Testing Landscape Indicators for Stream Condition Related to Pesticides and Nutrients: Landscape Indicators for Pesticides Study for Mid-Atlantic Coastal Streams (LIPS-MACS)

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September 2000

NOTICE

PROJECT SUMMARY

Title: Testing Landscape Indicators for Stream Condition Related to Pesticides and Nutrients: Landscape Indicators for Pesticides Study for Mid-Atlantic Coastal Streams (LIPS-MACS)

Principal Investigators: Ann Pitchford (EPA) and Judy Denver (USGS)

Project Goals:

This project is the first study in a long term, national research program, the Landscape Indicators for Pesticides Study (LIPS). The project is being conducted in the Mid-Atlantic Coastal Streams (MACS); the U.S. Geological Survey (USGS) is collaborating in the study through the National Water Quality Assessment (NAWQA) program. The main goal of the project is to develop landscape indicator models, also termed "landscape indicators," for pesticides, nutrients, and toxic chemicals in stream water and sediments. Landscape indicator model development involves the statistical comparison of physical or biological data characterizing streams (e.g., nutrient, pesticide, or toxic chemical concentrations, or biotic community composition and abundance), with corresponding spatial information for the stream and its valley. Besides surficial landscape features such as land cover, slope, and stream features, this study will include data on soils and hydrogeologic conditions in the analyses.

Approach/Methods:

With the experience gained from evaluating existing data, this study was designed to obtain collocated water quality, bed sediments, physical habitat, and benthic macroinvertebrate samples for first-order watersheds for a variety of geologic, hydrologic, and landscape settings, grouped by hydrogeologic conditions. The hydrogeologic conditions have been synthesized into a generalized framework of information on physiography, bulk texture of surficial sediments, topography, and subcropping geology. Seven units have been delineated within the Mid-Atlantic Coastal Plain (MACP). Each has relatively consistent, natural processes which are expected to govern the interchange of chemicals between surface and ground waters. Watersheds will be chosen to provide gradients in developed versus undeveloped land cover types. The field study will take place during the spring, providing a one-time-only "snapshot" of streams across the entire area. Water samples will be collected under conditions which represent shallow ground water contributions to the streams. Measurements proposed include pesticides, pesticide metabolites, nutrients, and major ions for stream water; physical habitat surrounding the stream at the sampling point; benthos community composition and abundance; and pesticides, mercury, arsenic, and PCBs in bed sediments. These data and indices based on these data will be the dependent variables in the landscape indicator models to be developed using independent variables such as land cover, topography, soil type, geologic and hydrologic characteristics, population density, length of roads in watersheds, and mean distance between roads and streams. The hydrogeologic framework unit will be evaluated as an explanatory variable in the landscape indicator models. In addition, the differences in results among the hydrogeologic framework units will be used to evaluate the hypotheses underlying the delineation of the units. Project resources

are leveraged with support from the USGS' NAWQA program and other smaller projects within the same geographic area.

Significance of Research:

In areas with substantial agriculture, industry, or urban development, pesticides and nutrients, industrial chemicals, pharmaceuticals, and other chemicals can dramatically affect water quality and biota in streams. The landscape setting, i.e., the location of a stream within its valley, and the relative proportions of land uses combined with the topography and related physical features, is expected to be a significant factor in assessing a watershed's condition in relation to these stressors. Landscape indicators can characterize the landscape setting by statistically combining and summarizing relevant spatial data. Since measurements are not possible in every watershed because of cost and practical constraints, these landscape indicators may offer a means to efficiently estimate the condition of streams with respect to pesticides, nutrients, and other chemicals in the MACP.

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INTRODUCTION

PURPOSE OF STUDY

This research plan for the Landscape Indicators for Pesticides Study -- Mid-Atlantic Coastal Streams (LIPS-MACS) describes the rationale and approach of developing a research project to evaluate statistical landscape indicator models for freshwater streams in the Mid-Atlantic Coastal Plain. This study is the first in a series of studies which will develop landscape indicator models for pesticides and toxic chemicals in selected areas, nationwide. These models, often termed "landscape indicators," will be developed for pesticides and nutrients in stream water and persistent organic pollutants, mercury, and arsenic in sediments.

In the statistical analysis, certain landscape characteristics, termed metrics, will be compared with dependent variables. Typical metrics include percent agricultural land cover, presence and extent of riparian zones, soil texture and permeability, percent agriculture on steep slopes, and soil erodibility. Typical dependent variables include the corresponding data characterizing streams, either biologically or chemically. In addition to these traditionally used landscape metrics, the LIPS-MACS study will include hydrogeologic parameters as additional landscape metrics in the evaluation process. The streams will be characterized with chemical analyses of both stream water collected during base flow conditions and sediments, and by measurements of benthic macroinvertebrates and physical habitat. Base flow conditions represent shallow ground water contributions to the streams and will provide a longer-scale, time integrated response, than characterizing storm flow, for example. The chemical analyses will include pesticides, nutrients, and major ions in stream water and historically used chlorinated pesticides, polychlorinated biphenyls (PCBs), and mercury and arsenic in stream sediments.

This study is intended to be consistent with several U.S. Environmental Protection Agency (EPA) approaches and guidelines including the Landscapes Approach (Jones et al., 2000); EPA's Guidelines for Ecological Risk Assessment (U.S. EPA 1998), EPA's Evaluation Guidelines for Ecological Indicators (Jackson et al., 1999), and the pesticide regulatory perspective.

RATIONALE FOR STUDY

Landscapes Approach

There is a growing interest among Federal agencies, States, and the public to evaluate environmental conditions at community, watershed, regional, and national scales. At the same time, the relatively high cost of collecting environmental data has limited the implementation of regional- and national-scale monitoring programs. However, alternatives to and adaptations of the traditional monitoring approach are possible using high resolution remotely sensed data and derivative products now available. Termed the "landscapes approach," this alternative applies a combination of concepts from landscape ecology, hydrology, and geography in conjunction with remotely sensed and other spatial data and geographic information system technology to the environmental assessment process (Jones et al., 2000, O'Neill et al., 1997). The landscapes approach relies on

- analysis of spatially explicit patterns (maps) of ecological characteristics (e.g., riparian zones near streams) to interpret ecological conditions;
- concepts from the field of landscape ecology, relating changes in landscape patterns to changes in ecological processes;
- an ecological hierarchy theory that analyzes the consequences of landscape change on ecosystems at multiple scales;
- digital maps of biophysical characteristics and human use to interpret landscape patterns relative to ecological condition; and
- inclusion of humans as part of the environment.

These characteristics distinguish the landscapes approach from the more traditional field or site-based monitoring programs. We hypothesize that the science of landscape ecology and related disciplines is integral to the assessment of the vulnerability and sustainability of ecosystem processes and functions.

The focus of EPA's landscapes approach is on aquatic resources because the EPA has primary responsibility in assuring their protection and restoration. However, the landscapes approach process evaluates many aspects of the terrestrial environment because these attributes are intricately linked to ecological and hydrological processes that influence aquatic resource conditions, as predicted from ecological hierarchy theory (O'Neill et al., 1986). Because regional-scale environmental factors and many local-scale factors are beyond human control, stream management efforts involve minimizing land use impacts that influence stream habitat (Richards et al., 1993). An understanding of both the aquatic resources and the terrestrial environment are important to understanding the role pesticides play in the environment.

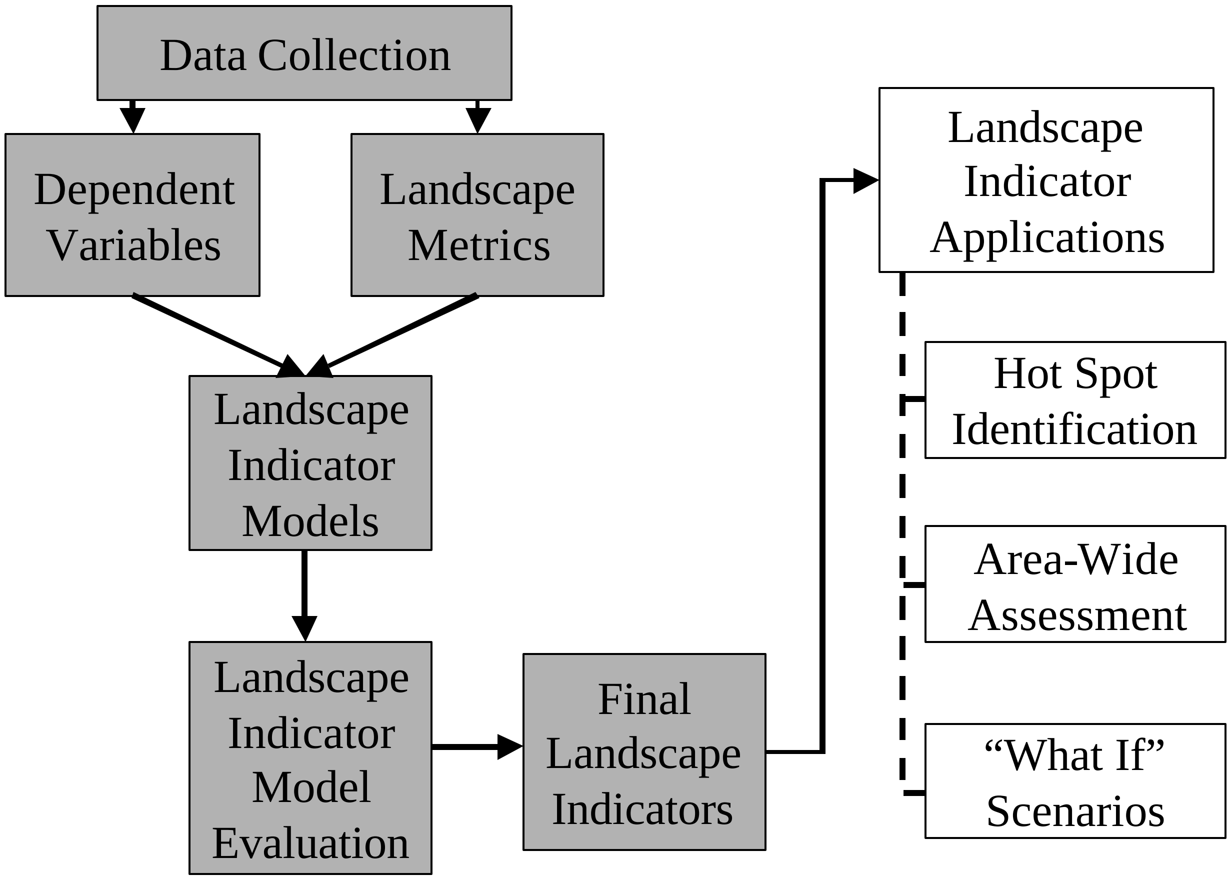

Figure 1. Steps in the landscapes approach.

The basic steps of the landscapes approach are summarized in Figure 1. The collection and synthesis of "landscape metrics," data characterizing specific spatial aspects of a watershed or area of interest, are the first steps in the process. Next, data for spatially and temporally comparable dependent variables are obtained, either from historical studies, or from new field studies. The landscape metrics are then ranked statistically for their importance in explaining the variance of dependent variables such as nutrient concentrations in streams (Jones et al., in press), or for LIPS-MACS, pesticide concentrations in stream water, benthic macroinvertebrate community composition and abundance, or toxic chemicals and metals in stream bed sediments. The statistical landscape indicator models are based on multivariate combinations of landscape metrics. The best indicator models are those with high predictive power, i.e., those which explain the largest amount of variance.

Once the landscape indicators have been developed and evaluated, a number of potential applications are possible. The landscape indicators can be used to classify geographic areas in a consistent, quantitative manner, for example, identifying relative ecological vulnerabilities. Thus, the indicators become a useful tool in deciding where to invest monitoring resources or in making other management decisions. By factoring the relative vulnerabilities into the decision process, the landscapes approach allows adaptation of a sampling design to focus on areas at highest risk. Because of its flexibility and applicability at multiple scales, the landscapes approach is widely recognized as the only cost-effective method to assess the potential impacts of complex natural and anthropogenic forces on the structure and function of ecological resources at various temporal and geographical scales. The implementation of the landscapes approach has begun only recently with the availability of high-resolution, remotely sensed data and the computer technology to manage these data (Jones et al., 1997). This study will be our first implementation of the landscapes approach for pesticides and toxic substances.

Guidelines for Ecological Risk Assessment

The Guidelines for Ecological Risk Assessment (U.S. EPA, 1998) describes basic elements for evaluating scientific information on the adverse effects of stressors on the environment. It is intended to be used as guidance for ecological risk assessments performed by the EPA. The three major phases of the framework are 1) problem formulation, 2) analysis, and 3) risk characterization. Because the landscapes approach provides tools that can characterize the geographic setting during initial problem definition, identify potential "hot spot" areas for more intensive evaluation, facilitate consistent comparisons across geographic areas, and assist in evaluating "what if" scenarios, it can play a multifaceted role in the risk assessment process (Graham et al., 1991, Hunsaker et al., 1990). After the landscape indicator models for pesticides and toxic chemicals are developed, the intent of LIPS-MACS is to apply the landscape indicators to provide examples of how these other aspects of the landscapes approach might be implemented for pesticides and toxics in streams.

Evaluation Guidelines for Ecological Indicators

EPA's evaluation guidelines for ecological indicators have been designed to encompass a wide variety of measurement types and assessment situations and are intended to be used for all EPA indicator development efforts. The 15 guidelines fall into four phases: conceptual foundation, feasibility of implementation, response variability, and interpretation and utility. Collectively, they provide a comprehensive, recognized framework and process for demonstrating indicator performance. The topics to be considered in the development of indicators include: 1) relevance to the assessment; 2) relevance to ecological function; 3) data collection methods; 4) logistics; 5) information management; 6) quality assurance; 7) monetary costs; 8) estimation of measurement error; 9) temporal variability-within season; 10) temporal variability-across years; 11) spatial variability; 12) discriminatory ability; 13) optimization to meet data quality objectives; 14) assessment thresholds; and 15) linkage to management action (Jackson et al., 1999). These topics have been considered in the conceptual formulation of the landscapes approach and landscape indicator development in general. LIPS-MACS will provide data and an opportunity to address many of these topics specifically for landscape indicators for pesticides and toxic substances.

Pesticide Regulatory Perspective

The United States and numerous other countries derive many benefits from manufactured chemicals, including improved health, food production, and quality of life. At the same time, these chemicals can cause serious problems for health of ecosystems. The challenge to society is to wield these chemicals wisely (Calow, 1998). The term "pesticides" is an umbrella concept for a wide range of chemical substances that can be used to control weeds, insects, and other pests. The active ingredients of pesticides are often combined into proprietary mixtures by manufacturers. The properties of the chemicals differ greatly; some are water soluble, some volatilize, some are adsorbed on soil particles, and some biodegrade rapidly. Unlike many manufactured chemicals, pesticides (including herbicides, insecticides, nematicides, and fungicides) are released directly into the environment and widely used in agricultural and urban areas and in water bodies, forests, and transportation corridors in the U.S. To assess product safety and evaluate potential risks to human and ecosystem health, and in accord with its statutory responsibilities, the EPA conducts a registration and evaluation process before any pesticide can be used. Pesticide- and toxic-substance-related research within the EPA supports this process by providing state-of-the-science measurements, methods, and models for development of ecological effects, exposure, and risk assessment protocols and guidelines, and it provides the scientific basis for credible ecological assessments and evaluations of the impacts of environmental stressors. Within this context, the Landscape Indicators for Pesticides Study is focused on improving assessments of the condition of streams and other water bodies with regard to pesticides, associated nutrients, and toxic chemicals at regional and sub regional scales.

The landscape indicator models developed in this project are expected to be useful to the U.S. Environmental Protection Agency's (EPA) Office of Prevention, Pesticides, and Toxic Substances (OPPTS); Office of Water (OW), and Regional Offices; and also State and local agencies with responsibilities for developing Total Maximum Daily Loads (TMDLs) or concerns about how water resources are affected by pesticides or toxic substances.

PARTICIPANTS

This study is a collaborative effort by EPA's National Exposure Research Laboratory (NERL) and USGS' Water Resources Division, Maryland-Delaware-District-of-Columbia District Office working with the National Water Quality Assessment (NAWQA) program. Discussions will also take place with the U.S. Department of Agriculture regarding their involvement in the study, particularly in providing pesticide application rate information.

Within EPA, the NERL Environmental Sciences Division in Las Vegas, Nevada is the lead for the study; other NERL participants include the Ecological Exposure Research Division in Cincinnati, Ohio, and the Ecosystems Research Division in Athens, Georgia. Other EPA participants include the Western Ecology Division of the National Health and Environmental Effects Laboratory in Corvallis, Oregon, and the Subsurface Protection and Remediation Division of the National Risk Management

Laboratory, in Ada, Oklahoma. EPA Regions 2, 3, and 4 and the Chesapeake Bay Program Office also are involved.

ORGANIZATION OF RESEARCH PLAN

The remainder of this research plan describes the details of LIPS-MACS. Separate sections provide a project overview, description of the study area, and literature reviews for key topics. Additional sections describe the field study, data analysis, hydrologic and multimedia modeling, landscape indicator applications, quality assurance (QA), milestones/ schedule, performance measures, potential for reducing uncertainty, and anticipated results and products.

PROJECT OVERVIEW

GENERAL

This overview identifies the key features of the project before delving into the details and specifics. Project elements at the broadest level flow from the hypotheses, to database development, to the final landscape indicators, and application of these indicators in decision making (Figure 2). In formulating this project and developing this plan, there are two major activities that are complete:

- Hypotheses Development: A number of hypotheses concerning pesticide and toxic chemical behavior, hydrogeologic characteristics, and landscape indicators are developed and are presented later in this section. These hypotheses are based on several general research objectives related to assessing condition of streams in the mid-Atlantic region of the U.S. and are driven by our understanding of agricultural land use and farming practices and urban pesticide practices in the area. The overarching issue is the risk to the aquatic environment from pesticides, nutrients, and toxic chemicals and metals.

- Project Design: The central component of this project is a comprehensive, geo-referenced database which will facilitate statistical analyses for landscape indicators and testing of the hypotheses. When these major objectives are completed, the database will continue to play a crucial role, supporting applications of the landscape indicators to answer "what if" type questions. This effort also may entail some process-based modeling. A major activity of the study, especially in terms of field sampling and laboratory analyses, is the development of this database. It will consist of data on water quality, stream bed sediments, benthic macroinvertebrates, physical habitat, landscape features, and pesticide loadings measured at, and geo-referenced to, all the study sites in the Mid-Atlantic Coastal Plain. These data categories are those considered pertinent during the development of the hypotheses and design of the analyses. The literature review and the evaluation of existing data are significant guides to the selection of the database components. Both existing and new data, and both spatial and point-based monitoring data, will be collected and included in the database.

To implement this study, there are two major activities:

- Existing Data Acquisition: Existing water quality, hydrologic, and biotic data were gathered to review for planning purposes as mentioned in the Project Formulation, above. Much of the data to be used is from existing USGS programs such as NAWQA. The data for interpreting the behavior of the land use/land cover

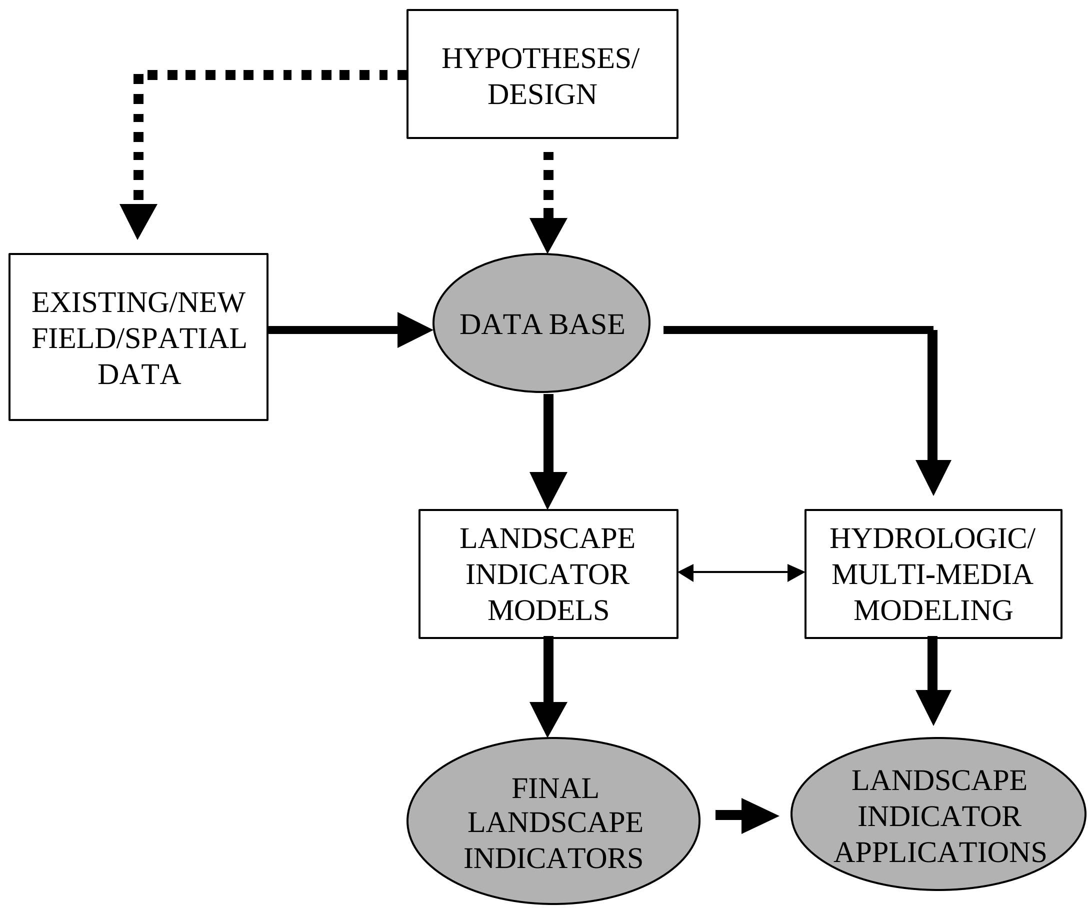

Figure 2. Conceptual framework for LIPS-MACS. Each rectangle corresponds with actions, while the gray ovals represent products. Note that since stakeholder involvement extends throughout the entire project, it is not shown explicitly. The arrows are either single-headed, implying a one-way progression, or double-headed, implying feedback and iteration.

imagery and related information will be compiled for the landscape analysis portion of the study and will be an essential component of the database. The remotely sensed landscape data and related spatial data (such as population) will encompass the entire study area, "wall-to-wall."

