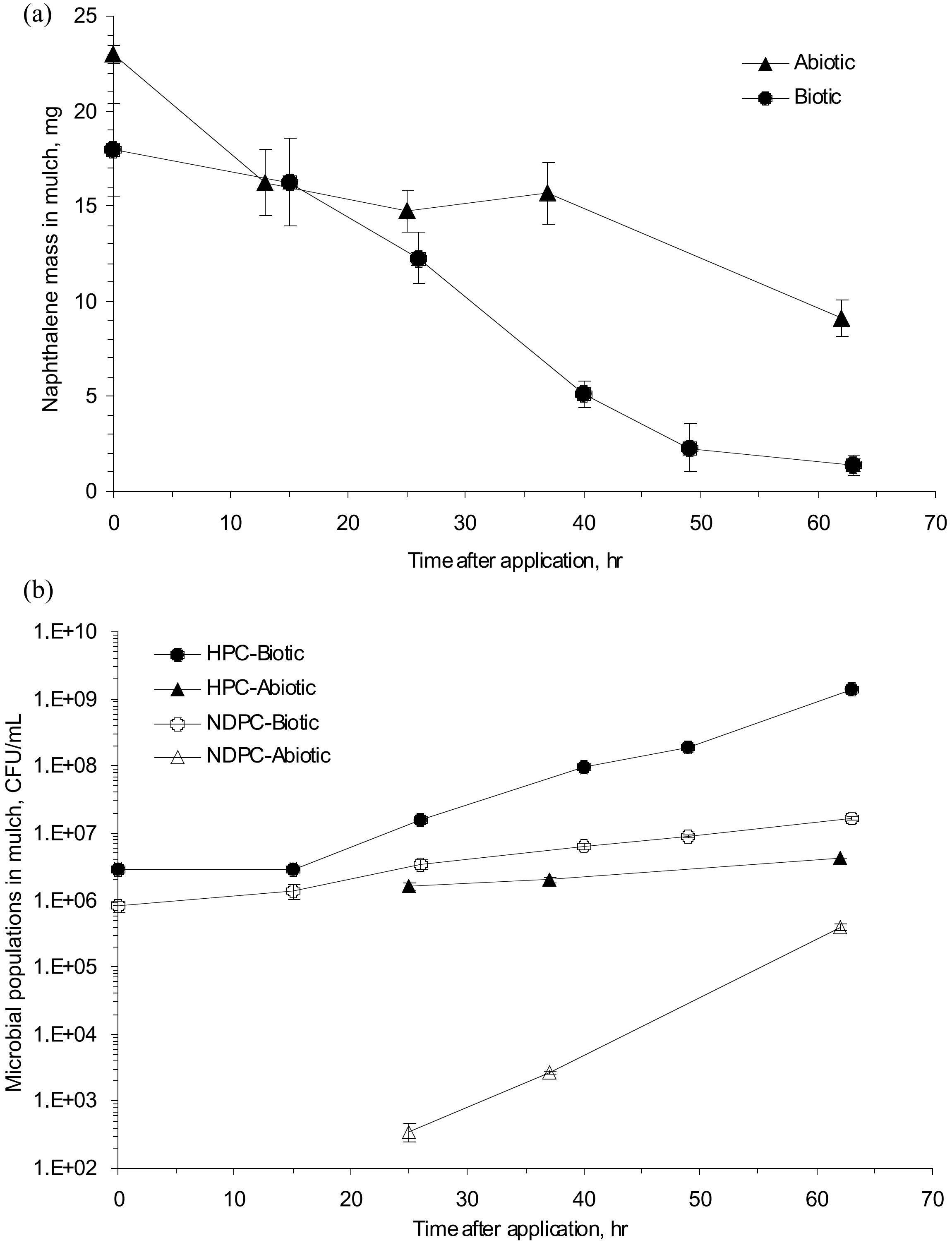

Figure 3. Microbial population change on naphthalene degradation: (a) Reduction of naphthalene in the mulch, and (b) Microbial growth based on total heterotrophic plate counts (HPC) and naphthalene-degrader plate counts (NDPC) in the mulch. Error bars represent the standard deviations.

