Gulf of Mexico Alliance

Nutrient Criteria Research Framework Appendices

Draft for Comments

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For more information: http://www2.nos.noaa.gov/gomex/nutrients/welcome.html

Gulf of Mexico Alliance
Nutrient Criteria Research Framework

Appendices

A. Ecosystem Budgets

Ecosystem budget are a simple yet effective way to describe a system and the key nutrient pathways affecting system dynamics. Budgets are simple models that result in mass balances for key variables. This framework adopts the methodology for ecosystem budgets developed by the International Geosphere-Biosphere Program's Land-Ocean Interactions in the Coastal Zone (LOICZ) project. LOICZ developed a modeling strategy to estimate the biogeochemical fluxes of nutrients to the coastal zone and transformations within coastal ecosystems (Gordon et al. 1996). The following describes the steps in the LOICZ budgetary modeling process and uses figures from Gordon et al. 1996.

1. Water budget:

Establish a budget of freshwater inflows (such as runoff, precipitation, groundwater, sewage) and evaporative outflow. There must be compensating outflow (or inflow) to balance the water volume in the system.

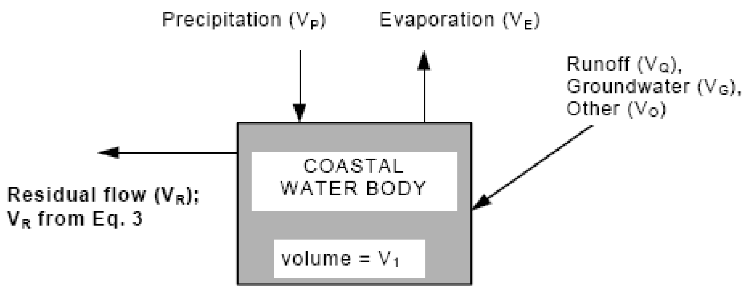


Figure 4. Generalised box diagram illustrating the water budget for a coastal water body. The arrows show the net water flow associated with each process. Quantities which are generally measured are shown in light typeface, while the quantity which is calculated to balance the budget (that is, V_R) is shown in bold typeface. In systems with net freshwater inflow, V_R will be negative (that is, out of system). System volume (V_1) is in units of volume, while all flow volumes are in units of volume per time.

Study questions:

- What are the net water volume and change of water volume through time?
- What is the flux of nutrients via water inflows and outflows?

Measurements:

- Flow in and out: units of volume per time
- Precipitation and evaporation: units of length per time
- Freshwater residence time of the system: units of days

2. Salt budget:

Salt must be conserved in the system. Therefore salt flux not accounted for by the salinities used to describe the freshwater flows in the water budget above, must be balanced by mixing. If there is no salinity difference between the system of interest and adjacent systems, or if the pattern of water exchange is too complex to be amenable to be described by the combined water and salt budgets, some more complex form of circulation analysis will be required. The water and salt budgets describe the exchange of water between the system of interest and adjacent systems by the processes of advection and mixing.

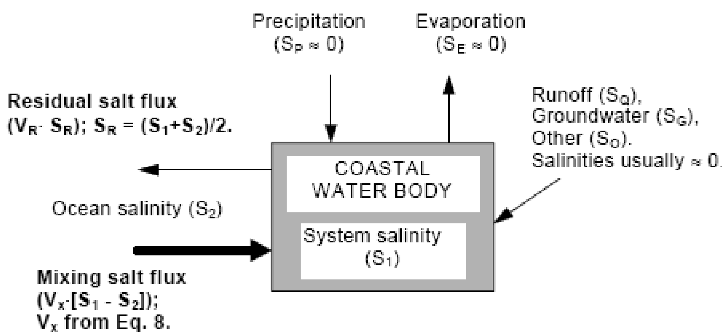


Figure 5. Generalised box diagram illustrating the salt budget for a coastal water body. The arrows show the net salt flux associated with each process. In general, residual flow (that is, $V_R \cdot S_R$) is negative indicating flow from the system. Under such conditions, mixing (V_X) is likely to transport salt into the system. Quantities which are generally measured are shown in light typeface, while quantities which are calculated within the budget are shown in bold typeface.

Study questions:

- What is the flux (exchange) of salt within the system and with adjacent systems?
- What is the dominant type of mixing? (tidal current, density-drive currents, or wind current)

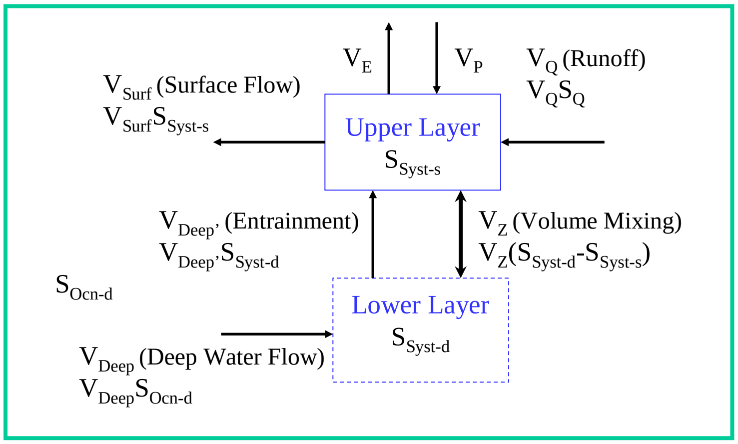
Measurements:

- Average salinity at the system boundary
- Salinity in stratified water layers (surface and bottom) and respective inflow and outflow

Modifications for Stratified Systems

Many Gulf of Mexico coastal systems are strongly stratified for part of the year. The LOICZ project has developed a modified methodology for water and salt budget for systems with strong vertical stratification to reflect a two-layer system model.

Two-layer water and salt budget model



$$V_Q + V_P + V_E + V_{Surf} + V_{Deep'} = 0$$

$$V_Q S_Q + V_{Surf} S_{Syst-s} + V_{Deep'} S_{Syst-d} + V_Z(S_{Syst-d} - S_{Syst-s}) = 0$$

The modified methodology identifies the following assumptions:

- the volume of outflow associated with freshwater inputs (i.e., V_R) all occurs in the surface layer, displacing water of the salinity of the surface portion of the system of interest ($S_{SYSTEM-s}$).
- a flow of oceanic water (V_{deep}) enters the deep layer, flows upward into the surface layer, and out again from the surface layer. The combined outflow from the surface layer to the ocean (V_{surf}) is equal to V_R - V_{deep} (remember, V_{deep} has positive sign, and both V_R and V_{surf} have negative signs).
- there is no simple 'exchange flow' term between the system and the ocean, as in the one-box model, salt balance is maintained by a vertical 'exchange flow', V_z, between the surface and deep layers

3. Budgets of nonconservative materials:

All dissolved materials will exchange between the system of interest and adjacent systems according to the criteria established in the water and salt budgets. Deviations of material concentrations from predictions based on these two previous steps are quantitatively attributed to net nonconservative reactions of materials in the system.

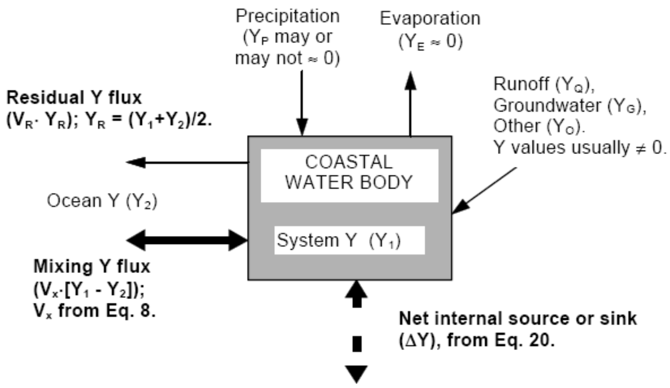


Figure 6. Generalised box diagram illustrating the budget for a nonconservative material, Y, in a coastal water body. The arrows show the net flux of Y associated with each process. Mixing (V_X) may be to or from the system. Quantities which are generally measured are shown in light typeface, while quantities which are calculated within the budget are shown in bold typeface. ΔY denotes the nonconservative flux of Y, and can be positive or negative with respect to the system.

Study Questions:

- What are the net internal fluxes of Carbon, Nitrogen, and Phosphorus?

Measurements:

- Net ecosystem metabolism: flux in DIP scaled by $(C:P)_{part}$ ratio
- Carbon fluxes: Dissolved inorganic carbon (temperature, salinity, pH, total alkalinity, partial pressure pCO2); Dissolved organic carbon (DOC)
- Phosphorus fluxes: Dissolved inorganic phosphorus (DIP)
- Nitrogen fluxes: denitrification, fixation: Dissolved inorganic nitrogen (NO_2^-, NO_3^-, and NH_4^+), dissolved organic nitrogen (DON)
- Dissolved nitrogen flux associated with production and decomposition of particulate matter (DP flux multiplied by $N:P_{part}$

4. Stoichiometric relationships among nonconservative budgets:

It can often be assumed that the nonconservative flux of dissolved inorganic phosphorus is an approximation of net metabolism at the scale of the ecosystem, because there is no gas phase for phosphorus flux. Nitrogen and carbon both have other major flux pathways (notably denitrification, nitrogen fixation, gas exchange across the air-sea interface, and [in some systems] CaCO3 reactions). The deviation of the fluxes of these materials from expectation based on C:N:P composition ratios of reactive particles in the system can be assigned to other processes in a quantitatively reproducible fashion.

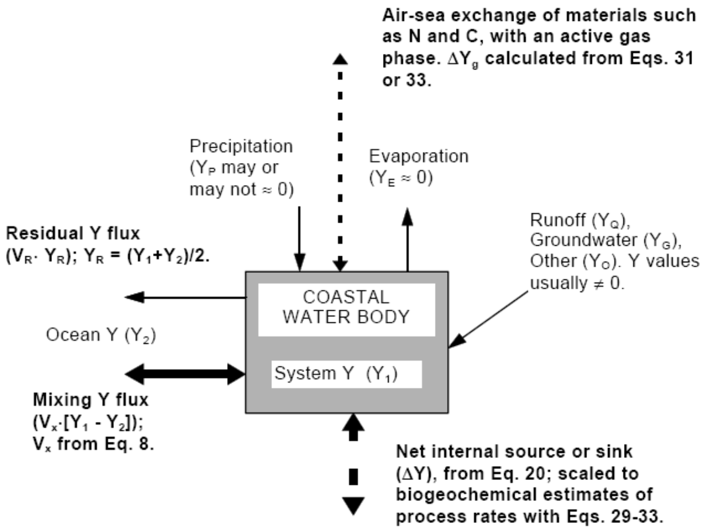


Figure 7. Generalised box diagram illustrating the budget for a nonconservative material, Y, which has an active gas phase in a coastal water body. In this case, appropriate stoichiometric linkages are used to scale the nonconservative fluxes (ΔY's) to system-scale estimates of internal biogeochemical processes. The arrows show the net flux of Y associated with each process. Quantities which are generally measured are shown in light typeface, while quantities which are calculated are shown in bold typeface.