- New Data Acquisition: New measures of stream water quality, bed sediments, and of stream benthic and physical habitat conditions, from a one-time-only field study, will be included in the database and used in the statistical analyses for landscape indicator development. These data will provide a "snapshot" of spring conditions using a consistent sampling design and established sampling and analytical methods. It is important to note that the same portfolio of measures will be obtained for all data categories at all the study sites. In addition to these field data, some process-modeling activities are expected to provide additional information for input to the statistical analyses. There will be no new aerial imagery developed specifically for this study.

The most important aspect of the study is the analysis effort which contains four major activities:

- Landscape Indicator Models: Traditional multivariate linear regressions will be applied to examine relationships between the data categories in the development of the landscape indicator models. The landscape metrics and hydrogeologic parameters will be the independent variables and stream water quality, sediment concentrations of toxic chemicals, and benthic condition data will be the dependent variables. In addition, Classification And Regression Tree (CART) analysis will be used. Landscape metrics, hydrogeologic parameters, and stream habitat characteristics will be the independent variables and the aquatic parameters the dependent variables. In a related series of analyses using comparative statistics, the generalized framework of seven hydrogeologic units will be evaluated for its contribution to our understanding of the natural processes which are expected to govern the interchange of chemicals between surface and ground waters.

- Hydrologic/Multimedia Modeling: This approach represents the application of existing, physically- and chemically-based process models to typical settings within the study area. Several hydrologic, pesticide fate and multimedia models will be used as needed to improve our conceptual understanding of the physical and chemical processes involved in the landscape. The model capabilities will include compartmental distribution, hydrologic flow, and fate and transport. We may use some data derived from the hydrologic and multimedia modeling in the landscape indicator modeling. Alternatively, the landscape modeling results may suggest scenarios for the hydrologic and multimedia modeling.

- Final Landscape Indicators: These indicators consist of the best models developed in the statistical analyses (see above) for use as indicators. Sensitivity analysis results; numbers and types of variables to be used; areas of applicability within the study area; and estimates of error will be considered. The landscape indicator model error estimates will rely on a randomly chosen subset of data, withheld from the initial analysis. A minimum detection level for the indicator models will be identified.

- Landscape Indicator Applications: Once the landscape indicators are selected, then it is possible to apply them for a number of different purposes: to identify relative "hot spots" in a region; to perform area-wide assessments; and to try out "what if" scenarios. For example, historic land cover data could be used as an input to the indicator and the older results compared with the more recent results. Alternatively, a projection of future land cover could be used as an input and the results compared with current status.

Finally, it is our intention to involve Program Offices, Regional Offices, and other stakeholders in the project to the degree they are interested. We will identify this group early and keep them informed during the process of selecting the sampling and modeling sites, as results become available. We will work extensively with this group in deciding how to present the results of this study, e.g., workshops, reports, news releases.

OBJECTIVES

The objectives of this study are to

1) develop landscape indicators for pesticides and toxic substances in stream water and bed sediments; and

2) demonstrate the application of the final landscape indicators for the Mid-Atlantic Coastal Plain

A key assumption in this approach is that first-order streams and their valleys represent the best scale for investigating landscape effects on streams because of the proximity of the stream to the landscape features, shorter residence times for ground water prior to discharge to surface water, and simplicity of the spatial land use patterns encountered.

HYPOTHESES

Two basic sets of hypotheses will be tested in this study, and organized according to the objectives listed above. The hypotheses are expressed in general terms, but are meant to apply to individual chemicals and groups of chemicals with similarities in properties and use. The hypotheses for objective 1 are:

H1.1 Concentrations of pesticides and agrochemicals in stream water and bed sediments, and concentrations of toxic substances in bed sediments are related to landscape metrics.

H1.1.a Concentrations of pesticides and agrochemicals in stream water and bed sediments are related to the amounts of pesticides applied to the land.

H1.1.b Concentrations of toxic substances in bed sediments above a background threshold due to atmospheric deposition are proportional to the amount of urban development in the watershed.

H1.2 Landscape metrics are related to underlying hydrogeologic variables.

H1.2.a Farmland is located in well-drained or artificially drained areas.

H1.3 Concentrations of pesticides and agrochemicals in stream water and bed sediments and concentrations of toxic substances in bed sediments are related to hydrogeologic variables.

H1.3.a Pesticide and agrochemical concentrations in stream water are related to the soil sand content in the watershed.

H1.3.b Pesticide and agrochemical concentrations are related to underlying geologic formations.

H1.3.c Pesticide and agrochemical concentrations in sediment are related to the soil sand content in the watershed and the amount of clay and organic material in the sediment.

H1.3.d Toxic metal concentrations in sediment are related to their content in the underlying geologic formations and atmospheric deposition.

H1.4 Concentrations of pesticides in stream water and bed sediments are related to a combination of landscape metrics and underlying hydrogeologic variables.

H1.4.a The relative importance of landscape metrics and hydrogeologic variables will be difficult to separate statistically because the two are interrelated.

A key assumption for the hypotheses below is that stream biotic condition is related to benthic macroinvertebrate community composition and abundance for first-order streams.

H1.5 Benthic macroinvertebrate community data are related to stream and bed sediment concentrations of pesticides, nutrients, and toxic substances, and physical habitat.

H.1.5.a Benthic macroinvertebrate community data are related to landscape metrics.

The hypotheses for objective 2 are:

H2.1 Landscape indicator models for pesticides and toxic substances are applicable to all the first-order, freshwater streams in the Mid-Atlantic Coastal Plain.

H2.2 Stream biotic condition can be estimated using landscape metrics and hydrogeologic variables.

H2.3. Landscape indicator models for stream biotic condition are applicable to all the first-order, freshwater streams in the Mid-Atlantic Coastal Plain (1990s data).

H2.4 Landscape indicator models for stream biotic condition demonstrate poorer conditions during the 1990s compared to similar analyses during the 1970s.

More detailed hypotheses for the hydrogeologic framework are described later (Table 1).

UNIQUE FEATURES

The following are unique features of this study:

- Testing landscape indicator concepts for pesticide and toxic chemical impacts on streams;
- Incorporating geologic and hydrologic data into the landscape indicator model development process;
- Choosing first-order streams and watersheds for landscape analysis;
- Incorporating a hydrogeologic framework into the sampling design to minimize hydrologic variability;
- Combining a gradient study sampling design (based on percent developed land cover) for landscape indicator development with a probability sampling design for characterizing hydrogeologic framework areas; and
- Characterizing pesticide metabolite concentrations for a large population of streams: the freshwater streams of the Mid-Atlantic Coastal Plain.

DESCRIPTION OF STUDY AREA

The Mid-Atlantic Coastal Plain is a physiographic region known for its rich farmlands, forests, marshes, and swamps. It extends from southern New Jersey to North Carolina. The eastern parts of four states; New Jersey, Maryland, Virginia, and North Carolina, the District of Columbia, and all of Delaware are included within the Coastal Plain (Figure 3). The western limit of the Coastal Plain is identified by the fall line, the location where waterfalls or rapids occur in rivers flowing to the Atlantic. The rapids originate at the boundary where the higher and relatively older, harder rocks transition to the lower, softer, and flatter sediments of the Coastal Plain. Fall-line cities on the edge of the Coastal Plain include Baltimore, Maryland; Washington, D.C.; Richmond, Virginia; and Raleigh, North Carolina. Land use/land cover data for the coastal plain show that urban, commercial, or residential designations comprise 9 percent of the area; agriculture 30 percent; forest 40 percent; wetland 20 percent; and other 1 percent. The Coastal Plain area is encompassed by three ecoregions (North Atlantic Coast, Chesapeake Bay Lowlands, Mid-Atlantic Coastal Plain) (Omernik, 1995) and three biotic communities (Northeastern Deciduous Forest; Southeastern Deciduous Forest and Evergreen Forest; and Southeastern Swamp and Riparian Forest) (Brown et al., 1998).

All the rivers of the Coastal Plain drain into the Atlantic Ocean. Major rivers include, from north to south on the Delmarva Peninsula, the Chester, Choptank, Nanticoke, and Pocomoke. On the west side of Chesapeake Bay, the rivers include the Susquehanna, Patuxent, Potomac, Rappahannock, York, and James, while in North Carolina the rivers include the Chowan, Tar, Neuse, New, and Cape Fear. Rivers are an important source of water supply to cities such as Baltimore, Washington, D.C., Richmond, and Raleigh, but many of the people on the Coastal Plain depend on ground water.

The Coastal Plain is well suited to agriculture; nearly all of the coastal plain is flat or gently sloped, although some areas have relief of 30 meters or more. Elevations across the Coastal Plain range from sea level along the coast to 230 meters (750 feet) on the western edge in North Carolina. Based on an analysis of a 30-meter digital elevation map, more than 75 percent of the Coastal Plain has elevations less than 40 meters (130 feet). The Coastal Plain is underlain by semiconsolidated to unconsolidated sediments that consist of silt, clay, sand, with some gravel and lignite (Trapp and Horn, 1997). In general terms, soils in the Coastal Plain include humus-laden loams near the coast, with sandy loams and clay more toward the west. Much of the land suitable for agriculture is farmed although suburbanization is encroaching on the farm lands. Agricultural products include chickens, dairy products, corn, soybeans, vegetables, and tobacco.

The climate in the Coastal Plain is humid and temperate. Average annual precipitation ranges from 132 cm (52 in) per year in the southern coastal portion of North Carolina to approximately 101 cm (40 in) per year in southern New Jersey, Northern Delaware, and west of the Chesapeake Bay. The growing season ranges from 200 days in New Jersey to 275 days in North Carolina.

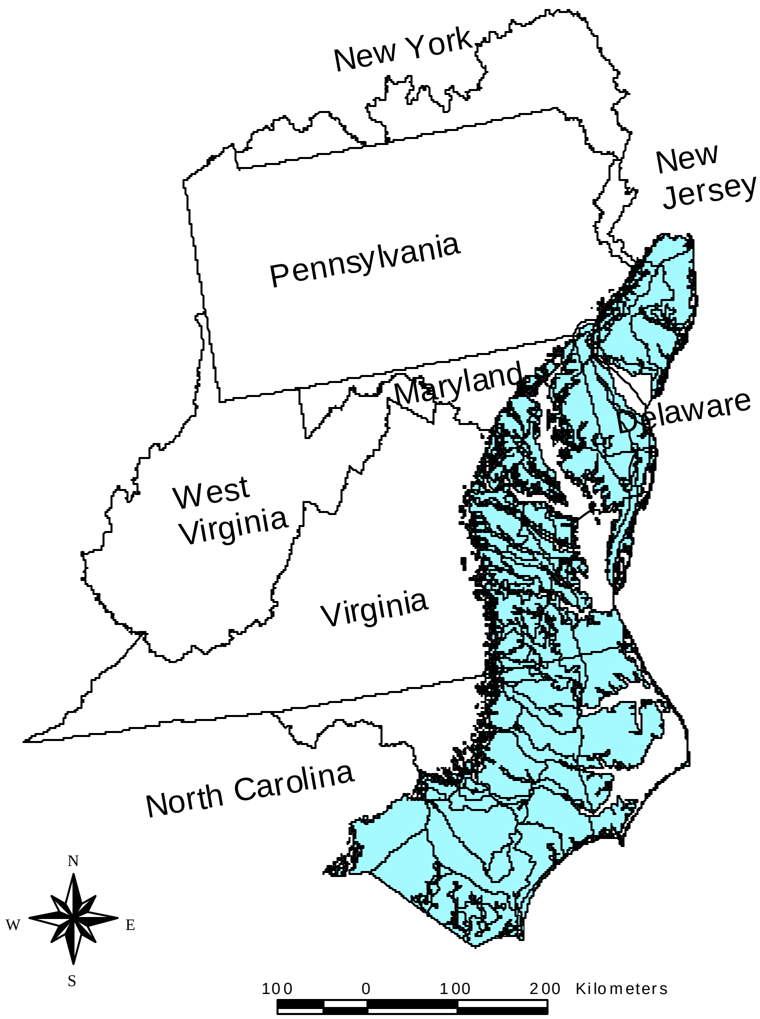

Figure 3. Mid-Atlantic Coastal Plain Study Area. State and the Mid-Atlantic Integrated Assessment (MAIA) boundaries are shown. The hydrogeologic framework is shaded with hydrologic framework units shown in outline only.

LITERATURE REVIEW

PESTICIDE AND FERTILIZER USE IN THE MID-ATLANTIC COASTAL PLAIN

According to the Federal Insecticide, Fungicide, and Rodenticide Act, pesticides are defined as any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, and any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant. Pesticides addressed in this plan include herbicides for weeds and insecticides for insects, mites, and nematodes. Pesticides in streams can have deleterious effects on aquatic life, as well as being a potential source of exposure for humans who may use the water. Fertilizers are defined as the primary plant nutrients: nitrogen, phosphate, and potash. An overabundance of nutrients in streams can promote algal growth, depress oxygen concentrations, and increase turbidity.

An understanding of pesticide and fertilizer use in agricultural and urban areas is critical to our study because these land use categories are the main source of the chemicals we will measure in the streams. Since stream samples are collected during base flow, the concentrations of pesticides and nutrients measured will represent the integrated result of short- and long-term flow paths of the shallow groundwater to the stream. The values measured will represent averages of usage over the past several years, rather than the year immediately past, or the most recent application. It would be ideal to have a decade of pesticide and fertilizer use information for each farm, roadside, and forest in each watershed we are studying, but this is not possible. In many cases, this type information is not available, or not saved. Even if it were saved, it would be considered proprietary business information. Information gathered for specific farms by federal government surveys is protected by confidentiality regulations. Finally, application estimates for household, urban area, highway right-of-way, and commercial forest uses of pesticides have proven difficult to find. Efforts to estimate these parameters will continue. The types of information that are available are summarized below.

Data on pesticide and fertilizer use varies widely in types of data available from state to state. Some data are available for all states from the National Agricultural Statistical Service (NASS), as part of their 5-year Census of Agriculture reports. These reports contain information on the number of acres for which broad categories of agricultural chemicals were used. These data are summarized at the state level, and by county (NASS, 1997). Additional reports are prepared annually by NASS for states in the “top-producer” category for selected crops and focus on specific topics, which often include pesticide and fertilizer use for selected crop types, at the state level. These reports provide application rates by specific active ingredient in pounds per acre for the states selected for the survey. Finally, some states prepare their own reports on pesticide use on an annual basis and these provide detailed summaries at the county level (Maryland Department of Agriculture, 1999).

In agriculture, pesticide and fertilizer use is determined by the type of crop planted and this in turn depends on the climate, soil, and microclimate of a particular farm field. Common crops in the five states containing the Coastal Plain include soybeans, corn for grain, fruits, nuts and berries (in New Jersey), tobacco, vegetables, sweet corn, melons, cotton, and wheat. For production of soybeans harvested for beans, North Carolina and Maryland are ranked 17th and 19th respectively among states nationwide. For production of corn harvested for grain or seed, North Carolina is ranked 16th. For tobacco production, North Carolina and Virginia are ranked first and fourth nationwide. For cotton production, North Carolina is ranked 7th nationwide.

Each crop type has a recommended pesticide application profile which is adapted by the farmer or commercial applicator to the specific conditions of the individual field. Factors which affect the use of pesticides include the condition of the field, whether conventional agriculture or no-till techniques are being used, what crops were previously grown, and the type of pest present. One application per year is typical for commonly used pesticides for corn, soybeans, and cotton (see Tables 1, 2, and 3). These data are based on surveys conducted in 1998 in North Carolina; other states in the Coastal Plain were not included in this survey.

Table 1. Pesticide and Fertilizer Usage for Corn in North Carolina based on Surveys Conducted in 1997 and 1998 (NASS, 1999).

Herbicide or Insecticide/ Fertilizer	Area Applied (percent)	Applications (number)	Rate per Application (pounds/acre)	Rate per crop year (pounds/acre)	Total Applied (1,000 pounds)
2,4-D	27	1.0	0.40	0.40	92
Alachlor	22	1.0	1.90	1.95	373
Atrazine	88	1.0	1.02	1.02	774
Glyphosate	14	1.0	0.64	0.64	77
Metolachlor	44	1.0	1.30	1.30	498
Paraquat	8	1.4	0.48	0.71	50
Simazine	2	1.0	1.25	1.25	16
Chlorpyrifos	8	1.0	1.17	1.17	81
Terbufos	21	1.0	1.14	1.14	201
Nitrogen	98	2.0	61	125	105,100
Phosphate	92	1.1	48	54	42,200
Potash	91	1.0	96	97	76,100

Table 2. Pesticide and Fertilizer Usage for Soybeans in North Carolina based on Surveys Conducted in 1997 and 1998 (NASS, 1999).

Herbicide or Insecticide/ Fertilizer	Area Applied (percent)	Applications (number)	Rate per Application (pounds/acre)	Rate per crop year (pounds/acre)	Total Applied (1,000 pounds)
Chlorimuron-ethyl	12	1.3	0.02	0.02	5
Flumetsulam	6	1.0	0.07	0.07	7
Glyphosate	59	1.2	0.85	1.07	932
Imazaquin	1	1.0	0.06	0.06	1
Metolachlor	9	1.0	2.30	2.30	322
Nitrogen	36	1.0	23	24	12,400
Phosphate	34	1.0	38	38	19,400
Potash	39	1.0	83	83	47,300

Table 3. Pesticide and Fertilizer Usage for Cotton in North Carolina (NASS, 1999).

Herbicide or Insecticide/ Fertilizer	Area Applied (percent)	Applications (number)	Rate per Application (pounds/acre)	Rate per crop year (pounds/acre)	Total Applied (1,000 pounds)
Clomazone	5	1.0	0.48	0.48	18
Cyanazine	9	1.0	1.01	1.09	69
Fluometuron	41	1.0	0.91	0.91	267
Glyphosate	65	1.6	0.73	1.21	556
MSMA	33	1.1	0.93	1.04	241
Pendimethalin	28	1.0	0.76	0.76	154
Prometryn	18	1.2	0.54	0.67	87
Pyrithiobac-sodium	5	1.0	0.06	0.07	2
Trifluralin	20	1.0	0.55	0.55	80
Aldicarb	28	1.0	0.69	0.69	138
Cyfluthrin	16	1.9	0.04	0.08	9
Disulfoton	3	1.0	0.49	0.49	10
Lambda-cyhalothrin	70	2.5	0.03	0.07	36
Phorate	25	1.0	0.8	0.8	140
PCNB	6	1.0	1.02	1.02	202
Cacodylic acid	12	1.0	1.37	1.42	124
Cyclanilide	42	1.0	0.13	0.13	40
Dimethipin	3	1.0	0.30	0.30	7
Ethephon	58	1.0	1.08	1.09	451
Mepiquat chloride	23	1.3	0.02	0.03	5
Paraquat	3	1.1	0.36	0.40	8
Thidiazuron	31	1.0	0.27	0.27	59
Tribufos	28	1.0	1.02	1.02	202
Nitrogen	98	1.9	46	87	60,200
Phosphate	90	1.1	52	55	35,000
Potash	93	1.1	96	108	71,600

PESTICIDES AND NITRATES MEASURED IN STREAMS IN THE MID-ATLANTIC COASTAL PLAIN

Pesticides and nitrates are routinely detected in some streams in the Mid-Atlantic Coastal Plain. Pesticides have been measured in streams and wells in the Mid-Atlantic mainly through the NAWQA program and some state programs; summaries of this information are available (Ferrari et al., 1997; Ator and Ferrari, 1997; Zappia and Fisher, 1997; Shedlock et al., 1999). Nitrates have been measured at more sites than pesticides, and summaries of these data are also available (for example, McFarland, 1995). Finally, river basin summaries, which discuss pesticides and nitrates and many other aspects of water quality, are available for all of the NAWQA study sites for example, the Lower Susquehanna and the Potomac, respectively (Lindsey et al., 1998; Ator et al., 1998). Some of the details of these studies are discussed further below. These data suggest that detectable concentrations of pesticides and nitrates will be measured at many of the study sites.

Chronic low levels of pesticides and much of the nitrate measured in Coastal Plain streams are attributed to ground-water discharge, i.e., ground water supplying the stream during base flow conditions (Barbash et al., 1996; Bachman et al., 1998; Shedlock et al., 1999). Base flow refers to the water that enters the stream from a persistent, slowly varying source (typically ground water) and maintains stream flow between storms (Dingman, 1994). Nitrate concentrations in Mid-Atlantic streams commonly exceed 0.15 mg/L as N, a level considered by the Chesapeake Bay Program to contribute to eutrophication in estuaries. Nitrate concentrations occasionally exceed 10 mg/L as N, the Federal maximum contaminant level for drinking water (U.S. EPA, 1994a). Pesticides are present year-round in some streams of the Mid-Atlantic Region in both urban and rural areas (Ferrari et al., 1997). Concentrations of most compounds are typically highest during the spring and summer when there are sharp increases shortly after application with relatively rapid declines in pesticide concentrations to near or below detection for the remainder of the year (Larson et al., 1997). Chronic low levels of common pesticides are attributed to ground-water discharge (Hallberg, 1987; Barbash et al., 1996; Shedlock et al., 1999). Higher levels are commonly related to runoff shortly after application periods and commonly occur in the spring and summer (Larson et al., 1997; Ferrari et al., 1997). Pesticide concentrations in Mid-Atlantic streams commonly increase with increasing stream flow (Ferrari et al., 1997). Herbicides are detectable in streams in many settings, but concentrations are generally higher in agricultural areas. Insecticide concentrations are typically highest in streams draining urban watersheds; however, data from such areas in the Coastal Plain are limited.

Detection of pesticides during late winter and early spring base-flow conditions should represent the contribution of ground-water sources of pesticides to surface water in the absence of recent pesticide application. The base flow conditions should be more representative of the time the water is in contact with the soil than other flow conditions, for example, when storm flow is present. Ground water is a major source of water to streams in the Mid-Atlantic Coastal Plain. The upper aquifer is shallow and relatively fast moving. The estimated median percentage of stream flow derived from ground water is more than 60 percent for the Coastal Plain part of the Chesapeake Bay drainage (Bachman et al., 1998). Ground water provides more than 90 percent of stream flow in parts of the

New Jersey Coastal Plain (Stackelburg and Ayers, 1994); between 40 and 85 percent of stream flow in parts of the Coastal Plain in North Carolina and southern Virginia (McMahon and Lloyd, 1995); and from 37 to 81 percent in the Delmarva Peninsula (Cushing et al., 1973).