Experiments using simulated stormwater runoff contaminated with ~2.7 mg/L dissolved toluene showed similar results. Biotic and two control ($HgCl_2$-amended and autoclaved abiotic) experiments were performed. Approximately 86% of the toluene in the runoff was removed through the mulch layer during the simulated storm events (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 naphthalene experiments. After completion of the simulated storm event, about 90% removal of toluene from the solid phase occurred in the biotic experiments within around 4 days (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 the toluene removal from the mulch that was not a result of volatilization was due to biodegradation (Figure 5 (b)). The population of the microorganisms in the mulch appeared to increase gradually with time based on both the heterotrophic plate counts and the toluene-degrader plate counts.

Experiments with motor oil contamination as well as experiments with particulate-associated hydrocarbon contamination will be performed next using similar methodology.

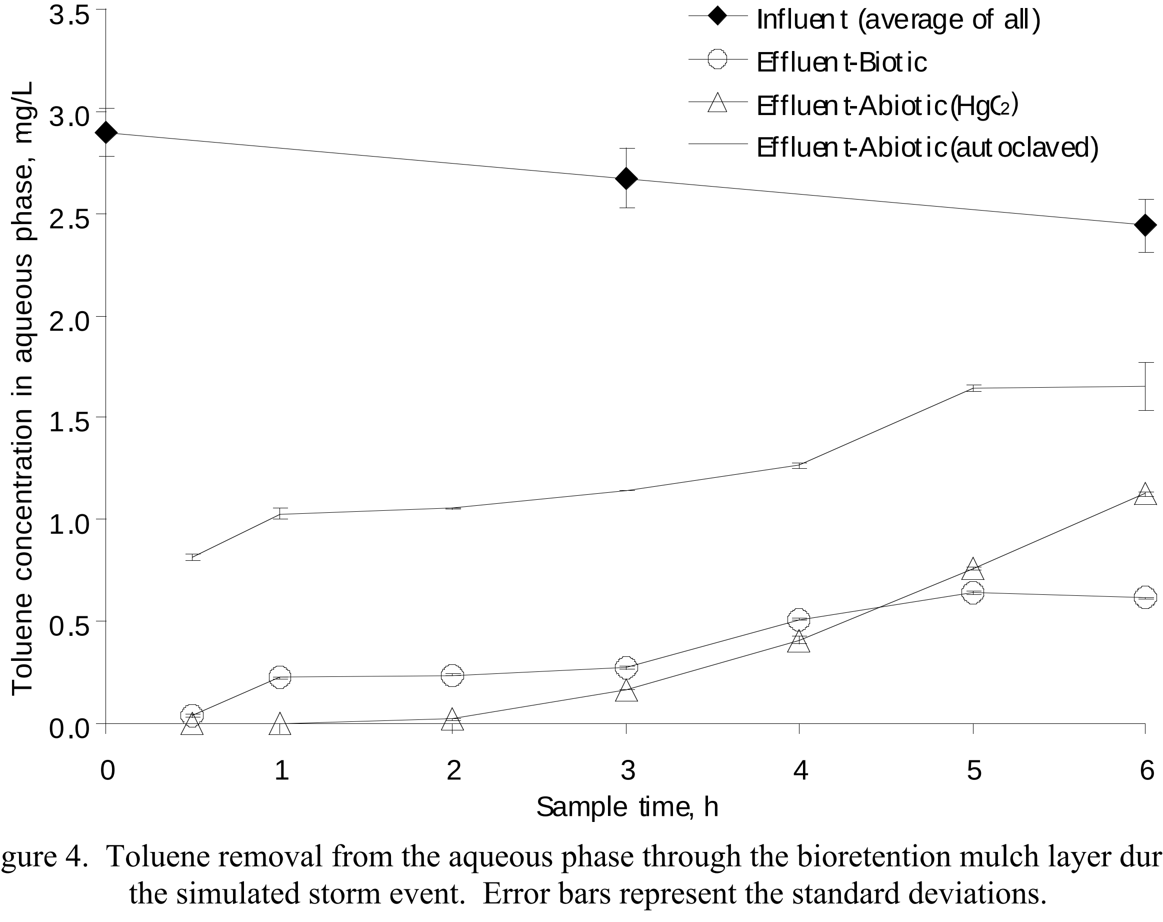

Figure 4. Toluene removal from the aqueous phase through the bioretention mulch layer during the simulated storm event. Error bars represent the standard deviations.

