Quality Assurance Plan

Project Title: **CISNet: Nutrient Inputs as a Stressor and Net Nutrient Flux as an Indicator of Stress Response in Delaware's Inland Bays Ecosystem**

Investigators: **William J. Ullman**, Associate Professor, College of Marine Studies (CMS), University of Delaware (UD); **Kuo-Chuin Wong**, Associate Professor, CMS, UD; **John M. Madsen**, Associate Professor, Department of Geology, UD; **Joseph R. Scudlark**, Research Associate, CMS, UD; **David E. Krantz**, Physical Scientist, U.S. Geological Survey; **A. Scott Andres**, Hydrogeologist, Delaware Geological Survey (DGS); and **Thomas E. McKenna**, Hydrogeologist, DGS.

1. Hypotheses/Objectives: The objectives of this study are: (a) to determine the magnitude, and spatial and temporal variability of nutrient (N and P) sources to Rehoboth and Indian River Bays, shallow interconnected estuaries with significant differences in flushing and circulation in Delaware's Inland Bays ecosystem; (b) to determine the magnitude of nutrient sinks in this system; and (3) to develop conceptual and simple quantitative models that relate these inputs and outputs to more easily measured and monitored forcing parameters, such as precipitation, temperature, season, ground water levels and surface water discharge.

2. Study Design: Atmospheric deposition will be measured on a daily/event basis at the Cape Henlopen NADP/AirMon site. Surface water inputs from ten tributary streams will be monitored biweekly to determine the seasonality of baseflow discharge of fresh water and associated nutrients into the Bays. Storm discharges of nutrients will be measured at one of these sites. Sites of focused ground-water discharge will be identified by evaluating thermal infrared images of the Bay margins for temperature anomalies. Several of these discharge areas will be instrumented to measure seasonal and annual ground-water and associated nutrient fluxes to the estuary. Ground-water discharge will be related to the underlying geology using ground-penetrating radar and marine seismics.

The outflow of water and associated nutrients from the Inland Bays ecosystem through Indian River Inlet will be determined using an acoustic Doppler current profiler to measure water flow and biweekly analyses of nutrient concentrations in waters moving through the inlet. Additional advective fluxes of water and nutrients will be determined at the connection between the two Bays, and in the connection between Rehoboth Bay and Delaware Bay to the north.

The internal cycling of nutrients within the Bays will be evaluated from nutrient mixing curves based on regularly collected samples from both Bays. The change in water-column storage of nutrients will be determined from the same data set. The loss of nutrients to sediments and the extent of temporary nutrient storage in these sediments will be studied in a suite of cores from the Bays available in the Delaware Geological Survey core collection.

The seasonal and temporal variability of all sources and sinks will be determined and conceptual and simple quantitative models describing these relationships and the effect of external forcing parameters, such as precipitation, temperature, surface and ground water discharge on component and net nutrient fluxes will be developed. These models will make it possible to determine the magnitude of gross fluxes (stressor) and net fluxes (stress response) characteristics under future sets of environmental forcing parameters.

3. Sample Handling: Water samples will be labeled in the field with a site designation and date and information about the sampling conditions will be recorded in a field notebook. All information from the original collection bottles will be transferred to subsequent containers and samples will be refrigerated at 4^{o}C in the dark or frozen until all analyses are completed. No samples will be discarded until analytical work is completed and verified (see below). Photocopies of field and laboratory notebooks will be made and archived and field and analytical data will be transcribed by the individual responsible for each aspect of the work. All data will be entered into spreadsheets and reviewed by one or more of the principal investigators prior to being made available to the U.S. Environmental Protection Agency (US-EPA), Delaware Department of Natural Resources and Environmental Control (DNREC), Center for the Inland Bays (CIB), and other interested agencies or archived (see below).

4. Analytical Methods: Samples for dissolved nutrients will be filtered in the field and unfiltered samples will be returned to the laboratory for further separation of particles for the determination of chlorophyll *a*, particulate nutrients, particulate organic carbon and total suspended solids.

