

Advances in Pesticide Environmental Fate and Exposure Assessments

PAMELA J. RICE,^{*,†} PATRICIA J. RICE,[§] ELLEN L. ARTHUR,[#] AND
 ALDOS C. BAREFOOT[⊥]

Agricultural Research Service, U.S. Department of Agriculture, University of Minnesota, 1991 Upper Buford Circle, St. Paul, Minnesota 55108; BASF Corporation, 26 Davis Drive, P.O. Box 13528, Research Triangle Park, North Carolina 27709-3528; Bayer CropScience, 17745 South Metcalf Avenue, Stilwell, Kansas 66085; and DuPont Crop Protection, Stine-Haskell Research Center, Newark, Delaware 19714

Globalization of markets and the growing world population increase threats of invasive and exotic species and place greater demands on food and fiber production. Pest management in both agricultural and nonagricultural settings employs established practices and new biological, chemical, and management technologies. Pesticides are an essential tool in integrated pest management. Without pesticides a significant percentage of food and fiber crops would be lost, infectious diseases would increase, and valuable native habitats would be devastated. Therefore, it is important to understand the environmental fate of pesticides and assess their potential exposure and associated risks to human health and the environment. This paper summarizes the *Advances in Pesticide Environmental Fate and Exposure Assessment* symposium held at the 231st National Meeting of the American Chemical Society (Atlanta, GA, 2006). The focus of the symposium was to provide current information on advances in pesticide environmental fate and exposure assessments. Thirty papers were presented on advances ranging from subcellular processes to watershed-scale studies on topics including chemical degradation, sorption, and transport; improved methodologies; use of modeling and predictive tools; exposure assessment; and treatment and remediation. This information is necessary to develop more effective pesticide use and management practices, to better understand pesticide fate and associated exposures and risks, to develop mitigation and remediation strategies, and to establish sound science-based regulations.

KEYWORDS: Pesticide; degradation; catabolism; sorption; transport; runoff; modeling; predictive tools; exposure assessment; treatment; remediation

INTRODUCTION

The U.S. Census Bureau projects the world population will reach 9.4 billion by the year 2050 with 419 million people residing in the United States (1). The growing population and greater requirements for food and fiber place increased pressures on agricultural production and the need for effective pest management. Globalization of markets and trading have also increased demands for pest management as invasive and exotic species threaten native habitats and indigenous organisms and further challenge food and fiber production (2, 3).

Pest management in both agricultural and nonagricultural settings employs established practices and new technologies to ensure an abundant food supply and control harmful and

nuisance pests. Although new biological, chemical, and management technologies are continually being developed to provide more sustainable production alternatives, it is expected the use of pesticides will continue to be an essential tool in integrated pest management. Pesticide use in the United States exceeds 2 billion kilograms annually with approximately 77% accounting for agricultural usage (4). Without pesticides a significant percentage of food and fiber crops would be lost, infectious diseases would increase, and valuable native habitats would be devastated by invasive species.

Pesticides are biologically active compounds designed to interfere with metabolic processes (5, 6). Therefore, it is important to understand the environmental fate of pesticides and assess their potential exposure and associated risks to human health and the environment. The application of pesticides to targeted areas inevitably results in the transport of a portion of these chemicals and their degradation products to surrounding nontarget areas. The detection of pesticides and their degradation products in soil (7, 8), water (9, 10), and air (11, 12) and reported

* Corresponding author [telephone (612) 624-9210; fax (651) 649-5175; e-mail pamelarice@ars.usda.gov].

† U.S. Department of Agriculture.

§ BASF Corp.

Bayer CropScience.

⊥ DuPont Crop Protection.

adverse effects of pesticides to nontarget organisms and ecosystems at environmentally relevant levels (13–15) have invoked public concern. Understanding the physical, chemical, and biological processes that control the behavior of pesticides in the environment, and their effects on target and nontarget species, is imperative for improving our ability to identify and develop pest management strategies that are effective yet have minimal adverse impacts to human health and the environment. This paper summarizes a symposium held at the 231st National Meeting of the American Chemical Society to examine advances in pesticide environmental fate and exposure assessments. Such information is necessary to develop more effective pesticide use and management practices, to better understand pesticide fate and associated exposures and risks, to develop mitigation and remediation strategies, and to establish sound science-based regulations.

DISSIPATION, DEGRADATION, AND SORPTION OF CHEMICALS

Many advances have been made in assessing the environmental fate of organic compounds over the past decade. With the ability to sequence genes, we can now understand the mechanisms associated with microbial degradation of man-made chemicals. Evaluation of degradative capabilities of microorganisms under various conditions can allow for optimization of remediation strategies. Although we have achieved a better understanding of degradation pathways and degradation mechanisms for many organic compounds, we have also gained insight into possible mechanisms of formation of naturally occurring compounds, such as perchlorate. Optimization of study designs has resulted in the ability to assess the fate of new formulations such as seed treatments, as well as to obtain paired data from aerobic soil metabolism and sorption–desorption tests. The data obtained from such studies can be used in models to evaluate expected environmental concentrations.

Sorption–Desorption. The most important process affecting the transport of pesticides through soil is sorption–desorption behavior because it controls the amount of pesticide available for transport (16). The traditional laboratory method of determining the leaching potential of a pesticide has been the use of the batch slurry equilibrium adsorption desorption testing. The resulting sorption coefficients are used as input parameters into pesticide transport models. Often the leaching potential of a pesticide is overpredicted when sorption coefficients obtained from the batch slurry method are used, which may be related to incomplete phase separation—for example, for strongly sorbed compounds such as pyrethroids—or to the high margin of error of the sorption coefficient due to errors in concentration measurement and degradation of weakly binding or readily degraded pesticides.

To better handle the issue of biphasic degradation and nonequilibrium sorption, researchers at this symposium presented a new study design which combines two sets of experiments that would allow for the simultaneous generation of both degradation and aged sorption parameters. For this approach, soil samples are incubated aerobically in the dark at standard temperature and constant field moisture, and at various intervals, samples are sacrificed and extracted sequentially with a CaCl_2 solution followed by organic solvents. The amount of pesticide extracted from soil using CaCl_2 provides an indication of the amount that can desorb from soil, whereas the solvent extraction provides an indication of pesticide which is more strongly bound or sorbed. The resulting degradation rate and sorption coefficient data obtained from this test can be used as input parameters for

a two-compartment kinetic sorption model to estimate pesticide environmental concentrations in groundwater (17).

Synthetic pyrethroids, a widely used class of insecticides in both agricultural and urban environments, bind strongly to soil. This class of compounds has traditionally been classified as immobile in the environment (18). Studies have shown that pyrethroids may move in runoff to surface water streams (19–23). Once reaching surface water, pyrethroids primarily associate with bed sediment, which is a potential water quality concern from the standpoint of sediment toxicity (21, 22). Pyrethroids bind readily to dissolved organic matter, and determination of sorptive behavior is difficult using the batch slurry equilibrium method because this method can be used only to determine the partition of a chemical between solid and aqueous phases. The partitioning of an organic compound between dissolved organic matter and water is more difficult to measure, as the two phases are not easily separated. Researchers presented a method that uses solid-phase microextraction (SPME) for detecting the freely dissolved chemical concentration (24). They tested this method for eight pyrethroid insecticides in two sediments. The sorption coefficient obtained with SPME was 2–34 times greater than that determined using the conventional solvent extraction method. The use of a selective method such as SPME to detect the freely dissolved chemical concentration may offer significant improvements in the determination of sorption coefficients for strongly hydrophobic pesticides.

