NCSR
National Centre for Sensor Research

Insight

In-Situ Monitoring of Key Water Quality Parameters

Dermot Diamond

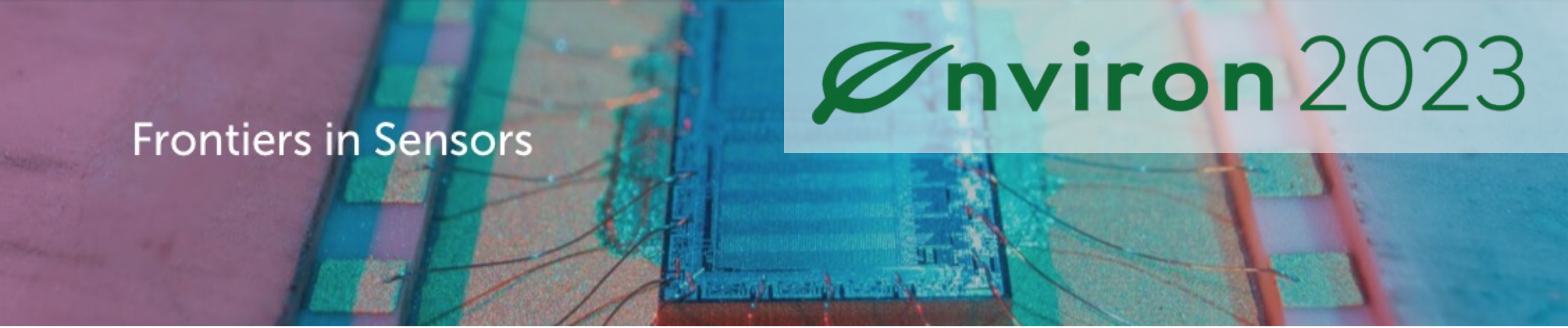
INSIGHT Centre for Data Analytics, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University

Invited Lecture presented at

33rd Irish Environmental Researchers Colloquium

Environ 2023: Evidence and Plans Towards Transitions to a Sustainable Future

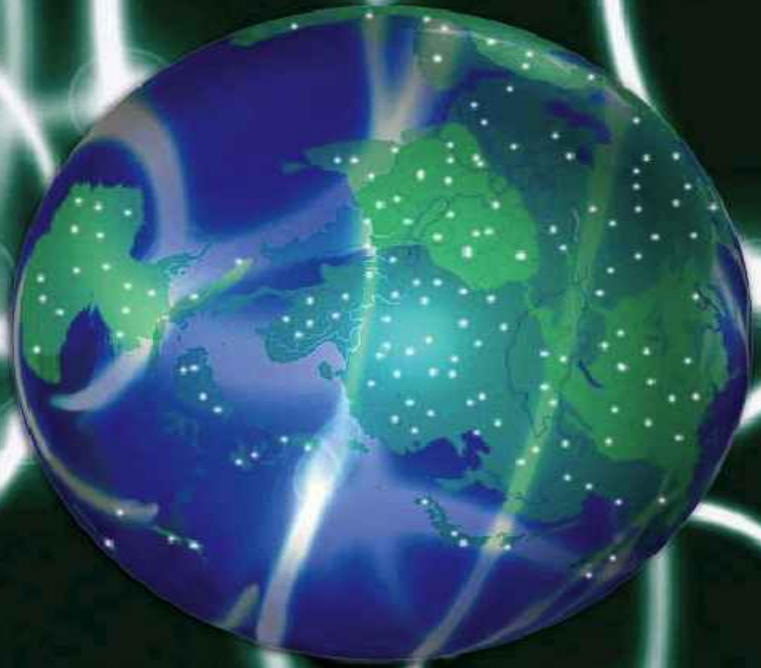
ESAI & Atlantic Technological University Donegal, 3rd-5th April 2023



Frontiers in Sensors **is delighted to support the upcoming Environ 2023 Conference at ATU Letterkenny through sponsorship of the best sensor related oral and poster prizes and the associated awards reception. Conference attendees involved in environmental sensing research are encouraged to consider submitting papers for publication to the journal, see;**

https://www.frontiersin.org/journals/sensors

Keynote Article: Anal. Chem., 76 (2004) 278A-286A



internet scale sensing

Dermot Diamond
Dublin City University
(Ireland)

Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email can instantly transmit complex documents to multiple remote locations, and websites provide a platform for instantaneous notification, dissemination, and exchange of information globally. This technology is now pervasive, and those in research and business have multiple interactions with this digital world every day. However, this technology might simply be the foundation for the next wave of development that will provide a seamless interface between the real and digital worlds.

