Name of Organization: Ohio State University

Type of Organization: College or University

Contact Information: Dr. Yu-Ping Chin

Department of Geological Sciences

125 S. Oval Mall

Columbus OH 43210

Phone: (614) 292 - 6953 **Extension:**

Fax: (614) 292 - 7688

E-Mail: yo@geology.ohio-state.edu

Project Title: Photolytic Destruction of Pesticides in Coastal Wetlands

Project Category: Pollution Prevention and Reduction - BNS

Rank by Organization (if applicable): 0

Total Funding Requested ($): 106,817 **Project Duration:** 2 Years

Abstract:

Coastal Great Lakes wetlands are highly productive and biologically diverse ecosystems than can treat large quantities of excess suspended solids, contaminants, and nutrients from runoff. Some of the diverse number and quantity of chemical constituents that enter wetlands are able to participate in the photo-transformation of potentially recalcitrant agricultural pesticides (e.g., atrazine and alachlor). The resulting indirect photolysis of pesticides by photosensitizers can be a major removal pathway for environmental contaminants in sunlit wetland surface waters, but remarkably this process has received little attention to date. We propose to study the fate of atrazine and alachlor to assess the role of indirect photolysis in wetlands. The specific photosensitizers that will be examined are nitrate and dissolved organic matter(DOM). These species when photolyzed are capable of forming radicals that can degrade pesticides. Nitrate levels, while low in most surface waters has been found up to mM quantities in wetlands. Natural dissolved organic matter is known to produce a number of reactive phototransient species in the presence of sunlight. Specific objectives to be addressed will include:

1. Study and characterize the environmental factors responsible for indirect photolysis of pesticides at two field sites (Old Woman Creek in Ohio and Metzgers Marsh in NE Ohio adjacent to Lake Erie) ;
2. Determine the pathways and kinetics transformation for atrazine and alachlor over a range of conditions (nitrate, DOM, pH, light intensity, etc.);
3. Identify the photoproducts formed and their fate in the wetlands and in Lake Erie; and
4. Provide a more detailed understanding of how specific hydrogeochemical processes control pesticide fate and release to the Great Lakes from coastal wetlands.

Geographic Areas Affected by the Project

States:

- [ ] Illinois
- [ ] Indiana
- [ ] Michigan
- [ ] Minnesota
- [ ] New York
- [ ] Pennsylvania
- [ ] Wisconsin
- [x] Ohio

Lakes:

- [ ] Superior
- [ ] Huron
- [ ] Michigan
- [x] Erie
- [ ] Ontario
- [ ] All Lakes

Geographic Initiatives:

- [ ] Greater Chicago
- [x] NE Ohio
- [ ] NW Indiana
- [ ] SE Michigan
- [ ] Lake St. Clair

Primary Affected Area of Concern: Black River, OH

Other Affected Areas of Concern: Applicable to all AOCs and areas of the Great Lakes that receive substantial nonpoint source agricultural pesticide inputs.

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

Agriculture is the prevalent land use application in the Great Lakes Basin. Nonpoint source (NPS) pollution from surface runoff contaminated with agrochemicals has been targeted as the most widespread water quality problem in the United States. Four times more waters were reported to be polluted from agricultural chemical runoff than from municipal sources (U.S. EPA, 1992). A long-term study that monitored pesticide concentrations in seven Lake Erie tributaries in Ohio from 1983-1991 indicated that monthly average concentrations of atrazine and alachlor generally exceeded maximum contaminant levels (MCLs) in at least one month following herbicide application (Richards and Baker, 1993). Thus, the significant reduction of NPS pesticides/herbicides prior to discharge to the Great Lakes through effective low-cost technologies would be highly desirable.

NPS contamination is difficult to control because it may be distributed across large areas of a watershed. Wetlands, however, may provide a means of managing water quality since the hydrology of a watershed will often result in the collection of water from diffuse sources into basins before final discharge to the Great Lakes. Typically, water quality improves as water moves through a wetland. Wetlands can also remove contaminants including some synthetic organic compounds and there has been increased interest in using them for this purpose (Duda, 1993; Deboer and Linstedt, 1985). To date the physical and chemical mechanisms controlling the fate of organic pollutants are poorly understood. For example many herbicides in current use are not readily sorbed by particles (e.g., atrazine), and subsequently are not easily removed by sedimentation processes. Nonetheless, a number of pesticides in Great Lakes coastal wetlands (such as Old Woman's Creek) are being removed through chemical transformations (Kolpin and Kahlkoff, 1993; Krieger, personal communication).