Leaching/Infiltration. Determining the mobility of a slow-release active ingredient applied as a seed treatment was investigated in soil columns in the greenhouse (25). Pesticide-treated seeds are increasingly being formulated for reducing environmental exposure (26–29). Many of the pesticides being used for seed treatment exhibit time-dependent sorption (30). Researchers designed a specialized column study that was conducted in the greenhouse over the normal life cycle of the corn plant. At the completion of the study, a cumulative 0.12% of the applied radioactivity moved through the 60 cm soil columns and was detected in the leachate. Ninety-six percent of the pesticide residues remained in the top 15 cm of soil. The amount of radioactivity in the leachate declined over time, indicating that the remaining residues became more tightly bound to the soil, thus reducing the potential for additional residues leaching into groundwater. Results of the column leaching study were modeled using the Pesticide Emission Assessment at Regional and Local scales (PEARL), a one-dimensional (vertical) model that simulates physical, chemical, and biological processes of an agricultural crop production system (31). The PEARL model is capable of modeling both instantaneous equilibrium and kinetic sorption using a linear two-site sorption model. The model was evaluated on the basis of soil and leachate concentrations monitored throughout the growing season of the plant. Measured concentrations were compared to model predictions for two scenarios: one assuming equilibrium sorption by specification of an organic carbon sorption coefficient and another assuming kinetic sorption by specifying a fraction of sorption sites undergoing kinetic sorption and the rate constant for desorption. With the scenario of instantaneous equilibrium, overprediction of the movement of peak pesticide concentrations in the profile resulted. With the scenario of sorption kinetics, the predicted movement of the compound in the soil profile was more in line with what was observed in the study. The combination of the soil column study and subsequent PEARL modeling shows that exposure assessments based only on the pesticide half-life and distribution coefficient alone result in overestimation of pesticide leaching

potential for compounds that exhibit time-dependent sorption characteristics.

While advances have been made in the laboratory to define appropriate input parameters to transport models to predict the mobility of pesticides in the environment, field dissipation studies provide a mechanism for empirically determining the degradation and mobility of pesticides through the soil profile. Researchers presented work on a two-year field dissipation study for isoxaflutole, a pre-emergence corn herbicide, which rapidly converts to its active diketonitrile degradate, DKN. The study was conducted in three soil types (sandy loam, loam, and clay loam) in west central Minnesota to indicate the rate at which isoxaflutole/DKN dissipates under the relatively cool, wet soil conditions typical of the northern Corn Belt. Separate plots were treated with isoxaflutole and potassium bromide, a nonsorbed, non-degraded tracer. Soil cores were collected to 1 m depth and sectioned into 0–10, 10–20, 20–40, 40–60, and 60–100 cm increments; bromide or herbicide concentration was measured at each depth. Leaching of both tracer and herbicide beyond 40 cm was observed. These results will provide information to aid in the development of best management practices for this herbicide (32).

Understanding and Enhancing Contaminant Degradation: Tools for Remediation. The intensive application of pesticides in modern agriculture to ensure production quantity and quality has resulted in contamination in soil, surface water, and groundwater by some heavily used pesticides. The remediation of contaminated soil is more complicated than that of contaminated water because the many components of soil can interact with the treatment chemicals. Anodic Fenton treatment (AFT) has been shown to be a promising technology in pesticide wastewater treatment. However, no research has been conducted on the AFT application to contaminated soils. The principal mechanisms and kinetics of Fenton-like reactions in simple and well-characterized aqueous systems have been consistently well documented. In contrast to aqueous systems, soils are complex, heterogeneous, and site-specific media. Due to the complexity, variety, and uncertainty of the soil matrix, the mechanisms and reaction kinetics of Fenton-like processes in soil have not been well understood, which hinders the application and improvement of remediation technologies. Researchers studied the applicability of this efficient, fast, and low-cost technology to help optimize the treatment conditions that must be used in contaminated soil to make it effective (33). In their study, the pesticide degradation kinetics of AFT in a soil slurry were investigated for the first time and were found to follow a two-stage kinetic model. During the early stage of 2,4-D degradation (the first 4–5 min), experimental data follow a pseudo-first-order kinetic model. In the later stage (i.e., after 6 min), the AFT kinetic model provides a better fit. The effects of initial 2,4-D concentration, Fe^{2+} delivery rate, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, humic acid concentration, and pH on the degradation kinetics have also been studied. Correlations between various experimental conditions and reaction rate constants and/or Fe^{2+}/OH lifetimes were developed, which could provide useful tools in the future treatment of pesticide-contaminated soils by AFT (34).

Formetanate hydrochloride is a bifunctional insecticide with high solubility and toxicity and has the potential to move in aqueous environments. To facilitate the design of more specific remediation technology for formetanate-contaminated surface water, researchers studied the relative stability of the formamidine and carbamate groups of this compound under various conditions. They found that the formamidine group is more labile than the carbamate group under strongly basic conditions,

as well as under predetermined field conditions, with a half-life of this group determined to be 3.9 h under strongly basic conditions (pH 12.6) and 14.4 h under mildly basic conditions (pH 7.6). In contrast, they found that the longevity of the carbamate group may exceed 6 months due to its resistance to base-promoted degradation. The relative stability of the formamidine and carbamate groups in this compound can be used to predict the identity of its degradation products in water. The results of this work may be used in the design of more specific remediation technology for formetanate-contaminated surface water. Currently, agricultural runoff laced with formetanate hydrochloride can be decontaminated via heterogeneous photocatalytic degradation with titanium oxide catalysts (35). The efficiency of this and other methods can be greatly enhanced by specifically targeting known byproducts such as *m*-formamidophenylmethylcarbamate. Details of this research are found in subsequent papers (36, 37).

Perchlorate is manufactured in large quantities as ammonium perchlorate, primarily for use as an oxidizer in solid rocket propellants. It is also used in fireworks, batteries, and automobile air bags. It occurs naturally in small concentrations in nitrate deposits in Chile and has been found in fertilizers derived from these deposits but not in other fertilizers (38–40). It has also been observed at low concentrations in surface water and groundwater in the southwestern United States distant from industrial sources. Studies were conducted using soils to determine if perchlorate could be formed when dry chloride salts were exposed to sunlight and laboratory UV light in the presence of desert soils and titanium oxide (41). Soils were obtained from Death Valley and Block Rock Desert and contained naturally occurring perchlorate at 29 and 16 $\mu\text{g}/\text{kg}$, respectively. Existing perchlorate was removed by washing soil. Additional chloride was added, and soils were exposed to sunlight and UV for 1–4 months. Perchlorate was generated in both sunlight and ultraviolet light on the soils (<4–29 $\mu\text{g}/\text{kg}$). Higher amounts were generated on titanium dioxide. The mechanism proposed for formation is a stepwise oxidation of chloride. Their data suggest a potential mechanism for natural generation of perchlorate on soil in the desert southwest.

Water-monitoring programs have shown that pesticides are found in surface water and groundwater (42, 43). The water in these monitoring programs, however, is raw water, which has not gone through any drinking water treatment processes. Drinking water for the majority of the U.S. population is treated. Exposure to pesticide residues via drinking water is a critical component of human risk assessments performed for registration or re-registration of active ingredients with the U.S. EPA. A general strategy was utilized by Bayer CropScience to determine the fate of pesticides in laboratory studies that mimic the drinking water treatment processes (44). The effects of flocculation, sedimentation, disinfection by chlorination, and treatment with activated carbon were determined using radiolabeled pesticides. Degradation of the parent compound and formation of degradates were determined for an experimental compound. Whereas the parent compound was stable in untreated raw water, it was completely degraded upon chlorination of the water. Powdered activated carbon removed the majority of the pesticide residues. Degradates formed were a mixture of small molecular weight acids of no toxicological concern. The effect of drinking water treatment on agrochemicals is an important issue. Laboratory-scale tests can be very useful in determining the effects of the various treatment processes. Additionally, the use of radiolabeled active ingredients will enable measurement of the formation of degradation products during these treatment processes.