The following methods will be used for the determination of dissolved and particulate nutrient concentrations: nitrate + nitrite (NO_3^- + NO_2^-) will be determined by the sulphanilamide/N(1-napthyl) ethylene diamine method after cadmium reduction of NO_3^- to NO_2^- (Glibert and Loder, 1977); ammonium (NH_4^+) will be determined by phenol hypochlorite (Glibert and Loder, 1977; Grasshoff and Johansen, 1972); phosphate (PO_4^{3-} = dissolved inorganic P = DIP) will be determined by the molybdenum blue method (Strickland and Parsons, 1972); total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) will be determined as NO_3^- + NO_2^- and PO_4^{3-} after persulfate oxidation (Glibert and Loder, 1977; D'Elia et al., 1977; Solarzano and Sharp, 1980b); particulate phosphorus (PP) will be determined as phosphate after acid digestion of the ashed filter on which the particles were collected (Solarzano and Sharp, 1980a); particulate nitrogen (PN) and particulate organic carbon (POC) will be determined either on a Carlo Erba CHN analyzer or Europa Carbon/Nitrogen analyzer by combustion and analysis of the combustion products. Dissolved organic nitrogen and phosphorus (DON and DOP) will be determined as the difference between the dissolved total concentrations (TDN and TDP) and inorganic concentrations (DIN = NO_3^- + NO_2^- + NH_4^+ and DIP = PO_4^{3-}). Chlorophyll *a* will be determined fluorometrically (Strickland and Parsons, 1972). Automated analytical methods based on these chemistries will be used whenever possible

All of these sampling and analytical methods are standard methods used by the US Geological Survey and the US Environmental Protection Agency for the analysis of seawater. A quality assurance plan covering most of the field and laboratory analytical methods was previously submitted to EPA (Ullman et al., 1992). Methods for particulate organic carbon and particulate nitrogen are still under development for this project and approval will be sought for these methods when the development is completed. The principal field instruments will be a conductive salinometer/ thermometer and this instrument will be calibrated using an NBS-traceable thermometer and KCl conductivity standards in the laboratory prior to each use. Salinities will be verified using an inductive salinometer, argentimetric titration or ion chromatography (for low levels). The principal laboratory instrumentation will be a Perstorp Analytical automated chemical analyzer for dissolved samples and either a Carlo Erba CHNS analyzer or Europa CHN analyzer for particulate samples.

5. Calibration and Evaluation: Commercial or laboratory standards (made from reagent grade materials) will be used to calibrate each analytical instrument on every day that it is used. Records of the reagent blanks and calibration curves will be kept with each set of analyses. Approximately 1 in every 15 samples will be replicated to determine analytical precision. All analytical results will be evaluated by either Scudlark or Ullman before acceptance. Acceptance criteria will include the linearity of standard curves, the level of the reagent blanks and the precision of replicate analyses. For each group of analyses, the level of analytical uncertainty will be reported.

6. Data Reduction and Reporting: Original field, analytical and remote-sensing results, as collected, will be reported electronically, graphically and/or in tabulated form to DNREC (water quality data), DGS (core logs, remote sensing, and seismic data), the National Atmospheric Deposition Program (atmospheric data) the US-EPA, the National Geophysical Data Center (NOAA), and/or the National Oceanographic Data Center (NOAA) and such data will be available from these agencies or the individual investigators. Further use of this data will be described in the papers and reports resulting from this work. The principal mechanism for the reporting of project results will be through presentations at state (CIB/STAC, see below) and national meetings and, above all, publication in peer-reviewed journals.

7. Use of Data: The data from this project will be used to: (a) determine the fluxes of water and associated nutrients (N and P) into Indian River and Rehoboth Bays; (b) to identify spatial and temporal trends in the data; and (c) to develop conceptual and simple quantitative models relating the component fluxes (inputs from surface- and ground-waters, precipitation, and the coastal ocean; outputs to sediments and to the coastal ocean) to more easily measured and monitored forcing parameters (rainfall, temperature, season, ground-water level, and surface discharge) which drive the fluxes in this and similar systems.

8. Project Evaluation: The evaluation of each component of the proposed research will be based on the application of the conceptual and simple quantitative models that relate the component fluxes (inputs from surface- and ground-waters, precipitation, and the coastal ocean; outputs to sediments and to the coastal ocean) to more easily measured and monitored forcing parameters (rainfall, temperature, season, ground-water level, and surface discharge). The models will be applied to new and previously collected data sets. For each component of the program, there exists some previous results or observations which provide a benchmark for the testing of the models by the hindcast method. On-going evaluation by peers will also be solicited (see below). The overall success of this effort will be evaluated by the users of our data and results. Success will be based on the inclusion of our models into the DNREC Hydrodynamic/Water Quality model that is used to determine the impact of nutrient loads of Inland Bay ecology. Success will also be based on the acceptance and publication of this work in peer-reviewed scientific and management journals.

9. Peer Review: We will use the resources of the Scientific and Technical Advisory Committee of the Center for the Inland Bays (CIB/STAC), which includes scientists and managers from US-EPA, UD, DNREC, and other federal and state agencies with expertise concerning estuarine oceanography and ecology to review our research plan in the first months of this project and then at regular intervals thereafter. The intermediate and final results of this program will also be reported and reviewed by the CIB/STAC.

