JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Agrochemical and Nutrient Impacts on Estuaries and Other Aquatic Systems

CATHLEEN J. HAPEMAN,*,† CHRISTOPHER P. DIONIGI,‡ PAUL V. ZIMBA,§ AND LAURA L. MCCONNELL†

Environmental Quality Laboratory, Agricultural Research Service, U.S. Department of Agriculture, 10300 Baltimore Avenue, Beltsville, Maryland 20705; National Invasive Species Council, 1951 Constitution Avenue, Suite 320, South Interior Building, Washington, D.C. 20240; and Catfish Genetics Research, Agricultural Research Service, U.S. Department of Agriculture, Experiment Station Road, P.O. Box 38, Stoneville, Mississippi 38776-0038

This paper summarizes the “Agrochemical and Nutrient Impacts on Estuaries” symposium held at the 220th National Meeting of the American Chemical Society. The focus of the symposium was to highlight ongoing research efforts to understand estuarine function and pollutant fate in these important ecosystems. Expanding urbanization and agricultural activity can result in increased particulate and chemical loads, resulting in decreased light penetration and degraded aquatic habitats. Legislative and regulatory protections, such as the Clean Water Act and Total Maximum Daily Loads (TMDLs), are considered here. Measurement of nutrient and pesticide loads and their ecotoxicological impacts are explored, as well as potential mitigation practices. The complexity and high visibility of estuarine ecosystem health will require continued examination to develop more effective agricultural and land management strategies and sound science-based regulations.

KEYWORDS: Estuaries; water quality; pesticides; nutrients; ecotoxicology; total maximum daily loads; nonpoint source; pollution

Estuaries are productive, important wildlife habitats that require special protection from agricultural operations. Encroachment of agriculture and human population on these areas can increase particulate and chemical loads, resulting in decreased light penetration and degraded aquatic habitats. The occurrence of agricultural chemicals and excess nutrients in water reflects a complicated interaction of chemical, biological, and physical factors. Additional complexities are embodied in public land and water policies, legislation, and social and economic factors. At the 220th National Meeting of the American Chemical Society (Washington, DC, 2000), the Agrochemicals and Fertilizer and Soil Chemistry Divisions cosponsored the “Agrochemical and Nutrient Impacts on Estuaries” symposium to highlight ongoing research efforts to understand estuarine function and pollutant fate in these important ecosystems. This information is necessary to develop more effective agricultural management strategies and sound science-based regulations.

CLEAN WATER ACT (CWA) AND TOTAL MAXIMUM DAILY LOADS (TMDLS)

The Clean Water Act of 1972, revised in 1977 (P.L. 95-217), 1981 (P.L. 97-117), and 1987 (P.L. 100-4), is the direct result of the severe degradation of water quality. Its stated goal is to make U.S. waters capable of sustaining quality fisheries and potable water. Although the CWA is credited with significant improvements in water quality, the U.S. Environmental Protection Agency (EPA) estimates that ~40% of U.S. waters do not meet minimum water quality standards (*1*). Furthermore, ~10% of these water impairments are due solely to point sources of pollutants. The remaining 90% of the waters are impaired by either non-point sources of pollutants alone or a combination of point source and nonpoint sources of pollutants (*1*).

The understanding that water pollution cannot be completely addressed unless all sources of pollutants are considered has led to the concept of a Total Maximum Daily Load (TMDL). Typically, TMDLs are developed by measuring pollutant concentrations and determining how much of the loadings of that pollutant from all sources would need to be reduced to bring the water into compliance with water quality standards. Nonpoint-source pollutants generally reflect land-use patterns within watersheds. (A watershed is an area of land in which all surface waters drain via a common outflow.) For example, 15% of the samples collected from shallow ground water under agricultural lands that receive nitrogen fertilizer exceeded the EPA drinking-water standards for nitrates, and the highest concentrations of insecticides used extensively by homeowners (such as diazinon, carbaryl, and malathion) were found in urban streams (*2*).

The National Water-Quality Assessment (NAWQA) Program within the U.S. Geological Survey (USGS) was established to

* Author to whom correspondence should be addressed [telephone (301) 504-6511; fax (301) 504-5048; e-mail hapemanc@ba.ars.usda.gov].
† Environmental Quality Laboratory, USDA.
‡ National Invasive Species Council.
§ Catfish Genetics Research, USDA.