Understanding Microbial Degradation of Pesticides: Tools for Bioremediation. Offsite movement of pesticides to surface water and groundwater is a major environmental concern. Atrazine, a herbicide that has been widely used over the past 30 years, has been detected in surface water and groundwater (45, 46). In an effort to find a viable bioremediation strategy to deal with atrazine-contaminated soils, a number of researchers have independently isolated atrazine-degrading bacteria from sites that were previously exposed to atrazine (47–51). Researchers working with atrazine-degrading bacteria have isolated genes responsible for the catabolism of atrazine and other triazines. With the determination of the complete genomic sequence of *Arthrobacter aurescens* TC1, researchers have found that atrazine catabolic genes are located on a large plasmid and that the *trzN* gene initiates this degradation (52). *Pseudomonas* strain ADP metabolizes atrazine as its sole nitrogen source via three enzymatic steps encoded by the genes *atzA*, *atzB*, and *atzC* (53). The *atzA*, *atzB*, and *atzC* genes were localized to a self-transmissible plasmid, pADP-1, and the complete nucleotide sequence of pADP-1 revealed the relative locations of these genes. Further analysis indicated the presence of three new catabolic genes, *atzD*, *atzE*, and *atzF*. Understanding the genomics and genetics of soil bacteria can provide insight into the evolution of plasmid-borne pathways to encode the catabolism of anthropogenic compounds.

Concerned with the environmental contamination by pesticides such as organophosphates (OP) as well as industrial chemicals such as polycyclic aromatic hydrocarbons (PAHs), researchers have been working to isolate PAH- and OP-degrading bacteria from a petroleum-contaminated soil and to study their taxonomy and degradation potential. Bacterial species isolated from contaminated soil can degrade a wide range of pesticides and PAHs. This degradative potential could be exploited as an effective bioremediation technology for environmental cleanup strategy. Researchers isolated and characterized 19 bacterial strains from a soil contaminated with 13 PAHs and 12 PAH metabolites. Some strains were capable of degrading phenanthrene completely after 7 days of incubation. One of these strains (C3) could also decompose nine carbamate pesticides, with up to 100% decomposition of aminocarb, carbaryl, and xylylcarb in 14 days. Metabolite and protein profiling showed a comprehensive metabolic network of the pesticides and PAHs (54).

Pentachloronitrobenzene (PCNB) is an organochlorine fungicide produced in the United States since 1962 (55), and it is used to control turf diseases. This pesticide has been found in surface water and groundwater. Efforts to find microbial means for bioremediation of this contaminant are being pursued. Researchers in this symposium presented their work on the effect of pH and temperature on the microbial reductive transformation of PCNB with a mixed fermentative/methanogenic culture developed from a contaminated estuarine sediment. Significant differences were observed in terms of biotransformation rate, extent, and products as a function of temperature. Details of this study are published in this issue (56). Overall, the results of this study indicated that pH and temperature are two important parameters which affect the reductive biotransformation rate and extent of PCNB. The microbial reductive transformation of PCNB will be useful in optimizing pH and temperature conditions for the enhancement of bioremediation applications related to soil and sediments contaminated with PCNB and cloranylins (56).

PESTICIDE TRANSPORT WITH RUNOFF

Chemical pollutants, including pesticides, have been detected in the surface waters of urban and agricultural areas (9, 10, 57).

A number of these compounds have been shown to reduce water quality and result in adverse effects to sensitive organisms, aquatic ecosystems, and human health, depending on their concentration and duration of exposure (13–15, 58, 59). Pesticides can be displaced from their site of application to nontarget surface waters via spray drift, volatilization, and transport with water. A greater understanding of pesticide transport with runoff and leachate, factors that influence runoff and associated pesticide loads, and evaluation of remediation strategies to reduce pesticide loads with runoff were discussed.

Runoff. The potential for pesticides to be transported with surface runoff have been evaluated with natural rainfall, simulated rainfall/irrigation, and computer model simulations in both agricultural and nonagricultural settings (60–64). In most simulated-rainfall studies precipitation is produced at a constant intensity or fixed rainfall rate, which is atypical of natural storm events demonstrating large within storm variations. To determine the impact of variable and constant rainfall intensities on the transport of herbicides with surface runoff, studies were initiated to quantify loads of two herbicides (fluometuron, pendimethalin) with runoff as influenced by rainfall intensity (constant or variable rainfall) and tillage practices (strip or conventional tillage). Variable rainfall intensity produced greater runoff rates of both herbicides from plots under conventional tillage, whereas no significant difference in herbicide runoff rates was observed between variable or constant rainfall intensity patterns from strip tillage plots. Results of this study suggest use of variable intensity rainfall patterns that simulate characteristics of natural rainfall can improve rainfall simulation-based estimates of pesticide runoff (65).

The influence of rainfall distribution on pesticide loss through runoff and subsurface drainage was also investigated. Researchers utilized the Root Zone Water Quality Model (RZWQM) to simulate pesticide transport with temporally discrete versus coarse rainfall data for three artificially subsurface-drained sites in Baton Rouge, LA, and Allen and Owen Counties, Indiana. RZWQM was calibrated on the basis of measured subsurface drain flow and bromide concentrations quantified in drain flow as a result of application of potassium bromide (KBr), a conservative tracer. Simulations were conducted with hourly rainfall, average storm duration, and distributed daily rainfall data. Rainfall intensity and duration had a greater impact on simulated subsurface drain flow than runoff. Details of this research are found in a subsequent paper (66).

Conservative tracers have historically been utilized as hydrologic tools for characterizing water movement through soil and tracking subsurface water flow (67–69). Massey et al. (70) reported the use of KBr and plastic tarps enhanced the understanding of solute movement with runoff from turf, the measurement of whole-plot rainfall application rates, and the integrity of runoff collection systems, improving site-to-site comparisons of multisite research projects. Other researchers have demonstrated conservative tracers can be utilized to develop pesticide and fertilizer application strategies to reduce off-site transport of chemicals with runoff from turf (71).

Vegetative Buffers: Mitigating Pesticide Transport with Runoff. Various remediation strategies have been designed and implemented to mitigate pesticide contamination (70–74). Multiple species riparian grass buffers are considered to be a cost-effective approach to reduce herbicide concentrations from edge-of-field runoff; however, design criteria important to meet sufficient removal rates are not well documented. Research was conducted to determine factors that will optimize riparian grass buffers, identifying physical, biological, and chemical processes

that are involved in herbicide mitigation. Growth-chamber and field studies revealed increased microbial enzymatic activity and greater degradation rates of herbicides in the rhizosphere of C4 warm-species plants relative to C3 cool-season species plants. C4 warm-species plants were most effective at reducing herbicide transport, and 8 m buffers containing native species reduced herbicide concentrations in surface runoff by 75–80%, demonstrating inclusion of native species in multiple species buffers will facilitate rapid mitigation of herbicides and reduce their off-site transport to surface and subsurface waters (75).

Another tool utilized to determine optimal design and placement of buffers is the Riparian Ecosystem Management Model (REMM) (76). This model has become an accepted tool for agricultural nutrient nonpoint runoff (77, 78). Recently, algorithms describing pesticide processes have been added to the model, including inputs for pesticides in runoff and subsurface flow, sorption by soils as affected by solute ionization, and transport and degradation within the buffer compartments. REMM can provide information for the design and placement of buffers as it evaluates plant/soil systems intended to intercept and remediate surface and subsurface flows from agricultural systems (79).

