Title

SEN 2: Scaleable Nitrate Sensors for Soil and Aquatic Observation Applications

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Scaleable Nitrate Sensors for Soil and Aquatic Observation Applications

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Introduction: Sensor fabrication in an environmentally relevant form factor

Applying nitrate as fertilizer in agriculture: what is the assimilative capacity of this heterogeneous soil-plant domain?

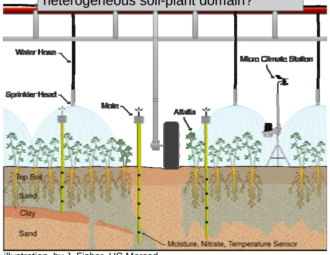
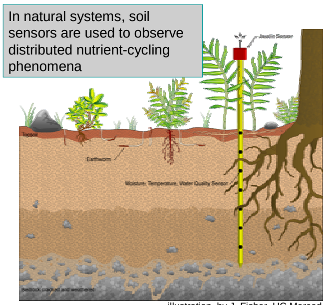


illustration by J. Fisher, UC Merced

Abstract. Many environmental, agricultural, and ecological water quality problems would be better understood and effectively managed if they could be efficiently and economically observed over time in a spatially distributed manner. Unfortunately, the current selection of commercially available chemical sensors is limited, and those that are available are relatively expensive ($200 to $500 ea.), and are generally not optimally packaged for field deployments. Over the past four years, the CENS Sensor group has directed substantial efforts at creating sensitive, selective nitrate sensors with modest power requirements and that are amenable to micro-fabrication methods which will allow the production of large numbers of small sensors. This poster highlights the results of these efforts with respect to (1) **potentiometric** and (2) **amperometric** nitrate microsensors. Prototypes of both types of sensors have been successfully tested in the laboratory, using real environmental samples. ***The amperometric version is more sensitive than the potentiometric, while the potentiometric sensor is easier to fabricate and has been tested in situ in both soil and river systems***.

In natural systems, soil sensors are used to observe distributed nutrient-cycling phenomena



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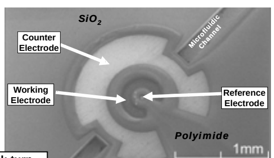
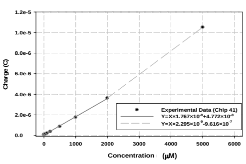
Proposed Solution: Potentiometric and Amperometric Nitrate Microsensors

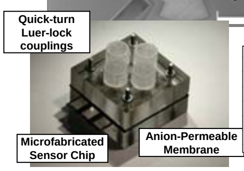
Approach:

- We are creating ***scaleable*** nitrate microsensors suitable for dense, spatially distributed deployment in environmental media.
- In addition to precise and accurate, our sensors must be ***inexpensive*** and have ***low impact*** on the observations (e.g, avoid flow disturbances)
- We have become adept at fabricating nitrate-doped ***potentiometric*** ion selective electrodes (ISEs), and are becoming so with an ***amperometric*** nitrate microsensor

Micromachined Amperometric Nitrate Sensing Chip



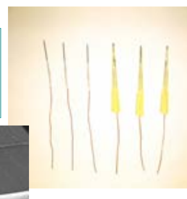


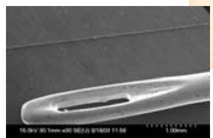


- Sensor performance
  - Broad linear response range (high to trace nitrate concentrations)
  - Detection limit as low as 4 uM (0.25 ppm)
- Sensor selectivity over interfering ions (mixture of 100-µM nitrate and interfering ions--100 µM each of PO_4^{2-}, SO_4^{3-}, F^-, Cl^-).

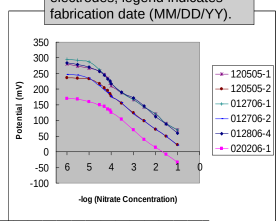
Conducting polymer-based nitrate ISEs

Potentiometric nitrate sensor prototypes: microfiber form (below); protectively packaged for soil deployments.





Calibration curves of $PPy(NO)_3$ electrodes; legend indicates fabrication date (MM/DD/YY).



- Sensor performance (competitive with commercial nitrate sensors
  - Broad linear response range Detection limit as low as 30-80 uM (2-5 ppm)
  - Highly selective over other ions (see below)
- Limitation: short-lived under flow-through conditions (but reconditionable!)

Results: Prototype testing in the lab; scale-up to CENS test beds

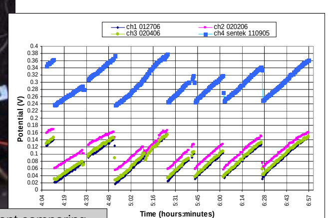
Testing microsensor utility: direct soil and water nitrate probing

- The potentiometric sensors have been tested for conditions ranging from the beaker to the field
- Results below are for:
  - Selectivity testing
  - Flow-through water and soil tests
  - In situ soil testing

Flow through experiment comparing fabrciated sensors with Sentek commercial sensor in soil box.

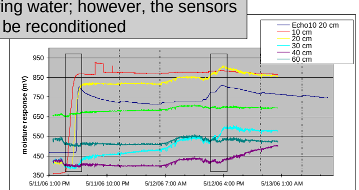
Prototype testing

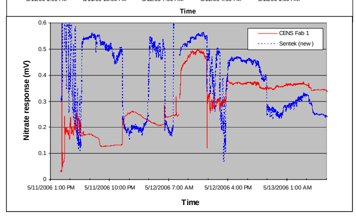
Deionized water test-bed experiment (continuous water flow). $PPy(NO_3)$ sensors (legend indicates sensor fabrication date) and Nitrate ISE (Sentek Ltd)



Deployment at Palmdale test bed

3-day deployment at Palmdale: $PPy(NO_3)$ sensors loose their sensitivity during direct exposure to flowing water; however, the sensors can be reconditioned





Selectivity

Potentiometric selectivity coefficients for PPy (NO_3) electrodes

J^- (interfering anion)	$PPy(NO_3)$ pencil lead -based ISE (K^{pot} values)
HCO_3^-	3.8 x 10^{-3}
Cl^-	1.20 x 10^{-2}
PO_4^{3-}	2.00 x 10^{-4}
Br^-	9.10 x 10^{-2}
NO_2^-	2.22 x 10^{-4}
ClO_4^-	2.93 x 10^{-3}

Future directions

Development of sensors suitable for long-term deployment will require:

- Incorporation of ***conductive polymers*** with longer life cycles
- Incorporation of materials ***resisting biofouling*** and/or development of systems for ***sample pretreatment*** (e.g., automated microfluidic prefiltration)
- Development of different types of sensor packaging for direct nitrate measurement in soil and local rivers

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