10.1021/jf020457n
Published on Web 06/22/2002

describe the quality of U.S. ground and surface waters and to determine the relationship between factors that affect water quality (*2*). Several water quality databases are maintained by the EPA's Office of Water and include >250 million data points from state and federal agencies on surface water and ground water quality, sediments, streamflow, and fish tissue contaminants.

Another important legislative measure impacting estuaries is the 1972 Coastal Zone Management Act (CZMA; P.L. 92-583; reauthorized 1996, P.L. 104-150), which created federal incentives for coastal states to manage their coastal and ocean resources. In 1990 with increasing pressure from population growth in coastal areas and its associated non-point-source water pollution, the U.S. Congress passed the Coastal Zone Act Reauthorization Amendments (CZARA) that require coastal states and territories to develop programs to address non-point-source pollution in coastal areas. The EPA identified several categories of non-point sources of pollution that affect coastal waters (agriculture, forestry, urban, marinas and recreational boating, and hydromodification). Thus, a tremendous need exists for pollution mitigation technologies, particularly for non-point sources.

NUTRIENT AND PESTICIDE INPUTS

Agricultural runoff is an important pesticide source to estuarine systems. The Susquehanna River provides 90% of the fresh water flow to the upper half of the Chesapeake Bay; much of its watershed is agricultural. To determine herbicide and insecticide mass loadings from the Susquehanna River, water samples were collected every 9 days over a 14-month period. Application practices and stream flow rates were found to be the most important factors in the prediction of pesticide loadings (*3*). Other research has focused on the management strategies to reduce runoff loads to estuaries. Subsurface drains were shown to reduce agricultural chemical losses from runoff by >20% and soil erosional losses by >50% (*4*).

Excess phosphorus (P) loading primarily affects aquatic life, whereas excess nitrogen (N) may affect both aquatic life and human health. However, the role of these nutrients, their transport mechanisms, particularly atmospheric deposition, and their linkages to endangered species, marine hypoxia, harmful algal blooms, and aquatic invasive species require further investigation (*2*). For example, the recent outbreak of *Pfiesteria piscicida* in Mid-Atlantic estuaries of the United States has prompted a reevaluation of nutrient cycling and transport to estuaries. Recent research emphasizes P cycling in soils and transport to surface waters to better mitigate P loss to water, which at high loadings is known to promote harmful algae blooms. A better understanding of N and P processes will aid environmental policy- and decision-makers in the development of scientifically sound, equitable standards for agricultural nutrient use (*5*).

Although chemical and physical parameters can objectively indicate contamination and provide quantitative data to compare with historical benchmark records, chemical data alone may not predict the amount of algae and other aquatic life (see, e.g., refs *6* and *7*). The National Stream Quality Accounting Network (NASQAN) and National Hydrologic Benchmark Network (HBN) of the U.S. Geological Survey provide data concerning long-term trends in water quality, with the HBN providing data concerning surface waters largely unaffected by human activities. Careful determinations of the statistical relationships between algal biomass and measured nutrient loads are needed to refine the predictive ability of chemical and physical measurements (*8*, *9*).

The Florida Bay ecosystem located in South Florida consists of a lagoonal series of embayments west of the Florida Keys archipelago. Seagrass vegetation historically dominated this region; however, in the 1990s seagrass die-offs were recorded, as well as an increase in water column algal blooms. Excess nutrient loads were implicated, and sources included runoff from agricultural fields located to the north and east of the major sloughs in the Everglades National Park and sewage-derived nutrients from the Florida Keys. Water column nutrient concentrations within impacted areas of Florida Bay were 2−4-fold higher than in pristine areas, and water column chlorophyll levels were an order of magnitude higher within these impacted zones. Primary productivity was shifted from seagrass−epiphyte-dominated components to one dominated by water column−sediment microalgae (*9, 10*).