Only a few pesticides have a strong potential to be delivered to surface water from ground water in appreciable quantities (Barbash and Resek, 1996). These include compounds such as the commonly used triazine and acetanilide herbicides that have moderate to high water solubility and stability and relatively low soil-sorption coefficients. Several of these compounds, including some metabolites of atrazine, have been detected in streams of the Mid-Atlantic Coastal Plain during winter base flow. Simazine, metolachlor, alachlor, desethyl atrazine, and deisopropyl atrazine were detected in base flow samples collected from January through March 1992 from a small stream on the Delmarva Peninsula located in an agricultural area with well-drained soils. Pesticide compounds were typically undetectable in samples collected during the same time period in two other small streams on the Delmarva Peninsula located in more poorly drained agricultural areas. The minimum laboratory reporting level for pesticides in the 1992 Delmarva samples was 0.05 micrograms per liter (ug/L); however, it is significantly higher than the 0.001 ug/L reporting level that has been used by the NAWQA program since 1993. We expect that with the lower reporting limits now in effect, pesticides will be detected more frequently than before.

Using current analytical techniques, pesticides are detectable in stream samples from a variety of Coastal Plain land-use settings. Surface water samples collected in two small Coastal Plain watersheds in North Carolina during December through March 1993 and 1994 typically contained atrazine, metolachlor, and alachlor; simazine and diazinon also were detected. Concentrations of these compounds ranged from below the method detection limit of 0.001 to 0.19 ug/L. The sampled streams drain mostly mixed agricultural and forested watersheds. Atrazine, desethyl atrazine, metolachlor, simazine, and alachlor were detected in samples collected between January and March 1997 from Great Egg Harbor River, which drains a developing urban watershed in New Jersey.

Concentrations of pesticides in surface water seldom exceed maximum contaminant levels or lifetime health advisory limits for those compounds that have them (Ferrari et al., 1997). In addition to parent compounds, metabolites of the common herbicide atrazine have been commonly detected in surface water throughout the Mid-Atlantic Region (Shedlock et al., 1999; Ferrari et al., 1997). Based on research from other areas where similar pesticides are applied (Kolpin et al., 1998), there is reason to suspect that metabolites of other commonly used pesticides, specifically the acetanilides, metolachlor and alachlor, would also be commonly detected in surface waters of the Mid-Atlantic Coastal Plain (Kalkoff et al., 1998; Phillips et al., 1999a; Phillips et al., 1999b).

Nitrate data provide additional insights on subsurface processes affecting stream concentrations. The importance of understanding subsurface conditions in interpreting the processes affecting surface-water quality has been demonstrated in several studies of riparian zone function in the Mid-Atlantic Region. Lower concentrations of nitrate in surface water than in upgradient ground water flowing toward surface-water discharge areas have been attributed to processes of uptake by riparian zone vegetation and denitrification (Lowrance et al., 1984; Correll et al., 1992; Osborne and Kovacic, 1993). Several recent studies have shown that differences between ground- and surface-water chemistry are dependent on a variety of other factors, as well, that relate to the opportunity for ground water to reach surface water (Böhlke and Denver, 1995; Phillips and Bachman, 1996; Speiran, 1996; Staver and Brinsfield, 1996).

Factors affecting concentrations of nitrate in streams include aquifer thickness, the chemical environment of the aquifer, the length of ground-water flow paths, the predominance of different land uses in a watershed, and changes in land use and chemical application rates over time. In a study of a small, well-drained agricultural watershed with a forested riparian buffer overlying a relatively thick surficial aquifer, Böhlke and Denver (1995) found that the lower concentrations of nitrate measured in surface water than in ground water were related to the lag time between nitrogen application and ground-water discharge, e.g., older ground water dates back to the time before fertilizers were used. Concentrations of nitrate in surface water resulted from mixing of younger, high-nitrate ground water from short flow paths with older, low-nitrate ground water from long flow paths, rather than denitrification in the aquifer sediments of the riparian zone. Typical residence times for ground water in these surficial watersheds range approximately from 1 to 40 years (Shedlock et al., 1999). Denitrification has been observed in saturated aquifer sediments upgradient of riparian zones or at depth beneath riparian root zones in other Coastal Plain settings (Böhlke and Denver, 1995; Böhlke et al., 1996; Speiran, 1996). Staver and Brinsfield (1996) measured relatively stable concentrations of nitrate and reported little evidence of denitrification or uptake by riparian vegetation in ground water discharging to surface water in a sub-estuary of the Chesapeake Bay. Phillips and Bachman (1996) demonstrated relations between base-flow stream chemistry and percentage of agricultural land use, soil characteristics, topography, and geology in well-drained and poorly drained stream basins. They found that in poorly drained basins, base-flow nitrate concentrations can be decreased if ground water discharging to streams is subject to anoxic conditions. These data show the importance of understanding the subsurface characteristics when interpreting the stream conditions.

BENTHIC MACROINVERTEBRATES AS THE ECOLOGICAL ENDPOINT

Characteristics of stream biota (algae, invertebrates, fish) have been used for many years to distinguish the degree and extent of human impacts on streams (Karr and Chu, 1999). We have chosen benthic macroinvertebrates for characterizing aquatic condition for the streams in this study for several reasons:

- The first- and second-order streams to be sampled are small and benthos will be present, while fish will be few in abundance and diversity (Paller, 1994).

- Macroinvertebrates play an important functional role in the stream ecosystem: as a food resource for demersal fish, as a link between lower and higher trophic levels, and frequently as the first step in bioaccumulation of pollutants in the food chain.

- Macroinvertebrates effectively monitor environmental conditions; they tend to be stationary or highly localized, and thus respond to the cumulative impacts of environmental perturbations over time. Benthic macroinvertebrate characteristics and indices have been successfully related to environmental factors for many locations in the U.S. and elsewhere, such as Wisconsin (Hilsenhoff, 1987), Idaho (Richards and Minshall, 1992), Virginia (Clements et al., 1992), Washington State (Cuffney et al., 1997), and New Zealand (Quinn and Hickey, 1990). The effects of contaminant stress may include a reduction in abundance and number of sensitive species, or a simultaneous increase in the proportion of pollution tolerant or opportunistic species (Wiederholm, 1984). Cuffney et al., (1997) identified agriculture as the primary factor causing degradation of biological communities in the Columbia River basin.

- Benthic macroinvertebrates are in wide use as biological endpoints for stream condition. Macroinvertebrates are easy to sample and standardized methods for sampling and taxonomic analysis have been developed by Federal agencies and many states (Plafkin et al., 1989; Cuffney et al., 1993; Kerans and Karr, 1994; Bode et al., 1996; Lazorchak et al., 1998; Stribling et al., 1998; Karr and Chu, 1999; Barbour et al., 1999). Statewide studies performed within the Coastal Plain include assessments for Delaware, Maryland, New Jersey, and North Carolina (Maxted and Dickey, 1990; Klauda et al., 1998; Kurtz et al., 1996; and Kennen, 1999; Lenat, 1993; respectively).

- Many factors can affect benthic macroinvertebrates; specific effects on benthos of pesticides applied at commonly used rates in first-order streams are rarely investigated (Schulz and Liess, 1999). In the case of herbicides, the potential impact is on the invertebrate food supply. In the case of insecticides, the potential impact is directly on the aquatic organisms. Results from a study on the insecticide lindane have shown that short-term but high contamination has greater effects on the aquatic fauna than long-term but low contamination with the same exposure (Abel, 1980). The high concentration conditions often occur when rainfall follows a pesticide application, resulting in overland flow into the stream. These high concentration conditions for pesticides (both insecticides and herbicides) are well documented for the Mid-Atlantic region in the late spring and early summer (Ferrari et al., 1997). Cuffney et al., (1984) found a shift in invertebrate species with the application of methoxychlor and reduced total invertebrate biomass. Schulz and Liess (1999) found that insecticide contamination has a strong negative effect on the aquatic macroinvertebrate community.

Macroinvertebrate community assemblages in streams are the result of many influences operating over a hierarchy of scales. Patterns in the distribution of invertebrates at the ecoregion scale are influenced by regional-scale natural factors such as climate, altitude, and geology (Corkum and Ciborowski, 1988). The Coastal Plain region selected for this study is relatively homogeneous with respect to these large scale factors (e.g., mid-latitude wet climate, sedimentary geology, elevations less than 100 m). This means that landscape- and local-scale influences become the distinguishing factors between sites. At the landscape scale, upstream land use and environmental factors explain some site-to-site variability (Klein, 1979; Corkum, 1992; Sweeney, 1993; Krug, 1993; Tate and Heiny, 1995; Richards et al. 1996; Johnson et al., 1997). Other factors which are important at this scale include stream size, gradient and flow regime, bed stability, nutrient enrichment, riparian zone characteristics, and food supply (Quinn and Hickey, 1990). Some of these factors depend on present and previous land use. Finally, unique characteristics of the sampling site can also introduce site-to-site variability due to differences in substrate extent and particle size, food availability, current velocity, pH, dissolved oxygen concentration, and temperature (Quinn and Hickey, 1990). Some of this variability can be minimized by using a standardized sampling protocol and compositing multiple samples from each site (keeping riffle and pool composites separate). In addition, in LIPS-MACS, the sampling location will be characterized using a quantitative physical-habitat assessment process (Lazorchak et al., 1998). The intent is to minimize regional and local scale impacts to focus on landscape-scale impacts.

Physical-habitat characterization data are essential to interpreting the benthos data because some of the differences observed in benthos composition and abundance are due to habitat variability. Physical-habitat data include stream dimensions, substrate qualities, gradient, habitat complexity and cover, riparian vegetation cover and structure, some anthropogenic disturbances, and stream-riparian interactions (Kaufmann, 1993). Anthropogenic alterations of riparian areas and stream channels, drainage of wetlands, grazing, agricultural practices, and modifications of stream banks, such as revetments or development, generally act to reduce the complexity of aquatic habitat and result in a loss of species and ecosystem degradation (Lazorchak et al., 1998). Noting and recording these features when a site is visited are essential to understanding the benthic survey results. A more detailed description of the stream sampling and characterization activities is provided in objective 3 in the Technical Approach section.

Macroinvertebrate populations can differ greatly between years depending on variations in weather and flow regime (Caspers and Heckman, 1981). Three recent events have probably affected the benthic macroinvertebrate populations over widespread areas within the Mid-Atlantic Coastal Plain. These events are the drought during the summer of 1999 and the flooding associated with tropical storms/ hurricanes Dennis and Floyd in August and September 1999. Under drought conditions, streams that would normally be flowing year-round have been dry during the summer and early fall. The dry conditions have the potential to severely stress aquatic organisms, depending on the timing of the drought compared to the timing of their life cycles (e.g., stonefly and mayfly nymphs) or their dependence on flowing water (e.g., mollusks). To estimate the impact of the drought, benthos reference sites will be sampled during the study. These data will be compared to data from previous years collected by state monitoring programs for the same location. The hurricanes have had a different effect: the associated flooding has resulted in major habitat modifications in some areas, especially in North Carolina (U.S. Federal Emergency Management Agency, 1999). We are in the process of determining to what extent the sampling sites are within the area of severe flooding. (Tidal streams, the area of greatest impact, are not part of this study.) Also in this case, the use of reference sites may provide insights about the biological impacts of the extreme variations in weather and stream flow.

Long-term viability of a macroinvertebrate population depends on potential for recolonization after catastrophe. Williams and Hynes (1976) cite drift from upstream as the most important mechanism of recolonization. First-order streams have been selected for sampling in this study. In areas where insecticides are used near first-order streams, depending on the specific location of the application, there may not be live organisms available upstream for recolonization by drift. The other mechanism for recolonization is oviposition by adults from other streams or migrating upstream. When insecticide use continues over a period of years near all streams in an area, the preconditions for reestablishment of species become adverse. In the Mid-Atlantic, insecticide concentrations tend to be higher in streams draining urban areas compared to agricultural areas (Ferrari and Ator, 1997) and this may result in different macroinvertebrate populations compared to agricultural areas. Because replenishment from upstream is compromised and nearby streams in developed areas are receiving similar insecticide applications, we expect that the benthic macroinvertebrate community composition and abundance in first-order streams may be significantly reduced, even in cases when physical habitat is conducive to healthy benthic populations.

We have learned that the states follow their own protocols for sampling with the exception of Delaware and Virginia which use the Mid-Atlantic Coastal Streams (MACS) Workgroup method for low gradient, nontidal streams (EPA, 1997; see Table 4). This may result in some differences when our data are compared to the historical reference-site data.

Table 4. Methods Used in State Sampling Programs for Benthic Macroinvertebrates

	North Carolina	**New Jersey**	**Delaware**	**Maryland**	**Virginia**
Method	own manual	own manual	MACS manual	own manual	MACS manual
Identification Level	Genus, species	Family	Genus, species	Genus	Family
Mesh Size (µm)	to be added	600	600	600	600

HYDROGEOLOGIC FRAMEWORK

Geologic and hydrologic characteristics, which have not always been considered directly in previous investigations of landscape indicators, could be particularly important in a coastal plain setting where surficial sediments are commonly permeable and much of the transport of contaminants to surface water takes place in the subsurface. The geologic material present at the earth's surface provides important controls on the shape of the landscape, the formation of soils, the flow of water, and the chemical environment that water encounters as it moves through the hydrologic system. In many cases, surficial landscape coverages, such as ones available for soils, topography, or land cover, are used as a proxy to represent subsurface conditions. However, processes that occur beneath the land surface in the shallow ground-water system, cannot be included in interpretations of landscape indicators and their relationship to water quality patterns without additional information. This information is provided by interpretation of the geologic characteristics of a region and their effect on hydrologic flow paths and geochemical reactions within the soil and aquifer materials. In some cases, geologic factors may exert a primary control on the transport or transformation of a particular water quality-related constituent, such as by a geochemical reaction. In other cases, a surficial landscape variable such as the percentage of a particular land use may be the primary control. It is useful to consider as many of the potential variables as possible, so meaningful relationships between landscape indicators and water quality can be quantified, at least to the extent needed to recommend appropriate management strategies. To properly address the hydrogeologic variables for this project, a digital map of surficial geology is needed. The underlying geology of the Coastal Plain is an important variable so we want to use a classification system which describes the important features consistently for our purposes. Some possible options are explained below.

The hydrogeology of the older, deeper, geologic units of the Coastal Plain has been mapped previously. These and related studies are described below:

- For Washington, D.C., to the north to Boston, the U.S. Geological Survey produced a map of engineering geology for the Department of Transportation in 1967.

- Brown et al. (1972) produced a 3-dimensional map of the Coastal Plain from North Carolina through Long Island using data from more than 2,200 wells (the first such model for the Mid-Atlantic Coastal Plain). Their purpose was to define the geometry and internal permeability distribution of each "mappable chronostratigraphic unit" (they mapped 17 plus the basement surface). The youngest unit was undifferentiated "post-Miocene."

- The Regional Aquifer System Analysis (RASA) program produced a series of reports detailing the hydrogeologic framework of the entire Coastal Plain in the 1980s. That program was mainly concerned with mapping and defining major regional aquifers, so they concentrated mostly on the older confined units and did not map the surficial units.

- Winner and Coble (1996) developed a hydrogeologic framework for the North Carolina coastal plain.

- A more recent regional study that treats the Mid-Atlantic Coastal Plain as one unit identified heterogeneities in the physical setting and land use within the Coastal Plain that were important in explaining the variations in ground-water quality (Ator and Ferrari, 1997).

- The Delmarva NAWQA study divided the Coastal Plain into seven subareas, referred to as hydrogeomorphic regions (HGMRs) that define different hydrologic settings. Each HGMR had a characteristic set of geologic and geomorphic features, drainage patterns, soils, and land use patterns. They were successfully used to look at differences in regional water-quality patterns and to transfer results from local-scale networks within the HGMRs to the regional-scale analysis (Shedlock et al., 1993, 1999).

Although useful, these mapping efforts either do not address the surficial (mostly Miocene and younger) units which are important to stream flow, or they do not provide consistent coverage over the entire study area.

To solve these problems, a hydrogeologic framework for the Coastal Plain was developed recently by USGS (see Figure 4, Table 5). Based on a regionally consistent map of surficial geology, and information on landform and geologic setting, it combines these primary natural factors affecting the flow and quality of near-surface ground water and small streams into one digital map (Denver and Ator, U.S. Geological Survey, Dover, DE, pers. commun., 1999). Seven areas are identified in which the occurrence and movement of chemicals into shallow ground water and streams are controlled by a relatively consistent set of natural processes. The framework will be combined with other spatial data, such as soils, topography, and subcropping geology, to represent the basic physical setting of the Mid-Atlantic Coastal Plain for the landscape indicator analysis process. The areas delineated by the framework are being used to stratify the selection of sampling sites for this study, to minimize hydrogeologic variability.

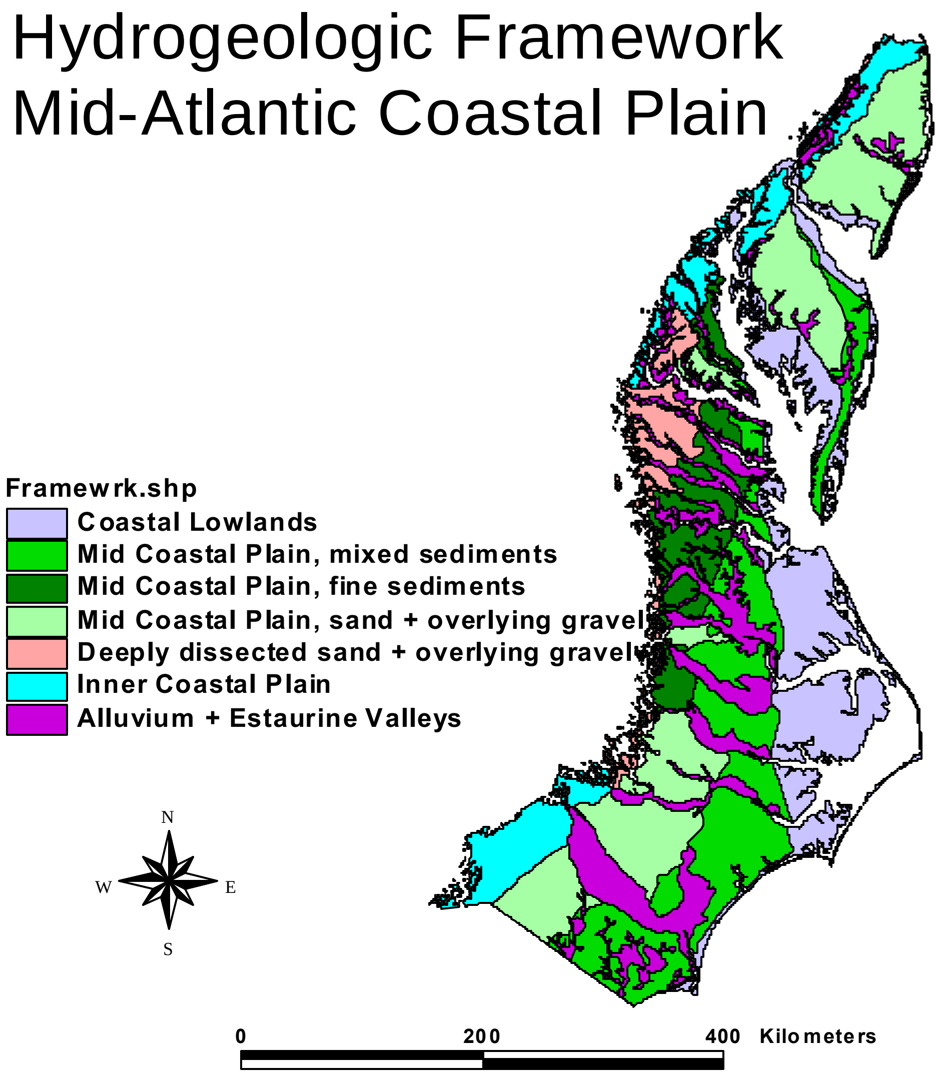

Figure 4. Hydrogeologic framework for the Mid-Atlantic Coastal Plain

Table 5. Hydrogeologic Framework Description and Hypotheses

Framework Area	Description	Hypothesized Potential for Pesticide Mobility
Coastal Lowlands	Low-relief platform of the Outer Coastal Plain and margins of the major estuaries. Area is very flat and low lying, with poorly developed stream drainage and numerous tidal wetlands. Streams are low gradient and largely tidal. Sediments are primarily fine-grained. Soils of swamps and marshes contain abundant organic matter. Soil types reflect chronic poor drainage and poor oxidation.	High potential for pesticides to be bound by fine-grained sediments and organic matter in poorly drained soils. There may be some transport of pesticides through sandy surficial sediments into ground and surface waters in areas where pesticides are applied. Pesticides may run off into drainage ditches.
Middle Coastal Plain, Mixed Sediment Texture	Broad platform of the Middle Coastal Plain. Land surface is moderately dissected by streams; local relief ranges from 25 to 30 feet. Sediment texture varies laterally and vertically and sizes are mixed, ranging from coarse sands to clays and silts.	Occurrence and concentrations of pesticides will vary widely in association with variations of sediment type and land use distribution.
Middle Coastal Plain, Fine Sediments	Dissected inner portion of Middle Coastal Plain with predominately fine-grained sediments at land surface. Local relief ranges from 20 to 60 feet.	The potential for pesticides to infiltrate into ground water is low because of confined conditions. Pesticides may be transported to surface water in overland runoff from areas where they are applied.
Middle Coastal Plain, Sands With Overlying Gravels	Inner Middle Coastal Plain; the original broad flat upland surface has not been completely dissected by developing stream networks. Local relief is less than 100 feet. Greater incision occurs near major tributaries that cut across the Middle Coastal Plain.	The potential for pesticides to be transported to ground water is relatively high. Pesticide transport will be affected by variability in land use and soil characteristics. The presence of organic matter in stream beds may limit transport from ground water to surface water in some areas.