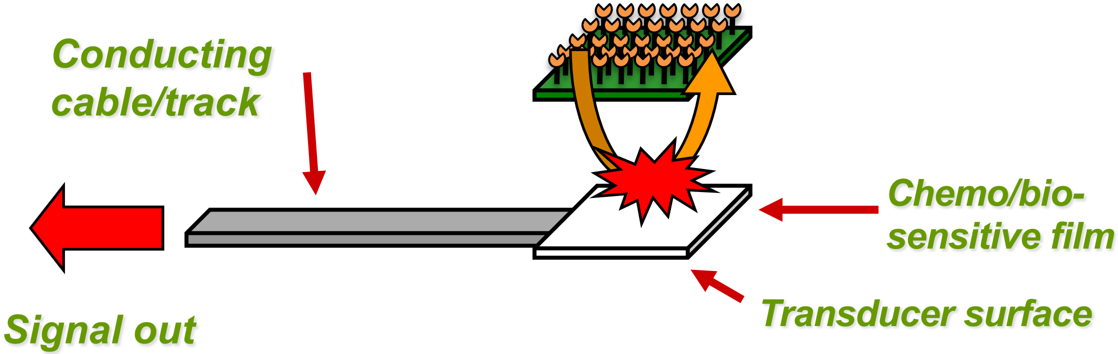
The crucial missing part in this scenario is the gateway through which these worlds will communicate: How can the digital world sense and respond to changes in the real world? Analytical scientists—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are

Internet of (Biochemical) Things
IO$_{BC}$T

- **Bridging the Molecular and Digital Worlds**
  - Emergence of ‘Internet of Analytical Things’, Internet of ‘Molecular Things’, ‘Internet of Biochemical Things’
- **Long-Term “Deploy and Forget” use model**
  - Embedded ‘smartness’
    - Sensing (temperature, light-level, imaging, vibration)
    - Communications (wireless)
    - Power (10-year battery life-time, energy scavenging capability)
  - Awareness of
    - Surrounding environment
    - Internal (functional) condition

What is a 'Bio/Chemical Sensor?

'a device, consisting of a transducer and a chemo/bio-sensitive film/membrane, that generates a signal related to the concentration of particular target analyte in a given sample'



Chemo/Bio-sensing involves selective **BINDING** & **TRANSDUCTION** on the device surface; this also implies the target analyte MUST interact the device surface (**LOCATION** & **MOVEMENT**). It provides a signal observable in the macroscopic world (**COMMUNICATION**)

Remote (Continuous) Sensing Challenges: Platform and Deployment Hierarchies

Physical Transducers – low cost, reliable, low power demand, long life-time

Thermistors (temperature), movement, location, power,, light level, conductivity, flow, sound/audio ……

Chemical Sensors – more complicated, need regular calibration, more costly to implement

Electrochemical, Optical, .. For metal ions, pH, organics…

Biosensors – the most challenging, very difficult to work with, die quickly, single shot (disposable) mode dominant use model

Due to the delicate nature of biomaterials enzymes, antibodies….

Increasing difficulty & cost

Increasing scalability

Gas/Air Sensing – easiest to realise

Reliable sensors available, relatively low cost

Integrate into platforms, develop IT infrastructure, GIS tools, Cloud Computing

On-land Water/ Monitoring

More accessible locations

Target concentrations tend to be higher

Infrastructure available

Marine Water

Challenging conditions

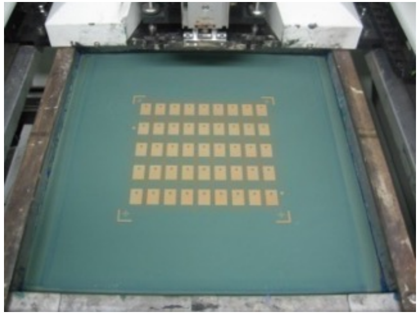
Remote locations & Limited infrastructure

Concentrations tend to be lower and tighter in range

Mass production of SCISEs and SCREs

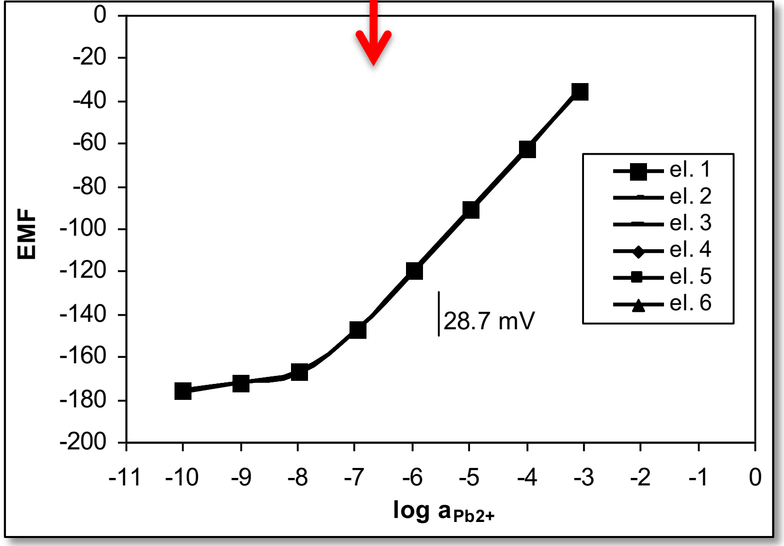
(Alek Radu and Salzitsa Anastasova)