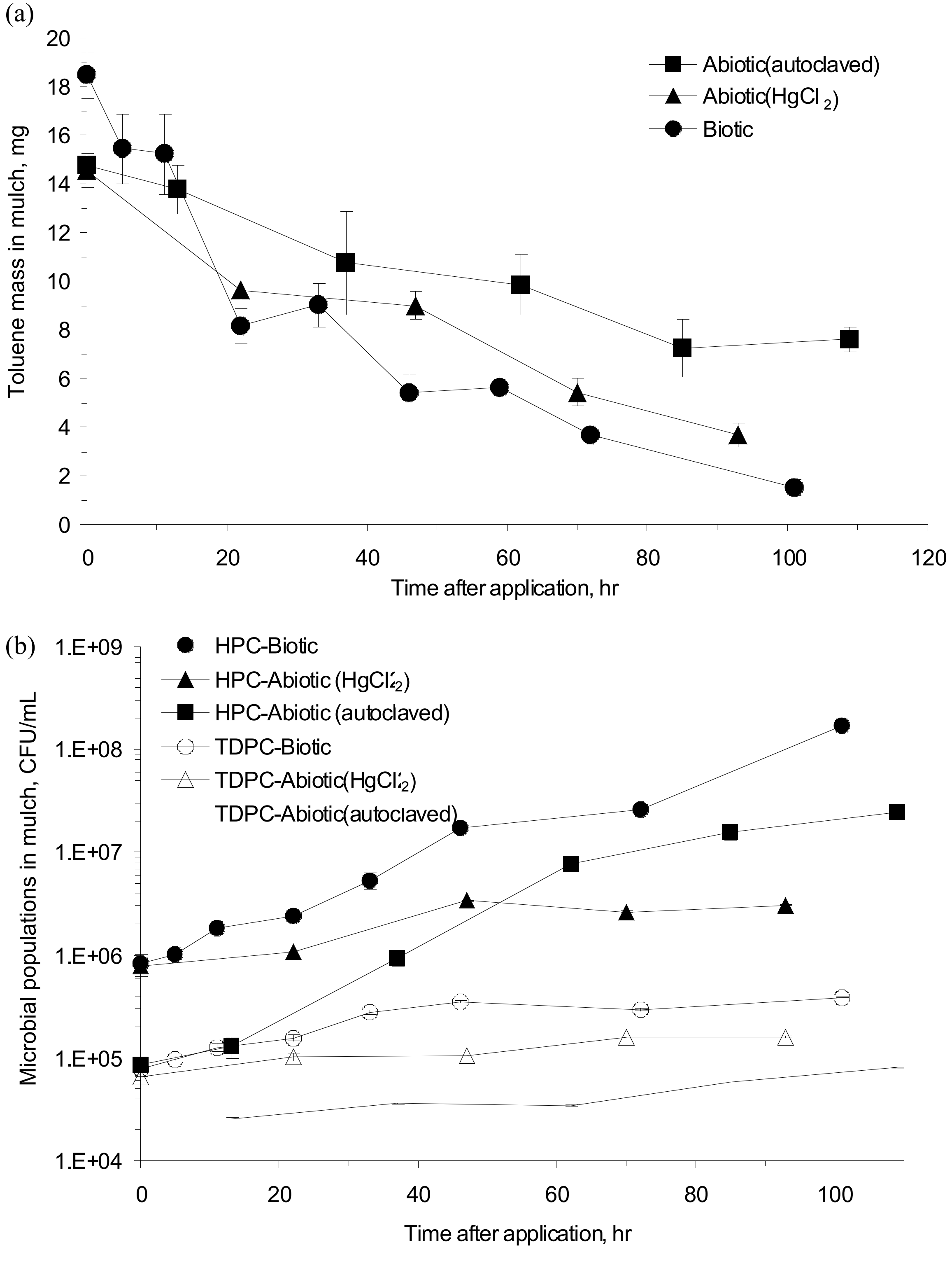

Figure 5. Microbial population change on toluene degradation: (a) Reduction of toluene in the mulch, and (b) Microbial growth based on total heterotrophic plate counts (HPC) and toluene-degrader plate counts (TDPC) in the mulch. Error bars represent the standard deviations.

