Reliable in-Situ Sensing of Water Quality Parameters Using Low Cost Autonomous Analysers - Opportunities and Challenges

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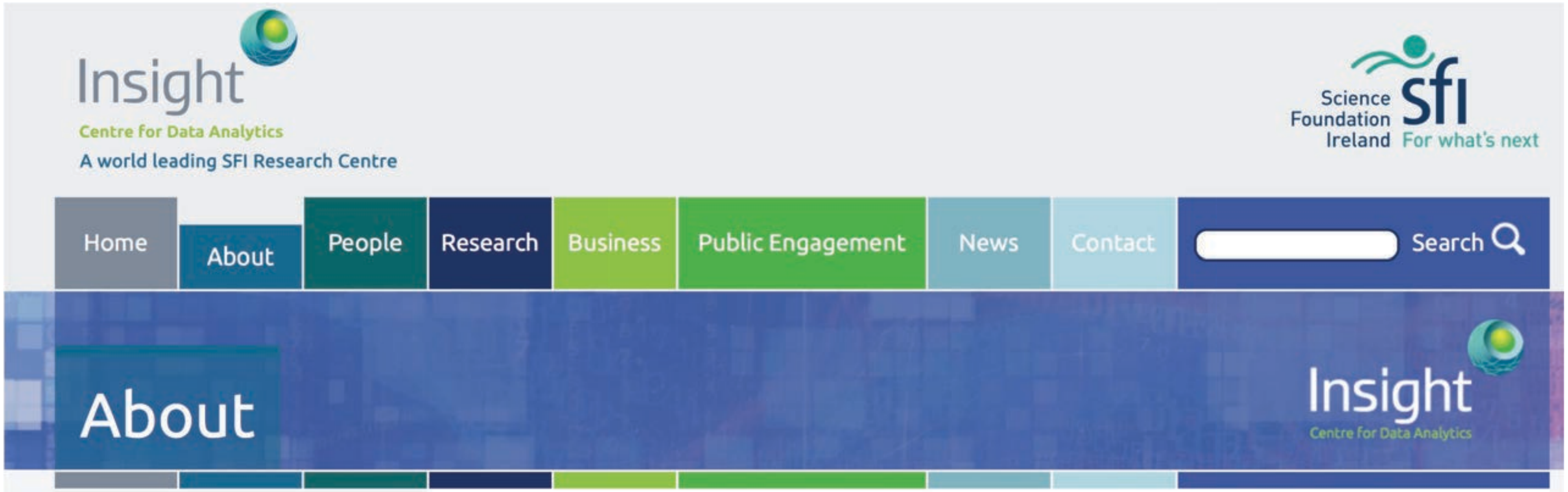
Keynote Lecture presented at
CEST 2019, Rhodes, Greece, 4-7 September 2019

Jean Louis Viovy (Fluigent-Curie), Mark Bowkett (TE Laboratories), Laurent Malaquin (LAAS-CNRS)

The Insight Centre for Data Analytics



Insight is one of the biggest data analytics centres in Europe. It undertakes high-impact research, seeks to derive value from Big Data and provides innovative technology solutions for industry and society by enabling better decision-making.

With **€88 million (ca.50% Industry)** in funding, Insight has 400 researchers across areas such as connected health, decision analytics, social media analytics, smart cities and the semantic web.

http://www.sfi.ie/sfi-research-centres/insight/

2nd Phase funding approved (ca. €50 million SFI) commencing autumn 2019

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

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.