MODELING AND PREDICTIVE TOOLS

Advances in Predictive Models and Interpretation. Groundwater is an important natural resource that needs to be protected from potential pesticide contamination due to agricultural practices. During pesticide registration, a compound is evaluated to assess its potential hazard to groundwater and human health via exposure by drinking water (www.epa.gov). Currently the U.S. EPA utilizes the SCI-GROW model for estimating groundwater concentrations. This tier I model considers information from the label and minimal chemical parameters. Results provided from SCI-GROW are a single fixed-point estimate of exposure that is assumed to represent the entire United States and does not consider regional differences in soil type and climate conditions or areas with greater vulnerability. A more refined tier II approach is desired by both regulators and industry to assess potential groundwater contamination on the basis of an intended use and regional area. Pesticide Leaching U.S. (PLUS) is a prototype modeling tool that was developed on the basis of the groundwater model Pesticide Root Zone Model (PRZM) and considers over 8000 soils and 184 weather stations (80). This tool provides more regional ranking of soil vulnerability, creates spatial and probabilistic exposure estimates, and provides daily concentrations that can be utilized in drinking water assessments. Jackson et al. (80) describes in detail the methods, results, and effectiveness of PLUS as a regional estimator of potential groundwater contamination.

Regulatory agencies use the PRZM-Exposure Analysis Modeling System (EXAMS) model to conduct aquatic exposure assessments for U.S. agrochemical registration. This predictive model utilizes standard scenarios with specific crop/soil/weather condition combinations that represent 90th percentile transport risk. Members of the Environmental Exposure Work Group within CropLife America (EEWG/CLA) have noted an over-prediction of erosion in a standard regulatory modeling scenario within PRZM-EXAMS (81). They examined the scenarios with EXPRESS model shell and compared resulting runoff and erosion outputs with baseline datasets developed to rank all soil/weather combinations. The EXPRESS predictions were reasonably agreeable with baseline values except for eight scenarios that predicted exceptionally high levels of erosion. Erosion factors were compared between three apple scenarios within

PRZM that considered different areas in the country (North Carolina, Oregon, and Pennsylvania) but had similar rainfall data. The authors noted that the erosion factor, C-Factor (crop/vegetation and management factor), in the Pennsylvania apple scenario differed dramatically (15–20 times higher) from those of the other two scenarios. Thus, as a consequence, when a pesticide evaluation is conducted, PRZM-EXAMS predicts unrealistic soil erosion, erosion pesticide flux, water concentrations, and benthic sediment concentrations. The unrealistic predicted soil erosion in the Pennsylvania apple scenario would result in the “standard pond scenario” (1 ha pond—2 m deep, 10 ha watershed) completely filling up with sediment after 36 years. The C-Factor for the Pennsylvania apple scenario considers a bare ground orchard with conventional tillage where in reality the common crop management practice for sloped orchards is to have a vegetative strip in the rows between the trees, which would reduce soil erosion. The authors conducted the same pesticide evaluation again with the Pennsylvania apple scenario but considered a reduced C-Factor. Results from this revised evaluation were reduced and more similar to those of the North Carolina and Oregon apple scenarios. This demonstrated the C-Factor has a significant impact on the predicted amount of soil erosion and on the estimated environmental conditions.

Degradation rates of pesticides and their metabolites are among the most essential parameters required in evaluating their potential environmental exposure. Approaches used in calculating the degradation parameters from experimental data can significantly affect the resulting degradation rates and thus the environmental risk assessments and evaluation of an agrochemical. For the European pesticide registration process it was evident there was a need for technical guidance and harmonization. FOCUS (Forum for the Co-ordination of pesticide fate models and their Use) formed a workgroup of experts that developed recommendations for calculating degradation kinetics of agrochemicals in the European Union (EU) registration process. The FOCUS Degradation Kinetics Workgroup provided a guidance document on the calculation of degradation/dissipation rates of parent compound and metabolites from laboratory, field, and water–sediment studies (82). A member of this workgroup and author in the symposium discussed the FOCUS guidance on the calculation of persistence and degradation kinetic endpoints for metabolites (83). It is important that relevant metabolites of pesticides be considered in the environmental risk assessments. Often the kinetics of metabolites are more complex because their formation and degradation occur simultaneously. FOCUS (82) gives detailed guidance on selecting the appropriate kinetic models for the parent compound and metabolites, deriving metabolite triggers and kinetic endpoints for metabolites from studies conducted with the parent compound, and following a stepwise approach for more complicated datasets.

Conceptual models serve as a frame of reference for the discussion of environmental variables that are involved in determining the fate and transport of pesticides in the environment. Although many models exist, there is no agreed upon standard conceptual model. Authors at this symposium presented the concept of a multiscale model for agrochemical fate and transport for agrochemical entry into flowing and static surface waters and subsequent environmental fate (84). This conceptual model addressed micro-, meso-, field, and watershed scales. Such a conceptual model would facilitate constructive discussion of factors that lead to discrepancies between various modeling approaches and results from environmental monitoring studies.

Predictive Tools for Understanding Environmental Fate and Efficacy of Pesticides. Predictive tools can be used to estimate chemical properties of pesticides when data are lacking. An example is the SPARC computer simulation program from The University of Georgia at Athens (85). This computer model can calculate accurate ionization equilibrium constants as a function of molecular structure. The majority of modern pesticides are often more hydrophilic than the older pesticide chemistry and thus can be acidic or basic. Understanding the acid–base properties of pesticides is important for evaluating their behavior in the environment. The authors noted that only 198 experimental pK_a values were found of 445 active ingredients. Ionic compounds with no documented pK_a values may be assumed as nonionic, which could lead to misinterpretation of the persistence and mobility in the environment. In the absence of data, SPARC can be a useful tool for predicting pK_a values for pesticides.

Soil fumigants play an important role in agriculture by controlling plant pests that would otherwise prevent growers from producing needed crops and commodities that are critical to human health and nutrition. These highly volatile pesticides are effective due to their ability to penetrate deep within the soil layers to reach plant pests such as soil nematodes and weeds. Emissions from soil fumigants can adversely affect the environment and human health; thus, there is a need to develop improved agricultural techniques for existing products that will reduce emissions while maintaining efficacy against plant pests. Typically, expensive and time-consuming field trials are needed to evaluate pest control efficacy, and therefore more inexpensive and rapid predictive tools are required. Yates and Dungan (86) investigated a new method to predict fumigant fate, transport, and control of plant pests after soil fumigation by using a 2-dimensional soil column and a simple model. The soil gas concentration and the volatilization of the fumigant (averaged over the 2-D box) were measured, the fate and transport of the fumigant was simulated with a model, mortality relationships for plant pathogen were developed, and control of pathogens was predicted using a concentration-time relationship. Comparison of the simulated and measured results indicated the model predicted the overall pathogen control well, and the minor observed differences would not change the fumigant application management. Throughout the experiment, soil gas concentrations and fumigant volatilization rates were overestimated by the model; though predictive cumulative emissions were accurate. Yates and Dungan (86) noted the soil degradation coefficient was important in describing the fate and transport of the fumigant throughout the study, but additional research is needed.

Geographic Information System (GIS) and other spatial data were used to evaluate the potential for spray drift exposure from agricultural pesticide applications near surface water (87). Utilizing knowledge of surface water characteristics along with detailed knowledge of the adjacent land cover, the potential for spray drift exposure can be efficiently estimated for thousands of water bodies over a large agricultural landscape. Information on distance from crop to water, direction, and composition of natural buffers can be assessed within a GIS. This information can be applied to standard methods for calculating drift-related concentrations in surface water such as AgDRIFT and FOCUS models. Using a GIS, the effect of no-spray buffers can also be quantified to examine the impact a specific label restriction may have on the exposure distribution. Estimated concentrations can be calculated for individual water bodies linked within a hydrologic network, creating the ability to assess potential watershed-level exposure.