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Evaluating the Influence of Diverse Riparian Leaf Litter Inputs on a Stream Food Web - Summer Student Project

Basic Information

Title:	Evaluating the Influence of Diverse Riparian Leaf Litter Inputs on a Stream Food Web - Summer Student Project
Project Number:	2001MD8B
Start Date:	5/1/2001
End Date:	9/1/2001
Funding Source:	104B
Congressional District:	5th Maryland
Research Category:	Biological Sciences
Focus Category:	Ecology, Conservation, Water Quality
Descriptors:	Riparian, Stream Ecology, Food Web, Invertebrates, Mesococms
Principal Investigators:	Allen Davis , Philip Kearney

Publication

EVALUATING THE INFLUENCE OF DIVERSE RIPARIAN LEAF LITTER INPUTS ON A STREAM FOOD WEB

Humans are altering the nature of our water resources at an alarming rate. One of the many strategies employed by environmental resource managers to attenuate this disturbance is to replant vegetation along stream margins. Establishing and conserving riparian vegetation serves many purposes. For example, root structure stabilizes stream banks, enhanced shading decreases the variation in water temperature, and autumn-shed leaf litter delivered to the stream provides food resources to benthic invertebrates. In fact, most stream ecosystems in North America rely heavily on this terrestrially-derived organic matter, and the invertebrates that feed on leaf litter account for a substantial portion of the food base of stream fishes. However, there are species-specific characteristics of riparian trees that make food available to detritivores differentially through time. Since it is known among ecologists that resource heterogeneity in general is related to high consumer feeding rates, stream invertebrate populations may respond positively to multi-species litter resources. Since riparian vegetation is the focus of many conservation and restoration efforts in streams (Sweeney, 1993; USDA Forest Service, 1996), the decisions made about what type of vegetation to protect or plant directly affects the level of resource heterogeneity that becomes available to aquatic food webs. **This research will test the hypothesis that increased heterogeneity in leaf litter will promote higher invertebrate abundance, and thus higher growth rates of stream fish.**

Many stream ecologists and resource managers assume that planting and protecting riparian vegetation directly enhances fish habitat by providing cover and enhancing habitat heterogeneity (e.g., log jams, pools, undercut banks; Schlosser, 1995), and thus fish production. There is little emphasis on what *type* of vegetation to plant, nor what groups of plant species together benefit the food web. Leaf litter becomes entrained by streambed substrates, after which invertebrates begin to colonize and degrade the leaf material. Stream fish forage across this "landscape" of patches, consuming the invertebrates on the streambed and in the leaf material (**Fig. 1**). If stream invertebrates respond positively to enhanced litter heterogeneity, then the expanded prey base may result in increased fish production. A high level of riparian plant diversity is one way the adjacent terrestrial habitat can enhance fish growth.

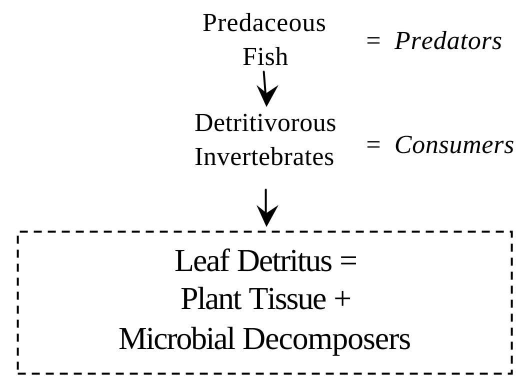

Figure 1. Summary of the trophic relationships and definitions of various components referred to in the text (*italics*).

SIGNIFICANCE

This work has important implications for applied ecology in that it relates riparian management and restoration decisions to stream food webs. By moving beyond the invertebrate community, I will touch on aspects of freshwater resources that are of more immediate concern to wildlife managers (e.g., fish production). The presence of woody vegetation in the riparian zone may be beneficial to stream fish by creating habitat and cover, decreasing variability in water temperatures, and stabilizing habitat structure (Schlosser, 1995). However, the extent to which individual species or groups of species are chosen for riparian planting has not been a priority for resource managers. Riparian diversity might be very important to fish production given that different leaf species vary in quality for stream invertebrate detritivores (i.e., that are prey for fish). The results of this research is intended to provide data that may ultimately guide how riparian restoration is done, by emphasizing the importance of riparian biodiversity as driver of food web function.