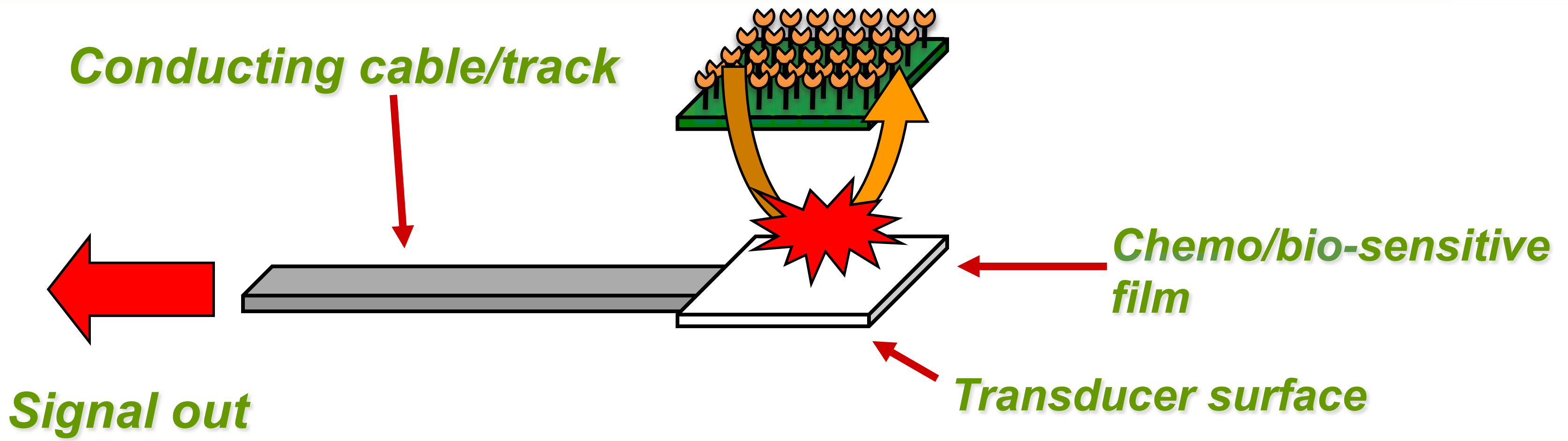
Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions 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

Ron Ambrosio & Alex Morrow, IBM TJ Watson

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 meet 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

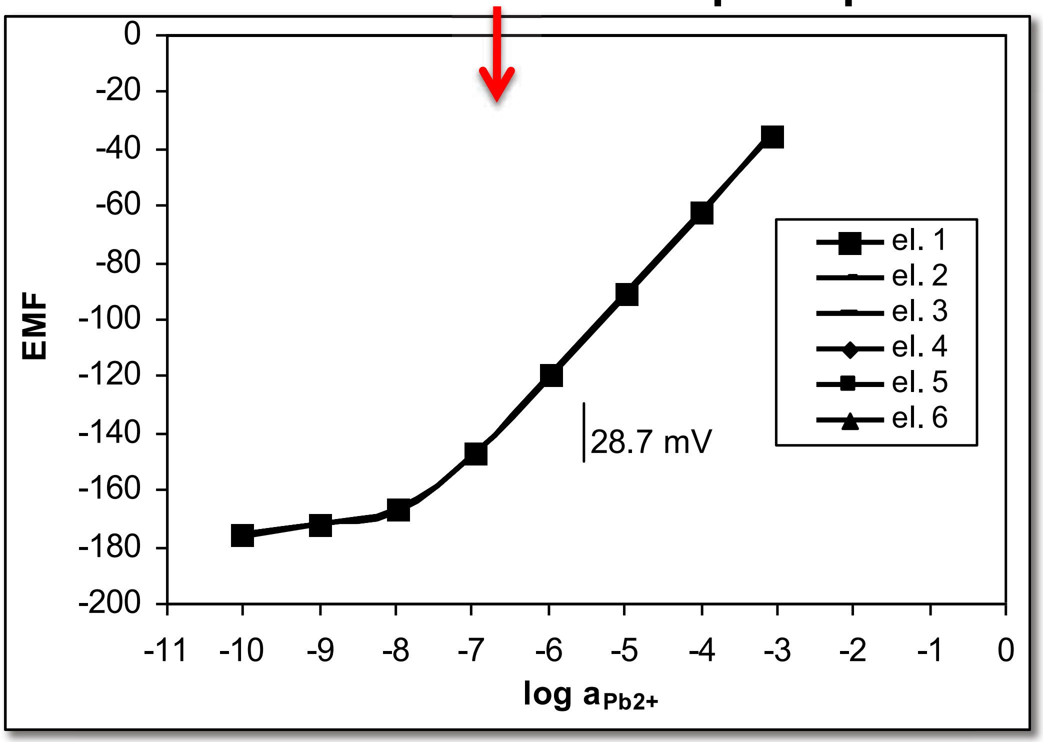
Challenging conditions

Remote locations & Limited infrastructure

Concentrations tend to be lower and tighter in range

EC-deposition of CP Layer -> highly Reproducible Sensors

6 calibration curves superimposed!