- Using Screen Printer DEK 248 silver paste was printed on plastic sheets.
- Next, carbon was printed twice, with 15 minutes of curing in oven at 200^{o}C between successive prints.
- After finishing carbon, the insulating layer was printed and UV-cured.
- Conducting polymer Poly (3-octylthiophene) (10^{-2} M in Chloroform) was dropcast (initially) or grown electrochemically (later) on printed platforms.
- The CP is covered with a PVC membrane cocktail containing active components for ISEs and reference electrodes (Fluka)



EC-deposition of CP Layer -> highly Reproducible Sensors

6 calibration curves superimposed!

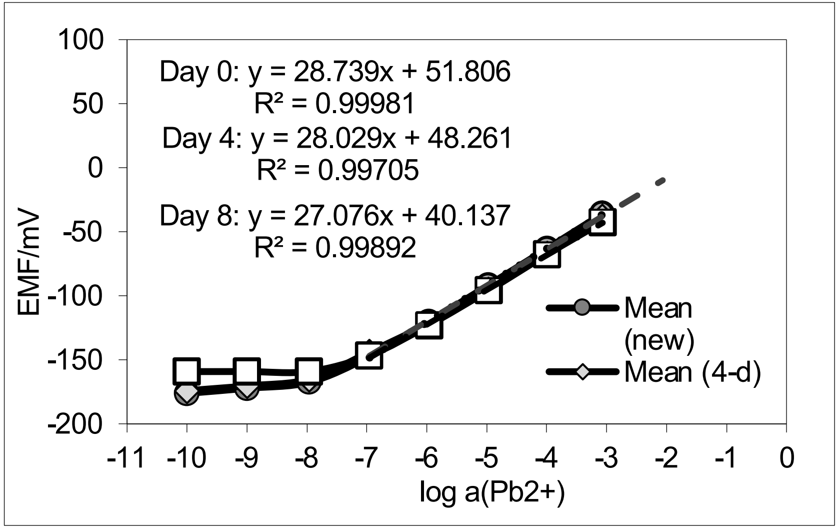


electrode number	Baseline, mV Day0	Slope, mV Day0	LOD Day0	Eo/mV Day0
1	-176.11	28.75	-8.00	53.87
2	-176.08	28.75	-8.00	53.90
3	-176.40	28.75	-7.95	52.14
4	-176.23	28.74	-7.90	50.83
5	-176.13	28.72	-7.92	51.32
6	-176.16	28.74	-8.00	53.73
Mean	-176.18	28.74	-7.96	52.63
SD	0.12	0.01	0.04	1.38

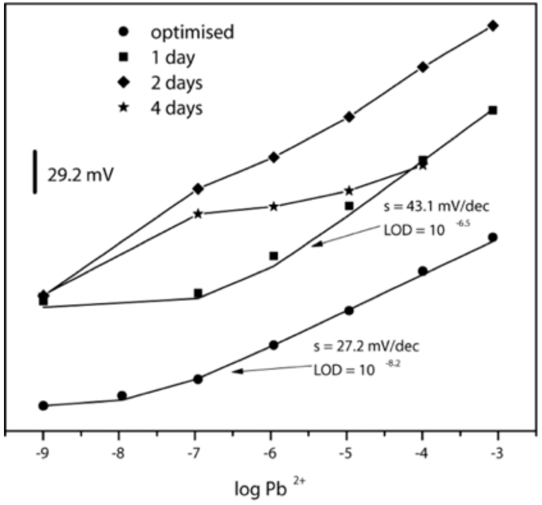
SP fabrication, **electrochemical deposition of CP (PEDOT)**, manual deposition of sensing layer;
Applied to analysis of river water samples

Radu, A.; Anastasova, S.; Fay, C.; Diamond, D.; Bobacka, J.; Lewenstam, A. Low Cost, Calibration-Free Sensors for In Situ Determination of Natural Water Pollution. In *2010 IEEE SENSORS*; IEEE Sensors; IEEE, 2010; pp 1487–1490.