Study questions:

- What type of metabolism dominates the system? (plankton, benthic algal, sedimentary materials)
- What is the dominant phase of C, N, and P? (dissolved, particulate, gaseous; organic, inorganic)

Measurements:

- Nutrient concentrations
- Suspended sediment load and C:N:P composition ratio

B. National Water Quality Monitoring Network Nutrients Design

The National Water Quality Monitoring Council (Council) has produced a design for the National Water Quality Monitoring Network for U.S. Coastal Waters and their Tributaries (the Network) as called for in the U.S. Ocean Action Plan. The Network is a framework for linking water quality monitoring in coastal bays, estuaries and the Great Lakes with observations in upland areas and offshore waters, and includes freshwater flows and contaminant input from inland and coastal rivers, groundwater, and atmospheric deposition. Wetlands and coastal beaches are also included in the design. A description of the Network design is available at http://acwi.gov/monitoring/network/design.

Nutrients in the design document:
Issues the Network was designed to address include nutrient enrichment, oxygen depletion, and habitat degradation. Table 3-1 in the Network report indicates that the following resource components should be monitored for nutrients: estuaries, near shore coastal waters, offshore coastal waters, Great Lakes, rivers, groundwater, and atmospheric deposition.

The Interagency Working Group charged the Nutrients Workgroup with several tasks.

1. Determine the specific constituents to be monitored and the performance requirements for analytical methods. Specify details such as total or dissolved nutrients in water and whether samples of sediment are to be analyzed. The goal is to provide guidance on nutrient concentrations and loads and to establish a basis for determining trends over time.
2. The Network is intended to provide data that will be collected primarily by Federal and State agencies. Thus, the methods used should be operational rather than approaches designed for research purposes. In recent years, the parameters measured and the performance limits of agencies and academic institutions have become increasingly similar.
3. The list of constituents to be monitored should be broad enough to address major management issues at regional and national scales but should not be so extensive as to make the Network prohibitively expensive. It is expected that at the local level, the basic Network design will be augmented by additional sample collection and analyses.

It is recognized that ambient nutrient concentrations in estuaries, near shore coastal waters, offshore coastal waters, Great Lakes, and rivers are of a similar nature. Concentrations of various forms of nutrient elements in groundwater and atmospheric deposition are often considered as loading parameters for input into aquatic systems. Wetlands are important to aquatic systems as either nutrient loading sources or sinks. Although the network design for the groundwater, atmospheric deposition and wetlands components are not complete, the Nutrients Workgroup recommendations include preliminary nutrient parameter recommendations for these components. The final recommendations for these components will be decided in consultation with those working groups. The Nutrients Workgroup's recommendations are described below.

The Nutrients Workgroup has developed a tiered list of nutrient parameters with corresponding analyses (Table 1). Tier I parameters represent the required constituents; Tier II parameters represent the constituents that would add significant value but may not be essential to some programs. The requirements for the river, Great Lakes, estuary, nearshore coastal and offshore coastal components are the same. However, some related analyses will differ between freshwater and marine systems. For example, conductivity will be measured in freshwater systems, while salinity will be measured in marine systems.

For all of the components except for wetlands, the Nutrients Workgroup recommends water sampling only. The Nutrients Workgroup does not recommend nutrient analysis in sediments except for wetlands. Sediments are very heterogeneous for many parameters on quite small spatial scales (meter or less).

Table 1 - Required nutrient parameters for National Water Quality Monitoring Network

Component	**Nutrient Analyses**		**Related analyses**	
	Tier 1	**Tier 2**	**Response Variables**	**Ancillary Analyses**
Rivers, Estuaries, Nearshore Coastal, Offshore Coastal	Total nitrogen* Dissolved ammonium Dissolved nitrate plus nitrite Total phosphorus⁺ Dissolved ortho phosphate Dissolved silica	Total dissolved nitrogen Total dissolved phosphorus Particulate nitrogen Particulate phosphorus	Chlorophyll *a* Dissolved oxygen Conductivity/salinity	Dissolved organic carbon Dissolved inorganic carbon pH Total suspended sediments Photosynthetically active radiation Particulate carbon
Groundwater	Dissolved nitrate plus nitrite	Dissolved ammonium Dissolved ortho phosphate		Dissolved organic carbon
Atmospheric deposition	Dissolved nitrate plus nitrite Dissolved ammonium Dissolved ortho phosphate			Major ions pH
Wetlands (sediment only)	Particulate nitrogen Ammonium Dissolved ortho phosphate Particulate phosphorus		Chlorophyll *a*	Particulate carbon

* May be determined by analysis of total dissolved nitrogen and particulate nitrogen (TN=TDN+PN)

[+] May be determined by analysis of total dissolved phosphorus and particulate phosphorus (TP=TDP+PP)

n.b. Dissolved refers to samples that are filtered through GF/F (or equivalent) filters before analysis. Total nitrogen (or phosphorus) refers to unfitered samples. Particulate nitrogen (or phosphorus or carbon) refers to samples collected on filters which are then analyzed.

Recommendations

Dissolved inorganic nitrogen (DIN) is comprised of nitrate plus nitrite and ammonium. These forms of nitrogen are readily available to phytoplankton and often control the formation of blooms. Total dissolved nitrogen (TDN) is comprised of dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON). Because there is no reliable way to measure DON directly, it is usually calculated from measured TDN and DIN values (DON=TDN-DIN). There is evidence that DON, particularly urea, may be important in triggering harmful algal blooms. The Nutrients Workgroup recommends that TDN be measured. The advantage of measuring TDN is that it provides a better estimate of the nitrogen that is likely to be most available to phytoplankton. The measurement of TDN plus particulate nitrogen (PN) is usually used to calculate total nitrogen (TN=TDN+PN). Because there is a significant historic dataset of total nitrogen values for a variety of systems, the Nutrients Workgroup recommends that total nitrogen (TN) be measured. These additional analyses would provide more detailed information about the sources of nitrogen in the system.

Phosphorus is also very important as a limiting nutrient, particularly in freshwater as well as tropical and subtropical estuarine marine systems. Total phosphorus (TP) is comprised of ortho phosphate, dissolved organic phosphorus and particulate phosphate (PP). Total dissolved phosphorus (TDP) includes dissolved organic phosphorus and ortho phosphate. Ortho phosphate is the dissolved inorganic form of phosphorus. Ortho phosphate concentrations are often very low and ortho phosphate is rapidly recycled. Similarly, the Nutrients Workgroup recommends that total phosphorus (or total dissolved phosphorus and particulate phosphorus (TP = TDP + PP)) be measured. As with nitrogen, the measurement of TDP gives more detailed information about the most available pools of phosphorus.

Dissolved silica controls the growth of diatoms and changing N:Si ratios in freshwater flow have been associated with changes in estuarine and marine phytoplankton communities (an increasing ratio is generally related to fewer diatoms relative to the other taxa).

In addition, the Nutrients Workgroup recommends that specific response variables and ancillary variables should be monitored. Chlorophyll *a* and dissolved oxygen concentrations are critical response variables that need to be monitored. Salinity or conductivity, while not response variables, are critical parameters that should be monitored. The ancillary analyses that would be useful to monitor include dissolved organic carbon, dissolved inorganic carbon, pH, total suspended sediments, particulate carbon, and photosynthetically active radiation. Dissolved organic carbon is a mixture of refractory and labile compounds. It is important in controlling the availability of trace metals as well as bacterial productivity of systems. Total suspended sediments and photosynthetically active radiation provide information about the light available for phytoplankton growth. Dissolved inorganic carbon and pH have traditionally been considered more significant in freshwater than marine waters. However, with the increasing atmospheric carbon dioxide concentration, ocean acidification is an increasing concern.

Groundwater and atmospheric deposition can be important sources of nutrients for many aquatic systems. Usually nitrate plus nitrite is the dominant form of nitrogen from these sources, although ammonium can be important in some systems.

C. Remote Sensing for the Nutrient Study Design

The following is a first draft of an attempt to define specific water quality parameters of interest for assessing the status of an estuary, and to develop their relationship to remotely sensed imagery. Included are a discussion of parameters to be measured, strategies for collecting data, a brief description of remote sensing of water optical properties, and some examples of empirical algorithms. Specific instruments and analysis methods can be found in the references.

Objectives:

1. Obtain feedback on the appropriateness and correctness of water quality parameters described below and to include missed parameters
2. Determine if there are standard methods currently being used for obtaining these measurements
3. Determine if the community believes remote sensing as described can be useful for their purposes.
4. Obtain feedback on the practical aspects associated with field data collection
5. Obtain feedback on the community's level of familiarity, experience and interest in using remotely sensed data

Remote Sensing for Estuarine Nutrient Source, Fate and Transport and Impairment Assessment

Remote sensing may be helpful in addressing water clarity and residence time, factors that determine susceptibility of an estuary to eutrophication by excess nutrient loading (Cloern, 2001). Each will be discussed briefly below.

Water Clarity

The term, "water clarity" is found throughout the literature and in numerous descriptions of characteristics of impaired water bodies. Water clarity in this context will be defined as light attenuation for 4 cases where irradiance at the top of the water column decreases to the indicated percentage due to absorption and scattering by water, CDOM, phytoplankton, organic detritus and mineral particles. K_d is the diffuse attenuation coefficient in units of m^{-1}. (In many, if not most, estuarine studies, K_d is discussed without reference to specific wavelength. For the purposes of this discussion, K_d will be synonymous with K_{PAR} unless a specific wavelength is included, e.g. $K_d(490)$.) K_d is defined as:

$$K_d(\lambda) \equiv -\frac{1}{E_d(\lambda)} \frac{dE_d(\lambda)}{dz}$$

If K_d is known, downwelling irradiance at some depth z, can be determined by:

$$E_d(z,\lambda) = E_d(0,\lambda)e^{-k_d(\lambda)z}$$

The depth at which downwelling irradiance has decreased to some level relative to that just below the surface is:

$$K_d(\lambda)z = -\ln\left[\frac{E_d(z,\lambda)}{E_d(0,\lambda)}\right]$$

The four cases often used in relation to water quality are:

Seagrass (SAV) Impairment Depth (Z_s) – 20 % => 1.6/ K_d (Eldridge et al., 2004)
Optical Depth ($Z_o(\lambda)$) – 10 % => 2.3/ $K_d(\lambda)$ (Mobley, 1994)
Photic Depth (Z_p) – 1 % => 4.6/ K_d (Cloern, 1987) (also known as Euphotic Depth)
Bottom Avoidance Depth ($Z_B(\lambda)$) – 0.08 % => 2.5/ $K_d(\lambda)$ (Mueller, et al., 2003)
Secchi Depth (Z_{SD}) – "*a simple visual index of water clarity*" (Preisendorfer, 1986)

K_d can be obtained by measurement of downwelling irradiance profiles in the water column and the use of equation 3 above. This measurement is often made with a broad band irradiance sensor with a cosine receptor, sometimes referred to as a 2π sensor or PAR sensor. K_d is an apparent optical property (AOP) and is therefore affected by a number of conditions including solar zenith angle, cloud, sky and atmospheric conditions and shading by the ship and measurement apparatus. K_d is not equivalent to Secchi depth and can not be derived directly from Secchi depth (See discussion of Secchi depth below).