DETECTION AND DISSIPATION OF PESTICIDES IN SURFACE WATER

Tools for Selecting Monitoring Sites. When it comes to large-scale monitoring studies, the selection of sampling locations on a regional and national basis can be challenging. The key is to minimize time spent during field data collection to assess as many potential monitoring sites on a watershed basis, especially when areas of interest span multiple states. Utilizing current data in a GIS prior to entering the field and during site selection can help narrow potential sites and streamline the selection process to meet study goals. The final goal is to select sites that meet study criteria on the ground that can be instrumented and monitored. Following a systematic process minimizes personnel time at each potential field site. GIS can be used to identify details of smaller watersheds that may be difficult to see in the field, and it provides some cross-check between national data sets and current conditions in the field. Researchers (88) presented a local sampling site selection process which began with a random spatially balanced selection of large watersheds (100–300 mi²) that described the bounds for smaller scale watershed selection. Major data criteria included land use, pesticide usage, precipitation, soils, hydrography, and drainage areas. A detailed GIS analysis using air photos, river networks, and raster watershed analysis helped to identify where smaller subwatersheds within these random larger areas met study objectives. Applicable river sections were identified where watershed criteria met the specific study criteria for size and composition. Field teams then identified bridges and sampling locations in the office prior to verification for suitability via field visits. GIS approaches integrated the whole process from the office to the field and made the process very efficient and successful. Examples were presented demonstrating where the procedure worked well and challenges to be resolved in future studies.

Chemical monitoring programs that are linked to river hydrology and weather data collection can be used to build confidence in environmental and ecological exposure estimates used to support pesticide registration and re-registration activities. A monitoring program is being conducted across the midwestern United States that involves extensive instrumentation activities. Snyder et al. (89) developed and deployed instruments using forms for electronic data handling matched with data redundancy approaches to ensure data delivery met or exceeded Good Laboratory Practice standards (GLPs). The study was planned to cover twice as many sampling stations during the second year of sampling; however, the year one efforts to establish an instrumentation methodology helped reduce costs and realize great efficiencies in the second year. In this presentation, the authors presented descriptions of the instrumentation design and installation challenges, data handling structure, and a review of the operational reliability of approximately 90 complex installations at unique/remote locations.

Surface Water Monitoring Studies. Large-scale water monitoring programs are conducted by the U.S. Geological Survey (USGS). During 2004, the occurrence of 14 herbicides and 41 herbicide degradation products was examined in 80 water samples collected from 10 major Iowa rivers flowing to the Missouri and Mississippi Rivers (90). All samples were analyzed for herbicides and herbicide degradation products using previously developed liquid chromatography–mass spectrometry (LC-MS) methods. Analysis for isoxaflutole (a restricted-use corn proherbicide) and its degradation products diketoneitrile (the compound containing the herbicidal activity) and benzoic acid used a new LC-MS/MS method. Similar to previous studies,

atrazine, metolachlor, and seven triazine or acetamide degradates were detected in almost every stream sample collected. By comparison, isoxaflutole was detected in only 5% of the stream samples, with diketonitrile (70%) and benzoic acid (55%) being detected much more frequently. Only sparse information is available on the occurrence of isoxaflutole and its degradates. These results suggest that isoxaflutole degrades rapidly after application and that its degradates are more likely to occur in the environment (similar to several other herbicides).

A multiyear surface water monitoring study was conducted in canals and Biscayne Bay of southern Florida. The area of the Everglades, Biscayne, and Florida Bays is a unique combination of highly productive agricultural lands: urban expansion, engineered canal structures for flood control, and critical terrestrial and aquatic wildlife habitat. Surface water samples from canals and Biscayne Bay were analyzed for 39 pesticides (10). Atrazine and chlorpyrifos concentrations were highest near corn production, whereas chlorothalonil and endosulfan concentrations were highest near vegetable production. No clear trend was observed for metolachlor, which was used on multiple crops. The calculated aquatic life hazard potential for the planting period (November) versus the harvest period (March) showed that a higher hazard potential occurs during harvest, primarily from the use of endosulfan. Coupling these data to the life cycles of the aquatic organisms will provide policy and decision makers with more realistic risk assessments and producers with information to reduce the impact of agricultural practices on sensitive ecosystems.

Pesticide Dissipation in Surface Waters. Surface runoff and subsurface drainage have contributed to the detection of pesticides in surface waters; however, surface waters may also be intended sites of chemical application when the control of nuisance or exotic invasive species in aquatic environments is desired (91, 92). 2,4-Dichlorophenoxyacetic acid (2,4-D), a commonly used herbicide for weed control in agricultural and turf environments, is also labeled for control of aquatic vegetation such as Eurasian watermilfoil (*Myriophyllum spicatum*) and water hyacinth (*Eichhornia crassipes*) (www.greenbook.net). Whether intentionally applied to surface waters (direct injection, foliar treatment) or inadvertently introduced (runoff, subsurface drainage, spray drift), understanding the dissipation of pesticides in aquatic environments and assessing their potential effects on nontarget organisms are important for protecting environmental and human health as well as product-use registration. Required data are often obtained from laboratory to in situ microcosm studies, monitoring activities, and model simulations. Researchers presented microcosm studies in surface waters of Minnesota and Florida that showed rapid dissipation of 2,4-D in treated areas to levels below the drinking water standard. Factors influencing the rapid dissipation include microbial processes, plant uptake, sediment binding, dispersion, and dilution (93, 94).

ENVIRONMENTAL FATE AND EXPOSURE ASSESSMENT

Requirements and demand for pest management will continue to change with ever-shifting social, economic, and environmental pressures. As new chemistries, crops, and practices emerge, it is important to recognize their beneficial and adverse impacts. Combinations of physical, chemical, and biological processes determine the behavior of pesticides in the environment and their effects on target and nontarget species. To improve our ability to identify and develop pest management approaches, we need to accurately measure and predict environmental concentrations of pesticides and apply new understanding and

technologies to pest management strategies. This paper summarized a symposium on the advances in the environmental fate and exposure assessment of pesticides. Thirty research projects were presented on topics ranging from subcellular processes to watershed-scale studies: evaluating pesticide degradation, sorption, and transport; improved methodologies; treatment and remediation strategies; and the utilization of models to predict environmental fate and exposure. Several of these research projects are presented in greater detail in subsequent papers. Use of the scientific advances discussed in this symposium will further improve science-based regulations and pest management strategies.