Continuous Use: Hg^{2+} in River Water



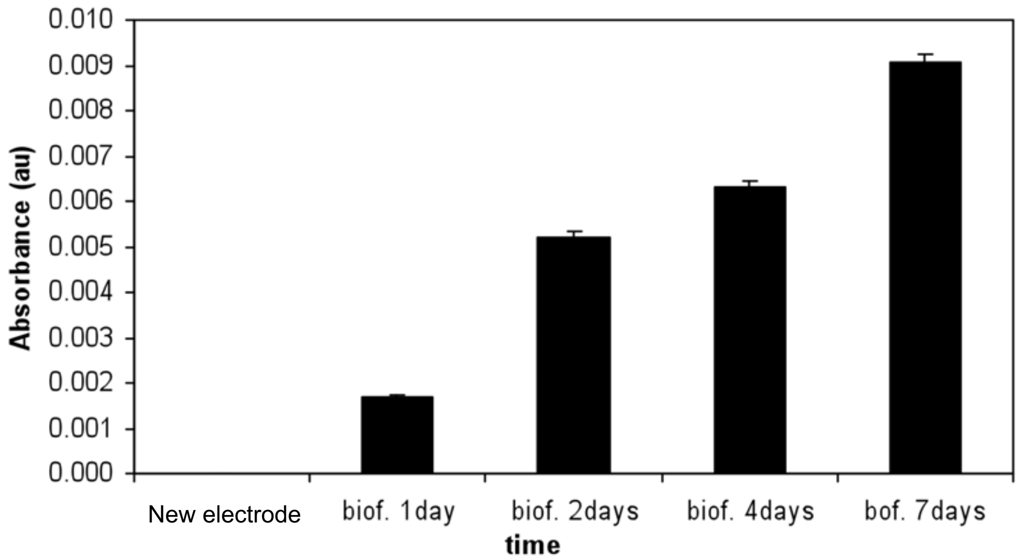
stored in 10^{-9}M Pb^{2+}, pH=4, in the lab



Continuous contact with river water

Anastasova, S.; Radu, A.; Matzeu, G.; Zuliani, C.; Mattinen, U.; Bobacka, J.; Diamond, D.; Disposable Solid-Contact Ion-Selective Electrodes for Environmental Monitoring of Lead with PPB Limit-of-Detection. *ELECTROCHIMICA ACTA* 2012, *73*, 93–97.

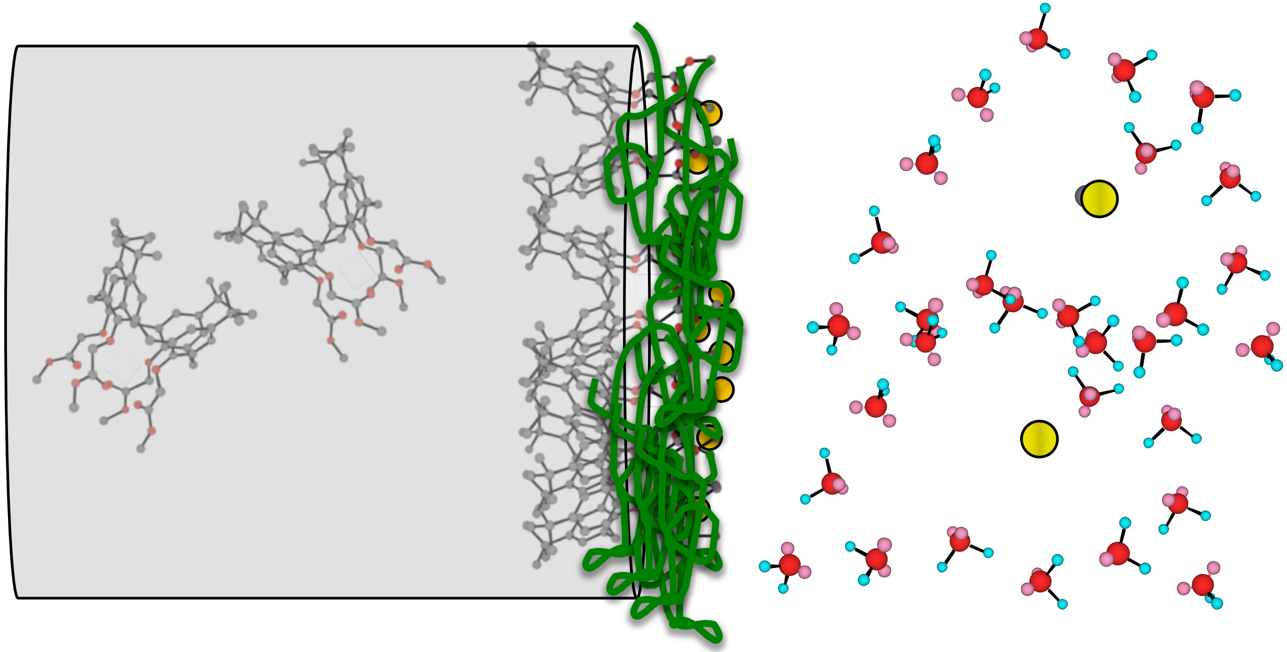
Biofilm Formation on Sensors



- **Electrodes exposed to local river water (Tolka)**
- **'Slime test' shows biofilm formation happens almost immediately and grows rapidly**

Anastasova, S.; Radu, A.; Matzeu, G.; Zuliani, C.; Mattinen, U.; Bobacka, J.; Diamond, D.; Disposable Solid-Contact Ion-Selective Electrodes for Environmental Monitoring of Lead with Ppb Limit-of-Detection. *ELECTROCHIMICA ACTA* 2012, *73*, 93–97.