Framework Area	Description	Hypothesized Potential for Pesticide Mobility
Middle Coastal Plain, Deeply Dissected, Sands with Overlying Gravels	Deeply dissected innermost Coastal Plain, adjacent to Fall Line, including sand and gravel caps on adjacent Piedmont hills. Local relief ranges from 100 to 150 feet. Sediments are dominated by coarse fluvial sands and gravels overlying marine sands or saprolite of crystalline rock. Surficial units are completely incised and there is no connectivity between upland surfaces on adjacent interfluves.	The potential for pesticides to be transported to ground water is relatively high. Pesticide transport will be affected by variability in land use and soil characteristics. Most pesticide occurrence in surface water will be associated with runoff because of stream incision int confined aquifers and confining beds.
Inner Coastal Plain	Outcrop and subcrop belt of lower Tertiary and Cretaceous formations, deeply weathered where exposed, with 250 to 300 feet of relief. Some units are leached and oxidized to depth of tens of feet. There is widely contrasting variability in the permeability and geochemistry of units. These contrasts affect aquifer recharge and water quality characteristics. The landscape is deeply dissected and streams typically cut into underlying units.	The potential for pesticides to be transported into ground water is moderate in areas with sandy surficial sediments because of loamy soils. Pesticide transport will be affected by variability in land use. Most pesticide occurrence in surface water will be associated with runoff because of stream incision into confined aquifers and confining beds.
Alluvial and Estuarine Valleys	Incised valleys of major rivers that cut across the Coastal Plain. Deeper parts of the valleys are filled by coarse-grained alluvial sediments. Upper portion of sequence is typically composed of fine-grained, organic-rich sediments. Valleys in North Carolina are broader with greater volumes of alluvial fill than are valleys to the north that drain to the Chesapeake and Delaware bays, which are more deeply incised.	The presence of fine-grained sediments, organic matter and shallow water table on valley terraces will limit pesticide mobility. In areas with sandy surficial sediments, pesticides may be present in ground water. Overland transport to surface water will be limited by flat topography.

LANDSCAPE INDICATOR MODELS

Ecological indicators are defined by the EPA as measurable characteristics of the environment, both abiotic and biotic, that can provide quantitative information on ecological resources (Barber, 1994; Jackson et al., 1999). In this plan, we are using the term in the inclusive sense; it is intended to encompass physical, chemical, and biotic indicators. Indicators can be classified into either the "condition" or "stressor" categories according to their purpose. In the broadest usage, an ecological indicator may be based on a single measure or a statistical combination of measures, or it may be an index based on multiple measures. Landscape indicators are a particular category of ecological indicators that are determined for a predefined area, which can be geographic, biogeographic (watershed, ecoregion) or political (State and county boundaries, Federal regions). They are usually based on remotely sensed data or other geographic information, and like ecological indicators, they can be based on a single measure or a combination of measures. The landscape indicator development and testing approach used in this project has evolved from the general approach to landscape indicators for the Environmental Monitoring and Assessment Program (EMAP) landscape monitoring and assessment research (U.S. EPA, 1994b; Kepner et al., 1995; Jones et al., 1997). Landscape indicator analysis has a number of unique features:

- ability to look past artificial boundaries and fit specific areas into a larger natural context;
- coverage of 100 percent of selected area, consistent with available data;
- adjustability of resolution of results, from fine to coarse scales;
- ability to test applicability of concepts from hierarchy theory; and
- ability to evaluate the importance of landscape features especially spatial pattern and adjacency metrics to stream conditions.

Because of the potential confusion between landscape models and the more complex landscape indicators based on multiple measures (i.e., soil erosivity based on the Universal Soil Loss Equation), we will use the term "landscape metrics" to refer to landscape indicators which are used as independent variables in the landscape indicator models to be developed. A landscape metric typically is based on one spatial measure or aspect; examples include population density, human use index (proportion of watershed with urban or agricultural land use), road density, and proportion of watershed with crops on steep slopes. A landscape indicator model combines these metrics to predict a dependent variable; for example, predicting nutrient concentration from land use/land cover information.

The most commonly used metrics involve percentages of land cover/land use (Jones et al., 1997), but a large number of indicators have been developed spanning landscape ecology, soil erosion, and wildlife management (Riitters et al., 1992; Jones et al., 1996). Research on the relationship of land use to stream water quality has largely focused on inorganic nutrients (Omernik et al., 1981; Osborne and Wiley, 1988; Hunsaker and Levine, 1995; Tufford et al., 1998; Cronan et al., 1999) rather than on organic chemicals such as pesticides. This is largely due to the lack of sufficient pesticide data, hence this study. The finest resolution of current landscape data is typically 30 m x 30 m, but new data will soon be available with 10 m and even 1 m resolution. However, results for indicators are often aggregated and reported for much larger areas, and identifying the appropriate scale(s) for a given indicator is important to its proper application (Carlile et al., 1989; O'Neill et al., 1991; O'Neill et al., 1996; Johnson, 1994; Keitt et al., 1997). The importance of the landscape setting and human influence in understanding benthic macroinvertebrate populations has been noted by Fore et al. (1996), May et al. (1997), Wang et al. (1997), Karr and Chu (2000) and others, which lends support to the usefulness of the landscape indicator approach in this context.

The general approach for developing landscape indicators is to assemble a large database of landscape metrics (independent variables) hypothesized to be important factors contributing to the variability of the conditions measured (dependent variables). The goal is to remove redundant metrics so the remaining ones are as independent as possible. A "weight of evidence" approach based on statistical tests is used to determine which independent variables explain the most variation in the dependent variables. One of the key precepts is that space can be traded for time within areas that are similar. In a traditional experiment, indicators would be tested over time in replicates of one or perhaps several locations, to provide a gradient of conditions for the same setting. Trading space for time assumes that looking at many locations within an ecoregion at one time provides snapshots of many different stages of an environmental situation. It has the disadvantage that initial conditions are not established and the areas may not be undergoing similar or parallel processes. The many locations will include responses to factors other than the ones of interest. However, this is the most practical approach, given the time scale of Federal careers compared to landscape evolution! For this study, chemical concentrations and biological condition are the conditions to be measured. Statistical techniques will be used to identify promising multivariate and hierarchical relationships. The result of this analysis will be the landscape indicator models, which relate a specific dependent variable to the independent variables. Multiple regression will be a primary statistical tool used for the landscape indicator models which take the general form below:

$$\text{dependent variable} = c_0 + 3\, c_i * x_i ,$$

where x_i is an independent variable, and c_0 and c_i are constants. Dependent variables include ecological condition as expressed by indices for benthic macroinvertebrates (different indices will be tested); physical habitat; and concentrations of pesticides, pesticide metabolites, nutrients, and major ions in streams. Independent variables include land use/land cover, topography, soil type, geologic and hydrologic characteristics, population density, metrics for roads in watersheds, pattern metrics for land use, and riparian zone characteristics. The hydrogeologic framework unit will be evaluated as an explanatory variable in the landscape indicator models. Amount of variability explained, both overall and by individual independent variables, will be used to evaluate the success of the model and the relative importance of the independent variables. In a study by Hunsaker and Levine (1995), for inorganic nutrients and conductivity in streams with the entire watershed as the source area, variance explained ranged from 53 to 86 percent for total nitrogen and total phosphorus, respectively. Another study (Jones et al., in press) had similar results.

Besides traditional multiple regression, one of the tools we are planning to use in our data analysis approach for landscape indicators is Classification And Regression Tree (CART) analysis (Breiman et al., 1984). CART offers a number of advantages for the analysis of environmental data; these data often have missing values, interactions between variables, non-normal distributions, large numbers of and different types of variables, high variability, and high dimensionality. CART is robust with respect to these problems because it makes no assumptions about the data distribution and is relatively insensitive to outliers (Brieman et al., 1984). When a variable is missing at a certain sample location, CART can use a surrogate variable. Environmental data often have location-specific relationships between variables; the CART technique can apply different decision rules for each location (Moore et al., 1991) or for each subset (Walker, 1990). CART is similar to stepwise regression in that it can deal with on-off type variables such as a pesticide used in one area and not in another.

CART is a heuristic technique which develops a hierarchical structure of rules by grouping observations into classes. It searches for a set of questions that is most efficient at discriminating between classes. The rule that provides the largest increase in class purity forms the first splitting rule of the decision tree (root node). The original data are split into two descendant nodes based on this rule (see Figure 5). Then the process is repeated iteratively to all subsequent nodes and their descendants until the tree has attained maximum complexity. Each splitting rule is fit onto the decision tree as a branch node (Moore et al., 1991). When a splitting rule is applied, data for which the answer is "Yes" are assigned to the left branch, while remaining data points are assigned to the right branch. The leaves of the tree are called terminal nodes (Efron and Tibshirani, 1991). Although rules have been developed to control the size of trees, a common practice is to construct a large tree and prune it working from the smallest subsamples toward the larger classifications. CART applications often use cross-validation to determine the best tree size, although many methods have been used (Sifneos et al., in preparation). This method is similar to using a test sample and works by dividing the data into 10 groups of equal size, creating a tree with 9/10 of the data and assessing the misclassification rate for the remaining group of data. Each group of data is tested against the remaining 9/10 in turn, and the total misclassification is computed for all 10 runs. The best tree is the one giving the lowest misclassification rate (Efron and Tibshirani, 1991; Clark and Pregibon, 1992).

Because the CART decision tree process is continually dividing data into smaller and smaller subsamples, the number of locations sampled, or observations, provides an inherent limit on the size and performance of the tree. Using a decision tree approach with a sample of 128 observations is considered minimally adequate for applying the technique (Miller, 1994). When data are binary (e.g., presence or absence of species), the classification aspect of CART is used. When data are continuous (e.g., concentration of chemicals), the regression capability of CART is used. Example applications of CART to ecological problems include modeling distributions of kangaroos in relation to climate (Walker, 1990); predicting vegetation distributions (Moore et al., 1991); explaining spatial factors related to bird biodiversity (O'Connor et al., 1996); and predicting species richness in fishes (Rathert et al., 1999). In this study, measures of stream ecological condition determined from benthic and stream water quality data will be the dependent variables, and physical habitat characterization and landscape metrics will be the independent variables.

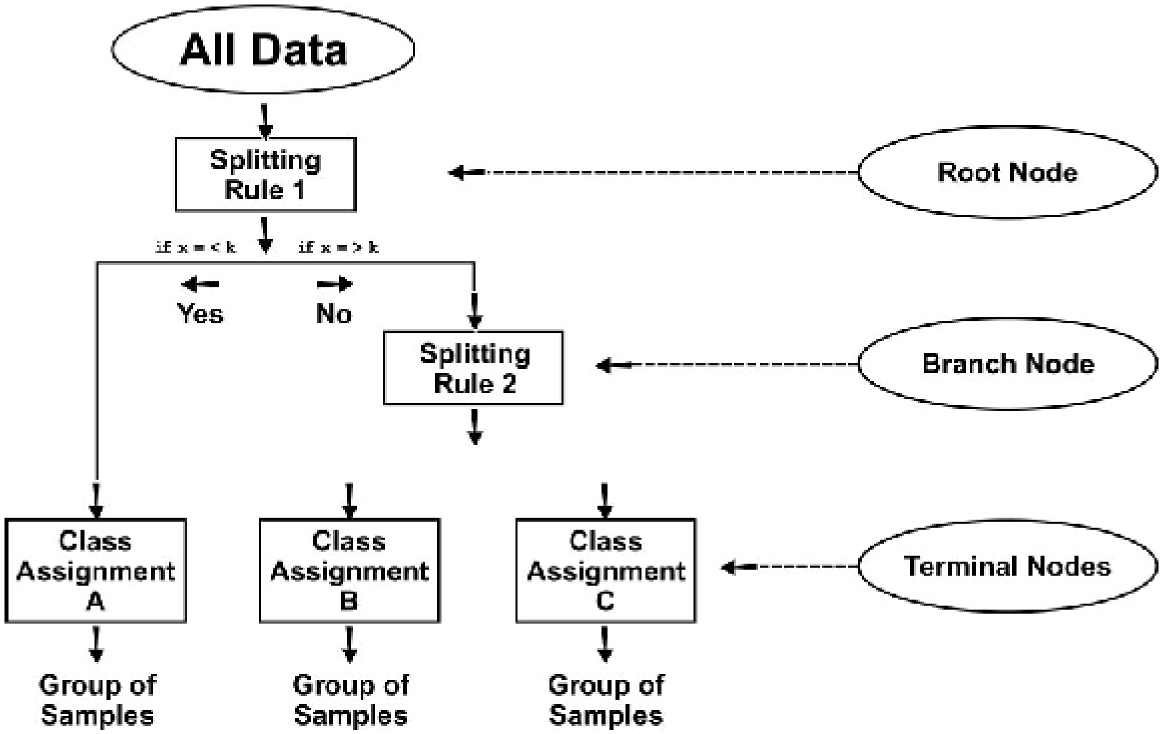

Figure 5. The CART decision process (after Moore et al., 1991). A CART analysis is prepared for each dependent variable of interest, for example, pesticide concentrations in stream water. Referring to the schematic framework, variables such as percent forest or percent developed land use/land cover may appear at the highest (root node) level as explanatory variables. Landscape factors may not be important below a certain threshold, and sites showing little response to landscape variables could be assigned to Class A. For sites with land use/land cover above the threshold, the variable at the next level of importance would appear in Splitting Rule 2. Possible variables for this branch node include the amount of riparian zone along the stream within the watershed, or the amount of clay in the soil of the watershed, resulting in the assignment of some sites to Class B and the rest to Class C. It is likely that additional splitting rules would be developed for some of these classes, extending the diagram further to include variables such as ecoregion, density of roads, and agriculture on steep slopes.

FIELD STUDY

STATISTICAL DESIGN

A particular challenge for the LIPS-MACS study design is to provide the necessary data for landscape indicator model development and validation, while at the same time providing adequate data to characterize regional hydrogeologic conditions with known bias. For landscape indicator model development, stream data for watersheds spanning a broad range of categories of land use/land cover are necessary. Because of the focus on pesticides, agricultural and urban land use are of particular interest. For the hydrogeologic framework unit characterization, stream data which are representative of the hydrogeologic framework unit with a good spatial distribution are important. The indicators being developed in this study will not be appropriate for addressing some kinds of questions, for example, assessing very small areas. The goal is to develop a consistent and comprehensive look at the entire region, and there are tradeoffs between the level of detail and the size of the area that can be considered. The spatial design (see Table 6) consists of a one-time survey:

- 175 sites representative of first-order streams (Figure 6) in the Coastal Plain;
- 3 nested sets of 5 sites each for a total of 15 sites; and
- 7 benthos reference sites.

In addition, three temporal sites will be sampled for a year. The 175 sites provide the basic data set for landscape indicator model development and evaluating the hydrogeologic framework. Subsets drawn from this larger set and held separately, will provide one form of landscape indicator model validation. A second type of validation data will be provided by the nested sites. These sites will enable a limited comparison of results for smaller watersheds nested within a larger one. The benthos reference sites are high quality, near-pristine sites which are part of the states' ongoing biological monitoring programs. The historical data available for these sites will be useful in interpreting our data. We have obtained site information from each of the states and will select a total of seven sites (one per hydrogeologic framework unit). These reference sites will be characterized physically and chemically in the same manner as the framework unit sites.

We will establish three temporal sites to evaluate the temporal variability of pesticide concentrations; each will have a full year of record (sampled biweekly in the spring, and monthly thereafter). Stream flow and pesticide concentration data will be available for comparison to the one-time survey being made across the entire Mid-Atlantic Coastal Plain. These sites will be selected from among those currently being sampled as part of other USGS or EPA programs to allow for maximum use of resources; our cost will be to pay for the pesticide analyses. Early results from this sampling should help identify the types and concentrations of pesticides to be expected from the regional sampling. Current choices for these sites are Chesterville Branch, an agricultural stream on the

Delmarva Peninsula in Maryland; Western Branch, which drains a mixed agriculture-forest-urban watershed near Washington, D.C.; and Lizzie Site, an agricultural stream in the Contentnea River drainage in North Carolina. Data from these watersheds will allow for a better understanding of the processes affecting the movement of pesticides at a finer scale and will help show how regional sampling results relate to local areas. These sites will be used in the case studies for the hydrologic and multimedia modeling.

Table 6. Summary of Types and Numbers of Sites

Type of Site	Purpose	Comment	Total Number of Sites
Framework unit	Unbiased description of stream water quality within framework units, weighted to provide a gradient over "developed" land use	25 per hydrogeologic framework unit x 7 units	175
Nested	Multiple smaller watersheds, nested within a larger one, to evaluate scale relationships	3 nests with 5 sites each	15
Temporal	Understand seasonal patterns in specific framework units	one site in each of 3 hydrogeologic framework units	3
Benthos reference	Historically unimpaired sites, to ensure suitable data for computing benthic macroinvertebrate metrics	one per hydrogeologic framework unit	7
TOTAL			200 (approx.)

The statistical process for the first-order watershed site selection is described in two stages below. In the first stage, we will establish the population of first-order streams and associated watersheds from which to select the sample. First-order streams will be identified using the Reach File 3 "start reach" codes (U.S. EPA, 1994c). Euclidean watersheds will be determined by using the Reach File stream coverage and determining Thiessen polygons, the boundaries of the polygons being formed by the perpendicular bisectors of the lines joining adjacent stream segments (Chow et al., 1988). The resulting shape approximates the watershed boundary. These Euclidean watersheds will be the "first cut" which provides our sampling frame of first-order watersheds. The sampling sites will be selected randomly from this set. Other alternatives for developing the watershed boundaries were considered, for example, basing them on digital elevations, but this is not practical because there are more than 10,000 first-order watersheds that make up the Coastal Plain. It is also not practical to use flow data since these are not available for most of these streams. Once the 200 hundred sampling sites are selected and visited by the sampling crews, we will recompute the watershed boundaries using digital elevations and actual sampling points. In addition, the watershed boundaries will be evaluated manually using topographic maps for the sites. This will ensure that the boundaries are as accurate as possible for the landscape indicator analyses.

Next, each watershed's land use/land cover composition will be determined by using land use/land cover data from the Multi-Resolution Landscape Characteristics (MRLC) Consortium. These land use/land cover data are derived from 30-meter resolution Landsat Thematic Mapper data, and classified into 15 land use/land cover classes (Vogelmann et al., 1998). We will define developed land use/land cover as all agricultural plus all urban, residential, and commercial land use/land cover categories. The goal is to select sampling sites so that roughly equal numbers of sites occur in each of 5 percentage categories of developed land use/land cover (0-19 percent, 20- 39 percent, ... and 80-100 percent). However, the actual distribution of sites within these categories shows that on average, there are more watersheds in the less developed rather than the more developed categories. Using a random selection from this population would result in too few sites in the upper categories of developed land use/land cover for developing the landscape indicator statistics.

To provide a more uniform distribution for the sampling sites, we will weight the selection probability of the first-order watersheds by the frequency of occurrence of developed land cover. The weighting process increases the probability that rare conditions will be included in the sample, thus ensuring that an adequate gradient will be available for the landscape indicator development. This can be accomplished conceptually by representing each watershed as a line segment having a unit length and placing these segments end-to-end, working methodically through all the possible watersheds in the study area. A simple random selection process would use a random start, and move along the line of segments at a fixed interval which selects the correct number of sites. The fixed interval is the total number of sites to be selected divided by the length of the total number of sites. If the line segment is of unit length, then this will be the same as the number of sites. The weighted random selection process is performed by adjusting the length of each segment for each watershed, by dividing the line segment length of 1 unit by the frequency of occurrence of the land use/land cover class for the watershed. The frequency of occurrence values are expressed as values within the range from 0 to 1. Since all the values are less than one, dividing by the frequency of occurrence has the effect of lengthening the segment. The segments for the rare conditions will be lengthened significantly, making them more likely to be selected, while the segments with the more frequently occurring conditions will be lengthened minimally in comparison, making them less likely to be selected. This technique was demonstrated for EMAP streams by Herlihy et al. (2000). The actual process is somewhat more complex than the conceptual approach just described, and that is described next.

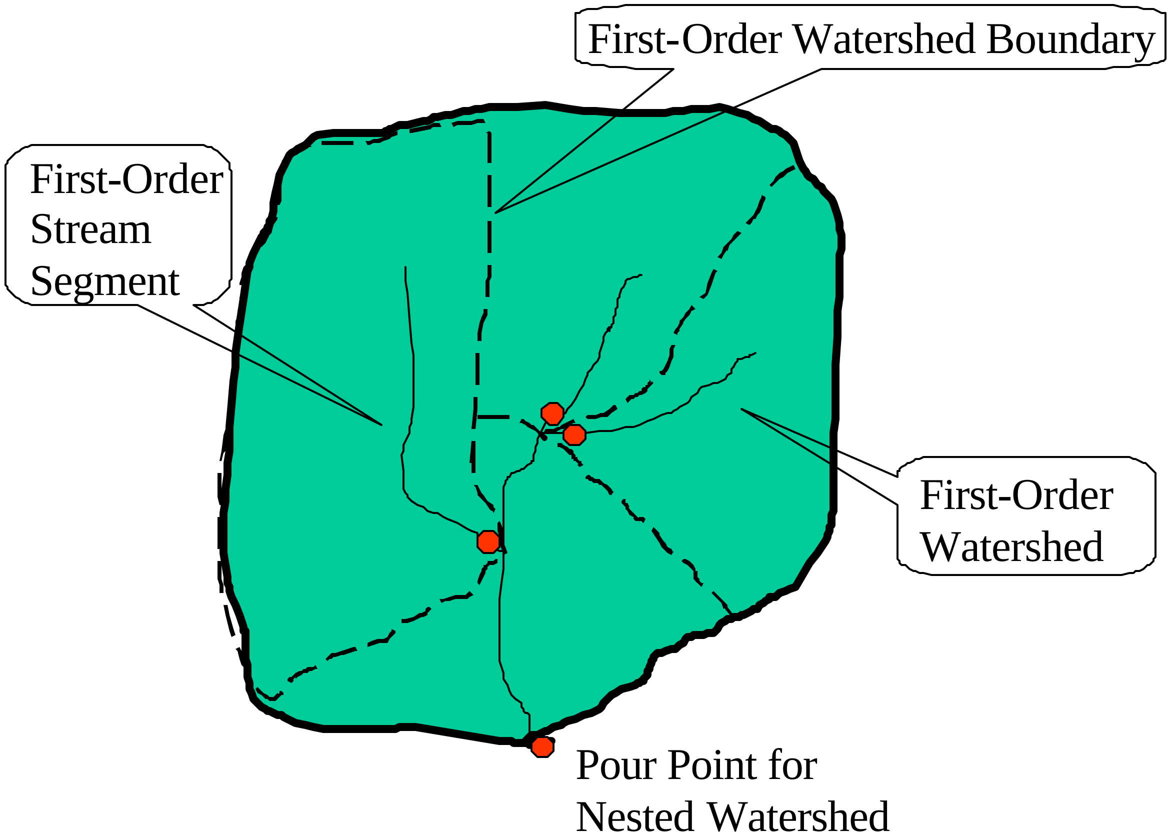

Figure 6. Example of first-order streams and watersheds. Unlabeled dots mark the sampling points (also called pour points) for first-order watersheds. These first-order watersheds are typical of the 175 sampling sites in the main part of the study; however, none of the actual sites are likely to be adjacent to each other as shown here. The dark outer boundary marks the edge of a larger watershed with a "nest" of first-order watersheds contained within. Nested samples will be collected at the pour points for the three first-order watersheds nested within the larger one and at the pour point for the larger watershed.