HYPOTHESIS & RATIONALE

Increases in leaf litter heterogeneity to aquatic food webs increases the abundance of invertebrate consumers and stream fish growth.

Ecologists know that resource heterogeneity can affect community structure (Naeem & Colwell, 1991), but the influence on consumer population dynamics is less studied. Variability in nutritional quality of plant tissue can stabilize temporal variability in herbivore feeding rates (Fox & Macauley, 1977) and possibly affect herbivore growth. There is evidence from terrestrial systems that the abundance and/or biomass (Blair et al., 1990; Keneko & Salamanca, 1999) of detritivorous invertebrates is higher when fed mixed-species vs. single-species litter. This is likely due to nutrient transfer among the different litter species by decomposer organisms (e.g., bacteria, fungi), promoting faster nutrient cycling and enhanced consumer growth (Taylor et al, 1989a). In aquatic systems, decomposition rate of leaf litter is species-specific and, therefore, the amount of edible detritus available to invertebrates varies among litter species (Webster & Benfield, 1986). Work I have done in the laboratory demonstrated that certain combinations of mixed-litter resources enhanced the growth of a common stream detritivore, while growth among single-species resources remains unchanged. Therefore, it is likely that resource heterogeneity (e.g., leaf species richness) may affect stream food webs by altering consumer abundance and/or biomass, and thus the availability of prey to higher trophic levels.

Litter consumption by invertebrates is a function of (1) when leaf material is available (Cummins et al., 1989), (2) leaf chemistry (Campbell & Fuchshuber, 1995; Findlay et al., 1996), and (3) microbial conditioning (Barlocher & Kendrick, 1975). In temperate ecosystems, leaf litter inputs vary through time in both quantity and species composition. There are known species-specific differences in the particular chemical characteristics of the leaves themselves (Webster & Benfield, 1986; Ostrofsky, 1993; Ostrofsky, 1997). The refractory:labile content (e.g., C:N, lignin:N) describes the “quality” of the leaf as a resource for microbial decomposers and consumers, and is directly related to litter decomposition rate (mass loss · time $^{-1}$; Melillo et al., 1982; Taylor et al., 1989b; Ostrofsky, 1997). Bacteria and fungi colonize freshly introduced leaf material, and begin to break the plant tissue down into a more palatable resource for consumers by degrading cellulose components and releasing tannins and phenols that are hard to digest (Barlocher & Kendrick, 1975). Invertebrate consumers use conditioned litter by feeding on both the microbial biomass *and* the plant tissue. Since the chemical attributes of a leaf control the decomposition process (and thus microbial biomass), the energy available to the consumers varies between leaf species (Herbst, 1982)**.**

Given the substantial temporal dynamics of allochthonous litter availability and decomposition, the consequence of multiple species of varying qualities being available has implications for consumers. Heterogeneous mixtures of leaf species can create a scenario where resource availability is more stable in time (Palmer et al., 2000a). In systems like streams where invertebrate abundance declines in response to reductions of allochthonous detritus (Richardson, 1991; Wallace et al., 1997), one can expect a positive response by the consumers to a stable resource base. Given this, I predict increases in leaf litter heterogeneity will increase both the abundance of invertebrates consumers, and thus fish growth.

EXPERIMENTAL APPROACH

I will use flow-through stock tanks (detailed in **Fig. 2a**) streamside to mimic riffle habitat (such tanks are routinely used successfully by stream ecologists, e.g. Peckarsky & McIntosh, 1998). I will create patches of leaf litter by enclosing leaf material collected from a local stream (the Middle Patuxent River) in coarse mesh bags, and securing them to the "streambed" in each of 30 mesocosms. These mesocosms are already built and in place at the University of Maryland's Agricultural Research Station (Clarkesville Facility). The mesocosms are lined with riffle sediments, with flow generated by a series of swimming pool pumps drawing water from a common location in the stream. Circulating flow is maintained by a center baffle and alternating nozzles, with flow velocity controlled by a valve for each tank. Screen covers are fitted on each tank to match natural light levels for a forested stream and inhibit additional windblown litter. Work this past year has shown that invertebrates readily colonize the mesocosm via water pumped from the stream, while larger predators (e.g., fish) are excluded. Photos of the mesocosm facility are available online at www.wam.umd.edu/~cmswan/projects.html.

