PESTICIDE TRANSPORT RESEARCH AT THE NSL: PAST, PRESENT, FUTURE

***S. Smith, Jr., *C. M. Cooper, *S. S. Knight, **G. H. Willis, **L. M. Southwick**

***Research Chemist, Supervisory Ecologist/Research Leader, Ecologist, respectively, Water Quality and Ecological Processes Research Unit, USDA-ARS-National Sedimentation Laboratory, Oxford, Mississippi**

****Supervisory Soil Scientist/Research Leader and Research Chemist, respectively, Soil and Water Research Unit, USDA-ARS, Baton Rouge, Louisiana**

BRIEF HISTORY/OVERVIEW OF NSL

The National Sedimentation Laboratory (NSL) opened in 1959 as a result of Senate Document #59 (86th Congress). The Laboratory was charged with being a national center for sedimentation research and with solving problems related to sediment transport and deposition in stream channels and reservoirs. Additions to the NSL occurred in 1969 and 1987 resulting in total building space of about 55,000 square feet. From the beginning, NSL researchers have been engaged in measuring stream flow and sediment transport in large watersheds. Research in the 117-square mile Pigeon Roost Creek Watershed (1957-1979) near Holly Springs, Mississippi, provided comprehensive sediment transport data used in the development and evaluation of sediment transport equations. Since 1982, NSL scientists have collected runoff and sediment discharge data from the 8-square mile Goodwin Creek Watershed located about 15 miles west of the Laboratory. This research watershed is part of the Demonstration Erosion Control (DEC) Project in the Yazoo Basin and is cooperative with the U.S. Army Corps of Engineers and the Natural Resources Conservation Service (formerly the Soil Conservation Service). Data from the Watershed are used to develop hydrologic model parameters and for model validation. DEC in-stream stabilization practices, ecological features, and other related measures are also being evaluated. For twenty years (1965-1985) the NSL was involved in sedimentation research in more than 1200 reservoirs throughout the United States. As early as 1968, NSL researchers were involved in agrichemical transport by sediments, fate in reservoirs, and impact on watershed ecosystems. This work continued through the 1970s and involved pioneering studies of sediment and agrichemical transport from Mississippi Delta flatland soils. Field and laboratory studies of upland infiltration and erosion began in the mid-1970s and the results have contributed significantly to the Water Erosion Prediction Project (WEPP) and to the Revised Universal Soil Loss Equation (RUSLE). The NSL is a partner with the University of Mississippi's Center for Computational Hydroscience and Engineering in developing computational methods related to hydrology, erosion, and sedimentation and the National Center for Physical Acoustics in conducting research and developing instrumentation for studying soil porosity, streambed elevations, and sediment movement via acoustical methods. Research at the NSL is currently divided among three organizational units: Upland Erosion Processes, Water Quality and Ecological Processes, and Channel and Watershed Processes. Scientific disciplines include: hydraulic engineering, agricultural engineering, agronomy, soil science, soil physics, geology, hydrology, ecology, biology, and chemistry.

PESTICIDE TRANSPORT AND RELATED RESEARCH

Early Studies

Studies in the late 60s focused on chlorinated hydrocarbon insecticide residues occurring in Mississippi River streambed sediments. At that time, environmental pollution problems associated with pesticides had only recently received intensive consideration in soil and water management programs (McDowell and Grissinger 1966). Streambed sediment samples collected from the lower Mississippi River (north of Memphis, Tennessee, to New Orleans, Louisiana) and from several of its Delta tributaries in Tennessee, Mississippi, Louisiana, and Arkansas were analyzed for chlorinated hydrocarbon insecticides then in current use (Barthel et al. 1966, 1969; McDowell et al. 1971). Results of the studies revealed two point sources of pesticide contamination. One was in the vicinity of plants where **endrin** (1,2,3,4,10,10-hexachloro-1*R*,4*S*,4a*S*,5*S*,6,7*R*,8*R*,8a*R*-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene) and **heptachlor** (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) were manufactured in the Wolf River-Cypress Creek complex in Memphis, Tennessee. The second point source was in Mississippi where several pesticide formulating plants were located on other tributaries of the Mississippi River.

