Development of an Autonomous Ammonium Fluorescence Sensor (AAFS) with a View Towards *In-situ* Application

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LONG-TERM GOALS

Our goal is to develop a portable autonomous ammonium sensor. Such a sensor could be deployed for periods of up to a month aboard ships, moorings or drifting buoys or used as a component in lowered or towed oceanographic instrument packages for vertical profiling.

OBJECTIVES

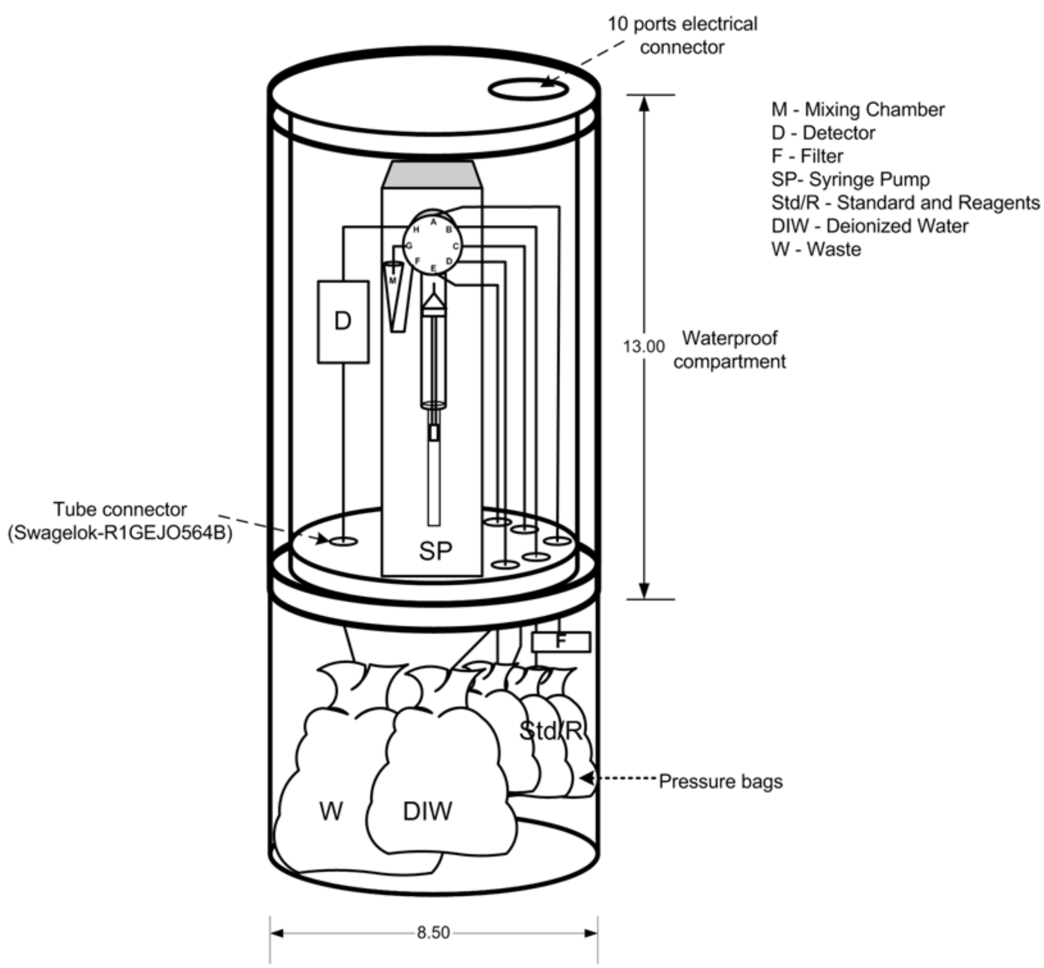
Our technical objective is to develop a robust, relatively simple, inexpensive, low power and compact instrument with a detection limit in the nM range and a sampling frequency of at least 6 samples per hour. Robustness, simplicity, low construction cost, lower power and small size are the practical desiderata for commercial application. Commercialization and the lowered instrument costs that will result are essential to permit wider application throughout the oceanographic community.

APPROACH AND WORK PLAN

Our approach has been to first design, assemble and demonstrate engineering prototypes suitable for benchtop laboratory use, take these aboard ship and once we have achieved the key design objectives test these first in an ongoing sampling program at coastal sewage outfalls along the east coast of Florida and second underwater by taking advantage of a “permanent” large mooring associated with the NOAA underwater habitat in the Florida Keys. Once we have achieved (and verified in the field) all our basic design objectives we will then concentrate upon further miniaturizing, reducing power consumption as much as possible and re-packaging for the possible alternative applications. These last efforts will be facilitated by the large and diverse South Florida user community and the related instrument development activities occurring both at UM/CIMAS and AOML. Key personnel in the initial steps are Drs. Amornthammarong and Dr. Zhang. Dr. Ortner, his graduate student and Mr. Shailer Cummings, while assisting in these initial steps, will take a much larger role with regard to underwater deployment and field testing.