An alternate approach to obtaining an indicator of light attentuation is to measure the spectral beam attenuation and absorption coefficient profile in the water column. These are inherent optical properties (IOP) and are not a function of the ambient conditions. This measurement is independent of the light field and will provide information on both absorption and scattering. The beam attenuation coefficient can be used to predict the radiance at some depth relative to that just below the surface as:

$$L_d(z,\lambda) = L_d(0,\lambda)e^{-c(\lambda)z}$$

The relationship between radiance L and irradiance E is

$E = L\mathrm{X}$, where X for a perfectly diffuse reflector is π. In the water column X can range from less than π to up to 2 π depending on the characteristics of the suspended particles.

Neither c, E_d nor K_d can be measured directly through remote sensing. A simplified description of the relationship between at sensor radiance and the absorption and scattering coefficients is provided below. An effective approach to developing a relationship between remotely sensed data and estuarine parameters of interest is through statistical regression analysis. The overall value or utility of such empirically derived relationships is a function many factors, including the atmospheric conditions and the need to correct the radiance measured by the sensor, the number and spatial distribution of sampling stations, the spatial distribution of estuarine water characteristics, the timing of the satellite overpass vs. sample time, and the relationship between measured biogeophysical water characteristics and the in-water light field.

Residence Time

Residence time, τ_e for an estuary is often defined in terms of the ratio of the rate of freshwater inflow to total volume of the estuary (Libes, 1992). Residence times for many Gulf of Mexico estuaries range from a few days to many months. (Bianchi et al., 2000). Estuaries with long residence times can have higher chl a concentrations than those with short residence times. Estuaries with multiple freshwater sources and segregated, within estuary bays, might have vastly different residence times and water clarity conditions throughout the estuary (Cloern, 1987).

Remote sensing can potentially support investigations related to residence times through multi-temporal synoptic views of a given estuary with widely varying conditions. These synoptic views may provide information on location and spatial extent of different conditions and dynamics within an estuary that could help determine locations of in situ monitoring stations. Repeat coverage within a predicted residence time or over multiple residence times may be useful for evaluating temporal variability within an estuary. This type of temporal coverage may also be useful for identifying periods of wind induced benthic resuspension events (Booth et al., 2000), wind driven buoyant plumes (Stumpf et al., 1993, Salisbury et al., 2004) or variability due to tidal cycles. Time series analysis may also provide an indication of primary productivity.

Archived satellite imagery may provide historical perspectives on long term changes and variability. This type analysis could conceivably be carried out with multiple sensors at different spatial and temporal resolutions. The major and significant difficulty is developing accurate inter-sensor calibrations and multi-temporal correction factors.

***IN SITU* SAMPLING STRATEGY for REMOTE SENSING**

In the relationship for remote sensing reflectance(see REMOTE SENSING below):

$$R_{rs}(\lambda,\theta,\varphi;\theta_0) = \frac{L_w(\lambda,\theta,\varphi;\theta_0)}{E_d(0^+,\lambda;\theta_0)} = \Re(\theta',W)\frac{f(\lambda)}{Q(0^-,\lambda,\theta',\varphi)}\frac{b_b(\lambda)}{a(\lambda)+b_b(\lambda)}$$

the *in situ* parameters that affect $a(\lambda)$ are CDOM, organic detritus and phytoplankton. $b_b(\lambda)$ is affected by the number and size distribution of suspended phytoplankton, organic detritus and mineral detritus. To support meaningful empirical relationships to remote sensing images, as much information about these parameters as possible should be measured. To enhance the linkage to radiometric quantities, profiles of the light field, absorption and scattering coefficients should be collected at the same time as the physical samples. An extensive list of *in situ* measurements and measurement procedures can be found in The *Ocean Optics Protocols for Satellite Ocean Color Sensor Validation, Rev. 4, Vol 1: Introduction, Background and Conventions*, (NASA/TM-2003-21621/Rev-Vol I, http://oceancolor.gsfc.nasa.gov/DOCS/). This document primarily describes sample collection for deep ocean and coastal continental shelf regions. Some of the strategies and methods must be modified to include shallow, small estuaries.

The spatial distribution of sampling should consider the spatial resolution of the sensor to be used, e.g. MODIS Ocean Color bands are ~1Km^2, MODIS medium resolution bands are 250 and 500 m^2. Samples throughout the total area of the estuary for which statistical correlation is desired should be collected. To account for spatial variability, a 2 x 2 pixel area (larger if possible) should be sampled in regions believed to have uniform water characteristics. Samples used for statistical correlation should be collected as close to the time of satellite overpass as possible. For many polar orbiting environmental satellites this will be approximately 10:30 am and 1 pm local U.S. standard time.

Extending discrete samples of dissolved and suspended particles to profiles of the water column is accomplished through the use of chl a and CDOM fluorometers, absorption and beam attenuation meters, scattering meters and beam transmissometers. The need for profiles will be dependent on the depth of the upper mixed layer relative to the estuary bottom depth, magnitude of the surface beam attenuation coefficients, stratification of the water column at each station. Profiles will always be necessary to obtain the best measurement of $K_{d.}$

An approach utilizing one or more of the following techniques can be used to develop relationships between remotely sensed imagery and water quality parameters:

1. statistical correlation between satellite DN (digital number) and *in situ* biogeophysical parameter of interest, i.e. CDOM, phytoplankton, suspended organic detritus and suspended mineral particles. K_d is estimated from concentration of measured parameters and thus linked to satellite DN.
2. *in situ* inherent and apparent optical properties (IOPs and AOPs) vs. *in situ* measured biogeophysical parameter of interest to obtain a direct connection to K_d and a statistical correlation to satellite DN. A simplified atmospheric correction such as a dark pixel subtraction method to improve the useability of the statistical relationships to a broader spatial range within an image.
3. analytic relationship between radiometrically and atmospherically corrected radiances measured by the sensor and IOP's and AOP's measured *in situ*, coupled with the biogeophysical parameters of interest. This process provides an analytical connection between satellite imagery and K_d and might provide a means to extend a single day/single scene empirical relationship to a multi-temporal, multi-location algorithm.

Satellites with imaging sensors available for estuarine assessment (currently, only MODIS and AVHRR are available for download without cost) (see Hu, et al. 2004, for an assessment of MODIS and Thematic Mapper instrument sensitivity)

USA Federal

MODIS (Aqua and Terra)
    Ocean color bands (1km)
    Medium Resolution bands (250 and 500 m)

Thermal bands (1 km)

Landsat (5 and 7 – status of both questionable) Thematic Mapper (30 m)

EO1-Hyperion (30 m hyperspectral, 7.5 km swath, limited coverage)
EO1-ALI (30 m, TM bands, limited coverage)

ASTER – combination of visible and IR bands

NOAA AVHRR

USA Commercial

Ikonos
SeaWiFS
Quickbird

International
MERIS
AWIFS
…

REMOTE SENSING (a simplified presentation relating water optical properties to radiance measured by the sensor)

Inherent Optical Properties (IOP) of estuarine waters are primarily determined by the absorption and scattering characteristics of the water, colored dissolved organic matter (CDOM), phytoplankton (ph), organic detritus (OD) and mineral particles (md). These characteristics are defined in terms of the beam attenuation coefficient, $c(\lambda)$, and the normalized Volume Scattering Function (VSF) or beta β where:

$$c(\lambda) = a(\lambda) + b(\lambda).$$

Each of these components is dependent on wavelength and written as:

$a(\lambda) = a_w(\lambda) + a_{ph}(\lambda) + a_{cdom}(\lambda) + a_{od}(\lambda) + a_{md}(\lambda)$ - total absorption coefficient

$b(\lambda) = b_w(\lambda) + b_{ph}(\lambda) + b_{od}(\lambda) + b_{md}(\lambda)$ - total scattering coefficient

Scattering is further segmented as forward and backscattering.

$b(\lambda) = b_f(\lambda, 0 \le \theta \le 90) + b_b(\lambda, 90 \le \theta \le 180)$ - forward and backscattering coefficients

Radiative transfer theory shows that propagation of light through the water is dependent on the beam attenuation c, and the scattering phase function, β. A version of the radiative transfer equation describing light transfer {Mobley 1994 #3670}(see text for complete description of parameters) is

$$\mu \tfrac{dL(z;\xi;\lambda)}{dz} = -c(z;\lambda)L(z;\xi;\lambda) + \int_{\Xi} L(z;\xi';\lambda)\beta(z;\xi' \rightarrow \xi;\lambda)d\Omega(\xi') + S(z;\xi;\lambda)$$

Because $c(\lambda)$ and β co-vary with CDOM and suspended particles, they must be measured in situ. However, because of cost and time constraints and other practical issues, these measurements are usually made at a few discrete stations. Satellite sensors measure only radiance at the sensor. These measurements are related to $a(\lambda)$ and $b(\lambda)$ by the following:

$L_S(\lambda,\theta,\varphi;\theta_0) = L_w(\lambda,\theta,\varphi;\theta_0) * \tau_a(\lambda) + L_a(\lambda,\theta,\varphi;\theta_0)$, at sensor radiance

where $L_a(\lambda,\theta,\varphi;\theta_0)$ is atmospheric radiance, and $\tau_a(\lambda)$ is atmospheric transmittance

$L_w(\lambda,\theta,\varphi;\theta_0) = \dfrac{L_S(\lambda,\theta,\varphi;\theta_0) - L_a(\lambda,\theta,\varphi;\theta_0)}{\tau_a(\lambda)}$, water leaving radiance

$E_d(\lambda,\theta,\varphi;\theta_0) = F_0(\lambda,\theta,\varphi;\theta_0) * \tau_a(\lambda) + E_a(\lambda,\theta,\varphi;\theta_0)$, downwelling irradiance

$R_{rs}(\lambda,\theta,\varphi;\theta_0) = \dfrac{\dfrac{L_S(\lambda,\theta,\varphi;\theta_0) - L_a(\lambda,\theta,\varphi;\theta_0)}{\tau_a(\lambda)}}{F_0(\lambda,\theta,\varphi;\theta_0) * \tau_a(\lambda) + E_a(\lambda,\theta,\varphi;\theta_0)}$, remote sensing reflectance

Remote sensing reflectance is often coupled to absorption and backscattering by the following model.

$$R_{rs}(\lambda,\theta,\varphi;\theta_0) = \frac{L_w(\lambda,\theta,\varphi;\theta_0)}{E_d(0^+,\lambda;\theta_0)} = \Re(\theta',W)\frac{f(\lambda)}{Q(0^-,\lambda,\theta',\varphi)}\frac{b_b(\lambda)}{a(\lambda)+b_b(\lambda)}$$

$$Q = \frac{E_u(0^-,\lambda)}{L_u(0^-,\lambda)}$$

A complete derivation of these parameters can be found in (Gordon, 1988) {Mobley 1994 #3670}{Mueller, Morel, et al. 2003 #3680}. The quantity

$$\Re(\theta',W)\frac{f(\lambda)}{Q(0^-,\lambda,\theta',\varphi)}$$

contains terms accounting for illumination and viewing geometry, light transmission through the air-sea interface, sea state, suspended particle composition and other conditions (Mueller, et al. 2003) and is often replaced by a constant value.