Starting with the key ideas above as a guide, and working in the broader context of Olsen et al., 1999, we will follow the approach of Stevens and Olsen (1999). They rely on a method (Madow, 1949) for combining systematic and random sampling to sample without replacement, with the probability that an item is included in the sample proportional to an arbitrary weight for each item. This method involves calculating the cumulative total weight for the items arranged in some order, and then drawing a systematic sample with a random start using a fixed length sampling interval along the cumulative weight totals. The steps in the Stevens and Olsen (1999) procedure are provided verbatim in italics below:

1. Overlay the population domain with an area grid, choose a random location in a cell designated as the origin cell, and then translate the entire grid so that the origin cell is centered on the random point.

2. Link each population element to its covering grid cell, and assign grid cell i an inclusion probability p_i equal to the expected number of samples in its associated portion of the population. The p_i may vary from cell to cell and may be zero [if it contains no item], but cannot exceed 1. (If any p_i exceeds 1, then a finer grid is required.) Then arrange the grid cells in hierarchically randomized order.

3. Draw a sample of grid cells from the randomized list, using Madow's (1949) technique, which guarantees that cell i is included in the sample with probability p_i. (Since p_i is the target number of samples in cell i, $\sum_i p_i = n$, where n is the target sample size and the sum is over the number of grid cells [or items].

4. For each selected grid cell, pick one sample point at random from its associated population elements, recognizing any differential weighting among such elements.

Variance estimation is performed by estimating pairwise inclusion densities by ignoring the spatial dependencies among the sample point locations and assuming an independent random sample design. Then the Horvitz-Thompson theorem for continuous populations yields a variance estimator (Cordy, 1993 and Stevens, 1997). If the population has spatial structure, then the resulting estimator will be conservative.

The advantages of this technique as it relates to the LIPS-MACS study are:

- it guarantees that the sample is well spread-out over the extent of the resource because the hierarchical randomization (Step 2 above) results in a random order that nevertheless preserves some spatial relationships;

- the design has enormous flexibility to accommodate design constraints; i.e., weights may be specified on a regional (e.g., by state boundaries) or elemental basis (e.g., stream order, or watershed land cover characteristic); and
- a variance estimator is available and conservative.

The flexibility is the key element of this design approach. It enables two design objectives to be addressed using systematic random sampling. Thus, each first-order watershed will have a known probability of being included. This has a number of advantages; stratification techniques can be applied to incorporate known characteristics of the population and unequal probability sampling can be applied to ensure rare conditions are included. This capability will allow the sampling of the more rare land-use patterns as necessary for the indicator testing, while enabling the use of these data for other purposes such as evaluating the hydrogeologic framework and characterizing the Coastal Plain.

LOGISTICS/METHODS

The field study effort has eight basic activities which are discussed further below:

- preliminary visit to sampling sites,
- collection of water samples,
- collection of benthic macroinvertebrate samples,
- performance of physical habitat assessment,
- collection of sediment samples,
- laboratory analyses of samples for pesticides, pesticide metabolites, inorganic nutrients, major ions, and identification of benthic macroinvertebrates,
- compilation of data into databases, including all laboratory analyses and physical habitat assessment and rapid visual assessment data, and
- ongoing quality assurance review of activities with both internal and external audits.

With the exception of the preliminary site visits, and the temporal sites, all the sampling activities will be conducted in the winter/spring sampling period. The choice of the winter/ spring sampling period is discussed later in this section. Laboratory analyses will follow immediately and continue for up to 9 months, depending on the parameter. Preliminary site visits will be conducted by the USGS during the fall and winter. These visits will confirm presence of the stream, arrange permission with the landowner, identify a convenient access route, and provide an initial assessment of the actual watershed size compared to the computer-drawn size. Practical considerations such as convenient lodging, shipping facilities, and health care facilities will be noted. A process for replacing sites that cannot be used is part of the study design.

To ensure consistency not only within this study but also to facilitate further use in other studies, we will use NAWQA procedures for stream sample collection and analysis and Environmental

Monitoring and Assessment Program (EMAP) methods for collecting sediments and assessing benthos and physical habitat (see Table 7). On-site measurements and stream chemistry will provide basic information about the stream and its setting. USGS Pesticide Schedule 2001 contains both urban and agricultural use pesticides and these compounds have been successfully identified in urban areas in this region (Ferrari et al., 1998). Pesticide metabolite concentrations are of interest to the Office of Pesticide Programs at EPA. Pesticide metabolites data may provide insights on transit times, degree of degradation, flow systems, and transport of chemicals. Benthic macroinvertebrates were chosen because of the lack of fish in these small streams. Sediments are being analyzed for the persistent chlorinated pesticides and PCBs. Mercury is included because of its potential for long range airborne transport and deposition; and arsenic is included as an indicator of poultry waste.

Table 7. Parameters Measured at All Sites

Activity	**Conducted by**	**Parameters**	**Reference**
Water sampling and on-site chemistry	USGS	DO, temperature, pH, stream discharge, dissolved alkalinity, specific conductance	Shelton, 1994
Water sample analysis (laboratory)	USGS	pesticide schedule 2001, major ions schedule 2701, nutrients schedule 2702, pesticide metabolites	Shelton, 1994; Zaugg et al., 1995; and Hostetler and Thurman, 1999. For analytes, see Appendices A, C, and D.
Benthic macroinvertebrate sampling	EPA NERL contractor	pool, riffle settings; community composition, and abundance	Lazorchak et al., 1998
Benthic sample analysis (laboratory)	EPA NERL contractor	300 count organism identification to genus and species	Klemm and Lazorchak, 1994
Physical habitat assessment	EPA NERL contractor	Thalweg profile, woody debris tally, channel and riparian characterization	Lazorchak et al., 1998; Kaufmann et al., 1999
Sediment sampling	EPA NERL contractor	Composite sample	Lazorchak et al., 1998
Sediment analyses	EPA NERL contractor	pesticides, PCBs, mercury, arsenic, gradation, organic content	Wesselman and Carr, 2000. See Appendix B.

Water samples will be collected, handled, and analyzed using procedures developed by the USGS for the NAWQA program (Shelton, 1994). Depth-integrated water samples will be collected from equal-width increments of a stream cross section using Teflon® or stainless steel equipment. Samples for pesticide analysis will be passed through a nominal 0.7 micron glass-fiber filter and collected in baked amber glass bottles. Samples for nutrients and selected major ions will be passed through a 0.45 micron filter. Samples will be chilled and shipped overnight to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado, and the USGS Laboratory in Lawrence, Kansas, for analysis of major ions, nutrients, and pesticides, and pesticide metabolites, respectively. All sampling equipment and supplies will be cleaned between sites with mild soap and methanol.

Benthic macroinvertebrate collection and 300-count analysis will follow the EMAP protocol (Lazorchak et al., 1998; Klemm and Lazorchak, 1994). Physical habitat characterization will be conducted following the EMAP protocol (Kaufmann and Robison, 1998), except for elements characterizing fish habitat which will not be assessed. Sediment samples will be collected from each of the 11 benthos transects. Samples will be collected from the top 2 cm of surficial sediment in depositional areas, using a plastic spoon. The sediment will be stored in 50 mL centrifuge tubes, one tube for each transect. Samples will be kept chilled but not frozen until delivery to the laboratory. The laboratory analyses will follow modified EMAP protocol to include additional analytes. The list of target analytes is provided in Appendix B. Additional parameters will also be noted during this phase; it will include performing an accuracy assessment for the MRLC land use/land cover designation for the area surrounding the site. Photographs will be taken of the site in four directions. Adjacent crop types, pesticide applications, and rills/gullies will be noted.

The field study will be conducted by USGS and contractor staff traveling separately to each site. The sampling location will be marked, identified with global positioning system coordinates in compliance with EPA's locational data policy, and maps will be provided so both crews sample from the same location. Considering crew activities, the expectation is that the water sampling crews can sample two to three sites daily, while the benthos and physical habitat crews will sample one or two sites daily depending on the proximity of the sites (see Table 8). This is nominally an 8-week sampling effort. Issues that are being considered include safety; having substitutes available in case a regular crew member becomes sick; and having additional crews available to keep the sampling on schedule.

The timing of the first-order watershed scale sampling was determined by identifying the best months based on a number of criteria (see Table 9). We will attempt to follow the transition from winter to spring as warmer temperatures advance from North Carolina to New Jersey. The months of late February, March, and April, with some variation allowed for weather conditions, are the best months for this sampling effort. The colder stream temperatures are important for minimizing biological activity and chemical reactions in the stream water. The timing is also chosen to occur before pesticides are applied to avoid effects of the initial pesticide surge, which occurs during the first storm after the pesticide is applied. In general, herbicides are used early in the planting season, while insecticides are used later when the crop is more mature. The insecticides have the potential to reduce populations of benthic macroinvertebrates, and this timing is a possible source of variability in the data from site to site.

We will consider using additional crews to shorten the time to cover all sites. Stream samples will be collected under base flow conditions and should mostly represent contributions from near-surface ground water which is most directly affected by land uses and other surficial activities. During these months, concentrations of chemical constituents in the water will be least affected by biological activity. This timing fits within the windows of acceptability for pesticide applications and benthic macroinvertebrate sampling.

Table 8. Activities and Time Estimates for Work at Sampling Sites

	Activity	**Group**	**Estimated Time Required per Site Visit**
Water Sampling Crew		3 persons	
	Travel to site		1 hour or more
	Verify site; establish sampling reach		1 hour
	Collect water chemistry samples; measure stream discharge; paperwork		1-2 hours
Totals		3 people, 3-5 hours	2-3 sites per day
Benthos Crew			
	Travel to site	2 persons	1 hour or more
	Collect and process benthos		2 hours
	Characterize physical habitat (modified procedure)		2 hours
	Sample tracking and packing		1 hour
Totals		2 people, 6- 8 hours	1 or 2 sites per day

Table 9. Timing of First-order Watershed Sampling Effort

Activity	Best months
Characterization of stream base flow	January through April
Minimal biological activity	December through March
Collection of benthos samples	March, April, May (Plafkin et al., 1989; Klauda et al., 1998) March 1 to May 1 (Stribling et al., 1998)
First pesticide application	late April, May
Sample collection time interval	Late February, March, April

DATA ANALYSIS

OVERVIEW

Data analysis includes all the systematic uses of the data and other information to address the LIPS-MACS hypotheses. Many of the analysis activities will be conducted in parallel. Some of the analysis activities are required to generate intermediate results necessary for understanding the data, while others provide direct results. A wide variety of data will be collected or calculated and summarized for each stream site or corresponding watershed (see Table 10). The overall data analysis approach which we will follow is described below:

- Descriptive statistics and maps will be developed for all the major categories of data to achieve familiarity with the data and add an additional level of data quality assurance and validation. Computation of benthic macroinvertebrate indices and physical habitat metrics are included here.

- Association statistics also will be developed for the major categories of data. These analyses are similar to descriptive analyses except that more than one parameter is considered at a time. Like descriptive analyses, association analyses promote data familiarity and they are an important step in data quality assurance and validation.

- Study period representativeness analyses will assess how representative the field study results are to other periods of time (other years). We will rely on existing data for these analyses, including stream data from USGS, weather data from the National Weather Service, and benthos data from the states of Maryland and North Carolina. If the study period is found to be significantly unusual compared to typical years or long-term composite conditions, the results will be interpreted in this light.

- Landscape indicator model analyses will rely on multiple regression techniques to develop predictions for the individual dependent variables as a function of the landscape metrics. This will be discussed further below.

- Multivariate analyses provide a top-down approach to organize many variables into a smaller number of unique groups. Classification and Regression Tree analysis will identify rules for grouping data into classes, for example, levels of human influence or hydrogeologic framework types. Taken together, these analyses will provide insights on the best approach for applying the landscape indicators. For example, the spatial applicability for each model will be evaluated, and the contributions of the hydrogeologic variables will be identified. This will also be discussed further below.

- Case study analyses will rely on hydrologic, pesticide fate and transport, and multimedia modeling at selected sites to help us articulate conceptual models and the relative importance of factors such as differing soil and hydrogeologic conditions. These case studies will start with a few sites and the simpler models and progress toward more complex models and additional sites. The models include a multimedia box model, a ground-water flow model, and pesticide fate and transport models for soil. This work will be conducted in parallel with the landscape indicator model development. The case studies and modeling are discussed in the next section.

Table 10. Parameters Measured or Calculated for Each Site or Watershed

Stream water chemistry	**Bed sediment data**	**Benthic macro-invertebrate**	**Physical habitat data**	**Rapid habitat assessment**	**Existing landscape data**	**Pesticide loading data**
<u>On-site</u> -DO, -tempera-ture -pH, -stream discharge -dissolved alkalinity -specific conduc-tance <u>Laboratory</u> -major ions USGS schedule 2701 -pesticides USGS schedule 2001 -nutrients USGS schedule 2702 -pesticide metabolites -see Appendices A, C, and D	<u>On-site</u> -composite of 11 samples per site <u>Laboratory</u> -Aldrin -Chlordane -DDD -DDE -DDT -Dieldrin -Endosulfan -Endrin -Hepta-chlor -Hepta-chlor epoxide -additional chlorinated pesticides -PCB Congeners, -As, Hg -see Appendix B	<u>On-site</u> -9 samples per site, combine into pool and riffle composites <u>Laboratory</u> -300 count organism identification to genus and species for pool and riffle composites -community composition -community abundance -various indices -see Appendix E	<u>On-site</u> -thalweg profile -woody debris tally -channel characteri-zation -riparian characteri-zation -compass bearings between stations -see Appendix F	<u>On-site</u> Riffle/run: -in stream fish cover -epifaunal substrate -embedded-ness -velocity/ depth -channel alteration -sediment deposition -frequency of riffles -channel flow status -condition of banks -bank vegetative protection -grazing/ other pressure -riparian vegetation width (Pool/glide similar)	<u>Databases</u> -stream hydrography -digital elevation -soil data -land use/ land cover -roads -county boundaries -population -precipitation -see Appendix G	<u>Databases</u> estimates: apportion to agricultural land use by -zip code -county

- Multiple comparison analysis techniques will utilize both new and available stream and ground-water monitoring data to test a) whether the hydrogeologic framework units are significantly different from each other; and b) whether a different grouping would be more optimal. This is discussed further below.

- Validation analyses will use reserved subsets of the field data, the nested site data; and existing data from previous ground water and surface water studies to evaluate the performance of the landscape indicator models. The reserved subsets will not be used in the landscape indicator model development process, ensuring that the model development is independent from the validation. Sensitivity analyses will also be performed on landscape model parameters.

- Reconciliation of results begins informally midway through the analysis effort and will be completed at the end of that phase. Sharing of results will encourage critical review, comparison with other results, and method refinements. Consideration of the validation results is part of this process. Ultimately, judgements of the technical credibility of the results will be made, and these findings will designate the final landscape indicators.

- Journal article and reports summarizing the above results will be produced throughout the analysis process, where appropriate.

Additional considerations in the preparation and analysis of the data are described below:

- Landscape metrics will be calculated for the actual sites and watersheds sampled, using the water sampling coordinates measured by the field crew as the pour point. Watersheds will be delineated using digital elevation data or hand drawn if necessary. We expect that a low percentage of the watersheds will require hand drawing. The spatial data types we expect to use, along with the data resolution, and sources are listed in Appendix G.

- For field study data, preparation includes traditional quality assurance and internal consistency checks. For existing data, preparation includes review of the methods and quality assurance information for the study that produced the data to identify data of questionable quality.

- Concentrations of pesticides in stream water and bed sediments will be tracked as individual compounds, as groups of compounds with similarities in properties and use, and as totals of herbicides and insecticides. These totals will be an initial indication of agricultural versus urban development. Major ions, including nutrients in stream water, will be treated individually, as will toxic compounds and arsenic and mercury in sediments. Base flow rates, stream size and temperature will also be considered in the analyses of the data.

- Indices for the macroinvertebrate data and physical habitat data will be computed; proposed benthic macroinvertebrate indices and physical habitat metrics are listed in Appendices E and F. Reference site data will be incorporated into these analyses, according to the process used to apply each metric, and will also be used for qualitative comparisons for other metrics. Each reference site will be characterized in the same manner as the framework unit sites to better explain the data observed. We intend to compare the reference sites with the framework sites, and examine the differences in benthic community composition and abundance between the developed and undeveloped watersheds. Data from the nested sites and other sites in the Coastal Plain will be used to look at scale issues.

- Ecological condition, as determined by macroinvertebrate and physical habitat data, will be compared to the data from the benthos reference sites that have been selected because they represent excellent conditions. The combination of the study sampling sites and the reference sites will give an indication of the relative range and variability of the macroinvertebrate responses over the study area. If unusually large spring storms occur in isolated portions of the study area, as indicated by the rainfall maps, that will increase the variability. Potential impacts of the 1999 hurricane season (Hurricane Floyd) and the drought of 1999 on benthic macroinvertebrate community composition and abundance will be considered in this analysis. This will be accomplished by obtaining hurricane flooding information from the Federal Emergency Management Agency. We will compare sampling sites with the flood locations from the previous year. This will enable us to identify sites which were severely affected by these storms, compared to those which were not. We also will have 4-kilometer resolution precipitation maps based on radar data available through the National Weather Service. This will enable us to compute rainfall received by a site for the previous 9 months of time. Drought has been an issue in some areas of the Coastal Plain for the past several years. The rainfall data will be useful in evaluating the extent of drought conditions at the sampling sites.

- The performance of the study design will be evaluated to determine if enough samples were collected, or if too many samples were collected, given the variability measured.

These results will support the analyses that follow.

LANDSCAPE INDICATOR MODELS

Model Development

The Landscape indicator analysis will rely heavily on multiple regressions and the CART technique described earlier. We expect to use SAS®, and CART® software. Various combinations of metrics will be tested for their success in explaining the variability encountered in the data. Many of the metrics are correlated with each other and care will be taken to use independent metrics (Riitters et al., 1995; Griffith and Amrhein, 1997). The best landscape indicator model will result from an iterative process of selecting statistically significant variables which are also physically and biologically meaningful. Each analyte will be treated individually and also grouped into totals, classes, and groups. We will conduct a preliminary analysis (pair wise correlations etc.) to determine preferred groups and minimize interdependencies. This will be followed by step wise regression. With the chemicals we will be looking at canonical correlations, and for landscape metrics, we will apply factor analysis.

Landscape indicator model relationships and hierarchical relationships using CART will be developed using data from the 175 sites which are representative of about 10,000 first-order, freshwater streams and their watersheds within the Mid-Atlantic Coastal Plain in New Jersey, Maryland, Delaware, Virginia, and North Carolina. The list of independent and dependent variables will be expanded and revised as we evaluate the performance of the landscape pattern metrics (see Table 11). Some variables, such as cropping pattern, are of interest but not available to us because of the scale and date (1992) of our land use/land cover data. We are treating agriculture as a bulk property. We will apply the method of Luther and Haitjema (1998) to estimate the mean ground water flow path and mean residence times for each watershed.

For the nested sites, watershed delineations and landscape characterization data will be prepared for each watershed pour point sampled within the nested series of streams. Since this data set is small, the data will be grouped by stream order and flow, and qualitative data analysis will be used to evaluate the results. These data will also be used for the model validation below. The nested watersheds will give us a way to consider how spatial scale affects our results. Our first-order watershed design will help us to understand processes in small scale watersheds while the data for the nested watersheds will help us to understand how the watersheds fit together. These data are not intended for the landscape modeling effort.

Table 11. Landscape Metrics and Dependent Variables for Analysis

Dependent variables: pH in water dissolved oxygen in water specific conductance in water dissolved alkalinity in water pesticides in water (Appendix A) pesticides in sediments (Appendix B) major ions in water (Appendix C) nutrients in water (Appendix D) benthic macroinvertebrates (Appendix E) physical habitat (Appendix F) pesticide metabolites in water
Landscape metrics: watershed area percentage of watershed in agricultural land use (MRLC data) percentage of contiguous agricultural land use percentage of watershed in urban land use (MRLC data) population density percentage of impervious surfaces (estimated from land use) length and width of riparian buffer zones road-to-stream distance percentage of agriculture on steep slopes gradient of stream Universal Soil Loss Equation soil erodibility soil texture, permeability hydrogeologic unit code depth to ground water mean length of ground-water flow path (Luther and Haitjema, 1998) mean residence time of ground water (Luther and Haitjema, 1998)

Model Validation/ Sensitivity Analysis

Model validation involves the calculation of landscape indicator values for watersheds which have associated pesticides and nutrient data for stream water and pesticide, PCB, arsenic and mercury for bed sediments. The calculated values will be compared to the actual values and percent differences will be determined. Some of the data used for validation will be subsets from the field data, which will not be used in the landscape indicator development process; this includes data from the 175 framework unit sites, as well as the nested sites. We have tentatively identified approximately 25 surface water sites and approximately 50 ground- water sites from previous studies which have pesticides and nutrient data. We will also evaluate these studies and perform comparisons with these data.

Sensitivity analysis will be performed by making incremental changes in the regression coefficients while holding the other coefficients constant. We may also test changes to ratios of coefficients. Some regression models may perform better in certain hydrogeologic framework units, compared to others. This hypothesis will be evaluated by comparing the goodness-of-fit statistics for the whole area to those for each hydrogeologic framework unit. The effect of using higher resolution Soil Survey Geographic (SSURGO) data instead of State Soil Geographic (STATSGO) data at sites where both are available will be investigated.