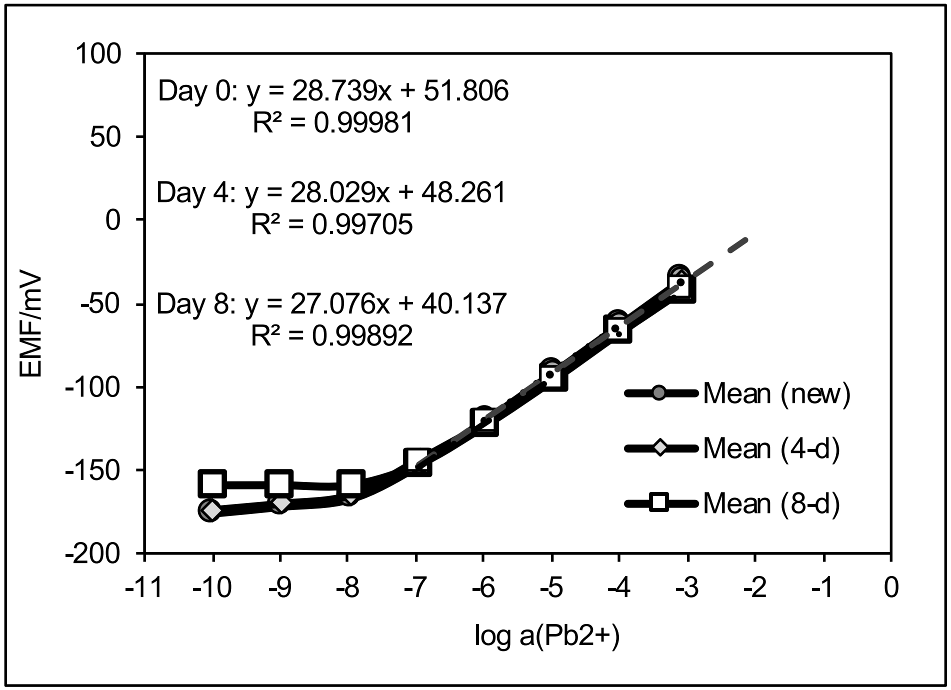


electrode number	Baseline, mV Day0	Slope, mV Day0	LOD Day0	Eo/mV Day0
1	-176.11	28.75	-8.00	53.87
2	-176.08	28.75	-8.00	53.90
3	-176.40	28.75	-7.95	52.14
4	-176.23	28.74	-7.90	50.83
5	-176.13	28.72	-7.92	51.32
6	-176.16	28.74	-8.00	53.73
Mean	-176.18	28.74	-7.96	52.63
SD	0.12	0.01	0.04	1.38

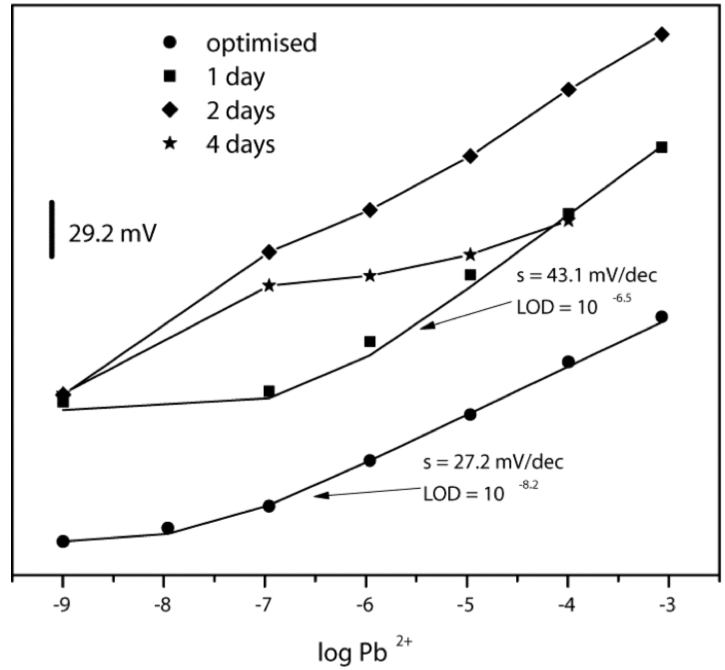
SP fabrication**, electrochemical deposition of CP (PEDOT)**, manual deposition of sensing layer;
Applied to analysis of river water samples