Ammonia emissions and transport to terrestrial and aquatic ecosystems are a major concern. Robust measurement technologies are required to facilitate research concerning transport of this reactive gas. Use of the passive sampler Williams Badge and the annular diffusive denuder provided similar results when ammonia concentrations near poultry houses were measured (*11*). Researchers have examined ammonia release from large-scale animal production facilities where animal wastes are disposed into lagoons or in stockpiles adjacent to the animal houses, resulting in substantial emissions of ammonia. Initial studies conducted in parts of eastern North Carolina with a relatively high density of large-scale animal production facilities (>700 swine/km^2) indicated that ammonia flux is seasonal (lowest in winter, highest in summer), with values ranging from 300 to >4000 μg of N m^{-2} min^{-1} (*12*). Throughfall and bulk N deposition to nearby forest canopies was measured. Adjacent to a swine facility, NH_4-N dry deposition was twice that from wet deposition. N loadings from both wet and dry depositions (NH_4-N plus NO_3-N) attenuated with distance from the animal facility (*13*).

Land use affects watershed nutrient cycles, especially agricultural practices that involve extensive land disturbance and fertilization. Agriculture has been estimated to contribute 80−90% of N inputs and 30−40% of P inputs to the Choptank estuary within the Chesapeake Bay watershed, where agriculture is the predominant land use. Waste water treatment plants account for most of the remaining N and P. Phytoplankton in the lower estuary can consume these excess nutrients, resulting in algal blooms, and contribute to bottom water anoxia and loss of submerged grasses (*15*).

TOXICITY

Ecotoxicological assessment of agricultural non-point-source pesticide runoff impacts on living marine resources of South Carolina and South Florida watersheds was performed. Significant concentrations of endosulfan and other pesticides were observed in runoff into both South Carolina and South Florida watersheds. Sediment toxicity tests with clams and copepods and in situ oyster bioassays found significant alterations in reproduction at areas adjacent to agricultural fields (*16*).

Initial studies have been conducted to assess endocrine disruption in nearshore habitats of the Chesapeake Bay using the killifish *Fundulus heteroclitus* and to determine if the effects are related to land use. Seven sites have been established around the Bay, representing urban, industrial, waste water treatment (or a combination), agricultural, or pristine areas. Although the egg protein vitellogenin and some gonadal anomalies have occasionally been observed in males, endocrine disruption as measured in *F. heteroclitus* appears to be at a low level and low frequency at these sites in the Chesapeake Bay (*17*).

The fate and transport of copper-based pesticides from tomato crops using plastic mulch was examined in field and greenhouse experiments. Grass shrimp and fish mortality rates were significantly higher in the agricultural runoff when compared to a control estuary, and these mortalities were attributed to high copper loadings (*18*). Two vegetable cultivation practices (plastic mulch and hairy vetch residue mulch) were evaluated for their impact on estuarine organisms. Toxicity was significantly higher in runoff water and sediments from the plastic mulch plots. In sediments, copper, esfenvalerate, and endosulfan correlated well with toxic effects observed with the amphipods. Dissolved copper concentrations correlated better than the dissolved organic pesticide concentrations to toxicity effects seen with the clams, diatoms, and copepods (*19*).

In some cases, pesticides are used to control pests in estuarine systems. Imidacloprid was evaluated for control of burrowing shrimp that interfere with commercial production of oysters. Imidacloprid dissipated very rapidly from the plots and nearby areas. In this study, hazard to nontarget aquatic organisms based on the residues detected was found to be minimal (*20*).

Riparian ecosystems are believed to improve the quality of water exiting agricultural production systems. The effectiveness of riparian buffer systems to remediate agricultural runoff is under investigation. Studies have shown that spatial heterogeneity within the riparian wetland system can affect its overall function for nutrient removal. The results further indicate that preferential movement of water through wetland ecosystems can limit the biogeochemical function of riparian buffers in removing agricultural pollutants (*21*).

RESEARCH GAPS

Several of the research projects summarized above have been described in detail in the subsequent full papers. The issues raised in the "Agrochemical and Nutrient Impacts on Estuaries" symposium remain in the public forum. More facile and robust methods to identify, monitor, and model impaired waters are needed. Research gaps persist in our understanding of the functionality of and species interplay within the estuarine ecosystems. Improved prediction methods to determine the impact of land-use changes on water quality, the pollutant loadings by multiple sources within a watershed, and the ability of management strategies to mitigate the negative impacts are also of considerable interest. The complexity and high visibility of estuarine ecosystem health will require continued examination.

LITERATURE CITED

(1) *The Quality of Our Nation's Waters: 1996, Executive Summary*; U.S. Environmental Protection Agency, Office of Water: Washington, DC, 1998; EPA 842-F-99-0003D.

(2) *The Quality of Our Nation's Waters, Nutrients and Pesticides*; U.S. Geological Survey: Washington, DC, 1999; Circular 1225, 82 pp.