HYDROGEOLOGIC FRAMEWORK

We will rely on both existing and new data for surface water and ground water in the evaluation of the hydrogeologic framework. Existing water-quality data will be used to determine if the regional aspects of the framework accurately represent factors that affect regional water quality. Results from local-scale, analyses of structure and function of the stream biota and habitat and the physical and chemical processes will be compared to the processes hypothesized as affecting water quality in different subregions of the framework. Available data will then be used to statistically evaluate the relevance of the framework to the description of actual water-quality conditions. This effort will include ground-water and surface-water data available from the NAWQA program and other data that are comparable in quality and study design. The statistics to be used will largely be determined by the data and are likely to include nonparametric tests and an analysis of variance to identify differences in chemical concentrations or other indicators among framework regions. If the data are too heavily censored for this (data below method detection limits which is common for pesticides), contingency tables could be used (with a consequent loss of power). We may also use correlations or regressions when comparing continuous variables. Hydrologic applications of these statistics are covered in general in Helsel and Hirsch (1992). Some examples of analysis-of-variance-type tests in environmental science include Blomquist et al. (1996); Ator and Denis (1997); and Ator and Ferrari (1997). For heavily censored data, probit or logistic regression can be used (Eckhardt and Stackelberg, 1995; Tesoriero and Voss, 1997; Liu et al.,1996). Blomquist et al. (1996) used parametric regressions. Ator and Denis (1997) used correlations and two-way ANOVA. Ator and Ferrari (1997) used contingency tables because the pesticide data were heavily censored.

DATA MANAGEMENT

Data storage and retrieval will be accomplished initially with Microsoft Access®, Arc Info®, and Arc View® computer software. Field data (water, macroinvertebrate, and sediment data) will be available to study participants via a USGS-operated website, while the large spatial files will be shared via compact disk. Eventually the data from the study will be incorporated into EPA’s Environmental Information Management System. A website describing the study and providing status reports and updates will be available to the public.

HYDROLOGIC AND MULTIMEDIA MODELING

Hydrologic, pesticide fate, and multimedia process models can provide additional insights about watersheds within the study area. By approaching selected sites from a case study point of view, we hope to gain added conceptual understanding of the physical and chemical processes involved. The temporal sites will be modeled first because of the more extensive data available. Starting with a few sites and simple models, we will expand the effort to include sites representative of all the hydrogeologic framework units. Because pesticide application rates are such an important factor, we are pursuing acquisition of specific pesticide application rate data for some of these sites. We may use some of the results derived from the hydrologic and multimedia modeling in the landscape indicator modeling. Alternatively, the landscape indicator modeling results may suggest scenarios and case studies for the hydrologic and multimedia modeling.

Many models are being considered to help us investigate the most significant processes as our data analysis develops (see Table 12). A key factor is data needed for the models. We are searching for the best available input data for these models and expect use values from the literature, for example, for atmospheric deposition and irrigation use. The modeling effort will be built progressively, starting with the simpler cases and models, and then moving to the more complex.

Table 12. Models Under Consideration

Model	**Purpose**	**Reference**
Mend-Tox™	multimedia compartmental estimates of pesticide concentrations over time	Cohen, 1986; Onishi et al., 1990
SESOIL	long term-fate and migration of pollutants in vadose zone	Bonazountas et al., 1997
PRZM-3	pesticide degradation and transformation; vertical leaching in crop root zone; run off from different land cover zones	Mullins et al., 1993
MODFLOW, MODPATH	ground-water flow (finite difference model), advective flow	Harbaugh and McDonald, 1996
GFLOW	ground-water flow (analytic element model) better advective flow	Kelson and Haitjema, 1994; Haitjema, 1995
MT3D	transport and transformations	Zheng, 1992
SPARROW	spatially referenced regression model, estimates source and fate of contaminants in streams	Smith et al., 1997

Mend-Tox™ is a multimedia model which estimates the distribution of organic chemicals for seven compartments in the environment: air, atmospheric aerosols, surface water, suspended solids in water, aquatic organisms, soil, and vegetation. Mend-Tox™ identifies significant and insignificant transport and exposure pathways, and it can estimate potential persistence of chemicals in the environment. Besides being useful in a case study, Mend-Tox™ may be useful in the landscape indicator application effort, for answering "What if?" type questions.

The hydrologic and pesticide fate and transport models (SESOIL, PRZM-2, MT3D with MODFLOW, and GFLOW) may be useful in understanding the relative behaviors of the pesticides in soils, surface water, and ground water. Further evaluation of their requirements and outputs will be needed before we decide which one(s) to use for the estimation process. Initial GFLOW modeling will be conducted by U.S. EPA NERL-Athens staff for two temporal sites in the Coastal Plain: the Chesterville Branch site in Maryland and the Lizzie site in the Contentnea River drainage in North Carolina. This modeling effort will share its results with this study and another research program at Athens. The modeling for the Chesterville Branch site depends on data collected by a study funded by the U.S. EPA's NRML-Ada and being shared with NERL-Athens and NERL-Las Vegas. The data being collected with NERL-Las Vegas funding are being shared with both of the other facilities.

The Spatially Referenced Regressions on Watershed Attributes (SPARROW) model (Smith et al., 1997) may be used as an adjunct to the landscape indicator evaluation process to help relate landscape characteristics to water quality. This statistical model reduces common problems associated with relating surface water quality to watershed landscapes, including sparseness of sampled locations, spatial bias in the sampling network, and drainage basin heterogeneity. To account for natural long-term hydrologic variation, SPARROW is typically used with estimated long-term average contaminant loads at sampling sites to estimate cumulative downstream loads based on watershed characteristics. A SPARROW model for nutrients in nontidal portions of the Chesapeake Bay Watershed has been developed (Preston and Brakebill, 1999) and the addition of the Delaware River Basin to this model is under consideration. However, surface-water stations with long-term, historical water-quality data are relatively scarce in the Mid-Atlantic Coastal Plain, particularly for pesticides (Ferrari et al., 1997). Initially, SPARROW model results which relate landscapes to stream quality in parts of the Mid-Atlantic Coastal Plain and overlap our study sites will be compared to the landscape indicator model results. The winter base flow data we collect may be useful for creating a SPARROW model to predict landscape effects on streams, although SPARROW has yet to be used in this way. This possibility will be investigated further and pursued if warranted. It may be possible to corroborate the landscape indicator model analysis with the SPARROW model results for selected, nested watersheds. The application of SPARROW for estimating pesticide concentrations in streams is a topic of current interest for the EPA Office of Pesticide Programs.

LANDSCAPE INDICATOR APPLICATIONS

POTENTIAL APPLICATIONS

Once the landscape indicator models are validated and the final selection of indicators is complete, it will be possible to use the results to gain a broader perspective. The landscape indicator models can be applied to the entire set of approximately 10,000 first-order, freshwater watersheds in the Coastal Plain to predict their status for selected dependent variables. Land use change scenarios can be applied to model the sensitivity of the watersheds and identify and rank the most vulnerable on a relative basis. The results can be displayed on detailed maps. New monitoring designs for different purposes (identifying most pristine areas, most vulnerable areas, or areas most suitable for restoration) can be demonstrated and can be evaluated using the landscape indicators and the underlying data bases. Watersheds with similar issues can be identified, so they can be treated as a group, such as for Total Maximum Daily Load development. Specific questions, and priorities will be addressed in conjunction with the stakeholders.

STAKEHOLDERS AND OUTREACH

One of the principles of the Landscape Ecology Branch (Jones et al, 2000) is to involve stakeholders early and throughout a project. Thus, meetings with representatives from Regions 2, 3, and 4, and the Office of Pesticide Programs and the Office of Water have already occurred in FY99 and FY00. An overview of the project has also been presented to representatives from state agencies within Region 3. The intent is to continue to find key individuals with interest in our activities, and build these relationships, involving these individuals in developing the landscape indicator applications. These individuals would bring different perspectives and needs into the project for consideration and often contribute substantial expertise gained from working in the area over a number of years. The decision points where stakeholder involvement is desired include

- selection of benthos reference sites;
- selection of case study sites;
- review of the hydrogeologic framework results;
- review of the landscape indicator results; and
- development of scenarios for landscape indicator applications.

Stakeholder contributions will help us to focus the study and meet their needs. We expect to work closely with the appropriate EPA Regional Offices to develop a pesticide indicator atlas for the Mid-Atlantic Coastal Streams, to provide public workshops to disseminate the results, and to publicize the availability of the reports, journal articles, and data which result from this study.

QUALITY ASSURANCE

The Mid-Atlantic Coastal Stream Study relies almost entirely on existing protocols and procedure manuals for its field and laboratory activities. Two large sampling programs, EMAP and NAWQA, have standardized many sampling and laboratory procedures, and we are taking advantage of their work. Table 7 (page 40) lists the methods and quality assurance manuals being followed in the study. Not only is there a substantial cost savings in using existing protocols, there is also a payoff in comparability of data, which enhances its value for the long term. Some quality assurance highlights for the study are listed below.

- Water sampling and on-site analysis of water samples will be conducted following USGS NAWQA sampling protocols. This includes independent audits of sampling crew activities.

- Macroinvertebrate sampling will follow EMAP QA protocols.

- Physical habitat assessment will follow EMAP QA protocol, with modifications.

- A methods, quality assurance, and safety workshop will be conducted for the macroinvertebrate and physical habitat field crews the week before spring sampling starts.

- All the laboratory water sample analyses for pesticides, major ions, and nutrients will be performed by the USGS National Water Quality Laboratory (NWQL). The NWQL uses quality-control data to measure and monitor bias and variability in analytical methods (Pirkey and Glodt, 1998). Three levels of quality control at the NWQL include continuing analyses of method performance, data review and blind sample programs, and participation in inter-laboratory performance evaluation studies.

- NWQL method performance is evaluated with results from quality control samples included with each batch of environmental samples. Quality control samples for inorganic analyses include blanks, standard reference materials, and laboratory replicates. Surrogate compounds and laboratory reagent blanks and spikes are used to monitor analyses for organic compounds.

- NWQL monitors method performance throughout the laboratory and over long periods using blind samples (Ludtke and Woodworth, 1997) and data reviews. Inorganic data are reviewed with logic checks such as cation-anion balances. Field and laboratory values and filtered and unfiltered values are also compared. For organic analyses, long-term data from the first level of quality control are analyzed to compute method control limits and acceptance criteria.

- NWQL participates in multiple inter-laboratory studies with the U.S. EPA, the National Oceanic and Atmospheric Administration (NOAA), and the National Water Research Institute of Canada (Glodt and Pirkey, 1998).

- Data management will follow the EPA guidelines and databases and metadata will meet the Federal Geographic Data Committee requirements. Data will be accessible through EPA's Environmental Information Management System.

- Modeling follows the EPA guidelines on use of existing models, with documentation of assumptions, parameter values and sources, boundary and initial conditions, validation and calibration of the model, and output. It includes periodic testing of the model with a standard data set and comparison to known results.

- The staff is trained in the use of software (for example, Arc View, Arc/INFO, SAS, CART, Mend-Tox), maintains their expertise through frequent use, and is available to mentor others in the use of these software packages.

- Data interpretation will be reviewed within the project group as results become available. When possible, results will be computed two or more ways and the results will be compared.

- The decision analysis tools will follow the EPA guidelines for use of existing software and for developing new software. When complete, they will be accessible through a website which will follow EPA website requirements.

- This plan will be externally peer reviewed. Interim and final results of the study will also be peer reviewed as part of the normal journal article submission process.

- Stakeholder input is planned at several stages of the study; this effort is described in detail in the section "Landscape Indicator Applications."

- Quality assurance reports are due from each of the major contributors after the data collection and sample analysis is complete (USGS, Benthos Sampling and Benthos Analysis contractors).

• Audits will be performed by the EPA as scheduled by the Principal Investigator and the Project Quality Assurance coordinator. Sampling procedure audits will be conducted once for each sampling crew during the field season to assess compliance with sampling protocols. A benthos laboratory sample audit will be conducted to assess compliance with standard laboratory procedures. The chemistry laboratories will not be visited because they participate in existing round-robin and other quality assurance activities, such as those mentioned for the NWQL, above.

C A central project file exists at NERL/ESD-Las Vegas, maintained by the Principal Investigator, with copies of the documentation described above. Project management records and budget information are also available.

SCHEDULE AND MILESTONES

A schedule and milestones for the study, including a Government Performance Results Act (GPRA) deliverable, have been developed for the years FY98-FY03 (see Table 13). The table provides a quick overview of the activities and responsibility for completing them.

Table 13. Detailed List of Milestones by Fiscal Year

Year	Event	Responsibility
FY98	Analyzed existing pesticide data for Mid-Atlantic	EPA, USGS
	Reviewed literature	EPA
	Initiated USGS interagency agreement	EPA
FY99	Complete hydrogeologic framework	USGS
	Begin analysis of hydrogeologic framework using existing data	USGS
	Augment GIS coverages	EPA
	Characterize watershed support areas for first- and second-order streams	EPA, USGS
	Begin statistical sampling design and select sites	USGS, EPA
	Select ground water-surface water models	EPA, USGS
	Initiate data and QA management	EPA
	Initiate arrangements for benthos sampling	EPA
	Identify scientific collaborators	EPA
	Contact stakeholders	EPA
FY00	Complete statistical sampling design and site selection	USGS, EPA
	Involve stakeholders in site selection where practical	EPA
	Collect and analyze water samples	USGS
	Collect and analyze benthos samples	EPA
	Complete analysis of framework performance using existing data	USGS
	Prepare database for water sample, benthos, and physical habitat data; derive interpretive measures and include in database; prepare metadata	EPA, USGS
	Initiate modeling (except for SPARROW)	EPA

FY01	Evaluate hydrogeologic framework with new data	USGS
	Evaluate landscape indicators with new data	EPA
	Develop Mid-Atlantic Coastal Stream assessment	EPA, USGS
	Complete modeling	EPA
	Conduct SPARROW modeling	USGS
	Prototype of decision analysis tool	EPA
	Share results with stakeholders	EPA, USGS
	GPRA Deliverable: Condition of streams and ground water with respect to pesticides and nutrients: development of landscape indicators for the Mid-Atlantic Coastal Plain, due 9/01	EPA
FY02	Make data available on Internet	EPA
	Deliverable: Landscape characterization of first order watersheds in the Mid-Atlantic Coastal Plain; Journal Article, 9/02	EPA
FY03:	EPA Report: Landscape Atlas for Pesticides and Nutrients in Mid-Atlantic Coastal Freshwater Streams. (due 9/03)	EPA

POTENTIAL FOR REDUCING UNCERTAINTY

Over the long term, the landscape indicators generated from this research are expected to contribute to assessments of condition, vulnerability, and risk to aquatic ecosystems due to pesticides and toxic substances at multiple scales across the U.S.

For the Mid-Atlantic Coastal Plain, this research should result in a validated hydrogeologic framework which will provide a context for the nutrients, pesticides, and toxic substance results. The combination of the framework and the pesticides and toxic substance indicators can be used to develop monitoring designs, identify similar watersheds, and estimate water quality for these parameters. It should also lead to an improved understanding of how landscape indicators for pesticides and toxic substances vary within hydrogeologic classes, versus how these parameters vary between these classes. From this information, we should be able to predict condition and relative ranking of stream segments. This will provide us with a complete case study showing how the elements of the pesticide and toxic substance data, landscape and water quality parameters, and ultimately landscape indicators can be integrated in a regional-scale water quality assessment. These results are expected to be useful to EPA's Office of Prevention, Pesticides, and Toxic Substances (OPPTS); Office of Water (OW), and Regional Offices; and also state and local agencies with responsibilities for managing water resources for pesticides and toxic substances.

The development of the hydrogeologic framework contributes to the following High and Medium Priority needs identified in "TMDL Scientific Needs: A Regional and Office of Water Assessment (March 18, 1998):

- High Priority Monitoring and Assessment Technical Support Needs: Monitoring designs for identifying impacted water bodies.

- High Priority Modeling Research Needs: Development of watershed similarity indices to extrapolate loading rates of key stressors.

- Medium Priority Monitoring and Assessment Research Needs: Development of extrapolation techniques to estimate water quality condition in nonmonitored segments.

- Medium Priority Data and GIS Technical Support Needs: Aquatic resource data: water column physical/chemical data linked to hydrographic coverages.

PERFORMANCE MEASURES

The EPA, to better account for the success of its actions, has developed a cascading set of goals, objectives, subobjectives, milestones, measures, tasks, and products in compliance with the Government Performance Results Act (GPRA). There are currently 10 longer-term goals for the EPA under the GPRA. Goal 8, "Provide sound science to improve the understanding of environmental risk, and develop and implement innovative approaches for current and future environmental problems," serves as the foundation, or core of the Office of Research and Development's (ORD) Ecological Research Program. The specific objective associated with ORD's ecoresearch under this "Sound Science" goal is to provide the scientific understanding to measure, model, maintain, or restore at multiple scales the integrity and sustainability of ecosystems now, and in the future.

In addition, the ORD's "Ecological Research Strategy" identifies major objectives, sub-objectives and products associated with its core research program areas of:

- Ecosystem monitoring research
- Ecological processes and modeling research
- Ecological risk assessment research, and
- Ecosystem risk management restoration research

Shorter-term accounting of success is accomplished by establishing and monitoring the response to the annual performance goals (APGs) and measures (APMs) under GPRA and progress toward completion of any additional critical research products identified in the ORD's "Ecological Research Strategy" and its subsequent updates. These goals and measures provide the "why" and the "what" of our research tasks and projects. This document, as a technical research plan, addresses not only the "why" and the "what" but also the "how" -- the approach to providing products that satisfy the specific performance goals associated with this activity.

This research project supports, Goal 2 (Water), Goal 4 (Preventing Pollution and Reducing Risk) and Goal 8 (Sound Science). Specific annual performance goals and measures are listed in the next section.

ANTICIPATED RESULTS/PRODUCTS

FY00:

Research Plan: Testing Landscape Indicators for Stream Condition Related to Pesticides and Nutrients: Landscape Indicators for Pesticides Study for Mid-Atlantic Coastal Streams (Due 9/00)

FY01:

GPRA Deliverable: Journal Article: Condition of streams and shallow ground water with respect to pesticides and nutrients: development of landscape indicators for the Mid-Atlantic Coastal Plain. This product provides the scientific basis for the use of landscape indicators which can identify a) similar watersheds and b) streams impacted by nutrients and pesticides. (due 9/01)

FY02:

Journal Article: Landscape characterization of first order watersheds in the Mid-Atlantic Coastal Plain. (due 9/02)

FY03:

EPA Report: Landscape Atlas for Pesticides and Nutrients in Mid-Atlantic Coastal Freshwater Streams. (due 9/03)

LITERATURE CITED

Abel, P.D., 1980. Toxicity of hexachlorocyclohexane (Lindane) to *Gammarus pulex*; mortality in relation to concentration and duration of exposure. Freshwater Biology, 10, 251-259.

Ator, S.W., and J.M. Denis, 1997. Relation of nitrogen and phosphorus in ground water to land use in four subunits of the Potomac River Basin. USGS WRIR 96-4268, 26 p.

Ator, S.W., and M.J. Ferrari, 1997. Nitrate and selected pesticides in ground water of the Mid-Atlantic Region. Water Resources Investigation Report 97-4139, 8 p.

Ator, S.W., J.D. Blomquist, J.W. Brakebill, J.M. Denis, M.J. Ferrari, C.V. Miller, and H. Zappia, 1998. Water quality in the Potomac River Basin, Maryland, Pennsylvania, Virginia, West Virginia, and the District of Columbia. 1992-96, USGS Circular 1166.

Bachman, L.J., B. Lindsey, J.W. Brakebill, and D.S. Powars, 1998. Ground-water discharge and base-flow nitrogen loads of non-tidal streams, and their relation to a hydrogeomorphic classification of the Chesapeake Bay watershed, Middle Atlantic Coast. U.S. Geological Survey Water-Resources Investigations Report 98-4059, 71 p.

Barbash, J.E, and E.A. Resek, 1996. Pesticides in ground water: distribution, trends, and governing factors. Chelsea, Michigan, Ann Arbor Press, Inc., 588 p.

Barber, M.C. ed., 1994. Environmental Monitoring and Assessment Program: Indicator Development Strategy, EPA/620/R-94/022, Athens, GA. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory.

Barbour, M.T., J. Gerritsen, B.D. Snyder, and J.B. Stribling. 1999. Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates and Fish, Second Edition. EPA 841-B-99-002. U.S. Environmental Protection Agency; Office of Water; Washington, D.C.

Battaglin, W.A., and D.A. Goolsby, 1994. Spatial data in geographic information system format on agricultural chemical use, land use and cropping practices in the United States. USGS, Water Resources Investigations Report 94-4176, http://water.usgs.gov/pubs/bat/bat000.html

Blomquist, J.D., G.T. Fisher, J.M. Denis, J.W. Brakebill, and W.H. Werkheiser, 1996. Water-quality assessment of the Potomac River Basin -- Basin description and analysis of available nutrient data, 1970-90. USGS Water Resources Investigations Report, 95-4221, 88 p.

Bode, R.W., M.A. Novak, and L.E. Abele, 1996. Quality assurance work plan for biological stream monitoring in New York State. New York State Department of Environmental Conservation, Albany, NY, 89 p.

Bohlke, J.K., and J.M. Denver, 1995. Combined use of ground water dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland, Water. Resources Research, Vol. 31, p. 2319-2339.

Bohlke, J.K., J.M. Denver, R.B. Wanty, and P.B. McMahon, 1996. Some hydrologic controls on distribution of nitrate on agricultural watersheds. Spring AGU meeting, 1996 Supplement, Vol. 77.

Bonazountas, M., D. Hetrick, and P. Kostecki, 1997. SESOIL in Environmental Fate and Risk Modeling, Amherst Scientific Publishers, Amherst, MA, 686 p.

Brieman L., J.H. Friedman, R.A. Oshen, and C.J. Stone, 1984. Classification and Regression Trees, Chapman & Hall, New York.

Brown, P.M., J.A. Miller, F.M. Swain, 1972. Structural and stratigraphic framework, and spatial distribution of permeability in the Atlantic Coastal Plain, North Carolina to New Jersey, U.S. Geological Survey Professional Paper 796, 79 p.

Brown, D.E., F. Reichenbacher, and S.E. Franson, 1998. A Classification System of North American Biotic communities. University of Utah Press, Salt Lake City, UT, 152 p.

Calow, P. 1998. Introduction: the chemical challenge. Environmental Monitoring and Assessment, 53: 391-394.

Carlile, D.W., J.R. Skalski, J.E. Batker, J.M. Thomas, and V.I. Cullinan, 1989. Determination of ecological scale. Landscape Ecology, 2(4), p. 203-214.

Caspers, H., and C.W. Heckman, 1981. Ecology of orchard ditches along the freshwater section of the Elbe Estuary. Arch. Hydrobiol. Supple. 43, 347-486.

Chow, V.T., D.R. Maidment, and L.W. Mays, 1988. Applied Hydrology, McGraw-Hill, Inc., New York, 572 p.

Clark, L. A., and D. Pregibon, 1992. Tree Based Models, in: Statistical Models in S.
T.J. Hastie, and J.M. Chambers, (Eds.), Wadsworth & Brooks California, 608 p.