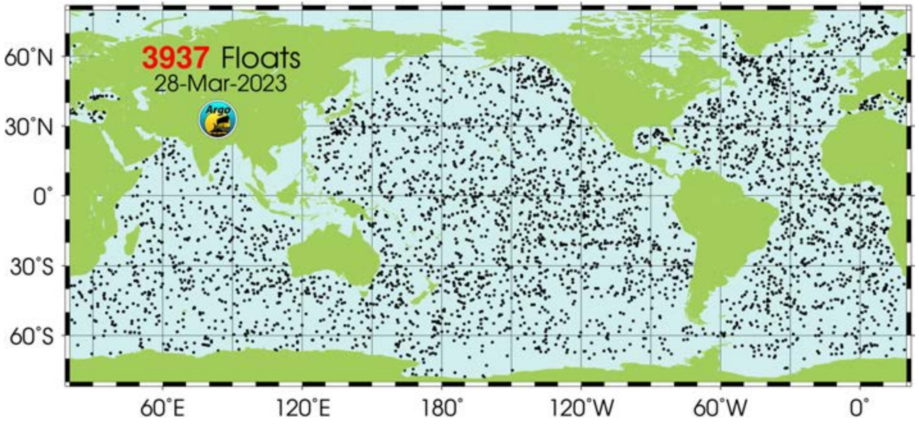
Control of membrane interfacial exchange & binding processes

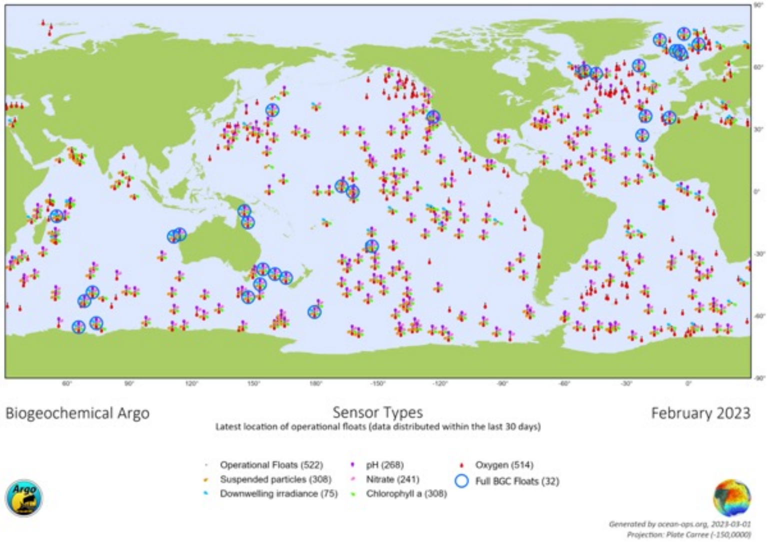


Remote, Long-term, autonomous chemical sensing is a tricky business! Regular calibration is essential.

Osberstown – 3 week deployment

Argo Project (accessed March 2023)





Core: ca. 4,000 floats (March 2023)
BioGeoChemical (BGC) Sensors: 522 ~ 13%

Chlorophyll: 308
pH: 268
Nitrate: 241

Suspended particles: 308
DO: 514
Full BGC Floats: 32 (<1%)

These are all optical measurements except DO – Clark Cell @ $60K each!

‘Calibration of the DO measurements by the SBE-IDO sensor remains an important issue for the future’,

Argo report “Thierry V., H. Bittig, D. Gilbert, T. Kobayashi, K. Sato, C. Schmid, 2018: Processing Argo OXYGEN data at the DAC level, v2.3.1, http://dx.doi.org/10.13155/39795”.

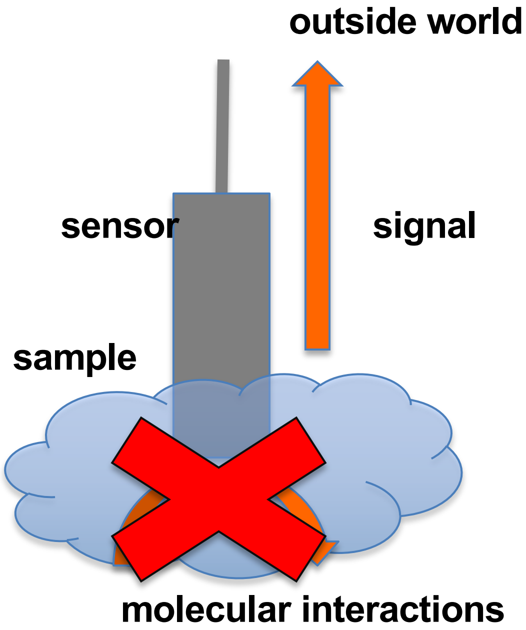
Issues with Argo BioGeoChemical (BGC) Sensors