EXAMPLE ALGORITHMS for CDOM, Chlorophyll Concentration, TSM, NTU

Notes:

1. NASA algorithms for K(490) and chl a are strictly case I (i.e. do not work in estuaries) as are all NASA Ocean Color data products
2. These are examples of empirical relationships and should not be used without validation

CDOM absorption

$a_y(\lambda) = a_y(\lambda_0) * \exp(x(\lambda - \lambda_0))$ (Bricaud et al., 1981)

$\lambda_0 = 440nm$ $, -0.014 \geq x \geq -0.019$ (Roesler et al., 1989)

$a_y(412) = -90X + 2.34$ (Delcastillo and Miller, in press)

$X = Rrs(510)/Rrs(670)$

TSM

Stumpf, 1988, J. of Coastal Research Vol 4, no. 1

$$R_{rs}(\lambda,\theta,\varphi;\theta_0) = \frac{\pi * L_w(\lambda,\theta,\varphi;\theta_0)}{\left|E_0(0^+,\lambda;\theta_0) * \sin(\theta)\right|}$$

$$L_w(\lambda,\theta,\varphi;\theta_0) = \frac{L_S(\lambda,\theta,\varphi;\theta_0) - L_a(\lambda,\theta,\varphi;\theta_0)}{\tau_a(\lambda)}$$

$$R_t = M * \log(n_s) + B$$

Stumpf and Pennock, 1989, Journal of Geophysical Research 94(C10),14,363-14,371

$$R(\lambda) = \frac{Y_{b_b}(\lambda)}{a(\lambda) + b_b(\lambda)}$$

$$R(\lambda) = \frac{Y1 * b_b^*(\lambda)}{\left(s^*(\lambda) + a_x(\lambda)\right)/n_s}$$

$$s^*(\lambda) = a_s^*(\lambda) + b_{bs}^*(\lambda)$$

$$a_x(\lambda) = a_w(\lambda) + a_d^*(\lambda)n_d + a_p^*(\lambda)n_p$$

Miller and McKee, 2004, Remote Sensing of Environment 93, 259-266
(1st order linear regression to dark pixel corrected MODIS red 250m band,

$$TSM = -1.91 + 1140 * R(645nm) \text{ for 0 to 60 mg/l .}$$

Hu et al. 2004, Remote Sensing of Environment 93, 423-441

MODIS medium spatial resolution bands

In situ measurements

$$TSM = 3.2 * c(660nm) - 7.83$$

$$Chla = 21.21 * chlfluorescence + 1.07$$

$$CDOM = 1.08 * CDOMfluorescence + 0.17$$

MODIS bands (e.g.)

$$TSS = 0.00522 * \exp(1002 * (Rt(645) - Rt(859)))$$

$$Chla = 26.04 * \exp(-1.225 * X)$$

$$CDOM = 2.00 * \exp(-1.0943 * X)$$

$$X = Rt(645) - Rt(859)$$

Recommendations for Remote Sensing in Estuaries from Tampa Bay survey

1. CDOM, chlorophyll a concentration, and TSS do not co-vary
2. CDOM shows inverse linear relationship with salinity though the slope varies over different locations
3. Sensitivity of MODIS medium spatial resolution bands is 4-5 times Landsat 7, ETM+ and are useful for estuarine studies.
4. In scenes where ground truth data is available, simple regressions of at-sensor radiances provided reasonable synoptic maps
5. Improvements of sensor calibration/characterization, atmospheric correction and bio-optical algorithms are required to make operational and quantitative use of the MODIS medium spatial resolution bands, 1,3,4.

NTU (nephelometric turbidity units)

Zhiqiang Chen, Chuanmin Hu, Frank Muller-Karger, 2007, Remote Sensing of Environment 109, 207-220.

$$turbidity(NTU) = 1203.9 * R_{rs}(645nm)^{1.087} \text{ (MODIS Aqua)}$$

NASA Ocean Color MODIS data product

$K(490)$

$$K(490) = K_w(490) + A\left[\frac{L_w(490)}{L_w(555)}\right]^B$$
$$K_w(490) = 0.016m^{-1}$$
$$A = 0.15465$$
$$B = -1.5401$$

Chl a concentration

NASA Ocean Color OC3M MODIS chlor_a

$$C_a = 10.0^{(0.2830-2.753R_{SM}+1.457R^2{}_{SM}+o.659R^3{}_{SM}-1.403R^4{}_{SM})}$$

Where, $R_{SM} = \log_{10}\left(\frac{Rrs(443)}{Rrs(550)} > \frac{Rrs(488)}{Rrs(550)}\right)$

SECCHI DISK

The following is taken from Preisendorfer, R.W., 1986, Limnology and Oceanography 31(5), 909-926

Secchi Depth is defined as:

$$Z_{SD} = \frac{\ln[\mathrm{T}C_0 / C_T]}{\alpha + K} \equiv \frac{\Gamma}{\alpha + K}$$

$C_0 = inherent\_contrast$

$C_T = threshold\_contrast$

$T = surface\_transmit\tan ce\_\ factor$, includes surface condition and sky reflectance.

$\Gamma = coupling\_cons\tan t$

$\alpha = photopic\_beam\_attenuation$, describes the upward *beam transmittance* for luminance

$K = photopic\_diffuse\_attenuation$, describes the downward *diffuse transmittance* for illuminance

$(\alpha + K)$, the upward *contrast transmittance*

Three reasons researchers use the Secchi disk:

1. a simple formula for euphotic depth, see eq. 69.
2. a connection between Z_{SD}, α and K
3. a curiosity about the observed characteristics of a white disk in natural waters

Note: use the 10 rules for secchi disk (see reference text).

"The net conclusion of the preceding observations is that:

(i) *the Secchi disk reading z_{SD} yields a quantitative estimate of the apparent optical property $\alpha + K$ of a medium.*

(ii) *(ii) The primary function of a Secchi disk is to provide a simple visual index of water clarity via z_{SD} or $\alpha + K$.*

(iii) *(iii) To extend the use of the disk with auxiliary objective measurements (of α or K, or both) is to risk obviating or abusing this primary function.*"

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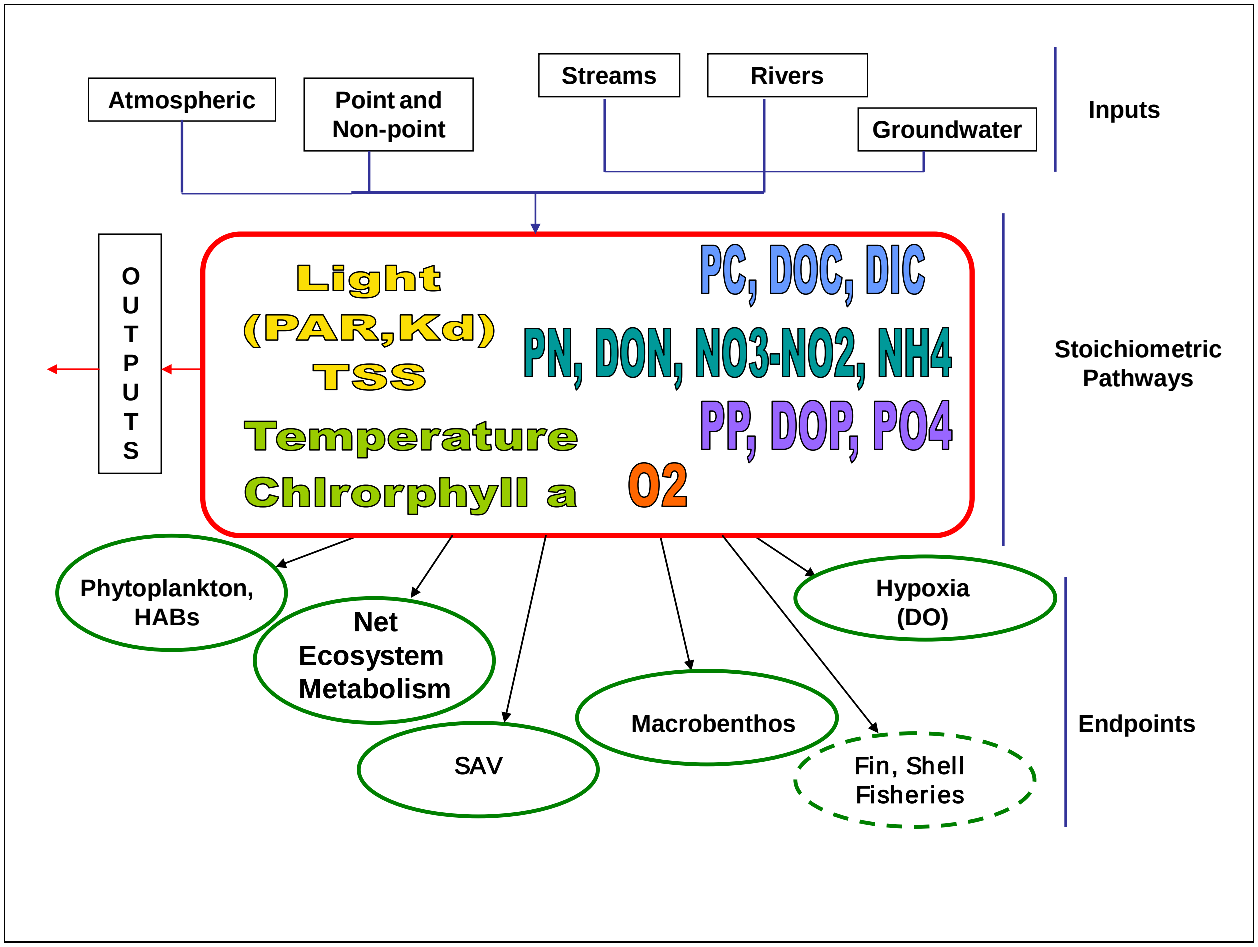
Web links:

NASA Remote Sensing tutorial at http://rst.gsfc.nasa.gov/

http://oceancolor.gsfc.nasa.gov/
http://oceancolor.gsfc.nasa.gov/DOCS/
Technical Memos
Ocean optics protocols for satellite ocean color sensor validation

Link to Volume 1 is http://oceancolor.gsfc.nasa.gov/DOCS/Protocols_Ver4_VolI.pdf

D. Nutrient Pathways and Endpoints



Conceptual model of nutrient pathways for Chlorophyll a.

Phytoplankton

Chlorophyll *a* is a pigment common to all phytoplankton; measures of accessory photosynthetic pigments unique to specific functional groups of phytoplankton will allow refinement of the understanding of phytoplankton community responses to nutrients and refinement of the application of water column chlorophyll as a management tool. Better understanding of spatial (both horizontal and vertical) and temporal patterns of phytoplankton community responses to freshwater inflows and nutrient loading will allow integration of this biological response into existing management schemes and will allow application over the appropriate scale taking into account areas where depth stratification is important.