Later Studies

In the early and middle 70s, NSL studies dealt with pesticides transported in runoff from Mississippi Delta flatlands and with pesticide volatilization/disappearance from crop canopies in the Mississippi Delta. In one study, **toxaphene** (chlorinated camphene) and sediment concentrations in runoff were measured from a 16-ha continuous cotton (*Gossypium hirsutum* L.) watershed from 1973-1975 (McDowell et al. 1981). Results indicated a linear relationship between toxaphene yield and sediment yield. Furthermore, toxaphene and sediment yields were greatest during the spring tillage/planting/cultivation period, but toxaphene concentrations in runoff and in sediment were greatest during the summer application period. Of the toxaphene losses in runoff in 1975, 93% was attached to sediment and only 7% was lost in the water phase. In a similar study on an adjacent 19-ha continuous cotton watershed, toxaphene, **DDT** [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane], **DDE** [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene], **trifluralin** (α,α,α-trifluro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine), and sediment concentrations in runoff were measured from 1973-1978 (Willis et al. 1983a). Storm yields for DDT, DDE, and trifluralin were found to be linearly related to storm sediment yields for all years of the study. Storm toxaphene and sediment yields were linearly related only in 1973 and 1978, the two years in which no toxaphene was applied. During years in which toxaphene was applied (1974-1977), relationships between storm yields of toxaphene and sediment were evident only when the data were separated into periods of similar tillage and application regimes. For all years, clay concentration in runoff was linearly related to sediment concentration, but sediment organic matter (OM) concentration was a nonlinear function of sediment concentration because of OM enrichment at low sediment concentrations. Data from these pioneering studies have been used over the last two decades by many researchers for developing and refining pesticide and sediment transport models.

To more fully understand other loss mechanisms of pesticides from agricultural fields, toxaphene volatilization from a mature cotton canopy was investigated using the momentum balance method (Willis et al. 1980). Windspeed profiles, temperature gradients, and atmospheric toxaphene concentration gradients above the cotton plant canopy were accurately measured for a 5-day period following application, and vertical flux densities of toxaphene were calculated. Volatilization rates of toxaphene were found to be greatest during mid-afternoon with additional evidence of high rates whenever cotton plant leaves were drying after heavy dew or light rain. The calculated volatile loss of toxaphene for the 5-day period of the study was 358g ha^{-1}, equivalent to 26% of the toxaphene present on the cotton plants at the start of the study. In a similar study, the contribution of volatilization to the overall disappearance of toxaphene and DDT from cotton was measured under Mississippi Delta field conditions (Harper et al. 1983; Willis et al. 1983b). Disappearance rates of both insecticides from the cotton canopy were found to be linear functions of their loads on the cotton plants. Calculated 50% disappearance times (DT_{50}s) for toxaphene were 4.7d (1st application) and 10.8d (2nd application) and for DDT was 10.3d. Volatile losses of toxaphene were 17% (1st application, 10.7-d sampling period) and 53% (2nd application, 32.7-d sampling period) of the amounts intercepted by the cotton plants. DDT volatile losses were 58% (32.7-d sampling period) of the amounts on the cotton plants. Micrometeorological methods determined that volatilization of both insecticides from cotton plant foliage was closely correlated with leaf or air temperature and windspeed and to a lesser degree with net radiation. These studies showed that post-application volatilization of foliarly-applied pesticides was a major pathway of loss from fields sites. Post-application volatilization of pesticides as well as drift and volatilization during application are the principal methods of pesticide dispersion over wide areas far removed from their sites of manufacture, use, and disposal.