‘Developing BGC sensors accurate and stable enough to be deployed on Argo floats is a challenge and different sensors are at different levels of readiness for inclusion on an operational BGC-Argo float.’
https://argo.ucsd.edu/expansion/biogeochemical-argo-mission/

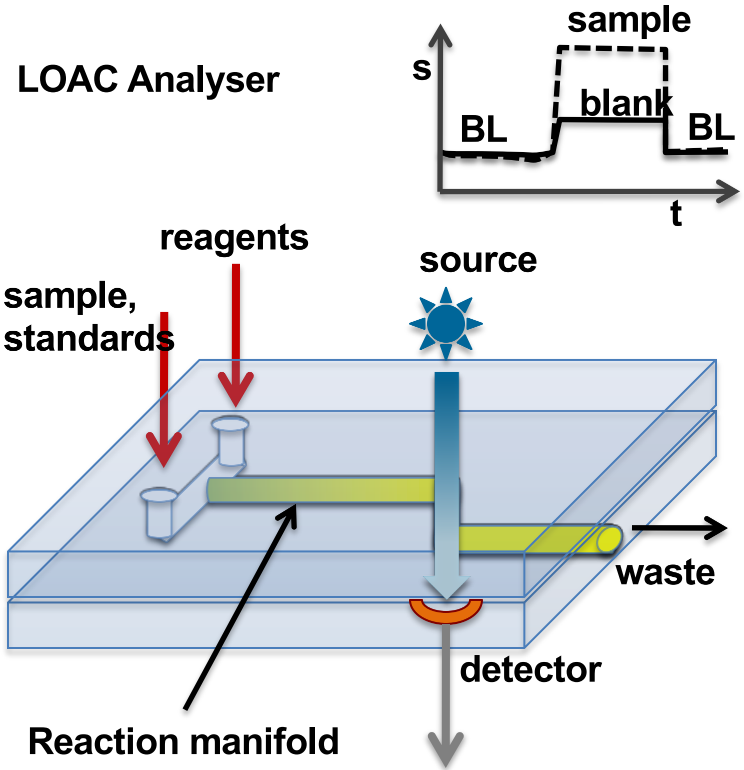
‘With a goal of 1000 floats equipped with the six core BGC sensors, system status ranges from nearly 30% complete for oxygen **to only 8% complete for pH and irradiance**. About 10% of the floats in the BGC array carry 5 of the six core sensors, but few research programs have merged all six on one float.’
On the Future of Argo: ***A Global, Full-Depth, Multi-Disciplinary Array, Roemmich et al., Frontiers in Marine Science, 6 (2019)*** https://doi.org/10.3389/fmars.2019.00439 (v highly cited paper, top 1% views)

Direct Sensing vs. Reagent Based LOAC/ufluidics

Direct Sensing



LOAC Analyser



Phosphate: The Yellow Method

Mixture (Reagent)

(NH_4VO_3) + $(NH_4)_6Mo_7O_{24}.4H_2O$, HCl conc.

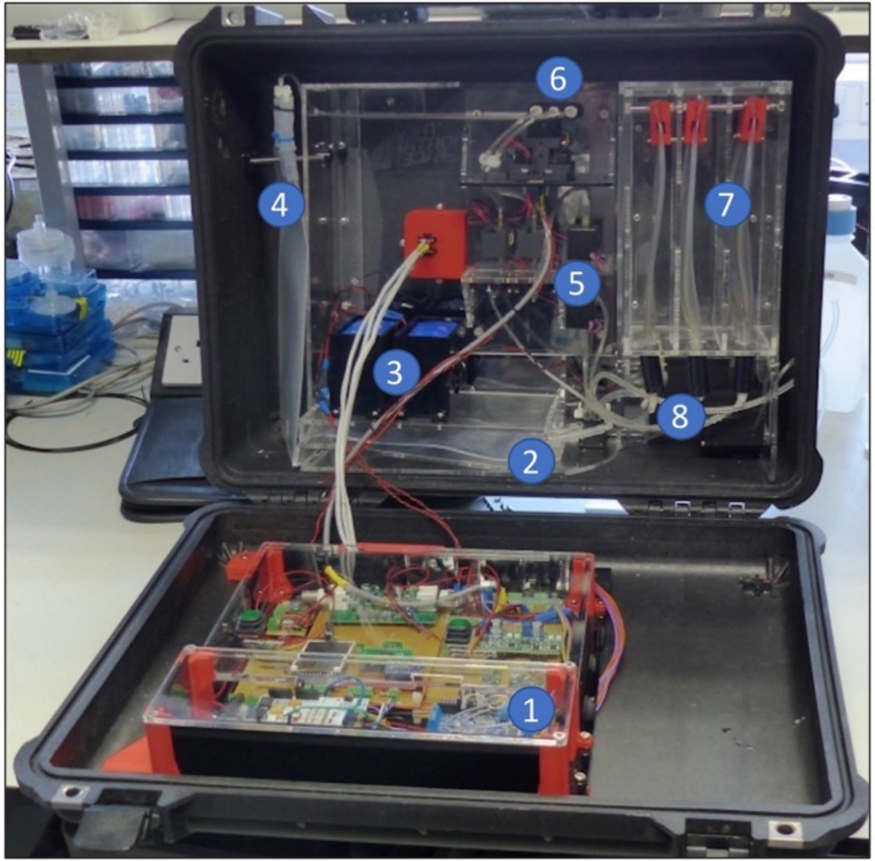
+

Sample

(KH_2PO_4)