WORK COMPLETED

Since the project started, progress has been rapid and specific advances made with regard to the basic mechanics of instrumentation. First an effective, simple mixing chamber was designed that could be used in conjunction with a syringe pump for flow analysis. Second a new design of fluidic system was developed incorporating this mixing chamber, the Autonomous Batch Analyzer (ABA) system, and the ABA was repeatedly tested in the field (on a ship, at a coastal inlet, etc.). Both have been described in the peer-reviewed literature (Amornthammarong et al, 2010 and 2011). Highlights of the results obtained are presented below. Building upon these advances a submersible, battery-powered system has been designed (see figure below) and is now under construction. The electrical port provides access to data logger, communication and battery modules. These will be either self-contained and submersible OR incorporated into larger integrated buoy or moored systems for longer deployment periods or to take advantage of pre-existing data communication channels.



RESULTS

A simple, effective mixing chamber used in conjunction with a syringe pump for flow analysis was developed and thoroughly evaluated in the laboratory. It was constructed using a conventional 5 ml pipette tip and its performance compared with a widely-used mixing coil. The results obtained demonstrated that the standard mixing coil does not rapidly and completely mix solutions. Utilizing a configuration that reversed solution positions in the chamber with each mixing cycle, the proposed mixing chamber was able to achieve complete mixing in a significantly shorter time than the mixing coil. The influence of injected sample volume on absorbance signals was then evaluated by calculating an $S_{1/2}$ value for the system. As tested with a minimal rinse, the system has no discernable carryover. Testing this new approach in our previously described silicate measurement system resulted in a more than two fold improvement in sensitivity (see Amornthammarong et al, 2010).

An autonomous batch analyzer (ABA) was then developed for the measurement of ammonium in natural waters. The system combined previously described batch analysis and continuous flow analysis methods and our new mixing chamber (see Amornthammarong et al, 2011). With its simpler design, the ABA system is robust, flexible, inexpensive, and requires minimal maintenance. The sampling frequency is ca. 8/hr and the potential limit of detection ca 1 nM which is comparable to the most sensitive flow through or batch analysis methods previously described and within the design specifications we had set for our project. In addition, the system produces a calibration curve by auto-dilution from a single ammonium stock standard solution with the same accuracy as traditional manual calibration methods. This last aspect is particularly important for extended (one month or longer) *in-situ* deployments.

Representative results obtained during the field tests are given below. Figure 1 plots underway measurements of ammonium in the surface seawater in South Florida coastal waters, including Florida Bay, Florida Key and Southwest Florida shelf waters taken aboard a cruise of the UNOLS vessel, RV/F.G. Walton Smith. Concentrations were elevated at several near shore locations near freshwater outflows from the Big Cypress/Southern Everglades. The shipboard system was remotely controlled and monitored from Miami over the Internet without any operating technician on board. It was then deployed at shore-locations. Figure 2 shows the ammonium concentrations in Lake Mabel (Port Everglades, Fort Lauderdale, FL) during May 17-20, 2011. The results clearly show a cycle with ca. 24-25 hr periodicity. Figure 3 shows the ammonium concentrations in the Port Everglades inlet from June 30 – July 6, 2011. There were two ammonium maxima around 4 am and 4 pm every day from 1-3 July. The ammonium cycles closely match the tidal cycles in the inlet with outflow water carrying high ammonium concentration. The ammonium concentrations were low during holidays (3-4 July) and a heavy rainfall day (5 July). The data were much more variable than those from Lake Mabel. In both cases the tested systems were self-contained and operated autonomously.

