Delaware Sea Grant Project:
Chemical and biological sensors for the in situ determination of biogeochemical processes (R/ETE-13)

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Project Abstract:

Prior to our development of the solid state gold-amalgam (Au/Hg) voltammetric microelectrode for environmental work (Brendel and Luther, 1995), it was not possible to measure non-gaseous species in freshwater and seawater solutions with microelectrodes because (i) the membrane covered electrodes are not permeable to ions (other than the proton) and (ii) the potentiostats for the application of potential were relegated to only one fixed potential where more than one species may be electroactive. These two features did not allow for the determination of the important redox metals Fe(II) and Mn(II). With our solid state gold/amalgam (Au/Hg) microelectrode, we have now demonstrated the measurement of dissolved oxygen, sulfide, iodide, Fe(II), Mn(II), FeS, Fe(III)species, S_x^{2-} or polysulfides (Luther et al, 1997, 1998a; Theberge and Luther, 1997; Huettel et al, 1998; Taillefert et al, 2000 and 2002; Rozan et al, 2000; Glazer et al 2002) because each redox species, if present, produces a current that can be detected in one potential scan [this is analogous to varying wavelength and monitoring absorbance in UV-VIS spectroscopy]. We have applied the electrode to make *in situ* measurements of these redox species in seasonally anoxic systems such as our local Inland Bays (Ma et al, 2007) and the Chesapeake Bay (Lewis et al, 2007) as well as the permanently anoxic Black Sea and the hydrothermal vents. With Sea Grant funding, we have now shown that they can be used as sensors for longer term *in situ* chemical monitoring for observatories because these solid-state electrodes are robust and have not biofouled to date (Moore et al, 2007, 2008).

In response to Ocean Observatory needs (see for example National Research Council, 2003; 2004), our Sea Grant program began the Delaware Bay Observing System (DBOS; http://www.udel.edu/dbos/), which was setup to measure only routine physical and meteorological parameters (no chemical or biological) from a lighthouse in lower Delaware Bay. In the present Sea Grant funding cycle, we have placed our electrodes, a CTD, an *in situ* electrochemical analyzer (ISEA developed with NSF funds) along with a fluormeter/nephelometer and PAR (photosynthetically active irradiance) sensor on a mooring at the junction of Delaware Bay with the Atlantic Ocean with success (Moore et al, 2008). Data acquisition, storage and transmission occurred via radio communication. This deployment provided the first chemical data set **with sensors that give biological proxy data** sets for the DBOS. Here, we propose to integrate our present sensors with an *in situ* version of a true biological sensor known as the **F**luorescence **I**nduction and **Re**laxation System (**FIRe**) from Satlantic (Gorbunov and Falkowski 2004). This instrument measures the quantum efficiency of oxygenic photosynthesis at photosystem center II, which is the center for O_2 production in plants/phytoplankton and is the primary gateway for solar energy to pass to the broader coastal ecosystem. It accomplishes the measurement through variable fluorescence of the photosystem center II, and thus is an indicator of how efficient a photosynthetic organism can utilize light energy to fix inorganic carbon and produce O_2. We propose to use our integrated sensor package

at our present lower Delaware Bay location for natural phytoplanktonic organisms. We will be able to assess the health of the ecosystem at the planktonic level and to assess photo-inhibition of the plankton during the summer.

This renewal proposal addresses two of the strategic plans identified by the University of Delaware Sea Grant program: (i) Expand the scientific and policy basis critical to sound ecosystem-based management in the wise use, protection, and restoration of coastal waters, estuaries, and watersheds, and their living marine resources, and (ii) Develop interactive observatories, sensors, autonomous samplers, and predictive models for real-time, continuous, cost-effective monitoring, forecasting, and assessment.