$(NH_4)_3PO_4.NH_4VO_3.16MoO_3$

- yellow vanaomolybdophosphoric acid is formed when ammonium metavanadate and ammonium molybdate (mixture) reacts with phosphate (acidic conditions)
- In conventional (molybdate) method, ascorbic acid is used to generate the well-known deep blue complex (v. fine precipitate)
- Could not be exploited in LOAC devices until UV-LEDs became available!!!!

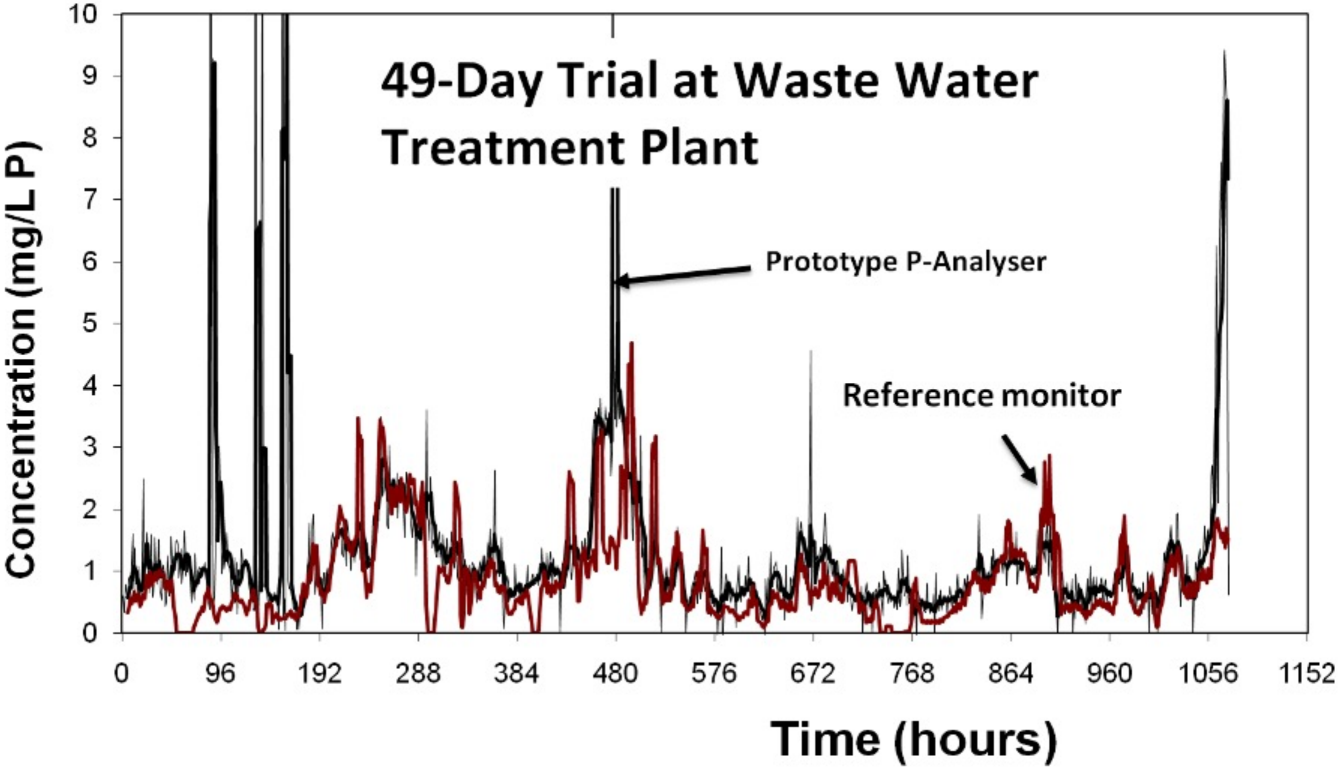


Nutrient Platform

(Phosphate PO_4^{3-})