Sunlight induced reactions may contribute to the chemical transformation of organic pollutants. The large surface areas and shallow waters of coastal Great Lakes wetlands provide a favorable environment for photoreactions as evidenced by the high primary productivity observed in most wetlands. Recent evidence suggests that organic pollutants may react through both direct and indirect photochemical pathways. Many wetlands are eutrophic (high productivity reflective of a good exposure to sunlight) and thus, contain higher amounts of dissolved organic matter (DOM) than other water bodies (lakes and rivers). Moreover, seasonal pulses of nitrate (up to 1 mM) can also occur. Both DOM and nitrate has been shown to catalyze (i.e., photosensitize) the degradation of pesticides and herbicides by sunlight (Canonica et. al, 1995; Chiron et. al., 1995; Hoigne', 1990; Minero, et al., 1992; Faust and Zepp, 1993; Torrents et al., 1997). The degree to which this can occur is highly dependent upon the composition and amount of photosensitizers present. Much of the DOM in natural waters are comprised of decomposed organic matter and/or extracellular products as well as amorphous humic substances which may contain a variety of chromophoric functional groups that absorb sunlight. Work done in our lab has shown significant enhancement of carbaryl photodegradation in the presence of DOM (relative to DOM-free controls) isolated from a coastal wetland adjacent to Lake Erie (Old Woman Creek NERR). Moreover when nitrate levels were high (0.1 to 1 mM) our degradation rates increased even more significantly. Therefore, due to (i) the abundance of DOM, nitrate, and sunlight in wetland surface waters and (ii) the evidence that these two substances act as a source of photochemically-generated, reactive intermediates, we believe that wetland surface waters could play a significant role in the photochemical transformation of agriculturally derived organic contaminants.

Proposed Work Outcome:

Objectives:

The specific objectives of the proposed research are as follows:

1. Study and characterize the environmental factors (irradiance, nitrate concentration, DOM concentration and composition) responsible for the direct and indirect photolysis of alachlor and atrazine at two field sites (Old Woman Creek in Ohio and Metzgers Marsh in NE Ohio adjacent to Lake Erie);

2. Determine the pathways and kinetics (i.e., speed) of transformation for atrazine and alachlor over a range of conditions (nitrate, DOM, pH, light intensity, etc.);

3. Perform univariate, multivariate, and/or time-series analysis (as appropriate) on the experimental results of objectives to obtain a more detailed understanding of how specific hydrogeochemical processes in wetlands control pesticide degradation; and

4. Identify the photoproducts formed and their fate in the wetlands and in Lake Erie.

Methodology

Water samples, from NOAA's Old Woman's Creek Estuarine Reserve and a wetland that is slated for restoration (Metzger's Marsh), will be collected seasonally at varying depths using a Fultz positive displacement pump. Samples will be analyzed for nitrate, total organic carbon, UV/VIS absorbance, and fluorescence. These later analyses will elucidate bulk water DOM properties. Larger volumes of surface water will also be collected for consolidation and ultrafiltration (using a crossflow ultrafiltration device) to concentrate the organic materials. The concentrated materials will be lyophilized and analyzed by 13C-NMR, FTIR, and elemental analyses to determine the DOM composition. Finally, we will quantify the amount and reactivity of the principal reactants (specifically, excited triplet states and hydroxide radicals that may form from the absorption of sunlight by DOM and/or nitrate) using chemical probes and trapping agents (Hoigne, 1990).

Photolytic degradation experiments will be conducted using alachlor and atrazine. The photolytic degradation of these substances will be examined in filtered surface waters taken from our wetland sites in Pyrex culture tubes. Clean controls (buffered water with no DOM and nitrate) will be run concurrently. Test tubes will be sacrificed periodically during the irradiation and assayed by HPLC for the parent compound and any detectable derivatives. Photochemical experiments will be conducted using a merry-go-round reactor equipped with a Xenon lamp housed in a borosilicate immersion well which mimics sunlight. Light intensity will be measured using chemical actinometry. Sampling will be comprised of withdrawing a small aliquot from each vial followed by either direct aqueous injection into our HPLC or an intermediate extraction followed by gas chromatography (for alachlor). The disappearance of the analytes as well as the appearance of the daughter compounds will be followed. Positive identification of the daughter species will be performed by either collecting aliquots from the HPLC or the performance of batch reactions and subsequent extraction and assay by GC/MS analyses. Polar derivatives will be identified and quantified by LC/MS.