LITERATURE CITED

- (1) U.S. Census Bureau. Available at <http://www.census.gov/ipc/www/worldpop.html> and <http://www.census.gov/ipc/www/usinteripproj>, accessed Nov 14, 2006.
- (2) Judge, C. A.; Neal, J. C.; Derr, J. F. Response of Japanese stiltgrass (*Microstegium vimineum*) to application timing, rate, and frequency of postemergence herbicides. *Weed Technol.* **2005**, *19*, 912–917.
- (3) Wu, Q. J.; Zhao, J. Z.; Taylor, A. G.; Shelton, A. M. Evaluation of insecticides and application methods against *Contarinia nasturtii* (Diptera: Cecidomyiidae), a new invasive insect pest in the United States. *J. Econ. Entomol.* **2006**, *99*, 117–122.
- (4) *Pesticides Industry Sales and Usage: 1996 and 1997 Market Estimates*; Aspelin, A. L., Grube, A. H., Eds.; U.S. Environmental Protection Agency, Office of Prevention, Pesticides & Toxic Substances: Washington, DC, 1999.
- (5) *Toxicology of Insecticides*; Matsumura, F., Ed.; Plenum Press: New York, 1985.
- (6) *Toxicological Chemistry*, 2nd ed.; Manahan, S. E., Ed.; Lewis Publishers: Ann Arbor, MI, 1992.
- (7) Kumar, M.; Gupta, S. K.; Garg, S. K.; Kumar, A. Biodegradation of hexachlorocyclohexane-isomers in contaminated soils. *Soil Boil. Biochem.* **2006**, *38*, 2318–2327.
- (8) Loague, K.; Soutter, L. A. Desperately seeking a cause for hotspots in regional-scale groundwater plumes resulting from non-point source pesticide applications. *Vadose Zone J.* **2006**, *5*, 204–221.
- (9) Hoffman, R. S.; Capel, P. D.; Larson, S. J. Comparison of pesticides in eight U.S. urban streams. *Environ. Toxicol. Chem.* **2000**, *19*, 2249–2258.
- (10) Harman-Fetcho, J. A.; Hapeman, C. J.; McConnell, L. L.; Potter, T. L.; Rice, C. P.; Sadeghi, A. M.; Smith, R. D.; Bialek, K.; Sefton, K. A.; Schaffer, B. A. Pesticide occurrence in selected South Florida canals and Biscayne Bay during high agricultural activity. *J. Agric. Food Chem.* **2005**, *53*, 6040–6048.
- (11) Buehler, S. S.; Basu, I.; Hites, R. A. Causes of variability in pesticide and PCB concentrations in air near the Great Lakes. *Environ. Sci. Technol.* **2004**, *38*, 414–422.
- (12) Goel, A.; McConnell, L. L.; Torrents, A. Wet deposition of current use pesticides at a rural location on the Delmarva Peninsula: impact of rainfall patterns and agricultural activity. *J. Agric. Food Chem.* **2005**, *53*, 7915–7924.
- (13) Clark, J. R.; Lewis, M. A.; Pait, A. S. Pesticide inputs and risks in coastal wetlands. *Environ. Toxicol. Chem.* **1993**, *12*, 2225–2233.
- (14) Margni, M.; Rossier, D.; Crettaz, P.; Jolliet, O. Life cycle impact assessment of pesticides on human health and ecosystems. *Agric. Ecosyst. Environ.* **2002**, *93*, 379–392.
- (15) Schulz, R. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: a review. *J. Environ. Qual.* **2004**, *33*, 419–448.
- (16) Koskinen, W. C.; Rice, P. J.; Anhalt, J. A.; Sakaliene, O.; Moorman, T. B.; Arthur, E. L. Sorption–desorption of “aged” sulfonilaminocarbonyltriiazolinone herbicides in soil. *J. Agric. Food Chem.* **2002**, *50*, 5368–5372.

- (17) Malekani, K. Study design for aged desorption and rate of degradation experiments and the use of the $K_{aged\ des}$ and DT_{50} in modeling of predicted environmental concentrations in groundwater. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 73, no. 80 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (18) Hill, I. R. Aquatic organisms and pyrethroids. *Pestic. Sci.* **1989**, *27*, 429–465.
- (19) House, W. A.; Long, J. L. A.; Rae, J. E.; Parker, A.; Orr, D. R. Occurrence and mobility of the insecticide permethrin in rivers in the Southern Humber catchment, UK. *Pest Manag. Sci.* **2000**, *56*, 597–606.
- (20) Kabashima, J. N.; Lee, S. J.; Haver, D. L.; Goh, K. S.; Wu, L. S.; Gan, J. Pesticide runoff and mitigation at a commercial nursery site. In *Pesticide Decontamination and Detoxification*; Gan, J., Zhu, P., Lemley, A., Aust, S., Eds.; American Chemical Society: Washington, DC, 2003; pp 213–230.
- (21) Weston, D. P.; You, J.; Lydy, M. J. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's central valley. *Environ. Sci. Technol.* **2004**, *38*, 2752–2759.
- (22) Weston, D. P.; Holmes, R. W.; You, J.; Lydy, M. J. Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ. Sci. Technol.* **2005**, *39*, 9778–9784.
- (23) Gan, J.; Lee, S. J.; Liu, W. P.; Haver, D.; Kabashima, J. N. Distribution and persistence of synthetic pyrethroids in runoff sediments. *J. Environ. Qual.* **2005**, *34*, 836–841.
- (24) Bondarenko, S. Improved methods for measuring K_d for strongly hydrophobic pesticides. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 73, no. 81 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (25) Shepherd, J. J.; Arthur, E. L.; Dominic, A. R.; Sabbagh, G. J.; Dyer, D. G. Mobility determination of an experimental compound as a seed treatment in a greenhouse. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 73, no. 82 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (26) Agarwal, V. K.; Sinclair, J. B. Seed Treatment. In *Principles of Seed Pathology*, 2nd ed.; Agarwal, V. K., Sinclair, J. B., Eds.; CRC Press: Boca Raton, FL, 1997; pp 423–460.
- (27) Maloy, O. C. Seed treatment and eradicant chemicals. In *Plant Disease Control: Principles and Practice*; Maloy, O. C., Ed.; Wiley: New York, 1993; pp 111–126.
- (28) Dawson, J. H. Herbicide-treated crop seed. In *Methods of Applying Herbicides*; Weed Science Society of America Monograph 4; McWhorter, C. G., Gebhardt, M. R., Eds.; Weed Science Society of America: Champaign, IL, 1987; pp 255–263.
- (29) Bateman, G. L.; Ehle, H.; Wallace, H. A. A. Fungicidal treatment of cereal seeds. In *Seed Treatment*, 2nd ed.; Jeffs, K. A., Ed.; Lavenham Press: Lavenham, Suffolk, U.K., 1986; pp 83–111.
- (30) Börjesson, B. J.; Stenstrom, L.; Johnsson, L.; Torstensson, L. Comparison of triticonazole dissipation after seed or soil treatment. *J. Environ. Qual.* **2003**, *32*, 1258–1261.
- (31) Sabbagh, G. J.; Fox, G.; Ma, L.; Malone, R.; Arthur, E. L.; Dyer, D. G. Modeling the fate and nonideal transport of pesticide from a slow-release, pesticide treated seed in a laboratory soil column. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 73, no. 83 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (32) Papiernik, S. K.; Koskinen, W. C.; Cox, L.; Rice, P. J.; Clay, S. A.; Werdin-Pfisterer, N. R.; Norberg, K. A. Sorption–desorption of imidacloprid and its metabolites in soil and vadose zone materials. *J. Agric. Food Chem.* **2006**, *54*, 8163–8170.
- (33) Friedman, C. L.; Lemley, A. T.; Hay, A. Degradation of chloroacetanilide herbicides by anodic Fenton treatment. *J. Agric. Food Chem.* **2006**, *54*, 2640–2651.
- (34) Kong, L.; Lemley, A. T. Kinetic modeling of 2,4-dichlorophenoxyacetic acid (2,4-D) degradation in soil slurry by anodic Fenton treatment. *J. Agric. Food Chem.* **2006**, *54*, 3941–3950.
- (35) Marinas, A.; Guillard, C.; Marinas, J. M.; Fernandez-Alba, A.; Aguera, A.; Herrmann, J. M. Photocatalytic degradation of pesticide–acaricide formetanate in aqueous suspension of TiO_2 . *Appl. Catal. B: Environ.* **2001**, *34*, 241–252.
- (36) Divito, C. B.; Davies, S.; Masoudi, S.; Muhuro, C. N. Relative stability of formamidine and carbamate groups in the bifunctional pesticide formetanate hydrochloride. *J. Agric. Food Chem.* **2007**, *55*, 5377–5382.
- (37) Muhuro, C. Studies on the aquatic chemical fate of formetanate hydrochloride. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 72, no. 76 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (38) Urbansky, E. T.; Magnuson, M. L.; Kelty, C. A.; Gu, B.; Brown, G. M. Comment on “Perchlorate Identification in Fertilizers” and the subsequent addition/correction. *Environ. Sci. Technol.* **2000**, *34*, 4452–4453.
- (39) Susarla, S.; Collette, T. W.; Garrison, A. W.; Wolfe, N. L.; McCutcheon, S. C. Response to comment on “Perchlorate Identification in Fertilizers” and the subsequent addition/correction. *Environ. Sci. Technol.* **2000**, *34*, 4454–4454.
- (40) Urbansky, E. T.; Collette, T. W.; Robarge, W. P.; Hall, W. L.; Skillen, J. M.; Kane, P. F. *Survey of Fertilizers and Related Materials for Perchlorate (ClO_4^-)*; Environmental Protection Agency: Cincinnati, OH, 2001; EPA/600/R-01/049.
- (41) Miller, G. C.; Lepak, V.; Kempley, R.; Awadh, J. Photooxidation of chloride to perchlorate in the presence of desert soils and titanium dioxide. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 72, no. 78 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (42) USGS National Water Quality Assessment (NAWQA) Program, 2006; available at <http://pubs.usgs.gov/fs/2006/3101/>.
- (43) Oregon Department of Environmental Quality (DEQ), 2006; available at <http://www.deq.state.or.us/lab/wqm/watershed.htm>.
- (44) Dominic, A. R.; Arthur, E. L.; Dyer, D. G. Drinking water treatment study procedures for evaluation of pesticide exposure. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 72, no. 79 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (45) Belluck, D. A.; Benjamin, S. L.; Dawson, T. Groundwater contamination by atrazine and its metabolites: risk assessment, policy and legal implications. In *Pesticide Transformation Products: Fate and Significance in the Environment*; Somasundaram, L., Coats, J. R., Eds.; American Chemical Society: Washington, DC, 1991; pp 254–273.
- (46) Seiler, A. P.; Brenneisen, P.; Green, D. H. Benefits and risks of plant protection products. Possibilities of protecting drinking water: case atrazine. *Water Supply* **1992**, *10*, 31–42.
- (47) Assaf, N. A.; Turco, R. F. Accelerated biodegradation of atrazine by a microbial consortium is possible in culture and soil. *Biodegradation* **1994**, *5*, 29–35.
- (48) Mandelbaum, R. T.; Allan, D. L.; Wackett, L. P. Isolation and characterization of a *Pseudomonas* sp. that mineralizes the s-triazine herbicide atrazine. *Appl. Environ. Microbiol.* **1995**, *61*, 1451–1457.
- (49) Moscinski, J. K.; Jayachandran, K.; Moorman, T. B. Mineralization of the herbicide atrazine by *Agrobacterium radiobacter*, abstr. Q-414. In *Abstracts of the 96th General Meeting of the American Society for Microbiology*; American Society for Microbiology: Washington, DC, 1996; p 458.