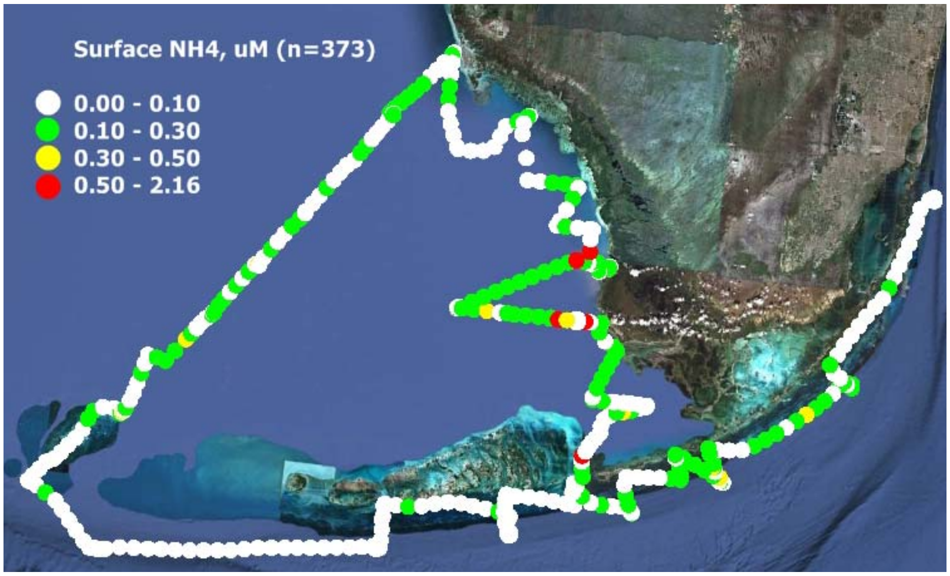


Figure 1. Surface ammonium concentrations in Florida Bay and vicinity during June 7-11, 2011.

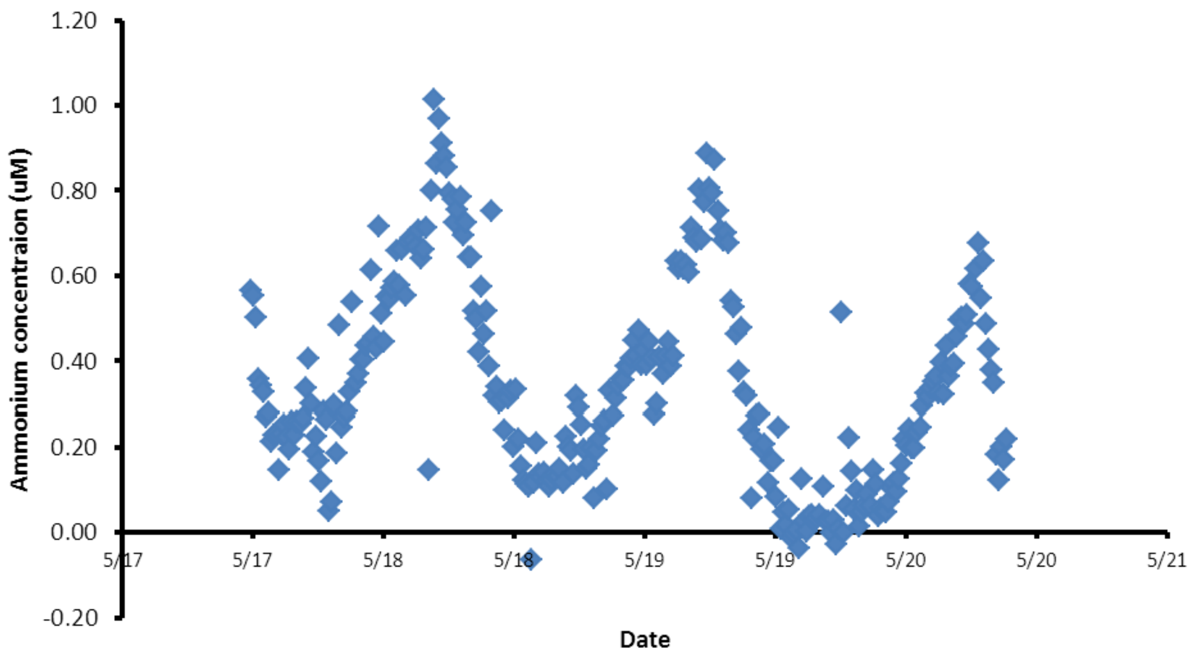


Figure 2. Ammonium concentrations in Lake Mabel (near Florida Atlantic University at Port Everglades, Fort Lauderdale, FL) during May 17-20, 2011.