(3) Liu, B.; McConnell, L. L.; Torrents, A. Herbicide and insecticide loadings from the Susquehanna River to the northern Chesapeake Bay. *J. Agric. Food Chem.* **2002**, *50*, 4385−4392.

(4) Southwick, L. M.; Grigg, B. C.; Kornecki, T. S. Potential influence of sugarcane cultivation on estuarine water quality of Louisiana's Gulf coast. *J. Agric. Food Chem.* **2002**, *50*, 4393−4399.

(5) Sims, J. T. Nutrient cycling and transport in the Chesapeake Bay watershed: Integrating research into agricultural policy and management. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 158.

(6) *Biological Indicators of Water Quality*; James, A., Evison, L., Eds.; Wiley: New York, 1979.

(7) *Biomarkers of Environmental Contamination*; McCarthy, J. F., Shurgart, L. R., Eds.; CRC Press: Boca Raton, FL, 1990.

(8) Carlson, R. E. A trophic state index for lakes. *Limnol. Oceanogr.* **1977**, *22*, 361−369.

(9) Richardson, L. L.; Zimba, P. V. Spatial and temporal patterns of phytoplankton in Florida Bay: Utility of algal accessory pigments and remote sensing to assess bloom dynamics. In *Linkages Between Ecosystems in the South Florida Hydroscape: The River of Grass Continues*; Porter, J., Ed.; CRC Press: Boca Raton, FL, in press.

(10) Zimba, P. V. Role of nutrient runoff in altering downstream ecosystems: Florida Bay, FL, USA. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 159.

(11) Whung, P.-Y. Gaseous ammonia emissions near poultry houses and swine operations. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 166.

(12) Robarge, W. P.; McCulloch, R. B.; Cure, W. Ammonia release from large-scale animal production facilities. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 165.

(13) Robarge, W. P. Ammonia release from large-scale animal production facilities in eastern North Carolina: Using throughfall to measure deposition Ammonia release from large-scale animal production facilities. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 167.

(14) Fisher, T. R. Effects of agricultural land use on export of N and P from the Choptank River basin in the Mid-Atlantic coastal plain. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 164.

(15) Benitez, J. A.; Fisher, T. R. Historical changes in land use and nutrient yield coefficients in the Choptank River basin. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 163.

(16) Scott, G. I.; Fulton, M. H.; Wirth, E. F.; Chandler, G. T.; Key, P. B.; Daugomah, J. W.; Bearden, D.; Chung, K. W.; Strozier, E. D.; DeLorenzo, M.; Siversten, S.; Dias, A.; Sanders, M.; McCauley, J. M.; Goodman, L. R.; LeCroix, M. W.; Thayer, G. W.; Kucklick, J. Toxicological studies in tropical ecosystems: An ecotoxicological risk assessment of pesticide runoff in south Florida estuarine ecosystems. *J. Agric. Food Chem.* **2002**, *50*, 4400−4408.

(17) Pait, T. S.; Nelson, J. Use of the killifish Fundulus heteroclitus to assess endocrine disruption in the Chesapeake Bay. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 138.

(18) Dietrich, A. M.; Gallagher, D. L. Fate and environmental impact of pesticides in plastic mulch production runoff: Field and laboratory studies. *J. Agric. Food Chem.* **2002**, *50*, 4409−4416.

(19) Hetzer, P. R.; Brown, S. S.; Rice, P. J.; Baker, J. E.; Harman-Fetcho, J. A. Comparative effects of cultivation practices (vegetative vs polyethylene mulch) on pesticide-related ambient toxicity in estuarine habitats. *Proceedings of the 220th National Meeting of the American Chemical Society*; American Chemical Society: Washington, DC, 2000; p 141.

(20) Felsot, A. S.; Ruppert, J. R. Imidacloprid residues in Willapa Bay (Washington state) water and sediment following application for control of burrowing shrimp. *J. Agric. Food Chem.* **2002**, *50*, 4417−4423.

(21) Angier, J. T.; McCarty, G. W.; Rice, C. P.; Bialek, K. Influence of a riparian wetland on nitrate and herbicides exported from an agricultural field. *J. Agric. Food Chem.* **2002**, *50*, 4424−4429.

Received for review April 18, 2002. Accepted April 25, 2002.

JF020457N