- (50) De Souza, M. L.; Wackett, L. P.; Sadowsky, M. J. The *atzABC* genes encoding atrazine catabolism are located on a self-transmissible plasmid in *Pseudomonas* sp. strain ADP. *Appl. Environ. Microbiol.* **1998**, *64*, 2323–2326.
- (51) Bouquard, C.; Ouazzani, J.; Promé, J.-C.; Michel-Briand, Y.; Plésiat, P. Dechlorination of atrazine by a *Rhizobium* sp. isolate. *Appl. Environ. Microbiol.* **1997**, *63*, 862–866.
- (52) Sajjaphan, K.; Shapir, N.; Wackett, L. P.; Palmer, M.; Blackmon, B.; Tomkins, J.; Sadowsky, M. J. *Arthrobacter aurescens* TCl atrazine catabolism genes *trzN*, *atzB*, and *atzC* are linked on a 160-kilobase region and are functional in *Escherichia coli*. *Appl. Environ. Microbiol.* **2004**, *70*, 4402–4407.
- (53) deSouza, M. L.; Newcombe Alvey, D. S.; Crowley, D. E.; Hay, A.; Sadowsky, M. J.; Wackett, L. P. Molecular basis of a bacterial consortium: interspecies catabolism of atrazine. *Appl. Environ. Microbiol.* **1998**, *64*, 178–184.
- (54) Seo, J.-S.; Keum, Y.-S.; Harada, R. M.; Li, Q. X. Isolation and characterization of bacteria capable of degrading polycyclic aromatic hydrocarbons (PAHs) and organophosphorus pesticides from PAH-contaminated soil in Hilo, Hawaii. *J. Agric. Food Chem.* **2007**, *55*, 5383–5389.
- (55) *Some Organochlorine Pesticides*; Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man 5; International Agency for Research on Cancer (IARC): Lyons, France, 1974; pp 211–218.
- (56) Tas, O. D.; Pavlostathis, S. G. Temperature and pH effect on the microbial reductive transformation of pentachloronitrobenzene. *J. Agric. Food Chem.* **2007**, *55*, 5390–5398.
- (57) Starner, K.; Spurlock, F.; Gill, S.; Goh, K.; Feng, H.; Hsu, J.; Lee, P.; Tran, D.; White, J. Pesticide residues in surface water from irrigation-season monitoring in the San Joaquin Valley, California, USA. *Bull. Environ. Contam. Toxicol.* **2005**, *74*, 920–927.
- (58) Scott, G. I.; Baughman, D. S.; Trim, A. H.; Dee, J. C. Lethal and sublethal effects of insecticides commonly found in nonpoint source agricultural runoff to estuarine fish and shellfish. In *Pollution Physiology of Estuarine Organisms*; Vernberg, W. B., Calabrese, A., Thurberg, F. P., Vernberg, F. J., Eds.; University of South Carolina Press: Columbia, SC, 1987; pp 251–273.
- (59) *Pesticide Toxicity Index for Freshwater Aquatic Organisms*, 2nd ed.; Munn, M. D., Gilliom, R. J., Moran, P. W., Nowell, L. H., Eds.; U.S. Geological Survey: Sacramento, CA, 2006; Scientific Investigations Report 2006-5148; p 81.
- (60) Ma, Q.; Hook, J. E.; Wauchope, R. D.; Dowler, C. C.; Johnson, A. W.; Davis, J. G.; Gascho, G. J.; Truman, C. C.; Sumner, H. R.; Chandler, L. D. GLEAMS, Opus, PRZM2beta, and PRZM3 simulations compared with measured atrazine runoff. *Soil Sci. Soc. Am. J.* **2000**, *64*, 2070–2079.
- (61) Rice, P. J.; McConnell, L. L.; Heighton, L. P.; Sadeghi, A. M.; Isensee, A. R.; Teasdale, J. R.; Abdul-Baki, A. A.; Harman-Fetcho, J. A.; Hapeman, C. J. Runoff loss of pesticides and soil: a comparison between vegetative mulch and plastic mulch in vegetable production systems. *J. Environ. Qual.* **2001**, *30*, 1808–1821.
- (62) Haith, D. A. TurfPQ, a pesticide runoff model for turf. *J. Environ. Qual.* **2001**, *30*, 1033–1039.
- (63) Heim, L. G.; Snyder, N. J.; Van Wesenbeeck, I. J. Runoff of 1,3-dichloropropene from field plots exposed to simulated and natural rainfall. *J. Soil Water Conserv.* **2002**, *57*, 16–23.
- (64) Potter, T. L.; Truman, C. C.; Bosch, D. D.; Bednarz, C. Fluometuron and pendimethalin runoff from strip and conventionally tilled cotton in the southern Atlantic. *J. Environ. Qual.* **2004**, *33*, 2122–2131.
- (65) Potter, T. L.; Truman, C. C.; Strickland, T. C.; Bosch, D. D.; Webster, T. M.; Franklin, D. H.; Bednarz, C. W. Combined effects of constant versus variable intensity simulated rainfall and reduced tillage management on cotton preemergence herbicide runoff. *J. Environ. Qual.* **2006**, *35*, 1894–1902.
- (66) Fox, G. A.; Pulijala, S. H.; Sabbagh, G. J. Influence of rainfall distribution on simulations of atrazine, metolachlor, and isoxaflutole/mtabolite transport in subsurface drained fields. *J. Agric. Food Chem.* **2007**, *55*, 5399–5407.
- (67) Jaynes, D. B.; Shao, M. Evaluation of a simple technique for estimating two-domain transport parameters. *Soil Sci.* **1999**, *164*, 82–91.
- (68) Kung, K.-J. S.; Klavivko, E. J.; Gish, T. J.; Steenhuis, T. S.; Bubenzer, G.; Helling, C. S. Quantifying preferential flow by breakthrough of sequentially applied tracers: silt loam soil. *Soil Sci. Soc. Am. J.* **2000**, *64*, 1296–1304.
- (69) Fox, G. A.; Malone, R.; Sabbagh, G. J.; Rojas, K. Interrelationship of macropores and subsurface drainage for conservative tracer and pesticide transport. *J. Environ. Qual.* **2004**, *33*, 2281–2289.
- (70) Massey, J. H.; Ampim, P. A. Utility of incorporating a conservative tracer and plastic tarp in turf runoff assessments. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 65, no. 47 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (71) Rice, P. J.; Horgan, B. P. Differential application of fluorobenzoic acids to evaluate surface runoff from turf grass. *Proceedings of the 230th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2005; p 72, no. 100 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (72) Sethunathan, N.; Megharaj, M.; Chen, Z. L.; Williams, B. D.; Lewis, G.; Naidu, R. Algal degradation of a known endocrine disrupting insecticide, alpha-endosulfan, and its metabolite, endosulfan sulfate, in liquid medium and soil. *J. Agric. Food Chem.* **2004**, *52*, 3030–3035.
- (73) Shea, P. J.; Machacek, T. A.; Comfort, S. D. Accelerated remediation of pesticide-contaminated soil with zerovalent iron. *Environ. Pollut.* **2004**, *132*, 183–188.
- (74) Lin, C. H.; Lerch, R. N.; Garrett, H. E.; George, M. F. Incorporating forage grasses in riparian buffers for bioremediation of atrazine, isoxaflutole and nitrate in Missouri. *Agrofor. Syst.* **2005**, *63*, 91–99.
- (75) Lin, C.-H.; Lerch, R. N.; Garrett, H. G.; George, M. F. Bioremediation of herbicides in vegetative buffers: considerations for design and species selection. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 65, no. 46 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (76) Lowrance, R.; Altier, L. S.; Williams, R. G.; Inamdar, S. P.; Sheridan, J. M.; Bosch, D. D.; Hubbard, R. K.; Thomas, D. L. REMM: The Riparian Ecosystem Management Model. *J. Soil Water Conserv.* **2000**, *55*, 27–34.
- (77) Dukes, M. D.; Evans, R. O. Riparian ecosystem management model: hydrology performance and sensitivity in the North Carolina Middle Coastal Plain. *Trans. ASAE* **2003**, *46*, 1567–1579.
- (78) Graff, C. D.; Sadeghi, A. M.; Lowrance, R. R.; Williams, R. G. Quantifying the sensitivity of the Riparian Ecosystem Management Model (REMM) to changes in climate and buffer characteristics common to conservation practices. *Trans. ASAE* **2005**, *48*, 1377–1387.
- (79) Wauchope, R. D.; Williams, R. G.; Lowrance, R.; Vellidis, G.; Gay, P. REMM: A simulation model for remediation of pesticide contaminants in runoff and leachate water by riparian buffer systems. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 63, no. 37 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (80) Jackson, S. H.; Hendley, P.; Cheplick, M. PLUS: a regional groundwater assessment and ranking tool. *J. Agric. Food Chem.* **2007**, *55*, 5408–5415.