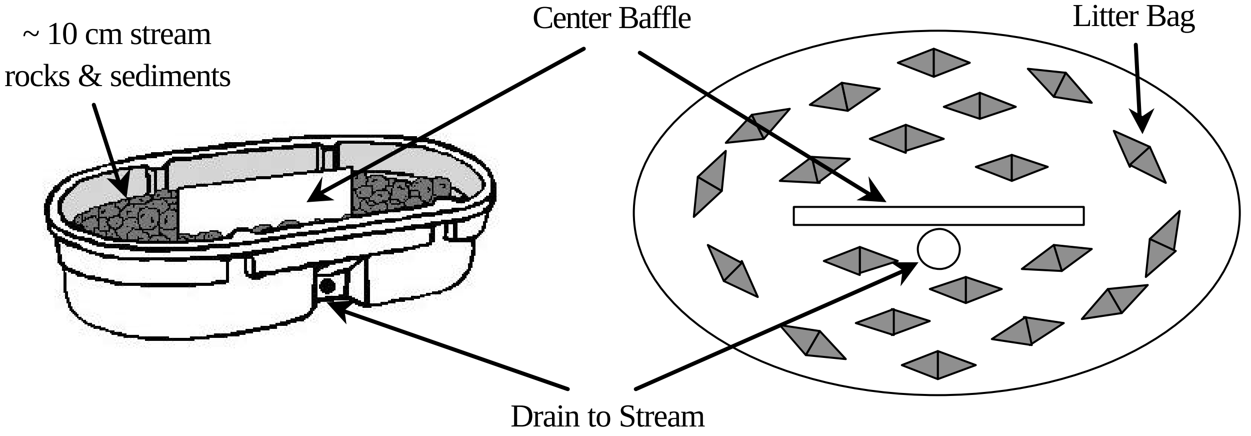

Figure 2. A. *(left)* Stock tank (132 cm L x 78 cm W x 30 cm D, ~1 m^2) to be used as a stream riffle mesocosm. Water will be delivered via a swimming pool pump drawing water from the river, and delivered with alternating nozzles to create circular flow. Flow direction is maintained by a center baffle. Water depth will be maintained at 5-10 cm with a standpipe. **B.** (*right*) Top-view schematic of proposed distribution of treatments as litter bags within the mesocosms.

There will be 10 litter treatments; 5 single-species treatments, and 5 four-species treatments (detailed in **Table 1**), and each will be replicated three times to utilize all 30 tanks. Litter for each treatment will be weighed out into 60-500 mg litter bags (20 bags/tank). Care will be taken to hold the *amount* of litter constant (20 x 500 mg = 25 g per tank; four-species treatments will have 500 mg/4 = 125 mg of each leaf species in each leaf pack), to isolate the effect of litter *heterogeneity.* The litter bags will constitute the patches the invertebrates will colonize, which have been used successfully for the same purpose in numerous stream studies examining invertebrate responses to leaf litter (e.g., Palmer et al., 2000b). Bags will be positioned so they are uniformly distributed across the tank bottom (**Fig. 2b**). The pumps will be turned on and the litter bags applied in early-summer (June, 2001) and allowed to colonize with stream invertebrates for two weeks. After this initial colonization, a single litter bag will be sampled from each tank to estimate initial invertebrate abundance, then a single tessellated darter (*Etheostoma olmstedi*, Family: Percidae), a common invertivore in the Middle Patuxent, will be measured for length and introduced to each tank. The experiment will be maintained for six more weeks, sampling a single leaf pack each week for invertebrate abundance. On the final sample date, each fish will be collected from the tanks, and length determined to estimate growth rate.

Table 1. Proposed litter treatments. Each Litter Species Combination will be applied to n=3 tanks, for a total of 30 tanks.