Recent Studies

By the late 70s and early 80s, NSL broadened the scope of its pesticide research by placing it in a more ecosystem-oriented setting. NSL scientists conducted watershed-scale/drainage network-scale studies of pesticide residues occurring in the major components (soil, water, sediment, fish) of Mississippi River alluvial stream and oxbow lake ecosystems. These studies also included comprehensive ecological evaluations. From 1976-1979 concentrations of toxaphene, DDT, **DDD** [1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethane], and DDE were measured in runoff, soils, surface waters, and bottom sediments of the intensively-cultivated 44,260-ha Bear Creek watershed (Cooper et al. 1987). Results of the study showed that low concentrations of the pesticides occurred in surface waters year round and that concentrations increased following seasonal winter and spring rains when vegetative cover was minimal. Furthermore, DDT concentrations were about what they were when the last applications occurred in 1972. In a 1978-1981 study of residual organochlorine insecticides in fishes of Lake Chicot, Arkansas (an oxbow lake of the Mississippi River), bottom feeding and piscivorus fish were found to contain higher pesticide concentrations than fish in the other feeding groups (Cooper and Knight 1987). Toxaphene, DDT, and DDD concentrations were also higher in fish from the main basin of the Lake where suspended sediment concentrations were significantly higher than in a smaller isolated basin. The pesticides also tended to be concentrated at relatively high levels in the viscera of the fish. In yet another study, the current-use insecticides **fenvalerate** [(*RS*)-α-cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate], **permethrin** [3-phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], and **methyl parathion** [*O,O*-dimethyl *O*-(*p*-nitrophenyl) phosphorothioate], along with residual toxaphene, DDT, DDD, and DDE were measured in soil, wetland and lake sediments, surface water, and fish of the 166 km^2 Moon Lake, Mississippi, watershed (Cooper 1991a, 1991b). DDT and metabolites were found in all watershed components ten years after discontinued use. The three current-use insecticides were not found in soil and were only occasionally detected in sediment, water, and fish. These on-the-cutting-edge ecological investigations led to a greatly expanded water quality and ecological processes research program at the NSL.

During the same time period, other NSL scientists, in cooperation with ARS researchers from the Baton Rouge, Louisiana, location, conducted in-depth field-scale studies related to pesticide persistence in and washoff from crop canopies. In one series of studies with toxaphene, fenvalerate, methyl parathion, **EPN** [*O*-ethyl *O* (*p*-nitrophenyl) phosphorothioate], permethrin, and carbaryl, rainfall amount was found to be of much greater importance than rainfall intensity in determining washoff losses of the insecticides (McDowell et al. 1984; McDowell et al. 1987; Willis et al. 1982; Willis et al. 1986; Willis et al. 1987). Another series of studies was concerned with washoff of fenvalerate, **azinphosmethyl** {*O, O*-dimethyl *S*-[(oxo-1,2,3-benzotriazin-3(4*H*)-yl)methyl] phosphorodithioate}, permethrin, **sulprofos** [*O*-ethyl *O*-(4-methylthiophenyl)-*S*-propyl phosphorodithioate], methyl parathion, and **malathion** [*S*-1,2-bis(ethoxycarbonyl)ethyl *O, O*-dimethyl phosphorodithioate] as affected by application method and/or formulation and/or time after application (McDowell et al. 1985; Willis et al. 1992a; Willis et al. 1992b; Willis et al. 1994a; Willis et al. 1994b). Results showed that the insecticides became more resistant to washoff with increasing time interval between application and first rainfall. Furthermore, ULV-oil application did not improve the rainfastness of some of the insecticides. Foliar deposition and persistence studies conducted with methyl parathion, fenvalerate, permethrin, and **parathion** (*O,O*-diethyl *O*-4-nitrophenyl phosphorothioate) showed no advantages of controlled-droplet applicators over application with conventional hydraulic nozzles, nor did application in soybean oil over application in soybean oil+water or water alone at ULV, VLV, or LV rates (McDowell et al. 1991; Willis et al. 1991). In a related study, microencapsulated formulations of methyl parathion and parathion were found to be more persistent on cotton foliage than conventional emulsifiable concentrate formulations (Smith et al. 1987). These studies led to the improved understanding of the dynamics of pesticide foliar persistence and washoff and have been important in developing pest management systems and in modeling environmental processes.

Present Studies

From the late 80s to the present, pesticide-related studies at the NSL have centered on non-point source stresses on upland stream watersheds and on farming systems for improved water quality. The distribution of residual organochlorine and current-use insecticides has been examined for the Otoucalofa Creek watershed in the loess hills of northern Mississippi (Knight and Cooper 1991). Analysis of watershed soils, transported sediments, surface water, and fish indicates that the residual pesticides are still contributing contaminants about two decades following their discontinued use and bioaccumulate in fish. Current-use insecticides also bioaccumulate but at significantly lower levels.