- (81) Hendley, P.; Jackson, S. H.; Chen, W.; Russel, M. H.; Sabbagh, G. J.; Ramanarayanan, T. S.; Wanner, U. Overprediction of erosion in standard regulatory modeling scenarios for agrochemicals. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 63, no. 36 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (82) FOCUS. Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration; Report of the FOCUS Work Group on Degradation Kinetics; EC Document Reference Sanco/10058/2005 version 1.0; 2005; 431 pp.
- (83) Beigel, C.; Boesten, J.; Jones, R. L.; Aden, K.; Beulke, S.; Dust, M.; Dyson, J.; Fomsgaard, I.; Karlsson, S.; Magrans, J. O.; Richter, O.; Soulas, G.; van der Linden, T. FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 63, no. 35 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (84) Hendley, P. D.; Wauchope, R. D. Conceptual models for understanding agrochemical occurrence in surface waters. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 76, no. 96 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (85) Edwards, J.; Wauchope, R. D. Acid and base equilibrium constants for pesticide active ingredients: molecular connectivity calculations vs. experimental values. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 62, no. 33 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (86) Yates, S. R.; Dungan, R. Predicting transport and the control of plant pests after soil fumigation. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 62, no. 32 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (87) Holmes, C.; Williams, R. Spatial approaches to estimating pesticide spray drift exposure to surface water at the landscape level using GIS and remote sensing. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 76, no. 98 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (88) Trask, J. R.; Harbourt, C. M.; Holmes, C.; Hendley, P. Site selection for surface water sampling locations in smaller watersheds using a GIS based procedure. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 76, no. 97 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (89) Snyder, N. J.; Harbourt, C. M.; Carver, L. S.; Hendley, P.; Burnett, G. A multi-state small-stream and weather monitoring network: equipment design, data handling, and reliability. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 76, no. 101 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (90) Meyer, M. T.; Kalkoff, S. J.; Scribner, E. A. Comparison between the transport of isoxaflutole and its degradates to triazine and acetanilide herbicides in ten Iowa rivers. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 76, no. 100 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (91) Rana, B. C.; Kumar, J. I. N. Observations on the effect of the herbicide isoproturon on aquatic targets and associated organisms. *Bull. Environ. Contam. Toxicol.* **1995**, *55*, 104–110.
- (92) Getsinger, K. D.; Petty, D. G.; Madsen, J. D.; Skogerboe, J. G.; Houtman, B. A.; Haller, W. T.; Fox, A. M. Aquatic dissipation of the herbicide triclopyr in Lake Minnetonka, Minnesota. *Pest Manag. Sci.* **2000**, *56*, 388–400.
- (93) Jacobson, B. R.; Balu, K. Dispersion and dissipation of 2,4-D residues associated with aquatic uses. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 66, no. 51 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).
- (94) Balu, K.; Ritter, A. M.; Williams, M. W. Exposure assessment of 2,4-D herbicide for aquatic uses. *Proceedings of the 231st National Meeting of the American Chemical Society*, Atlanta, GA; American Chemical Society: Washington, DC, 2006; p 66, no. 50 (available at <http://membership.acs.org/a/agro/Picogram.html>, accessed April 11, 2007).

Received for review December 28, 2006. Revised manuscript received April 15, 2007. Accepted April 25, 2007.

JF063764S