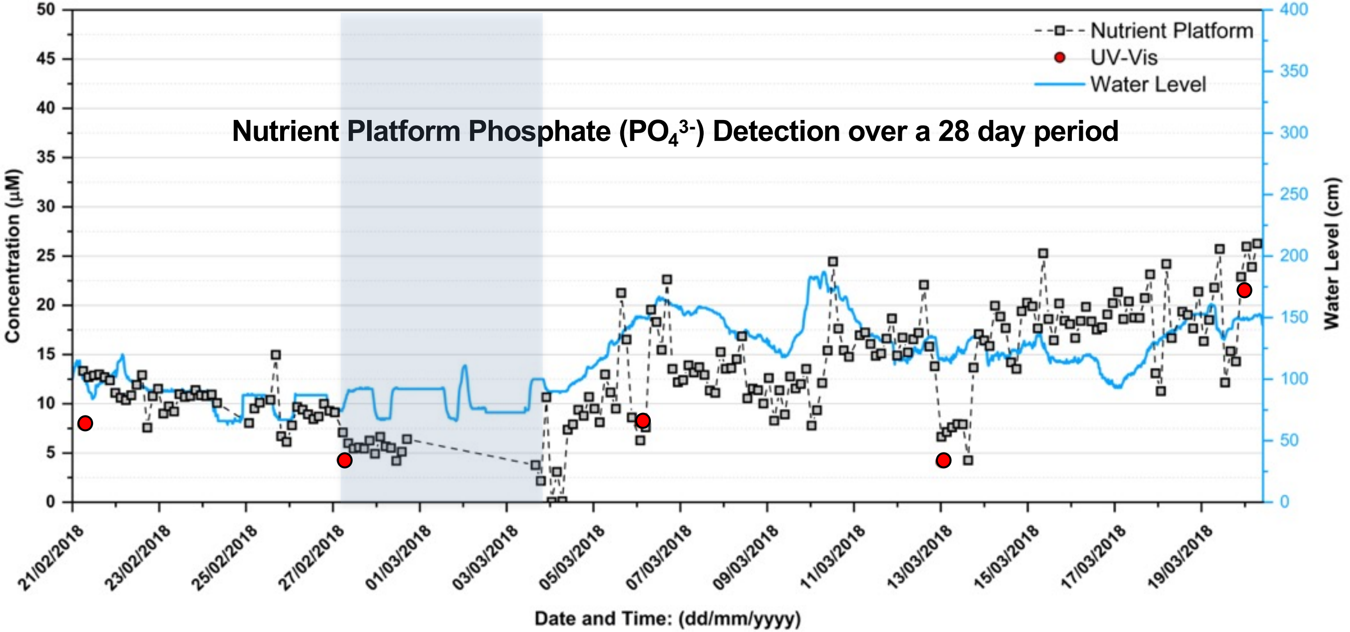
1. Electronics for Autonomous operation, Detection and Data Transmittance
2. Reagent Bag
3. Battery
4. Waste Bag
5. Pumps and Valves for Fluid Handling
6. Microfluidic Chip, LED (375nm) and Photodiode
7. Sample, High and Low Calibration standard bags
8. Inlet System

Autonomous Chemical Analyser



J. Cleary, C. Slater, D. Diamond, Analysis of phosphate in wastewater using an autonomous microfluidics-based analyser, World Academy of Science, Engineering and Technology. 52 (2009) 196–199.

River Liffey Deployment, Palmerstown, Dublin



636 measurements over 28 days recorded

From Multi-Part to Single Part Fluidic Chips

7 Parts : 3 days
~€50/chip

3 Parts : 1 day

1 Part : 1 hour
~€1/chip

With Laurent Malaquin (LAAS-CNRS)

Water Quality – Dublin Bay

Failure of Ringsend tank led to sewage discharge into Dublin Bay

An investigation into the cause of the incident is ongoing, Irish Water says

Tue, Feb 26, 2019, 06:00

Kevin O'Sullivan Environment & Science Editor

An aerial photograph taken at Poolbeg, Dublin, shows a large discharge was continuing at 5.45pm on Sunday evening. Photograph: Eoin O'Shaughnessy/ DublinCityShots

THE IRISH TIMES

LATEST NEWS MOST READ MEDIA IRELAN

Swimming banned at every south Dublin beach after overflow at treatment plant

Dún Laoghaire-Rathdown and city councils issue notices expected to last seven days

File image of Dollymount beach in Dublin. Photograph: Dara Mac Dónaill/The Irish Times

Mark Hilliard

Updated: about an hour ago

https://www.irishtimes.com/news/environment/swimming-banned-at-every-south-dublin-beach-after-overflow-at-treatment-plant-1.3917229

Date Accessed 6th June 2019

Conclusions

- Demand for long-term ‘continuous’ monitoring of remote environmental waters is increasing and will continue to grow.
- Regular calibration imposes the need for a fluidic system ->EXPENSIVE!
- 3d-Printing of fluidic chips will significantly decrease production cost AND improve reliability
- All components in a deployed instrument must be reliable and all reagents used must be stable for the duration of the service interval (3 Months?)

Thanks to…..

- NCSR, SCS, DCU
- Science Foundation Ireland & INSIGHT Centre
- Enterprise Ireland
- Research Partners – academic and industry
- Multiple PhD Students, PDs, RFs, RAs, Interns, UG Project students…
- Dr. Margaret McCaul – currently commercialising the platform with Yosef Yosef, Sonic BV (Netherlands)