In other upland studies, farming systems for minimizing agrichemical transport in runoff and shallow groundwater for restrictive layer (fragipan) soils are being investigated. For example, **metribuzin** (4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one) and **metolachlor** [2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-*o*-toluidide] losses in runoff from upland soybeans primarily depend on the amount of runoff in the first runoff event after herbicide application (Smith et al. 1991; Smith 1992; Smith et al. 1995). Herbicide losses in the water phase of runoff are independent of tillage practice, such as no-till, which reduces sediment concentrations in runoff by about two orders of magnitude compared to conventional tillage. Because the herbicides are primarily transported in the water phase in runoff, herbicide losses in the sediment phase of runoff are low even with conventional tillage, where sediment concentrations in runoff can reach 50,000 ppm or higher. In contrast, reductions in water phase runoff losses of **atrazine** (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), **alachlor** (2-chloro-2',6'-diethyl-*N*-methoxymethylacetanilide), and **cyanazine** [2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropionitrile], also relatively water soluble herbicides, in no-till and reduced-till upland corn compared to conventional-till corn are being observed (Smith et al. 1994). These reductions in herbicide losses are attributed to reductions in runoff volumes in no-till and reduced-till corn (a high residue crop). The no-till practice in upland soybeans and the no-till and reduced-till practices in upland corn appear to be facilitating greater herbicide leaching into the soil profile in shallow ground water, likely the result of the formation of conducting macropores and biochannels (earthworm burrows, old root channels, etc.) produced by soil faunal activity in these practices.

Future Studies

Because of this extensive experience in pesticide transport and pesticide toxicity/ecological studies, NSL and other ARS scientists will play major roles in the forthcoming Mississippi Delta MSEA (Management System Evaluation Area) research project. Major objectives of this study include the development and evaluation of alternative and innovative farming systems for improved water quality/ecology in the Mississippi Delta and the linking of proper farming practices to improved lake ecosystem health. Specific areas of research will be: 1) agrichemical transport in surface runoff and shallow ground water as affected by alternative farming systems composed of combinations of BMPs including but not limited to conservation tillage, grass filter strips and waterways, slotted-board riser impoundments/sediment ponds, and improved agrichemical application technology; 2) comprehensive ecological assessment of the oxbow lakes including water quality (temperature, conductivity, secchi visibility, nutrients, pesticides and metabolites, pH, dissolved oxygen, suspended solids, etc.), primary productivity (light vs. dark bottle, plankton, chlorophyll), macroinvertebrates, and fishes (spawning phenology, relative abundances, growth rates, body condition) prior to and after implementation of BMPs on adjacent lake watersheds; 3) soil tension crack development and influence on runoff and infiltration; 4) comprehensive chemical and biological characterization of watershed soils (OM, pH, initial sorption parameters for herbicides to be used in the study, microbial biomass, baseline microbial populations of general and specific organisms, and enzyme activities); and 5) socioeconomic evaluation of increased awareness and adoption by farmers/landowners of alternative farming systems to reduce adverse agricultural impacts on water resources and ecological processes.

SUMMARY

The National Sedimentation Laboratory (NSL) has conducted pesticide-related studies for about the past 25-30 years. All studies have dealt with national issues. Studies in the late 60s focused on chlorinated hydrocarbon insecticide residues occurring in Mississippi River streambed sediments. In the early and middle 70s, studies dealt with pesticides transported in runoff from Mississippi Delta flatlands and with pesticide volatilization from crop canopies in the Mississippi Delta. By the late 70s and early 80s, NSL scientists conducted watershed-scale/drainage network-scale studies of pesticide residues occurring in the major components (soil, water, sediment, fish) of Mississippi River alluvial stream and oxbow lake ecosystems. These studies also included comprehensive ecological evaluations. NSL scientists in cooperation with ARS researchers from the Baton Rouge, Louisiana, location concurrently conducted in-depth field-scale studies related to pesticide persistence in and washoff from crop canopies as affected by weather variables, application method, formulation, and time after application. From the late 80s to the present, pesticide-related studies at the NSL have centered on non-point source stresses on upland stream watersheds and on upland farming systems for improved water quality. Because of this extensive experience, NSL and other ARS scientists will play major roles in the forthcoming Mississippi Delta MSEA (Management System Evaluation Area) research project. Major objectives of this study include development and evaluation of alternative and innovative farming systems for improved water quality/ecology in the Mississippi Delta and will link proper farming practices to improved lake ecosystem health.

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