10. Project Management and Personnel: Dr. Ullman will be the Project Director and will be administratively responsible for meeting the technical and performance goals of this project. Together with the Research Associate, he will responsible for the internal nutrient cycling part of this work. With Mr. Andres, Mr. Scudlark and the Research Associate, he will be responsible for the surface-water input part of this study. Ullman, Andres and Scudlark will be jointly responsible for the sediment storage part of this project. He will supervise the Research Associate and, together with Scudlark, will be responsible for the review and quality assurance of the nutrient analytical work to be performed.

Dr. Wong will be responsible for the water flow parts of this program and will supervise and advise one of the graduate student research assistants. Mr. Art Sundberg (Marine Electronics and Operations) will assist Dr. Wong in the preparation, installation and maintenance of current meters to be used in the water flow parts of this study.

Dr. Madsen will be responsible, in collaboration with Drs. McKenna and Krantz, for the marine seismic and subsurface radar aspects of the groundwater program and will advise the graduate student assigned to the groundwater part of this project.

Dr. Krantz will be involved in the marine seismic and subsurface radar aspects of the groundwater program. Alternative funding for his contributions to this program is being sought.

Dr. McKenna will coordinate the groundwater part of this work and will work together with Drs. Madsen, Krantz and one graduate research assistant assigned to this aspect of the program. Dr McKenna will serve as Assistant Project Director, assisting and acting on behalf of Dr. Ullman in his absence. Dr. McKenna will also be responsible for approving Delaware Geological Survey expenditures on this project.

Mr. Andres will work together with Dr. Ullman on the surface water input part of this study and will be primarily responsible for the analysis of this part of the data set. He will also assist in the sediment parts of this study.

Mr. Scudlark will be responsible for the Cape Henlopen rain site and the data that is generated at this station. He will also assist with sediment sampling and analysis, methods development and the quality assurance of nutrient analytical work for this project.

The Research Associate with be responsible for laboratory analysis of particle and water samples collected as part of this study and for the maintenance of the data base describing this data. He/she will also be responsible for the field work associated with the internal cycling (together with Dr. Ullman) and surface water input (together with Mr. Andres and Mr. Scudlark) parts of this study.

Undergraduate students will assist Drs. McKenna, Madsen and Krantz in the field.

All collaborators, with the exception of the miscellaneous student and other professional personnel, will participate in the presentation of research results to the CIB, DNREC and other groups and will be involved in the preparation of reports and papers for more extensive dissemination of results.

11. Time Table:

Tasks by Year	1998-99				1999-00				2000-01			
Quarters	4	1	2	3	4	1	2	3	4	1	2	3
Surface Water (Andres, Scudlark)												
Baseflow Monitoring, Sampling and Analysis	■	■	■	■	■	■	■	■	■	■	■	■
Stormflow Monitoring, Sampling and Analysis		■		■		■		■		■		■
Analysis of Baseflow Results							■	■	■	■	■	■
Analysis of Stormflow Results										■	■	■
Atmospheric Deposition (Scudlark)	■	■	■	■	■	■	■	■	■	■	■	■
Groundwater Studies (Madsen, Krantz, McKenna)												
Thermal Imaging and Analysis		■	■	■								
Seismic and GPR Studies and Analysis			■	■	■	■						
Piezometer and Seepage Meter Installation						■	■	■				
Temperature/Conductivity Mapping									■	■		
Water Sampling and Analysis							■	■	■	■	■	■
Water Exchange (Wong)												
Indian River Inlet Study		■		■								
Analysis of New/Historical Data from Inlet					■	■	■	■				
Massey's Ditch Study									■		■	
Lewes/Rehoboth Canal Study									■		■	
Water Sampling and Analysis		■		■					■		■	
Internal Nutrient Utilization (Ullman)												
Water Sampling and Analysis		■	■	■		■	■	■		■	■	■
Analysis of Mixing Curves				■	■			■	■			■
Analysis of Water Column Storage				■	■			■	■			■
Sediment Storage (Ullman, Andres)												
Sediment Sampling					■	■						
Sediment Analysis									■	■		
Reporting (All Investigators)												
To CIB, DNREC, STAC, EPA	■	■	■	■	■	■	■	■	■	■	■	■
Data Transfer to DNREC, EPA					■	■	■	■	■	■	■	■
To Professional Meetings										■	■	■
To Peer-Reviewed Journals									■	■	■	■

12. References:

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