Clements, W.H., D.S. Cherry, and J.H. Van Hassel, 1992. Assessment of the impact of heavy metals on benthic communities at the Clinch River (Virginia): evaluation of an index of community sensitivity. Can. J. Fish. Aquat. Sci. 49: 1686-1694.

Cohen, Y. ed., 1986. “Intermedia transport modeling in multimedia systems,” in Pollutants in a Multimedia Environment, Plenum Press, New York.

Cordy, C., 1993. An extension of the Horvitz-Thompson theorem to point sampling from a continuous universe. Probability and Statistics Letters, 18, 353-362.

Corkum, L.D., and J.J.H. Ciborowski, 1988. Use of alternative classifications in studying broad-scale distributional patterns of lotic invertebrates. Journal of North American Benthological Society, 7: 167-179.

Corkum, L.E., 1992. Relationships between density of macroinvertebrates and detritus in rivers. Arch. Hydrobiol., 125: 149-166.

Correll, D.L., T.E. Jordan, and D.E. Weller 1992. Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient Transport to coastal waters. Estuaries, Vol. 15, No. 4. p. 431 - 442.

Cronan, C.S., J.T. Piampiano, and H.H. Patterson, 1999. Influence of land use and hydrology on exports of carbon and nitrogen in a Maine river basin. J. Environ. Qual., 28: 953-961.

Cuffney, T.F., B.F. Wallace, and J.R. Webster, 1984. Pesticide manipulation of a headwater stream: invertebrate responses and their significance for ecosystem processes. Freshwater Invertebrate Biology, Vol. 3, No. 4, 153-171.

Cuffney, T.F., M.E. Gurtz, and M.E. Meador, 1993. Methods for collecting benthic invertebrate samples as part of the National Water-Quality Assessment Program. U.S. Geological Survey Open-File Report 93-406, 66 p.

Cuffney, T.F., M.R. Meador, S.D. Porter, and M.E. Gurtz, 1997. Distribution of fish, benthic invertebrate, and algal communities in relation to physical and chemical conditions, Yakima River Basin, Washington, 1990. U.S. Geological Survey Water Resources Investigations Report 96-4280, 94 p.

Cushing, E.M., I.H. Kantrowitz, and K.R. Taylor, 1973. Water resources of the Delmarva Peninsula. U.S. Geological Survey Professional Paper 822, 58 p.

Denver, J.M., and S.W. Ator, 1999, personal comm.

Dingman, S.L., 1994, Physical Hydrology, Prentice Hall, Upper Saddle River, New Jersey, 575 p.

Eckhardt, D.A.V., P.E. and Stackelberg, 1995. Relation of ground-water quality to land use on Long Island, NY. Ground Water, vol. 33, no. 6, p. 1019-1033.

Efron, B., and R. Tibshirani, 1991. Statistical data analysis in the computer age, Science, Vol. 253, p. 390-395.

Ferrari, M.J., S.W. Ator, J.D. Blomquist, and J.E. Dysart, 1997. Pesticides in surface water of the Mid-Atlantic region. U.S. Geological Survey Water Resources Investigations Report 97-4280, 12 p.

Fore, L.S., J.R. Karr, and R.W. Wisseman, 1996. Assessing invertebrate responses to human activities: evaluating alternative approaches. J. N. American Benthological Society, 15(2), p. 212-231.

Gianessi, L.P., and C.A. Puffer, 1990 (revised 1991). Herbicide use in the United States. Resources for the Future, Quality of the Environment Division, Washington, D.C., 128 p.

Gianessi, L.P., and C.A. Puffer, 1992a. Fungicide use in the United States. Resources for the Future, Washington, D.C.

Gianessi, L.P., and C.A. Puffer, 1992b. Insecticide use in the United States. Resources for the Future, Washington, D.C.

Glodt, S.R., and K.D. Pirkey, 1998. Participation in performance-evaluation studies by U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Fact Sheet FS-023-98, 6 p.

Graham, R.L., C.T. Hunsaker, R.V. O'Neill, and B.L. Jackson, 1991. Ecological risk assessment at the regional scale. Ecol. Appl. 1: 196-206.

Griffith, D.A., and C.G., Amrhein, 1997. Multivariate Statistical Analysis for Geographers, Prentice Hall, Upper Saddle River, New Jersey, 345 p.

Haitjema, H.M., 1995. Analytic Element Modeling of Ground-water Flow. Academic Press, New York.

Hallberg, G.R., 1987. Agricultural chemicals in ground water: extent and implications, American Journal of Alternative Agriculture, Vol. 11, No. 1, p. 3-15.

Harbaugh, A.W. and M.G. McDonald, 1996. Users documentation for MODFLOW-96, an update to the U.S. Geological Survey modular finite-difference ground-water flow model, OF 96-0485, 56 p.

Helsel, D.R., and R.M. Hirsch, 1992. Statistical Methods in Water Resources, Elsevier, Amsterdam, Netherlands, 522 p.

Herlihy, A.T., D.P. Larsen, S.G. Paulsen, N.S. Urquhart, B.J. Rosenbaum, 2000. Designing a spatially balanced, randomized site selection process for regional stream surveys: the EMAP Mid-Atlantic Pilot Study, Environmental Monitoring and Assessment, 63 (1): 95-113.

Hilsenhoff, W.L., 1987. An improved biotic index of organic stream pollution. The Great Lakes Entomologist, Vol. 20, p. 31-39.

Horn, R.C., and W.M. Grayman, 1993. Water-Quality modeling with EPA Reach File System. Journal of Water Resources Planning and Management, Vol. 119, No. 2, p. 262-274.

Hostetler, K.A., and E.M. Thurman, 1999. Determination of chloroacetanilide herbicide metabolites in water using high-performance liquid chromatography-diode array detection and high-performance liquid chromatography/mass spectrometry. Morganwalp, D.W., and H.T. Buxton, Eds., U.S. Geological Survey Toxic Substances Hydrology Program. Proceedings of the technical meeting, Charleston, South Carolina, March 8-12, 1999, Volume 2, Contamination of hydrologic systems and related ecosystems. U.S. Geological Survey Water Resources Investigation Report 99-4018B.

Hunsaker, C. T., R. L. Graham, G. W. Suter, II, R. V. O'Neill, L. W. Barthouse, and R. H. Gardner, 1990. Assessing ecological risk on a regional scale. Environmental Management 14: 325-332.

Hunsaker, C.T., and D.A. Lavine, 1995. Hierarchical approaches to the study of water quality in rivers. Bioscience 45: 193-203.

Jackson, L.E., J.C. Kurtz, and W.S. Fisher, 1999. Evaluation guidelines for ecological indicators. EPA/620/R-99/005, U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC 27711,
http://www.epa.gov/emap/html/pubs/docs/resdocs/ecol_ind.pdf

Jones, B., J. Walker, K.H. Riitters, J.D. Wickham, and C. Nicoll, 1996. Indicators of landscape integrity, in J. Walker and D.J. Reuter, (Eds.), Indicators of Catchment Health: a technical perspective. CSIRO, Melbourne, p. 155-168.

Jones, K.B., K.H. Riitters, J.D. Wickham, R.D. Tankersley Jr., R.V. O'Neill, D.J. Chaloud, E.R. Smith, and A.C. Neale, 1997. An ecological assessment of the United States Mid-Atlantic region: A landscape atlas. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., EPA/600/R-97/130.

Jones, K.B, L.R. Williams, A.M. Pitchford, T.E. Slonecker, J.D. Wickham, R.V. O'Neill, D. Garofalo, K.H. Riitters, W.G. Kepner, and Goodman, I.A., 2000. A national assessment of landscape change and impacts to aquatic resources, a 10-year research strategy for the landscape sciences program. U.S. Environmental Protection Agency, EPA/600/R-00/001.

Jones, K.B., A.C. Neale, M.S. Nash, R.D. VanRemortel, J.D. Wickham, K.H. Riitters, and R.V. O'Neill, in press. Predicting nutrient and sediment loadings to streams from landscape metrics: A multiple watershed study from the United States Mid-Atlantic Region, Landscape Ecology.

Johnson, A.R., 1994. Spatiotemporal hierarchies in ecological theory and modeling. GIS and Environmental Modeling, p. 451-456.

Johnson, L.B., C. Richards, G.E. Host, and J.W. Arthur, 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. Freshwater Biology, 37: 193-207.

Kalkoff, S.J., D.W. Kolpin, E.M. Thurman, I. Ferrer, and D. Barcelo, 1998. Degradation of chloroacetanilide herbicides: the prevalence of sulfonic and oxanilic acid metabolites in Iowa ground waters and surface waters. Environmental Science and Technology, Vol. 32, p. 1738-1740.

Karr, J.R., and E.W. Chu, 1999. Restoring Life in Running Waters, Better Biological Monitoring, Island Press, Washington, D.C. 206 p.

Karr, J.R., and E.W. Chu, 2000. Sustaining Living Rivers, Hydrobiologia, 422/423, p. 1-14.

Kaufmann, P.R. (Ed.), 1993. Physical Habitat, p. 59-69 in R.M. Hughes (Ed.), Stream Indicator and Design Workshop, EPA/600/R-93/138, U.S. Environmental Protection Agency, Corvallis, Oregon.

Kaufmann, P.R., and E.G. Robison, 1998. Physical habitat characterization, in Lazorchak, J.M, Klemm, D.J., and Peck, D.V. (Eds.), Environmental Monitoring and Assessment Program - Surface Waters: Field Operations and Methods for Measuring the Ecological Condition of Wadeable Streams. EPA/620/R-94/004F, U.S. Environmental Protection Agency, Washington, D.C.

Kaufmann, P.R., P. Levine, E.G. Robison, C. Seeliger, and D.V. Peck, 1999. Quantifying physical habitat in wadeable streams. EPA/620/R-99/003, U.S. Environmental Protection Agency, Washington, D.C.

Keitt, T.H., D.L. Urban, and B.T. Milne, 1997. Detecting critical scales in fragmented landscapes. Conservation Ecology [online] 1(1): 4. Available from the Internet, URL: http://www.consecol.org/vol1/iss1/art4

Kelson, V.A., and H.M. Haitjema, 1994. GFLOW Users Manual. Haitjema Software, Indianapolis, IN.

Kennen, J.G., 1999. Relation of macroinvertebrate community inpairment to chatchment characteristics in New Jersey streams. Journal of American Water Resources Association, 35: 4, p. 939-955.

Kepner,W.G., K.B. Jones, D.J. Chaloud, J.D. Wickham, K.H. Riitters, R.V. O'Neill, 1995. Mid-Atlantic landscape indicators project plan, Environmental Monitoring and Assessment Program. EPA620/R-95/003, U.S. Environmental Protection Agency, Washington, D.C.

Kerans, B.L. and J.R. Karr, 1994. A benthic index of biotic integrity (B-IBI) for rivers of the Tennessee Valley, Ecological Applications, 4(4), p. 768-785.

Klauda, R., P. Kazyak, S. Stranko, M. Southerland, N. Roth, and J. Chaillou, 1998. Maryland biological stream survey: a state agency program to assess the impact of anthropogenic stresses on stream habitat quality and biota. Environmental Monitoring and Assessment, 51: 299-316.

Klein, R.D., 1979. Urbanization and stream quality impairment. Water Resources Bulletin, 15(4): 948-963.

Klemm, D.J. and J.M. Lazorchak, 1994. EMAP 1994 Pilot Laboratory Methods Manual for Streams, EPA/620/R-94/003, U.S. Environmental Protection Agency, Washington, D.C.

Kolpin, D.W., E.M. Thurman, and S.M. Linhard, 1998. The environmental occurrence of herbicides: the importance of degradates in ground water. Archives of Environmental Contamination and Toxicology, 35, 385-390.

Krug, A., 1993. Drainage history and land use pattern of a Swedish river system - their importance for understanding nitrogen and phosphorus load. Hydrobiologia 251: 285-296.

Kurtz, J, B. V. Kurtz, T. Poretti, D. Miller, C. Bryson, C. Lawless, and J. Sell, 1996. Ambient monitoring network: Atlantic coastal drainage basin. Water Monitoring Management, New Jersey Department of Environmental Protection, Trenton, New Jersey, 15 p.

Larson, S.J., P.D. Capel, and M.S. Majewski, 1997. Pesticides in surface waters: distribution, trends, and governing factors. Chelsea, Michigan, Ann Arbor Press, Inc., 373 p.

Lazorchak, J.M., A.T. Herlihy, H.R. Preston, and D.J. Klemm, 1998. Introduction, in Lazorchak, J.M., D.J. Klemm, and D.V. Peck, (Eds.), Environmental Monitoring and Assessment Program-surface waters: field operations and methods for measuring the ecological condition of wadeable streams. EPA/620/R-94/004F, U.S. Environmental Protection Agency, Washington, D.C.

Lenat, D., 1993. A biotic index for the southeastern United States: derivation and list of tolerance values, with criteria for assigning water quality ratings. J. N. Am. Benthol. Soc.12(3): 279-290.

Lindsey, B.D., K.J. Breen, M.D. Bilger, and R.A. Brightbill, 1998. Water quality in the lower Susquehanna river basin, Pennsylvania and Maryland, 1992-95. USGS Circular 1168.

Liu, Shiping, S.T. Yen, and D.W. Kolpin, 1996. Atrazine concentrations in near-surface aquifers - A censored regression approach. Journal of Environmental Quality, Vol. 25, p. 992-999.

Lowrance, R., R. Todd, J. Fail, Jr., O. Hendrickson, Jr., R. Leonard, and L. Asmussen, 1984. Riparian forests as nutrient filters in agricultural watersheds. BioScience 34(6): 374-377.

Ludtke, A., and M. Woodworth, 1997. USGS blind sample project – Monitoring and evaluating laboratory analytical quality. U.S. Geological Survey Fact Sheet FS-136-97, 2 p.

Luther, K.H., and H.M. Haitjema, 1998. Numerical experiments on the residence time distributions of heterogeneous ground watersheds. Journal of Hydrology, 207, 1-17.

Madow, W.G., 1949. On the theory of systematic sampling II. Annals of Mathematical Statistics 20: 333-354.

Maxted, J.R., and E.L. Dickey, 1990. Invertebrate community of coastal stream habitats. Technical Report 1-01, Delaware DNREC, Dover, DE.

May, C.W., R.R. Horner, J.R. Karr, B.W. Mar, E.B. Welch, 1997. Effects of urbanization on small streams in the Puget Sound lowland ecoregion, Watershed Protection Techniques, Vol. 2, No. 4, 6/97, pp483-493.

Maryland Department of Agriculture, 1999, Maryland Pesticide Statistics for 1997, MDA 256-99.

McFarland, E.R., 1995. Ground-Water flow, geochemistry, and effects of agricultural practices on nitrogen transport at study sites in the Piedmont and coastal plain physiographic provinces, Patuxent River Basin, Maryland. USGS Open File Report 94-507.

McMahon, G., and O.B. Lloyd, 1995. Water-quality assessment of the Albemarle-Pamlico Drainage Basin, North Carolina and Virginia – Environmental setting and water-quality issues. U.S. Geological Survey Open-File Report 95-136, 72 p.

Miller, T. W., 1994. Model selection in tree-structure regression. Proceedings of the ASA Statistical Computing Section, American Statistical Association, p. 158-163.

Moore, D.M, B.G. Lees, and S.M. Davey, 1991. A new method to predicting vegetation distributions using decision tree analysis in a geographic information system. Environmental Management, 5(1) 59-71.

Mullins, J.A., R.F. Carsel, J.E. Scarbough, and A.M. Ivery, 1993. PRZM-2, A model for predicting pesticide fate in the crop root and unsaturated soil zones: Users manual for release 2. U.S. EPA 600/R-93/046.

NASS, 1997, 1997 Census of Agriculture, AC97, available at http://www.nass.usda.gov/census/

NASS, 1999, Agricultural Chemical Usage 1998 Field Crops Summary, available at http://usda.mannlib.cornell.edu/reports/nassr/other/pcu-bb/agch0599.txt

Novak, M.A., and R.W. Bode, 1992. Percent model affinity: a new measure of macroinvertebrate community composition. J.N. Am. Benthol. Soc., 11(1): 80-85.

O'Connor, R.J., M.T. Jones, D. White, C. Hunsaker, T. Loveland, B. Jones, and E. Preston, 1996. Spatial partitioning of environmental correlates of avian biodiversity in the conterminous United States. Biodiversity Letters, Vol. 3, p. 97-110.

Olsen, A.R., J. Sedransk, D. Edwards, C.A. Gotway, W. Liggett, S. Rathbun, K.H. Reckhow, and L.J. Young, 1999. Statistical issues for monitoring ecological and natural resources in the United States. Environmental Monitoring and Assessment, Vol. 54, p. 1-45.

Omernik, J.M., A.R. Abernathy, and L.M. Male, 1981. Stream nutrient levels and proximity of agricultural and forest lands to streams: some relationships. J. Soil Water Conserv. 36: 227-331.

Omernik, J.M., 1995. Ecoregions of the conterminous United States. Annals of the Association of American Geographers Vol. 77, p. 118-125.

O'Neill, R.V., D.L. DeAngelis, J.B. Waide, and T.F.H. Allen, 1986. A hierarchical concept of ecosystems. Princeton University Press, Princeton, NJ.

O'Neill, R.V., S.J. Turner, V.I. Cullinan, D.P. Coffin, T. Cook, W. Conley, J. Brunt, J.M. Thomas, M.R. Conley, J. Gosz, 1991. Multiple landscape scales: an inter site comparison. Landscape Ecology, 5(3): 137-144.

O'Neill, R.V., C.T. Hunsaker, S.P. Timmins, B.L. Jackson, K.B. Jones, K.H. Riitters, and J.D. Wickham, 1996. Scale problems in reporting landscape pattern at the regional scale. Landscape Ecology, 11(3): 169-180.

O'Neill, R.V., C.T. Hunsaker, K. B. Jones, K.H. Riitters, J.D. Wickham, P.M. Schwartz, I.A. Goodman, B.L. Jackson, and W.S. Baillargeon, 1997. Monitoring environmental quality at the landscape scale, Bioscience 47(8): 513-519.

Onishi, Y., L. Shuyler, and Y. Cohen, 1990. Multimedia modeling of toxic substances, in Proceedings of International Symposium on Water quality Modeling of Agricultural and Non-Point Sources, Part II. DeCoursey, D.G., Ed., U.S. Department of Agriculture, ARS-81, pp 479-509.

Osborne, L.L., and M.J. Wiley, 1988. Empirical relationships between land use/cover and stream water quality in an agricultural watershed. Journal of Environmental Management, 26: 9-27.

Osborne, L.L., and D.A. Kovacic, 1993. Riparian vegetated buffer strips in water-quality restoration and stream management. Freshwater Biology, 29, 243-258.

Paller, M.H., 1994. Relationships between fish assemblage structure and stream order in south Carolina coastal plain streams. Transactions of the American Fisheries Society, Vol. 123, p. 150-161.

Phillips, P.J., and L.J. Bachman, 1996. Hydrologic landscapes on the Delmarva Peninsula–Part 1: Drainage basin type and base-flow chemistry. Journal of the American Water Resources Association, Vol. 32, p. 767-778.

Phillips, P.J., G.R. Wall, E.M. Thurman, D.A. Eckhardt, J. vanHoesen, 1999a. Metolachlor and its metabolites in tile drain and stream runoff in the Canajoharie Creek watershed. Environmental Science and Technology, 33(20), p. 3531-3537.

Phillips, P.J., D.A. Eckhardt, E.M. Thurman, and S.A. Terraciano, 1999b. Ratios of metolachlor metabolites in ground water, tile drainage discharge, and surface water in selected areas of New York State. Morganwalp, D.W., and H.T. Buxton, eds, U.S. Geological Survey, Water Resources Investigations Report 99-4018B, p.383-394.

Pirkey, S.R., and K.D. Glodt, 1998. Quality control at the U.S. Geological Survey National Water Quality Laboratory. U.S. Geological Survey Fact Sheet FS-026-98, 4 p.

Plafkin, J.L., M.T. Barbour, K.D. Porter, S.K. Gross, and R.M. Hughes, 1989. Rapid assessment protocols for use in streams and rivers: benthic macroinvertebrates and fish. EPA/444/4-89-001, U.S. Environmental Protection Agency, Washington, D.C.

Preston, S. D., and J. W. Brakebill, 1999. Application of spatially referenced regression modeling for the evaluation of total nitrogen loading in the Chesapeake Bay watershed. U. S. Geological Survey Water-Resources Investigations Report, 99-4054, 12 p.

Quinn, J.M., and C.W. Hickey, 1990. Characterisation and classification of benthic invertebrate communities in 88 New Zealand rivers in relation to environmental factors. New Zealand Journal of Marine and Freshwater Research, 24: 387-409.

Rathert, D., D. White, J.C. Sifneos, and R.M. Hughes, 1999. Environmental associations of species richness in Oregon freshwater fishes. Journal of Biogeography, 26(2): 257-273.

Richards, C., and G.W. Minshall, 1992. Spatial and temporal trends in stream macroinvertebrate species assemblages: the influence of catchment disturbance. Hydrobiologia, 241: 173-184.

Richards, C., G.E. Host, and J.W. Arthur, 1993. Identification of predominant environmental factors structuring stream macroinvertebrate communities within a large agricultural catchment. Freshwater Biology, 29: 285-294.

Riitters, K.H., B.E. Law, R.C. Kucera, A.L. Gallant, R.L. DeVelice, and C.J. Palmer, 1992. A selection of forest condition indicators for monitoring. Environmental Monitoring and Assessment, 20: 21-33.

Riitters, K.H., R.V. O'Neill, C.T. Hunsaker, J.D. Wickham, D.H. Yankee, S.P. Timmins, K.B. Jones, B.L. Jackson, 1995. A factor analysis of landscape pattern and structure metrics. Landscape Ecology, 10: 23-39.

Richards, C., L.B. Johnson, G.E. Host, 1996. Landscape-scale influences on stream habitats and biota, Canadian Journal of Fisheries and Aquatic Sciences 53(Suppl. 1): p. 295-311.

Schulz, R., and M. Leiss, 1999. A field study of the effects of agriculturally derived insecticide input on stream macroinvertebrate dynamics. Aquatic Toxicology, 46, 155-176.

Shedlock, R.J., P.A. Hamilton, J.M. Denver, P.J. Phillips, 1993. Multiscale approach to regional ground-water-quality assessment of the Delmarva Penninsula. Chapter 23 in Regional Ground-Water Quality, W.M. Alley, Ed., Van Nostrand Reinhold, New York.