Changes in nutrient availability can be related spatially and temporally to community composition and water column light environment. The importance of various algal groups as food for benthic organisms and fishes could then be integrated into a phytoplankton management scheme for the body of water of concern that goes beyond what a single indicator (*e.g.*, chlorophyll *a*) will be able to provide. A management tool that will allow for efficient transfer of biomass through the food web by maintaining an appropriate balance of phytoplankton community populations will further help to avoid the creation of 'dead zones' due to organic matter deposition to environments where only microbial decomposition occurs rather than transfer through macroinvertebrates to higher trophic levels.

Optical properties of water (*e.g.*, transmittance), particularly as influenced by phytoplankton, turbidity, and colored dissolved organic matter, will be related to traditional water quality data (e.g. Secchi depth) by measuring these optical properties continuously along transects (with both vertical and horizontal components) between long-term sampling stations. Relationships between these optical and traditional measures will allow estimation of historical light environments for benthic habitats and allow refinement of existing targets and goals for seagrass recovery. These relationships will also help to better understand changes in water quality over time as they relate to historical management activities and the changing light environment available to benthic habitats.

Optical measurements can be collected in real-time using a suite of sensors that have been used extensively to characterize the light fields in estuarine and coastal systems throughout Florida and the Gulf of Mexico. The optical package was developed in the Ocean Optics Laboratory at the University of South Florida (USF). The following optical parameters would be measured: percent transmittance, chlorophyll fluorescence, remote sensing reflectance, phytoplankton absorption, color absorption, scatter, backscatter, and others. Monthly data would be collected at existing fixed stations together with traditional optical (PAR and Secchi disk) and water quality measurements so that direct comparisons can be made. Every quarter, real-time optical measurements could be collected to provide a synoptic picture of the light environment by "connecting the dots" between existing fixed stations. Using the relationships between the light field and water quality, a detailed history of the light field could be reconstructed using historical data from those fixed stations that date back over ten or more years.

Refinement of the spectral information generated for monitoring purposes will assist in development of airborne tools for managing water quality and benthic habitat, as well as defining spatial and temporal constraints on such applications. With this information it will be possible to define a combined fixed station, flow-through and airborne assessment protocol that will enable more cost-effective and system-wide assessment of water column and benthic habitat changes over time and space. Ultimately, this information can be used to implement a satellite-based water column and habitat quality management tool for estuarine and coastal waters of the Gulf of Mexico. Phytoplankton monitoring should consider the following:

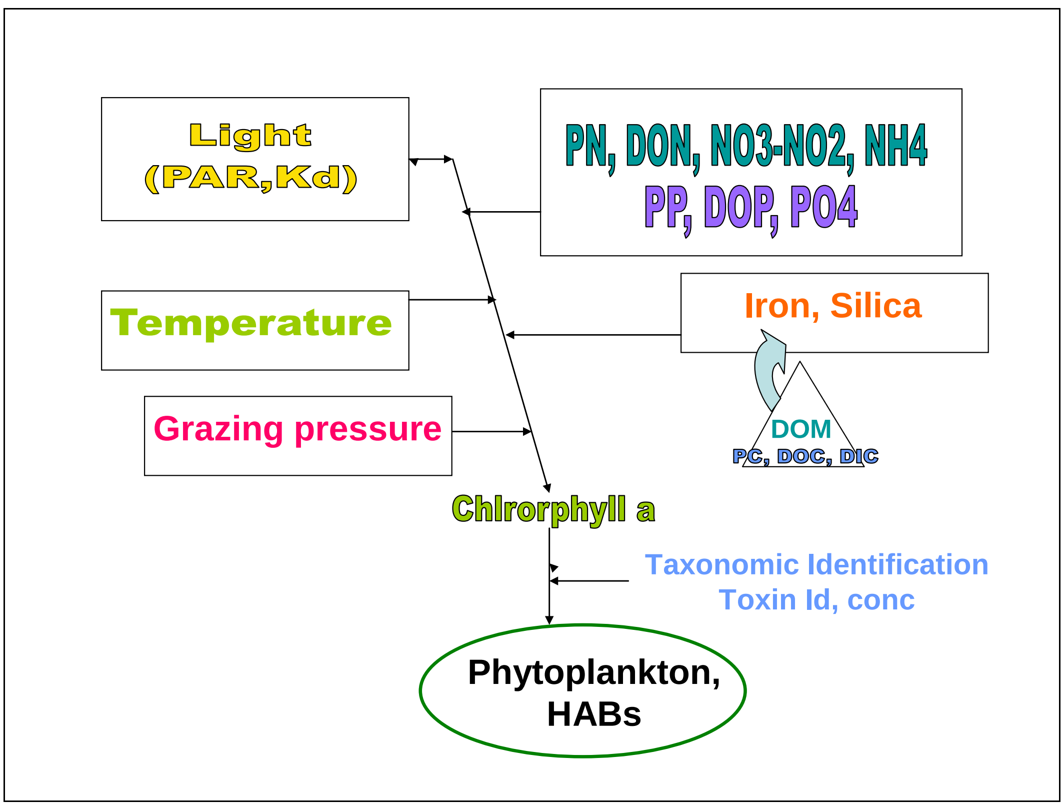
- Perform taxonomic and HPLC analyses in conjunction with ambient nutrient sampling and speciation.
- Refine relationship between nutrient form, concentration and load with phytoplankton community composition.
- Define a monitoring program utilizing phytoplankton community responses to nutrient loading.

- Examine relations between chlorophyll *a*, accessory pigments and phytoplankton community composition.
- Propose refinement of chlorophyll *a* target levels.
- Perform limiting nutrient bioassays utilizing multiple nutrient species.
- Determine if there are spatial-temporal and/or community relationships with limiting nutrient responses.
- Refine routine sampling to ensure appropriate data is collected to monitor trends in time and space of phytoplankton community responses to nutrient loads.
- Evaluate trophic transfers as they relate to phytoplankton community composition.
- Integrate a measure of production into water quality management schemes.
- Refine monitoring programs to ensure data collection to continue this type of evaluation and refinement into the future.
- Measure optical water quality parameters, in conjunction with traditional water quality measures.
- Establish relationships between optical water quality measures and traditional water quality measures.
- Develop conceptual historical light environment based on applying optical relationships with traditional, historical water quality data.
- Calculate spectral distribution of light energy reaching benthic habitats under various conditions.
- Refine light targets for seagrass recovery taking into account observed relationships.
- Refine monitoring programs to ensure continued generation of data required to effectively manage the benthic light environment.
- Extrapolate flow-through and fixed station data to integrate water quality estimates across the bay.
- Propose minimum data requirements for establishing an operational airborne water quality and habitat monitoring program for the bay.
- Propose minimum data requirements for establishing a satellite-based water quality and habitat monitoring program for the bay.

Phytoplankton experiments that examine responses to nutrients similar to the approach described below may provide useful information. A fixed suite of parameters could be characterized for each station prior to bioassays, including bacterial abundance, phytoplankton community composition, size-fractioned chlorophyll and accessory pigments. Bioassay experiments would be conducted using N, P, and N+P combined additions as well as a control. Silica may also be added in some types of ecosystems as a nutrient parameter. The level of N and P additions could be determined based upon the ambient nutrient concentration in the regions and will be comparable to a bolus of nutrients found in the environment associated with a rain event. The preferred frequency of bioassays is every other month with the potential to sample two additional events annually. Duplicate bioassays of each of the four treatments would be set up using water from each site. Incubations are conducted in “cubitainers” at ambient field temperature and light intensities. A 48 hr time period is used to determine change in size fractionated chlorophyll *a* content as a result of nutrient additions. However, 48-hours may not provide enough information regarding the extent that biomass is N or P limited.

Biomass can be used as an indicator to determine which nutrient additions from each site are being utilized. Response of the phytoplankton communities to the nutrient additions can be quantified based on changes in size-fractionated chlorophyll *a* and phytoplankton community composition using concurrent pigment analyses, microscopic analysis (identification and cell counts), and bacterial enumerations. These data will allow determination the extent to which different components of the biota responds to nutrient additions, which nutrient are being used, and whether all biotic components are responding to the same or different nutrients.

Phylogenetic-group composition can be characterized using chemosystematic (photopigment) enumeration *via* high performance liquid chromatography (HPLC). Briefly, extracted pigments (in 100% acetone) will be injected directly into a Waters 600E HPLC equipped with a monomeric and polymeric reverse-phase C_{18} columns in series and an in-line, Waters 2996 photodiode array (400-700 nm) detector. Mobile phases, solvent flow rates, and temperature regimes will follow that described by Pinckney *et al*. 1996. This methodology provides excellent resolution of ‘marker’ carotenoids and chlorophylls necessary for chemosystematic characterization of estuarine and coastal microalgal groups. Pigments will be quantified by integrating chromatographic peaks and calibrated from authentic standards. The absolute and relative chlorophyll *a* concentrations of microalgal phylogenetic groups will be derived from photopigment suites by CHEMTAX matrix factorization.



Conceptual model of nutrient pathway for Phytoplankton and HABs endpoints.

Phytoplankton:

1. Refine understanding of chlorophyll *a* – nitrogen load relationship for refining chlorophyll *a* target levels for the water column.
2. Relate chlorophyll *a* to phytoplankton community composition through taxonomic and accessory pigment analyses.
3. Examine shifts in limiting nutrients through limiting nutrient bioassays with natural phytoplankton populations.
4. Propose a phytoplankton community composition metric as a management tool for ensuring efficient transfer of energy through the food web, as a tool for preventing 'dead zone' creation through excessive organic matter loading to the benthos, and as a first warning or sentinel indicator.
5. Establish relationships between traditional water quality measures and optical measures, enabling reconstruction of historical light environment.
6. Refine our understanding and application of existing light targets for seagrass recovery.
7. Propose modification to existing monitoring programs to allow for airborne/satellite monitoring of water and habitat quality and change over time.

Nitrogen Effects on Ecosystem Metabolism and Hypoxia

Spatiotemporal volatility in the relationship between ecosystem respiration and photosynthesis leads to hypoxia events. The tendency for high R:P to cause hypoxia can be offset by physical gas exchange via water exchange or local vertical mixing and diffusion. As a result, the interaction between hydrodynamics and local geomorphology will influence local susceptibility to hypoxia. Two estuaries with the same general chl a concentrations may have very different susceptibilities to hypoxia.

Because of these implications, we suggest that R:P volatility be included as an ecological endpoint in the monitoring program. There are several methods for determining R:P that do not rely on intractable flux parameters; two or more of these methods should be cross-referenced during the pilot period. Note that these methods reflect "effective" R:P, wherein the compensatory/depensatory effects of gas exchange are included.

1. DO vs. CO_2 curves:

CO_2 can be calculated (alkalinity must be known), measured directly using a sensor (OxyGuard or other) or titration, or measured indirectly using pH as a locally validated proxy. This method appears to work well in Florida estuaries.

2. δ^{18}O of dissolved oxygen.

Respiration enriches δ^{18}O, photosynthesis depletes δ^{18}O, and equilibrium is near 24.5 per mil. This method provides a natural standard (24.5 per mil).

3. Nonconservative behavior of DIC (or phosphorus, see Gordon et al. 1996)

When compared to conservative water and salt budgets, nonconservative DIC behavior indicates net production (decreasing DIC) or net consumption of organic matter (increasing DIC).

4. δ^{13}C of DIC.