Heterogeneity Level (# Leaf Species)	Litter Species Combination
1	Boxelder
	Sycamore
	Slippery Elm
	Silver Maple
	Black Willow
4	Boxelder + Sycamore + Slippery Elm + Silver Maple
	Boxelder + Sycamore + Slippery Elm + Black Willow
	Boxelder + Sycamore + Silver Maple + Black Willow
	Boxelder + Slippery Elm + Silver Maple + Black Willow
	Sycamore + Slippery Elm + Silver Maple + Black Willow

Analysis: Invertebrate abundance will be analyzed with a nested ANCOVA, with Day Sampled as the covariate. The effect of Litter Species Combination will be tested as a nested effect within level of Litter Heterogeneity (1 vs 4; **Table 1**). Fish growth rate will be estimated as (initial length - final length / days in mesocosm). Fish growth will be analyzed with a nested ANOVA, similar to the invertebrate data, excluding the effect of time.

Summary of Results

Studies of litter decomposition in aquatic and terrestrial ecosystems have revealed that species-specific differences in litter chemistry mediate complex interactions between community and ecosystem processes. Litter species with refractory chemical attributes and low nutrient concentrations tend to slow microbial activity, alter decomposition rates, and adversely affect the growth and abundance of detritivorous invertebrates. While research in terrestrial ecosystems has revealed that mixing litter can further alter these patterns and processes, often in non-additive ways, such studies in aquatic ecosystems remain rare. We performed a field experiment where we placed packs of leaves from five species of common riparian trees as single-species and four-species mixtures in a piedmont stream. We documented strong differences among single species treatments in C processing, N accumulation, microbial respiration, decomposition rates, and invertebrate abundance. Among mixed treatments, N accumulation rates were greater than could be predicted from averaging single-species estimates in two of our mixed treatments. Furthermore, decomposition rates were slower than predicted in one instance, and microbial respiration was lower than predicted in another. Certain species combinations, especially those with highly labile, high N attributes, resulted in higher than expected estimates than would be predicted by simply averaging single-species effects, while refractory species in mixtures tended to lower estimates. Given the extent to which riparian habitats are being altered, it is evident that not just the number, but also the composition of tree species present are important to stream ecosystem properties.

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Information Transfer Program

The Center sponsored a lecture series on Pharmaceuticals in the Environment during the spring semester of 2001. A distinguished group of speakers from EPA, FDA, CDC, Johns Hopkins University, Institut for Water Research and Technology, Wiesbaden, Germany, Bristol-Myers Squibb and Smith Kline Beecham gave presentations. The course (CHEM 729) was open to the scientific community in the Washington area and University faculty. The course was also televised to two Universities in the University System of Maryland, i.e., Frostburg University and University of Maryland, Baltimore County. Dr. Britt Erickson, Associate Editor, Environmental Science and Technology, American Chemical Society, attended the lectures. We supplied her with all of the taped lectures and from this material she wrote the feature article on "Analyzing the Ignored Environmental Contaminants" ES&T, April 1, 2002, 140-145.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	0	0	0	3
Masters	5	0	0	0	5
Ph.D.	0	0	0	0	0
Post-Doc.	0	0	0	0	0
Total	8	0	0	0	8

Notable Awards and Achievements

Publications from Prior Projects

1. Kim, H., E.A. Seagren, A.P. Davis. 2000 Engineered Bioretention for Removal of Nitrate from Storm water Runoff. In Water Environment Federation 73rd Annual Conference and Exposition, WEFTEC North America. 2000
2. Rock, M.L. B.R. James, G.R. Helz. 2001 Hydrogen Peroxide Effects 0n Chromium Oxidation State and Solubility in Four Diverse, Chromium-Enriched Soils. Environ. Sci & Technol. 35, 4054-4059
3. Davis, A. P., and Matthew Burns. 1999 Evaluation of Lead Concentration in Runoff from Painted Structures. Water Research 33, 2949-2958.
4. Kim, H. , Seagren, E.A. , and Davis, A.P. "Engineered Bioretention for Removal of Nitrate from Stormwater Runoff," Water Environ. Res., accepted for publication, December 2002.
5. Baer, N.A. and W.O. Lamp. 2001.Macroinvertebrate community structure vs. leaf decomposition: a comparison across two Maryland coastal plain streams. Bulletin of the North American Benthological Society. 18(1):232.
6. Baer, N.A. and W.O. Lamp. 2001.Macroinvertebrate community structure vs. leaf decomposition: a comparison across two Maryland coastal plain streams. Chesapeake Bay Conference to be held September 23-26, 2002.