Shedlock, R.J., J.M. Denver, M.H. Hayes, P.A. Hamilton, M.T. Koterba, L.J. Bachman, P.J. Phillips, and W.S.L. Banks, 1999. Ground-water assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia: Results of investigations, 1987-1991. Water-Supply Paper 2355-A, 42 p.

Shelton, L.R., 1994. Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment program. U.S. Geological Survey Open-File Report 94-455, 44 p.

Sifneos, J. C., D. White, N.S. Urquhart, D. Schafer, (in preparation). A Comparison of Pruning Methods for Regression Trees: Evidence From Simulation and Published Studies.

Smith, R.A., G.E. Schwarz, and R.B. Alexander, 1997. Regional interpretation of water-quality monitoring data. Water Resources Research, Vol. 33, No. 12, p. 2781-2798.

Speiran, G.K., 1996. Geohydrology and geochemistry near coastal ground-water-discharge areas of the Eastern Shore, Virginia. U.S. Geological Survey Water-Supply Paper 2479, 73 p.

Stackelburg, P.E., and M.A. Ayers, 1994. National Water-Quality Assessment Program—Long Island-New Jersey coastal drainages. U.S. Geological Survey NAWQA Fact Sheet FS 94-012.

Staver, K.W., and R.B. Brinsfield, 1996. Seepage of ground water nitrate from a riparian agroecosystem into the Wye River Estuary. Estuaries, Vol. 19, p. 359-370.

Stevens, D.L. Jr., 1997. Variable density grid-based sampling designs for continuous spatial populations. Environmetrics, 8: 167-195.

Stevens, D.L., and A.R. Olsen, 1999. Spatially restricted surveys over time for aquatic resources. Journal of Agricultural, Biological, and Environmental Statistics, Vol. 4, No. 4, p. 415-428.

Stribling, J.B., B.K. Jessup, J.S. White, D. Boward, M. Hurd, 1998. Development of a benthic index of biotic integrity for Maryland streams. Maryland Department of Natural Resources, Annapolis, MD, CBWP-EA-98-3.

Sweeney, B.W., 1993. Effects of stream side vegetation on macroinvertebrate communities of White Clay Creek in eastern North America. Proceedings of The Academy of Natural Sciences of Philadelphia, 144: 291-340.

Tate, C.M., and J.S. Heiny, 1995. The ordination of benthic invertebrate communities in the South Platte River Basin in relation to environmental factors. Freshwater Biology, 33: 439-454.

Tesoriero, A.J., and F.D. Voss 1997. Predicting the probability of elevated nitrate concentrations in the Puget Sound Basin - Implications for aquifer susceptibility and vulnerability. Ground Water, vol. 35, no. 6., pp 1029-1039.

Trapp, H. Jr., and M.A. Horn, 1997. Ground Water Atlas of the United States, Segment 11, Hydrologic Investigations Atlas 730-L, U.S. Geological Survey, Reston, Virginia.

Tufford, D.L., H.N. McKellar, and J.R. Hussey, 1998. In-stream non-point source nutrient prediction with land-use proximity and seasonality. J. Environ. Qual., 27: 100-111.

U.S. Environmental Protection Agency, 1994a. National primary drinking-water standards. U.S. Environmental Protection Agency Fact Sheet 810-F-94-001, 2 p.

U.S. Environmental Protection Agency, 1994b. Landscape monitoring and assessment research plan. EPA 620/R-94/009.

U.S. Environmental Protection Agency, 1994c. EPA Reach File Version 3.0 Alpha release (RF3-Alpha) technical reference. Office of Wetlands, Oceans, and Watersheds, Office of Water.

U.S. Environmental Protection Agency, 1997. Field and laboratory methods for macro-invertebrate and habitat assessment of low gradient, nontidal streams. Mid-Atlantic Coastal Streams Workgroup, Environmental Services Division, Region 3, Wheeling, WV; 23 pages with appendices.

U.S. Environmental Protection Agency, 1998. Guidelines for Ecological Risk Assessment. EPA/630/R-95/002F.

U.S. Federal Emergency Management Agency, 1999, Declared Counties Map, Remote Sensing Damage, DR 1292, North Carolina. http://www.gismaps.fema.gov/1999pages/dr1292.htm

U.S. Geological Survey, 1999. The quality of our nation's waters–nutrients and pesticides. U.S. Geological Survey Circular 1225, 82 p.

Vogelmann, J.E., T.L. Sohl, P.V. Campbell, and D.M. Shaw, 1998. Regional land cover characterization using Landsat and ancillary sources. Environmental Monitoring and Assessment, 51: 415-428.

Walker, P. A., 1990. Modeling wildlife distributions using a geographic information system: kangaroos in relation to climate. Journal of Biogeography, Vol. 17, p. 279-289.

Wang, L., J. Lyons, P. Kanehl, R. Gatti, 1997. Influences of watershed land use on habitat quality and biotic integrity in Wisconsin streams, Fisheries, Vol. 22, No. 6, 6/97, p. 6-12.

Wesselman, R. and R. Carr, 2000, personal. comm.

Wiederholm, T., 1984. Responses of aquatic insects to environmental pollution, in The Ecology of Aquatic Insects, Praeger, New York, p. 508-557.

Williams, D.D., and H.B.N. Hynes, 1976. The recolonization mechanisms of stream benthos. Oikos 27, 265-272.

Winner, M.D., and R.W. Coble, 1996. Hydrogeologic framework of the North Carolina coastal plain. U.S. Geological Survey Professional Paper 1401-I, 106 p.

Zappia, H., and G.T. Fisher, 1997. Water quality assessment of the Potomac River Basin: Analysis of Available Data 1972-90. USGS, WRIR 97-4051.

Zaugg, S.D., M.W. Sandstrom, S.G. Smith, and K.M. Fehlberg, 1995. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory–Determination of Pesticides in Water by C-18 Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry with Selected-Ion Monitoring. U.S. Geological Survey Open-File Report 95-181.

Zheng, C., 1992. MT3D version 1.8, Documentation, and User Guide. S.S. Papadopulos and Associates, Bethesda, MD.

APPENDIX A
U.S. Geological Survey Pesticide Schedule 2001

The following information is excerpted from Zaugg et al., 1995. *This method is suitable for the determination of low-level concentrations (in micrograms per liter and nanograms per liter) of pesticides and pesticide metabolites in natural-water samples. The method is applicable to pesticides and metabolites that are (1) efficiently partitioned from the water phase into an octadecyl (C-18) organic phase that is chemically bonded to a solid inorganic matrix, and (2) sufficiently volatile and thermally stable for gas chromatography. Suspended particulate matter is removed from the samples by filtration, so this method is suitable only for dissolved-phase pesticides and metabolites... The method was developed in response to the request for a broad spectrum pesticide method for use in determining their occurrence and distribution as monitored by the NAWQA program. Pesticides were selected initially because of their widespread use in the United States, according to information in ...Gianessi and Puffer, 1990, 1992a, and 1992b, and their compatibility with the general analytical plan. Other criteria included published studies of pesticide fate and occurrence of metabolites, responses from NAWQA Study Unit personnel regarding pesticides of local significance, and U.S. EPA health advisories. Finally restrictions in the analytical software on the number of ions scanned for specific time intervals limited the number of pesticides chosen to about 50.*

The calibration range is equivalent to concentrations from 0.001 to 4.0 µg/L for most pesticides. Widely and abundantly used corn herbicides-atrazine, metolachlor, cyanazine, and alachlor–have upper concentration limits of 20 µg/L. Method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero. The MDL is compound dependent and dependent on sample matrix and instrument performance and other operational sources of variation. For the listed pesticides, MDLs vary from 0.001 to 0.018 µg/L. Analytical results are not censored at the MDL; if a pesticide meets the detection criteria (retention time and mass spectra compared to that of a reference standard) the result is calculated and reported.

Summary of method: The samples are filtered at the collection site using glass-fiber filters with 0.7-µm pore diameter to remove suspended particulate matter...Filtered water samples are pumped through disposable polypropylene SPE columns containing porous silica coated with an octadecyl (C-18) phase that is chemically bonded to the surface of the silica. The SPE columns are dried using a gentle stream of carbon dioxide or nitrogen to remove residual water. The adsorbed pesticides and metabolites then are removed from the SPE columns by elution with hexane-isopropanol (3:1). The eluant is further evaporated using a gentle stream of nitrogen. Extracts of the eluant are analyzed by a capillary-column GC/MS operated in the SIM mode.

Table A1. USGS Pesticide Schedule 2001 (complete list) and the Estimated Amount of Active Ingredient Applied in the Mid-Atlantic (Gianessi and Puffer, 1990 and 1992 a,b).

USGS Pesticide Schedule 2001	**Detected in Ground Water[1]**	**Detected in Surface Water[2]**	**Estimated Active Ingredient Applied in Mid-Atlantic Region (lbs/yr) [3]**
2,6,-Diethylaniline		U	
Acetochlor		U	
Alachlor	U	U	3,630,000
Atrazine	U	U	4,900,000
Azinphos-methyl	U	U	
Benfluralin	U	U	
Butylate	U	U	1,260,000
Carbaryl	U	U	453,000
Carbofuran	U	U	992,000
Chlorpyrifos	U	U	2,340,000
Cyanazine	U	U	1,090,000
Dacthal		U	
Deethylatrazine		U	
Diazinon	U	U	
Diazinon-d10 (sur.)		U	
Dieldrin	U	U	
Disulfoton			
EPTC	U	U	1,070,000
Ethalfluralin		U	
Ethoprofos			
Fonophos		U	
Lindane	U	U	
Linuron	U	U	485,000
Malathion		U	
Metolachlor	U	U	4,270,000
Metribuzin	U	U	

USGS Pesticide Schedule 2001	Detected in Ground Water[1]	Detected in Surface Water[2]	Estimated Active Ingredient Applied cont. (lbs/yr) [3]
Molinate		U	
Napropamide	U	U	
Parathion		U	
Parathion-methyl			
Pebulate	U	U	
Pendimethalin	U		975,000
Phorate		U	
Prometon		U	
Propachlor	U	U	
Propanil		U	
Propargite		U	
Proyzamide			
Simazine	U	U	730,000
Tebuthiuron	U	U	
Terbacil	U	U	
Terbufos		U	
Terbuthylazine (sur.)			
Thiobencarb		U	
Tri-allate		U	
Trifluralin	U	U	
alpha-HCH		U	
alpha-HCH-d6 (sur.)		U	
cis-Permithrin		U	
p,p'-DDE	U	U	

[1]Ator, S.W. and Ferrari, M.J., 1997.
[2]Ferrari, M.J., et al., 1997.
[3]Gianessi and Puffer, 1990, 1992 a,b.

APPENDIX B
Target Analytes for Sediment Analyses

Table B1. Analytes for Sediments

Analyte (CAS Number)

Pesticides
Aldrin (309-00-2)
Chlordane-cis (5103-71-9)
Chlordane-trans (5103-74-2)
2,4'-DDD (53-19-0)
2,4'-DDD (72-54-8)
2,4'-DDE (3424-82-6)
4,4'-DDE (72-55-9)
2,4'-DDT (789-02-6)
4,4'-DDT (50-29-3)
Dieldrin (60-57-1)
Endosulfan l (959-98-8)
Endosulfan ll (33213-65-9)
Endrin (72-20-8)
Heptachlor (76-44-8)
Heptachlor Epoxide (1024-57-3)
Hexachlorobenzene (118-74-1)
Hexachlorocyclohexane [Gamma-BHC/Lindane] (58-89-9)
Mirex (2385-85-5)
trans-Nonachlor (3765-80-5)
cis-Nonachlor (5103-73-1)
Oxychlordane (27304-13-8)

Poly Chlorinated Biphenyl (PCB) Congeners
2,4-Dichlorobiphenyl, #8 (34883-43-7)
2,2',5-Trichlorobiphenyl, #18 (37680-65-2)
2,4,4'-Trichlorobiphenyl, #28 (7012-37-5)
2,2',5,5'-Tetrachloroblphenyl, #52 (35693-99-3)
2,2',3,5'-Tetrachloroblphenyl, #44 (41464-39-5)
2,3',4,4'-Tetrachloroblphenyl, #66 (32598-10-0)
2,2',4,5,5'-Pentachlorobephenyl, #101 (37680-73-2)
2,3',4,4',5'-Pentachlorobephenyl, #118 (31508-00-6)
2,2',4,4',5,5'-Hexachlorobiphenyl, #153 (35065-27-1)
2,3,3',4,4'-Pentachlorobiphenyl, #105 (32598-14-4)
2,2',3,4,4',5-Hexachlorobiphenyl, #138 (35065-28-2)
2,2',3,4',5,5',6-Heptachlorobiphenyl, #187 (52663-68-0)
2,2',3,3',4,4'-Hexachlorobiphenyl, #128 (38380-07-3)

2,2',3,4,4',5,5'-Heptachlorobiphenyl, #180 (35065-29-3)
2,2',3,3',4,4',5-Heptachlorobiphenyl, #170 (35065-30-6)
2,2',3,3',4,4',5,6-Octachlorobiphenyl, #195 (52663-78-2)
2,2',3,3',4,4',5,5',6-Nonschlorobiphenyl, #206 (40186-72-9)
Decachlorobiphenyl, #209 (2051-24-3)
3,3',4,4' Tetrachlorobiphenyl, #77* (32598-13-3)
3,3',4,4',5 Pentachlorobiphenyl, #126*
3,3',4,4',5,5' Hexachlorobiphenyl, #169* (32775-16-6)

Metals

Arsenic (7440-38-2)
Mercury (7439-97-6)

Additional Measurements
Percent Moisture
Size distribution
Organic matter content

APPENDIX C
U.S. Geological Survey Schedule 2701
Major Ions

Table C1. U.S. Geological Survey Major Ions Schedule 2701

Calcium, dissolved (mg/L as Ca)
Silica, dissolved (mg/L as SiO_2)
Chloride, dissolved (mg/L as Cl)
Iron, dissolved (mg/L as Fe)
pH, wH, laboratory, standard units
Sodium, dissolved (mg/L as Na)
Potassium, dissolved (mg/L as K)
Manganese, dissolved (µg/L as Mn)
Specific conductance (microsiemens/cm)
Magnesium, dissolved (mg/L as Mg)
Sulfate, dissolved (mg/L as SO_4)
Residue, dissolved 180c (mg/L)
Fluoride, dissolved (mg/L as F)

APPENDIX D
U.S. Geological Survey Schedule 2702
Nutrients

Table D1. U.S. Geological Survey Nutrients Schedule 2702

Phosphorus, dissolved (mg/L as P)
Nitrogen (ammonia + organic) (mg/L as N)
Phosphorus, total (mg/L as P)
Phosphorus, ortho (mg/L as P)
Nitrogen (amn & organic) (mg/L as N)
Nitrogen, nitrite (mg/L as N)
Nitrogen, ammonia (mg/L as N)
$NO_2 + NO_3$, dissolved (mg/L as N)

APPENDIX E
Benthic Macroinvertebrate Indices

Table E1. List of Benthic Macroinvertebrate Indices (primarily from Bode et al., 1996)

COMMUNITY INDICES	DESCRIPTION
Species richness (taxa number)	This is the total number of species or taxa found in the sample. High species richness values are associated with clean-water conditions.
EPT richness	EPT denotes the total number of species of mayflies (Ephemeroptera), stoneflies (Plecoptera), and caddisflies (Trichoptera) found in a 100-organism subsample. These are considered to be mostly clean-water organisms, and their presence generally is correlated with good water quality.
Hilsenhoff Biotic index	The Hilsenhoff Biotic Index (HBI) is calculated by multiplying the number of individuals of each species by its assigned tolerance value, summing these products, and dividing by the total number of individuals. On a 0-10 scale, tolerance values range from intolerant (0) to tolerant (10). Tolerance values are listed in a species list for Wisconsin, developed by Hilsenhoff (1987). High HBI values are indicative of organic (sewage) pollution, while low values are indicative of clean-water conditions.
Percent model affinity	This is a measure of similarity to a model, nonimpacted community based on percent abundance in seven major groups (Novak and Bode, 1992). Percentage similarity as calculated in Washington (1984) is used to measure similarity to idealized kick sample or Ponar sample communities.
Species diversity	Species diversity is a value that combines species richness and community balance (evenness). Shannon-Wiener diversity values are calculated using the formula in Weber (1973). High species diversity values usually indicate diverse, well-balanced communities, while low values indicate stress or impact.
Dominance	Dominance is a simple measure of community balance or evenness of the distribution of individuals among the species. Simple dominance is the percent contribution of the most numerous species. Dominance-3 is the combined percent contribution of the three most numerous species. High dominance values indicate unbalanced communities strongly dominated by one or more very numerous species.
NCBI	The North Carolina Biotic Index (NCBI) (Lenat, 1993) is similar to the HBI, with tolerance values developed for North Carolina stream invertebrates and seasonal factors to correct data to mean summer values. Stream size does not have a large effect on NCBI.
Maryland B-IBI	The Benthic Index of Biotic Integrity for Maryland coastal plain streams (Stribling et al., 1998) includes taxa number, EPT taxa number, percent Ephemeroptera, percent Chironomidae that are Tanytarsini, percent clinger taxa, percent scrapers, and Beck's Biotic Index.
10-Metric B-IBI	This B-IBI was proposed by Karr and Chu (1999) based on examples for the Tennessee Valley, Puget Sound, southwestern Oregon, north central Oregon, northwestern Wyoming, and Japan, and was designed to detect human impact.

APPENDIX F

Physical Habitat Metrics

Table F1. Calculated Reach-Level Physical Habitat Metrics (after Kaufman et al., 1999)

Depth: mean and standard deviation (SD)
Wetted width: mean and standard deviation (SD)
Width: Depth ratio
Width-Depth product
Habitat class: percent of reach in each class
Reach aggregate and individual residual pool metrics
Reach slope: mean and SD
Reach sinuosity from backsighted bearings
Substrate size: percentage by class, mean and SD of size; median, lower and upper quartiles (Q_1 Q_3), and interquartile range of size class; Log_{10} of geometric mean diameter
Bankfull width: mean and SD
Bankfull height: mean and SD
Incision height: mean and SD
Bank angle: mean, SD, Q_1 and Q_3, and interquartile range
Undercut distance: mean, SD, Q_1 and Q_3, and interquartile range
Large woody debris size classes: counts and volumes
Canopy densiometer values (mid-channel): mean and SD
Canopy densiometer values (bank): mean and SD
Riparian vegetation cover metrics
Riparian vegetation presence metrics
Riparian vegetation type: proportion of reach with each type
Presence of human influences: proximity weighted

APPENDIX G
Spatial Databases

Table G1. Spatial Databases

Coverage	Scale/ Resolution	Source
Stream Hydrography	1:100,000	U.S. EPA, Office of Water, RF3 files
Hydrogeologic Framework	1:1,000,000	U.S. Geological Survey, Water Resources Division, Maryland-Delaware-District of Columbia District Office
Digital elevation	30 m, 90 m	U.S. Geological Survey, EROS Data Center
STATSGO soil data	1:1,000,000	U.S. Department of Agriculture, NRCS
SSURGO soil data	1:100,000	U.S. Department of Agriculture, NRCS
Soils 5 soil data	point locations	U.S. Department of Agriculture, NRCS
MRLC Land use/land cover	30 m	U.S. Geological Survey, EROS Data Center
Roads, Railroads, Pipelines	1:100,000	U.S. Geological Survey, Digital Line Graph files
County and State boundaries	1:100,000	U.S. EPA, NERL-RTP
Population (census blocks)	1:24,000	U.S. Bureau of Census
Agrochemical Application Data; and confined animal feeding operations (CAFOs)	County and possibly zip code polygons for agrochemicals; exact coordinates of CAFOs	U.S. EPA, ORD, NERL; NASS; individual states
Agrochemical Application Data (1989)	County scale	U.S. Geological Survey (Battaglin and Goolsby, 1994)
NEXRAD precipitation	4 km grid, 24-hour cumulative total	National Oceanic and Atmospheric Administration

A wide variety of spatial databases will be acquired for this study (Table G1). These coverages will be acquired, edge-matched as needed and “clipped” to the Coastal Plain boundary. The most critical of the spatial coverages is the stream hydrography data because the selection of watersheds for sampling is based on the overall delineation of streams in the study area. We plan to use Reach File 3 (RF3) data at a scale of 1:100,000 (U.S. EPA 1994; Horn and Grayman, 1993) as our basis for identifying streams to be sampled. The RF3 data provide stream segment locations at the best available resolution, covering the entire study area at a consistent scale. It has codes which designate the segments according to type of segment which is useful in the selection process. Soil particle size distributions, permeability, and depth to water table are available from the National Resource Conservation Service’s STATe Soil GeOgraphic database (STATSGO, available for the entire area); and from their higher resolution Soil SURvey GeOgraphic database (SSURGO, available for approximately half the area). These data will be used in both the landscape indicator analysis and the hydrologic modeling. The land use/land cover data are from the Multi-Resolution Landscape Characteristics (MRLC) Consortium. These data were derived from 30-meter resolution Landsat Thematic Mapper (TM) data, and classified into 15 land use/land cover classes (Vogelmann et al., 1998). Agrochemical coverages include both fertilizer and pesticide application data and will be compiled from several sources. One source is from existing published data, such as the 1997 Census of Agriculture. These data are compiled as pounds of active ingredient applied by county (for certain states only). Total acres in which pesticides were applied are also available by county. These data will be entered onto a spreadsheet, identified by Federal Information Processing Standard (FIPS) county code, and attributed to the agricultural portion of the county polygon coverage. Another source of these data at a finer resolution is by special request to the state offices of the National Agricultural Statistical Survey (NASS). Through arrangements with their staff, the application rate data are assembled according to zip code (confidentiality is preserved by not reporting data for zip codes containing only one or two farms). We are currently having discussions with NASS regarding the application of this approach for the Coastal Plain states. We are also considering the possibility of a direct request for application rate information for selected locations, to the American Crop Producers Association. Gianessi and Puffer, 1990, 1992a, and 1992b have identified the twenty most commonly used pesticides in the Mid-Atlantic. We will compile physical and biological data for these chemicals from readily available sources as needed for the modeling effort; these data include type of compound (triazine; carbamate, etc.), physical constants (solubility in water, Henry's Law constant, etc.), type of crops treated; application method, wildlife lethal dose information, and toxicological information. Additional data for use in the hydrologic models will also be compiled as needed. Once the data sets are complete, they will be assembled onto a compact for distribution among the participants. The data will also be available for viewing at an EPA intranet website. It is not our intention to become distributors for these data except in their role as part of the final products of the study.