Respiration depletes δ^{13}C and photosynthesis enriches δ^{13}C. Depletion or enrichment is determined via comparisons with source waters.

E. Classification of Study Areas

Classification frameworks are logical approaches to organizing and grouping information about ecological systems. Although coastal areas are diverse, complex and heavily utilized, they may show similar patterns that can be useful for classifying coastal systems. This monitoring framework will incorporate the collection and analyses of data needed to evaluate classification approaches or combination that will best meet state needs.

In the mid-1990s, the National Interagency Technical Team (NITT) was formed to develop a common framework of ecological regions for the nation. Ecoregions are areas with generally similar ecosystems and with similar types, qualities, and quantities of environmental resources. Variables such as vegetation, animal life, geology, soils, water quality, climate, and human land use, as well as other living and non-living ecosystem components were used to delineate ecoregion boundaries. These general purpose regions are critical for structuring and implementing ecosystem management strategies across federal agencies, state agencies, and non-government organizations that are responsible for different types of resources within the same geographical areas (Omernik and others, 2000). At level III, the continental United States contains 104 ecoregions and the conterminous United States has 84 ecoregions (United States Environmental Protection Agency [USEPA], 2003). Level IV is a further subdivision of level III ecoregions. Explanations of the methods used to define the USEPA's ecoregions are given in Omernik (1995), Omernik and others (2000), Griffith and others (1994), and Gallant and others (1989).

The NOAA Coastal and Marine Ecological Classification Standard (CMECS) provides a framework to classify coastal and marine waters and potential reference areas throughout the region. Broadly, the framework applies to nearshore coastal waters and estuarine systems. CMECS was created to provide ecological classifications; however where possible, nutrient classifications that result from this study should remain compatible with this system for both site classification and to facilitate mapping.

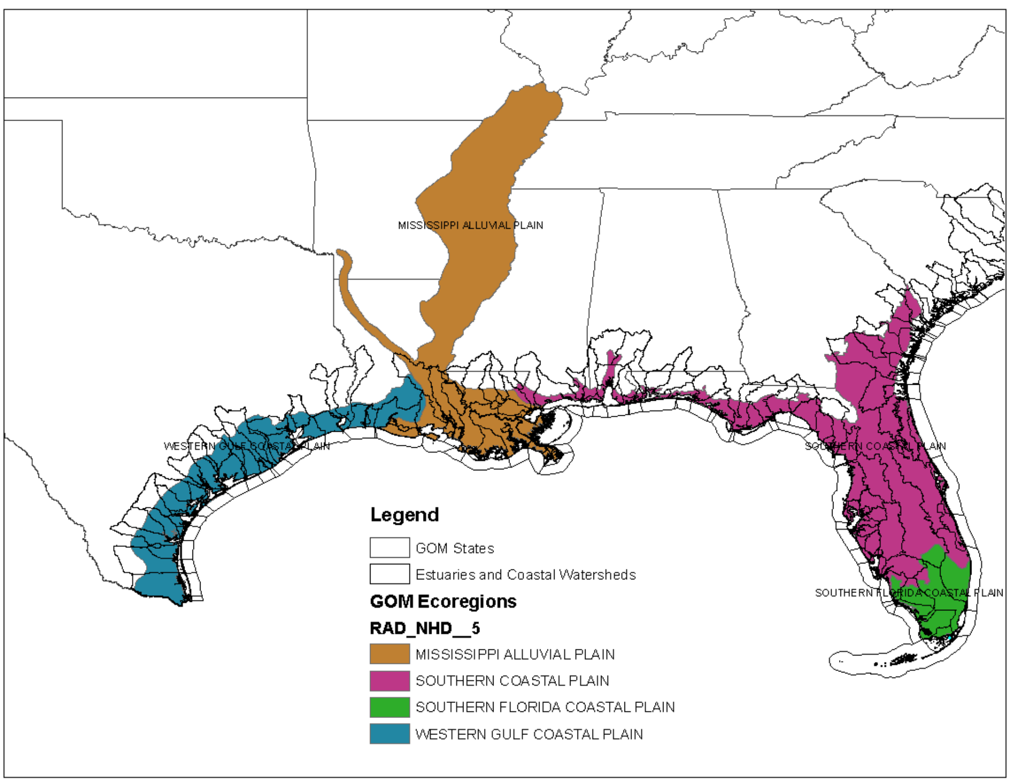
The NOAA Coastal and Marine Ecological Classification Standard (CMECS) provides a framework to classify coastal and marine waters and potential reference areas throughout the region. Broadly, the framework applies to nearshore coastal waters and estuarine systems. Nearshore coastal waters may be truly marine in character (> 30 psu throughout the year) or freshwater influenced (marine waters are periodically diluted by freshwater flow that originates from land) and extend from the land margin to approximately the 30 m depth contour. CMECS was created to provide ecological classifications; however where possible, nutrient classifications that result from this study should remain compatible with this system.

Freshwater-influenced systems are waters that have no distinctly enclosing morphology, yet receive a significant amount of freshwater input from land during at least part of the year. In such cases, an unenclosed marine water column may be influenced by freshwater in the form of an active river plume, an overlying freshwater lens or a ground water seep discharge. The freshwater-influenced system can occur in nearshore, neritic or oceanic depths, provided the region is influenced by freshwater input that reduces salinity to below 30 psu.

Estuarine systems consist of tidal habitats and adjacent tidal wetlands that are usually semi-enclosed by land but have open, partly obstructed, or sporadic access to the open ocean, and in which ocean water is at least occasionally diluted by freshwater runoff from the land. The salinity may be periodically increased above that of the open ocean by evaporation. The estuarine system extends between (1) an upstream and landward point to where ocean-derived salts measure less than 0.5 psu during the period of average annual low flow; and (2) an imaginary line closing the mouth of the river, estuary, bay, or sound.

For mapping purposes, the CMECS framework classifies coastal and marine waters by system, subsystem (subtidal, intertidal), cover (colonized or bare), class (e.g., aquatic bed) and subclass. CMECS further classifies these waters ecologically by group, biotope complex and biotope. These ecological units are uniquely associated with a given habitat type which results from a combination of the higher hierarchical levels.

The Land-Ocean Interactions in the Coastal Zone (LOICZ) program has adopted a classification process of geospatial clustering based on a broad spectrum of environmental variables. LOICZ web-based tools have also been developed, WebLOICZ and DISCO, which applications linked to a global typology database. The National Estuarine Eutrophication Assessment (NEEA) effort is in the process of developing a U.S. database that is more detailed than LOICZ that consists of estuary and catchment variables (Bricker et al. 2007).

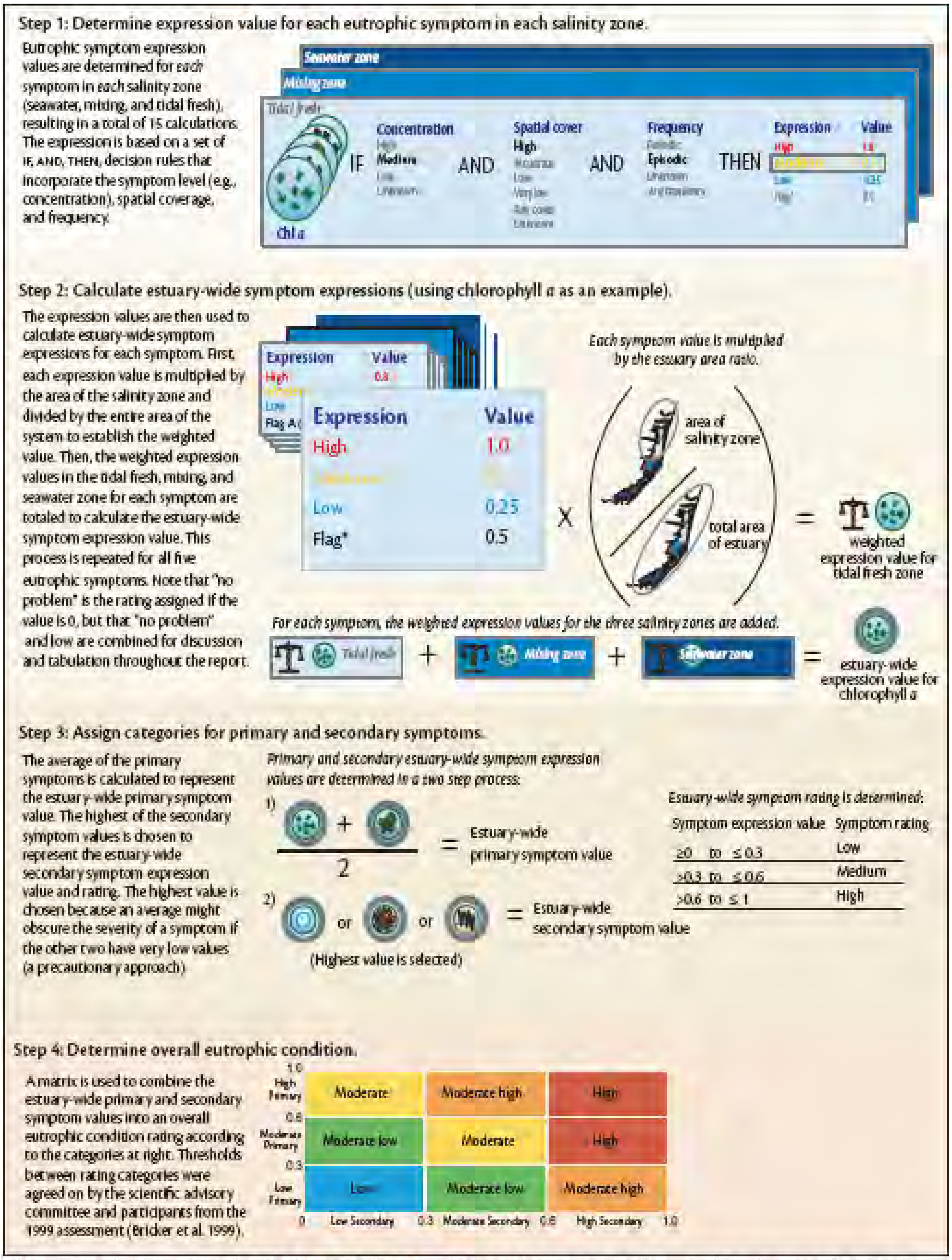


Level III Gulf of Mexico Ecoregions

In addition to classification systems based on shared ecosystem characteristics, classification can be based on commonalities in sensitivity to stressors and the physical characteristics affecting that sensitivity. This type of classification may result in groupings of systems most similar in responses, critical thresholds, and potential for management approaches. The NRC (2000) publication summarized approximately a dozen factors deemed important to characterize the susceptibility of estuaries to nutrient loading.

1. System dilution and water residence time or flushing rate
2. Ratio of nutrient load per unit area of estuary
3. Vertical mixing and stratification
4. Algal biomass (e.g., chlorophyll *a*, and chlorophyll *a* corrected for nonchlorophyll *a* light attenuation over seagrass/SAV beds and macroalgal biomass as AFDW)
5. Wave exposure (especially relevant to seagrass potential habitat)
6. Depth distribution (bathymetry and hypsographic profiles)
7. Ratio of side embayment (s) volume to open estuary volume or other measures of embayment influence on flushing.