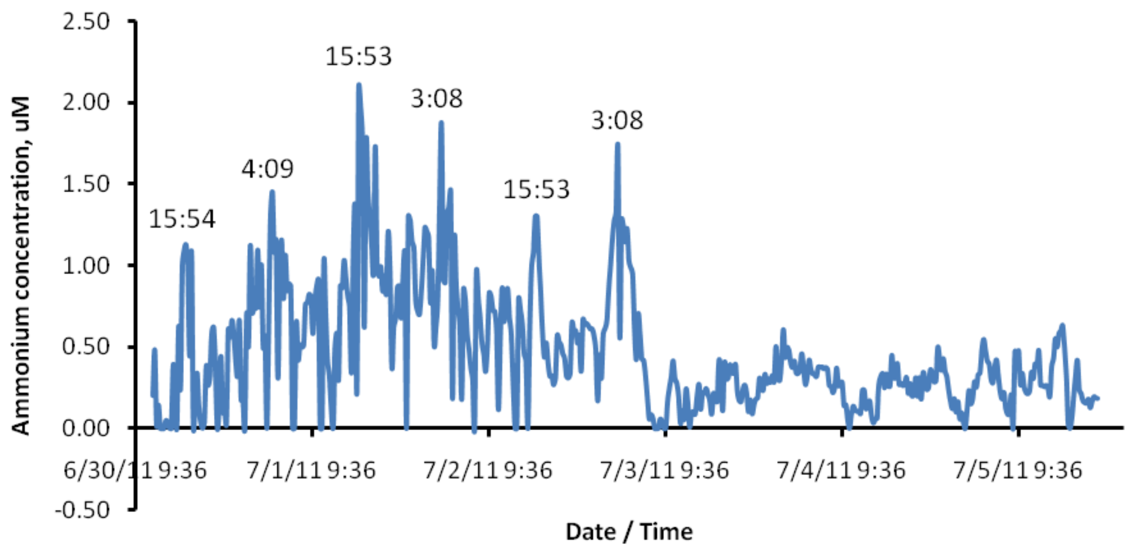


Figure 3. Ammonium concentrations at Port Everglades inlet, Fort Lauderdale, FL from 6/30/11 to 7/6/11.

IMPACT AND APPLICATIONS

Economic Development

The sensor system being developed will have broad applicability as a research tool in biological oceanography but more significant with respect to economic development is its wider market potential for regulatory-required monitoring of ammonium. Moreover, the basic design we have pioneered through the ABA system can be adapted to automating other wet chemical reactions such as nitrate, nitrite and phosphate, etc. extending its commercialization potential.

Quality of Life

Given the central ecological significance of ammonium in coastal and oceanic ecosystems a sensor system permitting long-term and near real-time cost effective measurements will be of significant assistance with regard to ecosystem based management of coastal living marine resources.

Science Education and Communication

With respect to science education the primary relevance will be incorporation of the system (and the measurements it permits) in graduate theses and dissertations within the marine science community. Moreover data streams from contexts of local political significance (e.g. documenting the extent of pollution associated with individual point sources like sewage outflows or groundwater springs could be useful for public outreach and education.

When the development and testing is complete we will be able to deploy such an instrument to monitor in situ ammonium in the coastal and ocean water column to study the variable influx of this rapidly assimilated nutrient that is associated with migration of zooplankton populations in benthic communities (including coral reefs), zooplankton and mesopelagic fish vertical migration, grazing by schooling herbivorous fishes and intermittent physical processes such as breaking internal waves, wind-mixing etc.

TRANSITIONS

Economic Development

Contacts have already been established (and interest expressed) by commercial instrument manufacturers.

Quality of Life

The instrument has already been used in the Florida Area Coastal Environment (a federal/state/private industry partnership) to monitor surface concentrations of ammonium in the coastal waters of the Florida Keys and south-eastern coastal waters with respect to point sources like inlets adjacent to population centers and sewage outfalls.

REFERENCES

Amornthammarong, N. and Zhang, J.-Z. (2008). Shipboard Fluorometric Flow Analyzer for High-Resolution Underway Measurement of Ammonium in Seawater. *Anal. Chem.* 80, 1019-1026.

PUBLICATIONS

Amornthammarong, N.; Ortner, P.B. and J.-Z. Zhang (2010). A Simple, Effective Mixing Chamber Used in Conjunction with a Syringe Pump for Flow Analysis. *Talanta.* 81, 1472-1476.

Amornthammarong, N.; Zhang, J.-Z. and P.B. Ortner (2011). An Autonomous Batch Analyzer for the Determination of Trace Ammonium in Natural Waters Using Fluorometric Detection. *Anal. Methods.* 3, 1501-1506.

PATENTS

The University of Miami Patent and Copyright Committee has accepted the AAFS (Case Number UMJ-178) and is proceeding with test marketing to determine commercial interest.

Should the submersible system is successfully tested; another patent application will be filed by the University of Miami Patent and Copyright Committee.

OUTREACH MATERIALS

This work was highlighted in an internal newsletter of Atlantic Oceanographic and Meteorological Laboratory: AOML Keynotes, May-June 2011, Vol. 15, No. 3, Page 6 as in the following link.

www.aoml.noaa.gov/keynotes/PDF-Files/May-June11.pdf