Outcome:

The results of the proposed research will hopefully demonstrate that wetlands in conjunction with sunlight will prove to be an effective and passive means of treating pesticides generated from agricultural practices. More importantly it will identify the constiuents resposible for pesticide photodegradation and ascertain their effectiveness as photosensitizers. If such a technology proves viable this would encourage the preservation of existing coastal wetlands and the construction of new wetlands. Given the rapid disappearance of wetlands in the Great Lakes basin, the project will provide an impetus to preserve and utilize these unique ecosystems to treat pesticides associated with agriculture in the Great Lakes Basin.

References

Richards, R.P., Baker, D.B. (1993) Environ. Toxicol.Chem. 12,13.
Faust B. Zepp R. (1993) Env. Sci. Technol., 27, 2517.
Hoigne J (1990)Aquatic Chemical Kinetics p. 43
Kolpin D., Kalkhoff S. (1993) Env. Sci. Technol., 27, 134.
Chiron, S. Abian, J. Ferrar, M. Sanches-Baes, F. Messguer, A. Barcelo, D. (1995) Environmental Toxicology and Chemistry, 14, 1287-1298.
Canonica, S. Jans, U. Stemmler, K. HoignÈ, J. (1995) Environ. Sci. Technol., 29, 1822-1831.

Duda, A.M. (1993) Wat. Sci. Tech, 28, 1-11.
DeBoer, J. Linstedt, K.D. (1985) Advances in Water Reuse Applications. Water Res., 19, 1455-1461.
U.S. Environmental Protection Agency (1992). 1990 National Water Quality Inventory-305(b) Report to Congress. Washinton.
Minero C., Pramauro E. Pelizetti E., Dolci M., Marchesini A., Chemosphere , 24, 1597.
Torrents A, Anderson b., Biboulian S., Johnson W., Hapeman C. (1997) Env. Sci. Technol., 31, 1476.

Project Milestones:	**Dates:**
Collect samples from the OWC site.	09/2000
Isolation of DOM consituents	10/2000
Solar simulator experiments	01/2001
Field experiments at OWC	06/2001
Collect samples at Metzgers site.	09/2001
Solar simulator experiments	12/2001
Transient trapping experiments	06/2002
Write report/papers and present data	08/2002

☒ Project Addresses Environmental Justice

If So, Description of How:

This project will comply with the guidelines of environmental justice in that if proven succesful will result in an improvement in coastal Great Lakes water quality to all inhabitants that utilizes coastal resources for both recreation and potable water supplies. The passive technology proposed will also aid those communities that may experience episodic increases in pesticide levels, but lack the means to properly treat their drinking water for these events. The construction of wetlands upstream of their water intake may provide an inexpensive alternative to insure that pesticides never exceed MCLs in potable water.

☒ Project Addresses Education/Outreach

If So, Description of How:

The proposal will fund one graduate student and we will set-up a summer internship for high school students to aid the graduate student and P.I. on the project. The internship will be actively recruited high school students from under-represented minorities. This will hopefully provide the selected individual with an experience that will attract him/her to the environmental sciences as a career.

In addition to our education component, we will actively be involve in the education of interested parties that may benefit from this technology. These include coastal communities in the Lake Erie basin, farmers using the watershed resources, and government officials responsible for the stewardship of these ecosystems. This will be accomplished through Extension programs at Ohio State and the Ohio Sea Grant Program, and would involve the production of pamphlets for general distribution, a website that can be accessed through OSU's extension program, and informal town meetings in communities that may be affected by NPS pollution .

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	49,980	0
Fringe:	3,759	0
Travel:	2,500	0
Equipment:	0	0
Supplies:	16,500	0
Contracts:	0	0
Construction:	0	0
Other:	0	18,000
Total Direct Costs:	72,739	18,000
Indirect Costs:	34,078	0
Total:	106,817	18,000
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

A proposal to study constructed wetlands (using the OSU Olentangy Wetland Park) on photolytic processes is being considered by the USDA NRI Program. The amounts for this proposal is $248,000 of which approximately half will be committed to my research group.

Description of Collaboration/Community Based Support:

Ohio Sea Grant Extension Program (Dr. Jeff Reutter: Director) We will use Ohio Sea Grant's Extension offices as a means for outreach and data dissemination to the general public.

Old Woman Creek NERR (Dr. David Klarer: Science Director) We will use the facilities at Old Woman Creek to conduct our research.