The NEEA utilized classification based on susceptibility, an estimate of the natural tendency to retain or flush nutrients. The NEEA used physical and hydrologic data to separately define dilution and flushing rating for an index of susceptibility. (Bricker et al. 2007)



*Flags are used to identify components for which data were inadequate or unknown. In these cases, assumptions were made based on conservative estimates that unknown spatial coverage is at least 10% of a zone, frequency at least episodic, and duration at least days.

Bricker, S., B. Longstaff, W. Dennison, A. Jones, K. Boicourt, C. Wicks, and J. Woerner. 2007. Effects of Nutrient Enrichment in the Nation's Estuaries: A Decade of Change. NOAA Coastal Ocean Program Decision Analysis Series No. 26. National Centers for Coastal Ocean Science, Silver Spring, MD 322 pp.

F. Sampling Design

The following sampling design will be applied at study sites to develop a working blueprint for sampling to assess nutrient related water quality conditions and trends and effects on biota in Gulf of Mexico coastal waters and their tributaries. Resource components included in the design are estuaries, near shore marine waters (out to about 3 nautical miles), and adjacent offshore waters out to beyond the influence of coastal input where background conditions exist (out to approximately the 30-m isobath). The design also monitors rivers that flow directly into estuaries, coastal marine waters, and rivers draining upland watersheds that are tributary to these waters, because fluxes of nutrients from these rivers are typically the dominant source of nutrients to coastal waters. Atmospheric deposition near the coasts will be included as will ground water in those areas where aquifers discharge directly to coastal waters. Data from the proposed design will make a significant contribution to local evaluation of the effectiveness of management actions, identification of problems, and other objectives as described in this section. In combination with studies in other locations around the Gulf that follow the same core design, data will also provide information toward a Gulf-wide evaluation of the minimum necessary monitoring necessary to develop coastal nutrient criteria.

Data from each resource component could stand alone and would be valuable for that reason alone. However, the design was constructed as a whole so that its value is greater than the sum of its parts. Several features of this integrated design are worth noting. First, the design recognizes that the environmental components are linked by the hydrologic cycle through which water is constantly moving. The quality of coastal waters as related to nutrients is determined in large part by the sources of tributary waters that carry materials including sediment, naturally-occurring and anthropogenic nutrients, and many types of organisms that can process/alter in situ nutrients. Second, the monitoring plan has a common set of analyses that will further strengthen the linkages established by the flow of water among the resource components. Thus, the sampling design will provide insights into the onshore sources of water and nutrients, and to their effect on the coastal resources. Third several different methods of data collection are used in the design, each of which is appropriate for the scale of the specific resource component and monitoring purpose.

I. Resources to monitor

The two primary resource compartments to be monitored are estuaries and near coastal oceans. Offshore waters must also be monitored to the extent necessary to provide end points for coastal hydrodynamic models and nutrient fate and flux models. In some cases, understanding nutrient fate may necessitate nutrient and effect monitoring beyond state waters in order to understand the mechanisms sufficiently to identify the critical points to monitor as part of reduced monitoring designs. Coastal rivers, groundwater and atmospheric deposition will also be monitored as “fluxes” rather than resource compartments.

Many of the measurements are made in all resource components but some measurements are resource specific (*e.g.* it makes no sense to measure dissolved oxygen in atmospheric deposition). This is an important aspect of the overall design because this continuity of measurements will allow linkages among the resources. For example every constituent group measured in rivers is also measured in estuaries and offshore. Where appropriate, ground water and atmospheric deposition will also be monitored for the same group of constituents. Thus, for example, it will be possible to identify at a broad scale the inland sources of nutrients and determine loads of nutrients to estuaries and the coastal ocean. Similarly, many of the constituents measured in estuaries will also be monitored in the near shore oceans to strengthen our understanding of the linkages among these marine resource components. Gathering information to allow creation of flux and load models is highly desirable.

II. General approaches to site selection

This design includes inventories and remote sensing, targeted monitoring and probability-based surveys, and intensive monitoring. An inventory is a census of the entire resource at a particular point in time, such as that available from remote sensing programs. To be useful in a monitoring program, the inventory must be available in near-real time or within a few months. At the opposite end of the spectrum of spatial coverage, intensive monitoring is characterized as site-specific and is typified by either repeated measurements at a single site or the use of a large number of sites in a relatively small area.

III. Data collection approaches

There are three basic approaches for data collection: remote sensing, continuous sampling, and discrete sampling.

- **Remote Sensing** platforms include *non in situ* measurement methods such as atmospheric-based (*i.e.*: aircraft deployed) measurements and space-based (satellite deployed) measurements. The great advantage of remote sensing is that this tool allows for an inventory of the entire resource at a particular point in time. Remote sensing is typically applied for continuous observation and measurement of physical variables such as water temperature, wind speed and direction, current speed, wave height, sea level, and sea ice distribution. With a few exceptions, such as ocean color and chlorophyll concentrations, most chemical and biological measurements are not amenable to remote sensing at this time, although improvements in sensing technology may allow these measurements in the future.

- **Continuous Sampling** results in multiple, evenly spaced *in situ* measurements over a time interval. This type of data is normally collected electronically (sensors with data logger) and may or may not be available in real time through cell phone or satellite communications. *In situ* sensors can monitor temperature, pH, dissolved oxygen, specific conductance, light spectra, currents (direction and speed), and waves. The drawbacks to continuous sampling are that sensors and auto analyzers must be visited periodically for maintenance and calibration. Parameters that cannot currently be measured with continuous sampling, but for which sensors are under development, include: plankton and many macro and micro nutrients.

- **Discrete Sampling** is the collection of individual samples, usually by an observer, which result in measurements with a larger sample interval than for continuous sampling (for example, monthly). Discrete samples may also be collected with an unequal sample interval. The great advantage of discrete sampling is that the sample can be analyzed for a great range of chemical characteristics. The collection of discrete data can provide spatial patterns of variables. If collected at the same points, over the long-term (several years) the discrete data become an invaluable tool for identifying water quality trends and variability and developing measures for addressing ecosystem changes.

IV. Summary of monitoring design

The condition of the resource will be assessed for estuaries and the near shore marine environment out to approximately the 30-m isobath. Each of these resources is also assessed using targeted sampling and remote sensing. Rivers will be monitored to determine the flow of water and loads of nutrients into estuaries. Because estuaries are the connection between fresh water flowing from land to the oceans, each estuary will also be monitored along a salinity gradient to gain insights into the transport of water and waterborne constituents. In some places, where ground water flows directly into coastal waters, that resource will be monitored. Atmospheric deposition, which can be a significant source of some nutrients will be monitored in the coastal zone. Finally, recreational beaches will be monitored for HAB related issues.

V. *Sampling design for estuaries*

In order to address the stated goals of the monitoring plan, targeted and probabilistic site selection may be used, as well as continuous and discrete sampling. Changes and trends over time can be detected by repeated collection of data within the individual estuaries and by re-visiting randomly-selected sites used to determine conditions of estuaries. Each of the purposes and the approach taken will be described briefly. The core study time period will be establish to ensure that variability is captured to improve ecosystem understanding. It is recommended that studies be a minimum of annual and a reduced study design will be developed for studies over 2 to 3 years to capture inter-annual variability.

Conditions Regionally: Sites may be selected probabilistically from among all estuaries, with approximately 50 total sites selected for the region. Thus, it would be possible to make statistically valid statements about the conditions of estuaries in the Gulf region compared to other regions. Comparisons between and among regions would be possible.

Conditions in Individual Estuaries: In general, the assessment of overall conditions for individual estuaries or portions thereof can employ a total of approximately 50 sites per estuary, selected using a probability-based method that will provide geographic coverage. Note that sampling sites for the estuaries extend to the head of tide in the major tributaries. The selected sites could be sampled monthly for water column nutrients and physical characteristics (conductivity, pH, dissolved oxygen, temperature). The intensive sampling of each estuary would provide managers with a statistically valid picture of overall conditions within the estuary.

Transport through Estuaries: This component of estuarine monitoring will provide data to help understand the timing and flow paths for water and waterborne constituents moving from major riverine inputs through the estuary and seaward into the near shore environment. A targeted approach based on professional judgment will select a maximum of 15 sites (fewer in the smallest estuaries) located along the major salinity gradient of each of the estuaries. These sites will be sampled monthly for water column nutrients and physical characteristics (conductivity, pH, dissolved oxygen, temperature). For those locations where the average water depth is greater than 5 meters, samples will be collected at the top and bottom of the water column. Properly selected transects can provide information on: (1) processing of nutrients within the estuary, (2) export of nutrients to the coastal zone, (3) nutrient and suspended sediment loads from rivers and streams, and (4) residence time within the estuary.

Short-term Variability: Sites in each estuary that are used for the transport component can also be instrumented for continuous monitoring of constituents such as depth, temperature, salinity, dissolved oxygen, pH, and turbidity. Other possible constituents such as chlorophyll and other plant pigments and nutrients may also be included as technology improves and these measurements become more feasible. Specific information this monitoring could provide includes (1) timing and duration of conditions like hypoxia, (2) timing and duration of freshwater pulses, and (3) effects of hurricanes and other extreme events on estuarine water quality.

VI. Sampling design for near-shore coastal waters

Three different monitoring approaches will be used to address conditions in near shore waters. First, a probability based survey will allow an assessment of the resource across the region. This is similar in design to that for the condition assessment in estuaries except that an appropriate number of sites would be chosen for the coastal segment. Previous national designs have used a total of 50 sites for coastal waters. These sites would be sampled once per year or at additional frequency as required for physical conditions or water column nutrient chemistry. This sampling effort will be based on discrete samples collected from research vessels. A second, targeted, approach will also be used to assess near shore conditions. These sites could be located at fixed locations, where appropriate such as small islands. The frequency of data collection and the constituents to be monitored will be determined by the needs of the individual study design. The third approach for near shore waters is the use of remote sensing which will allow the entire resource to be assessed for those constituents (e.g. surface water chlorophyll) that can be monitored remotely.

VII. Sampling design for ground water

Determining the significance of ground water to coastal water quality involves the characterization of local and regional hydrogeologic settings, hydraulic relationships between surface waters and ground water, and natural and manmade nutrient sources. Because this effort is regional in scale, the focus is on ground water resources that could be termed “major aquifers,” in relation to the potential impact on coastal resources. More information about ground water monitoring is included in Appendix E.

Ground water monitoring is important to the design but has less detail and specificity when compared to other resources. The primary reason for the difference in treatment within the overall design is that the relative impact of ground water on coastal waters will vary by location. In some areas, ground water monitoring will be critical to understanding loads of constituents to coastal waters. In other areas, ground water will be relatively insignificant when compared to surface water; however, ground water must always be considered in the overall budget of sources of nutrients.

Challenges in Designing a Ground Water Monitoring Network for Coastal Water Quality Contributions

Designing a regional monitoring network component for ground water is complex. The challenges include:

- Spatial variability and the significance of site-specific problems make it difficult to develop a generalized approach.
- Ground water aquifers have “response times” and “delivery rates” that extend over longer time periods than surface waters, extending the duration of nutrients-discharge impacts in comparison to similar-scale surface water bodies.
- Effective sampling of ground water is hampered by accessibility and representative-volume problems.
- Solving problems that involve ground water quantity and quality seems to suffer more (than equivalent surface water system-generated problems) from the lack of data, and gathering data once a problem is identified is generally more difficult and expensive.
- Historically, ground water problems predominantly revolved around quantity and hydraulics issues; thus, in general, the historic database of ground water quality information still lags that of surface water quality.

Basic Design Approach for Ground Water

With these challenges in mind, a set of recommendations has been developed to provide the basic design approach for the ground water resource component. Overall, the design approach should follow a logical, stepwise process that relies upon oversight by a nationwide group of ground water experts, and local implementation by ground water experts in each defined local ground water area.

The following overall guiding principles are recommended:

- The local ground water experts should reach a consensus on appropriate levels of monitoring in each local area to be monitored. In addition, they should provide input to the national group of experts on the areas appropriate to local studies, and on the national framework for ground water monitoring.
- Existing data collection programs should be utilized to the extent possible. Within the U.S., the National Water-Quality Assessment (NAWQA) efforts undertaken by the USGS serve as one "model" program, as well as that agency's State Water Office implemented efforts toward long-term monitoring of ground water levels and ground water quality, tied together through national data portals on the Internet. The hallmark of these efforts is regional monitoring coverage that includes spatially distributed monitoring at appropriate frequencies for providing important ground water hydraulic, hydrologic, and water quality information.
- Overlay mapping should be conducted to identify the relative significance of ground water to coastal water quality, using maps of surface water hydrologic networks, hydrogeologic formations/aquifers, land use and population density, ground water quality, and existing coastal water quality problems related to ground water. This will help to focus the efforts of local ground water experts by identifying the coastal areas where ground water discharge and ground water-borne contamination are known to be, or are likely to be, the predominant factors in coastal water quality.
- The most pressing ground water related problems should be identified, and a list of ground water parameters to be measured should be developed, based on the identified problems. Most of the parameters will be monitored through direct sampling of ground water in drilled wells; however, the design should also incorporate innovative methods, including remote sensing and imagery. For example, the use of satellite imagery to identify temperature changes and contrasts in coastal waters could be used to indicate the relative magnitude and significance of ground water discharges.

VIII. Sampling design for atmospheric deposition

The focus of the atmospheric deposition component is the deposition that falls directly on estuaries and coastal waters and the loads of substances that are present in wet and dry deposition. This monitoring of direct deposition is distinguished from the water and associated constituents that enter coastal waters through storm water runoff. At present very little is known about the importance of atmospheric loadings to coastal waters (Valigura and others, 2000); thus, the monitoring proposed here will make a significant contribution to our current understanding.

This effort will address the atmospheric deposition by monitoring wet and dry atmospheric deposition near the mouths of coastal HUC 6 outflows (Hydrologic Unit Code, sixth level). Actual sites will be selected by resource management agencies and other technical experts. This will provide data for estimates of direct atmospheric deposition to coastal waters. Although these sites are likely to be land based, if they are located near the coast, they will capture dry deposition that is representative of the area to be monitored and wet deposition from widespread storms. These sites will not capture the effects of localized events but this is consistent with the overall design which is focused on a larger (regional) spatial scale.

At present, the primary atmospheric deposition monitoring program is the National Atmospheric Deposition Program (NADP). The NADP is a cooperative that includes federal and state agencies, tribes, universities, industry, and non governmental organizations.

G. Quality Assurance Project Plan

The Quality Assurance Project Plan (QAPP) should document the planning, implementation, and assessment procedures of, and how specific quality assurance (QA) and quality control (QC) activities will be applied during a particular project. It is important to understand the terminology of quality assurance and quality control in order to develop a QAPP. Key definitions include:

Precision -- the degree of agreement among repeated measurements of the same characteristic. It may be determined by calculating the standard deviation, or relative percent difference, among samples taken from the same place at the same time.

Accuracy -- measures how close your results are to a true or expected value and can be determined by comparing your analysis of a standard or reference sample to its actual value.

Representativeness -- the extent to which measurements actually represent the true environmental condition or population at the time a sample was collected.

Completeness -- the comparison between the amount of valid, or usable, data you originally planned to collect, versus how much you collected.

Comparability -- the extent to which data can be compared between sample locations or periods of time within a project, or between projects.

A. Steps to Developing a QAPP

Step 1: Establish a QAPP team
Step 2: Determine the goals and objectives of your project
Step 3: Collect background information
Step 4: Refine your project
Step 5: Design your projects sampling, analytical and data requirements
Step 6: Develop an implementation plan
Step 7: Draft your standard operating procedures (SOPs) and QAPP
Step 8: Solicit feedback on your draft SOPs and QAPP
Step 9: Revise your QAPP & submit it for final approval
Step 10: Begin your monitoring project
Step 11: Evaluate and refine your QAPP

While most QA Project Plans will describe project- or task-specific activities, there may be occasions when a generic QA Project Plan may be more appropriate. A generic QA Project Plan addresses the general, common activities of a program that are to be conducted at multiple locations or over a long period of time; for example, it may be useful for a large monitoring program that uses the same methodology at different locations. A generic QA Project Plan describes, in a single document, the information that is not site or time-specific but applies throughout the program. Application-specific information is then added to the approved QA Project Plan as that information becomes known or completely defined. A generic QA Project Plan shall be reviewed periodically to ensure that its content continues to be valid and applicable to the program over time.

The level of detail of the QA Project Plan should be based on a graded approach so that the level of detail in each QA Project Plan will vary according to the nature of the work being performed and the intended use of the data. As a result, an acceptable QA Project Plan for some environmental data operations may require a qualitative discussion of the experimental process and its objectives while others may require extensive documentation to adequately describe a complex environmental program.

B. Content Requirements

The QA Project Plan is a formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. The QA Project Plan must provide sufficient detail to demonstrate that:

- the project technical and quality objectives are identified and agreed upon;
- the intended measurements, data generation, or data acquisition methods are appropriate for achieving project objectives;
- assessment procedures are sufficient for confirming that data of the type and quality needed and expected are obtained; and
- any limitations on the use of the data can be identified and documented.

Most environmental data operations require the coordinated efforts of many individuals, including managers, engineers, scientists, statisticians, and others. The QA Project Plan must integrate the contributions and requirements of everyone involved into a clear, concise statement of what is to be accomplished, how it will be done, and by whom. It must provide understandable instructions to those who must implement the QA Project Plan, such as the field sampling team, the analytical laboratory, modelers, and the data reviewers. In all aspects of the QA Project Plan, the use of national consensus standards and practices are encouraged.

In order to be effective, the QA Project Plan must specify the level or degree of QA and QC activities needed for the particular environmental data operations. Because this will vary according to the purpose and type of work being done, EPA believes that the graded approach should be used in planning the work. This means that the QA and QC activities applied to a project will be commensurate with:

- the purpose of the environmental data operation (e.g., enforcement, research and development, rulemaking),
- the type of work to be done (e.g., pollutant monitoring, site characterization, risk characterization, bench level proof of concept experiments), and
- the intended use of the results (e.g., compliance determination, selection of remedial technology, development of environmental regulation).

The QA Project Plan shall be composed of standardized, recognizable elements covering the entire project from planning, through implementation, to assessment. These elements are presented in that order and have been arranged for convenience into four general groups. The four groups of elements and their intent are summarized as follows:

Project Management - The elements in this group address the basic area of project management, including the project history and objectives, roles and responsibilities of the participants, etc. These elements ensure that the project has a defined goal, that the participants understand the goal and the approach to be used, and that the planning outputs have been documented.

Data Generation and Acquisition - The elements in this group address all aspects of project design and implementation. Implementation of these elements ensure that appropriate methods for sampling, measurement and analysis, data collection or generation, data handling, and QC activities are employed and are properly documented.

Assessment and Oversight - The elements in this group address the activities for assessing the effectiveness of the implementation of the project and associated QA and QC activities. The purpose of assessment is to ensure that the QA Project Plan is implemented as prescribed.

Data Validation and Usability - The elements in this group address the QA activities that occur after the data collection or generation phase of the project is completed. Implementation of these elements ensures that the data conform to the specified criteria, thus achieving the project objectives.

All applicable elements, including the content and level of detail under each element, defined by the organization(s) sponsoring the work must be addressed in the QA Project Plan. If an element is not applicable, state this in the QA Project Plan. Documentation, such as an approved Work Plan, Standard Operating Procedures, etc., may be referenced in response to a particular required QA Project Plan element to reduce the size of the QA Project Plan. Current versions of all referenced documents must be attached to the QA Project Plan itself or be available for routine referencing when needed. The QA Project Plan shall also address related QA planning documentation (e.g., Quality Management Plans) from suppliers of services critical to the technical and quality objectives of the project or task.

H. Human Use Assessment

The human use assessment will not quantify nutrients from human sources, which would be done as part of a Total Maximum Daily Load process. Instead the assessment will concentrate on the magnitude of inputs to the system, dominant transport mechanisms, and dominant chemical composition of nutrient inputs. In addition, data will be collected on human uses of the system that are affected by excess nutrients. The assessment will provide critical data to understand nutrient dynamics and focus on direct measures of nutrient inputs and fluxes.

Human Use Data to Be Collected

Broad land use categories and pathways for nutrient sources
Point sources input

Current & historical:
Hydrography: National Hydrography Dataset, topography, bathometry
Land Use: consistent Gulf-wide categorization scheme or equivalent
Event Mean Concentration (EMC) compilation for region

Active Use: commercial – fisheries + industry
Recreational Use: boating, fishing, swimming, nature watching
Passive Use: aesthetic/spiritual/sense-of-place

Human Use Endpoints

Percent of watershed area within main categories of nutrient sources
Land cover
Percent of area meeting designated uses

I. Watershed Assessment

The fate and transport of nutrients in coastal ecosystems are affected by both aquatic and terrestrial components of the watershed. Information on habitat, including distribution, extent, composition, and connectivity is important to characterize key factors that affect nutrient dynamics and the biological communities that affect nutrient dynamics. In addition, community information is important to characterize fate and associated impacts and defining the habitat and communities of interest will aid in the selection of boundaries for the study design.

Watershed boundaries will be identified using NOAA boundaries for coastal watersheds and key site information. The Meterological and Physical section above provides additional references for watershed data

Watershed Data to be Collected

- Rainfall (nutrient concentration)
- Temperature
- Wind/tides
- Slope
- Hydric soils acreage
- Erodible soils acreage
- Freshwater flow - peak, wet-weather, dry-weather, baseline
- Groundwater flow
- Residence time/flushing rate
- Offshore to inshore: chemical, physical, and biological variables
- Residence time/flushing rate
- Key Species abundance, distribution, and health
    - Shrimp
    - Fish
- Key Communities abundance, distribution, and health
    - Benthic community
    - Macroinvertebrate community
    - Riparian habitat
    - Wetland habitat
    - Submerged aquatic vegetation (SAV) community
    - Shellfish beds
- Harmful Algal Blooms (HAB) occurrence and origination
- Hypoxia occurrence
- Impervious surface area