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



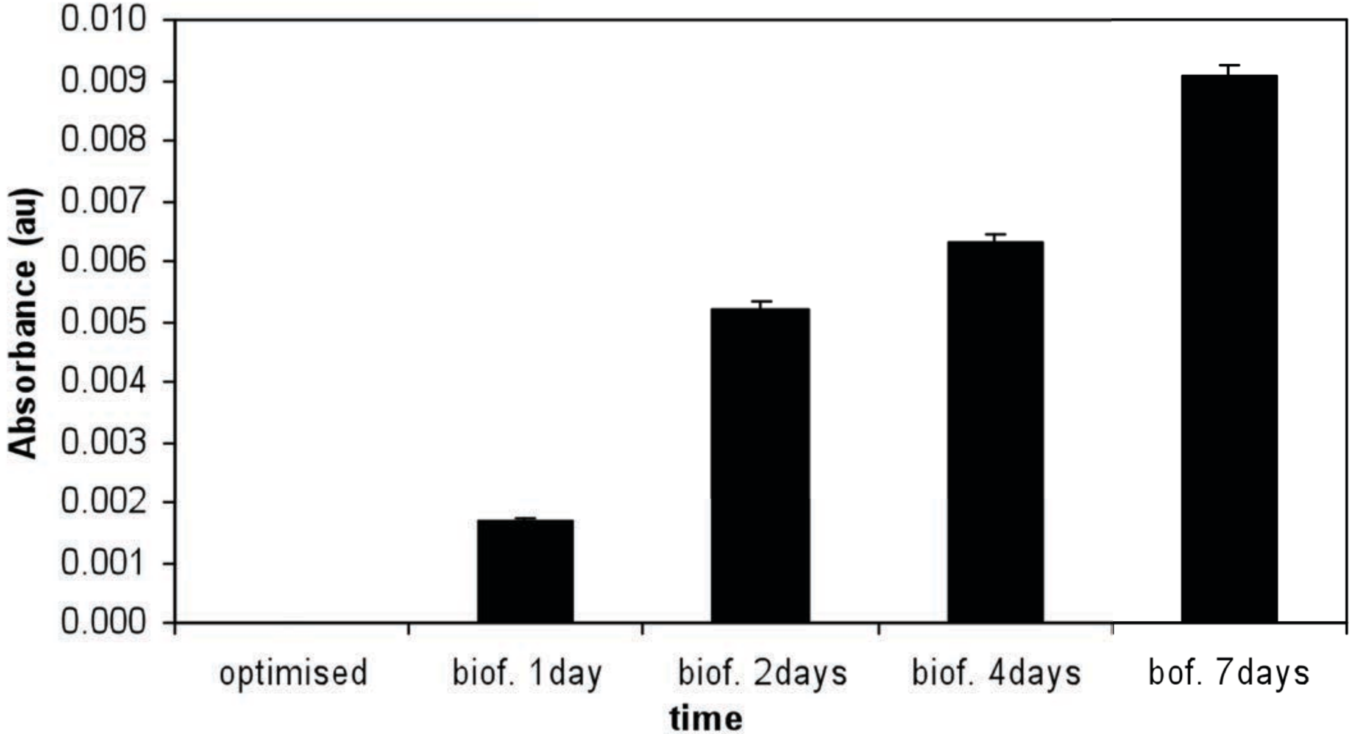
stored in 10^{-9}M Pb^{2+}, pH=4, in the lab



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



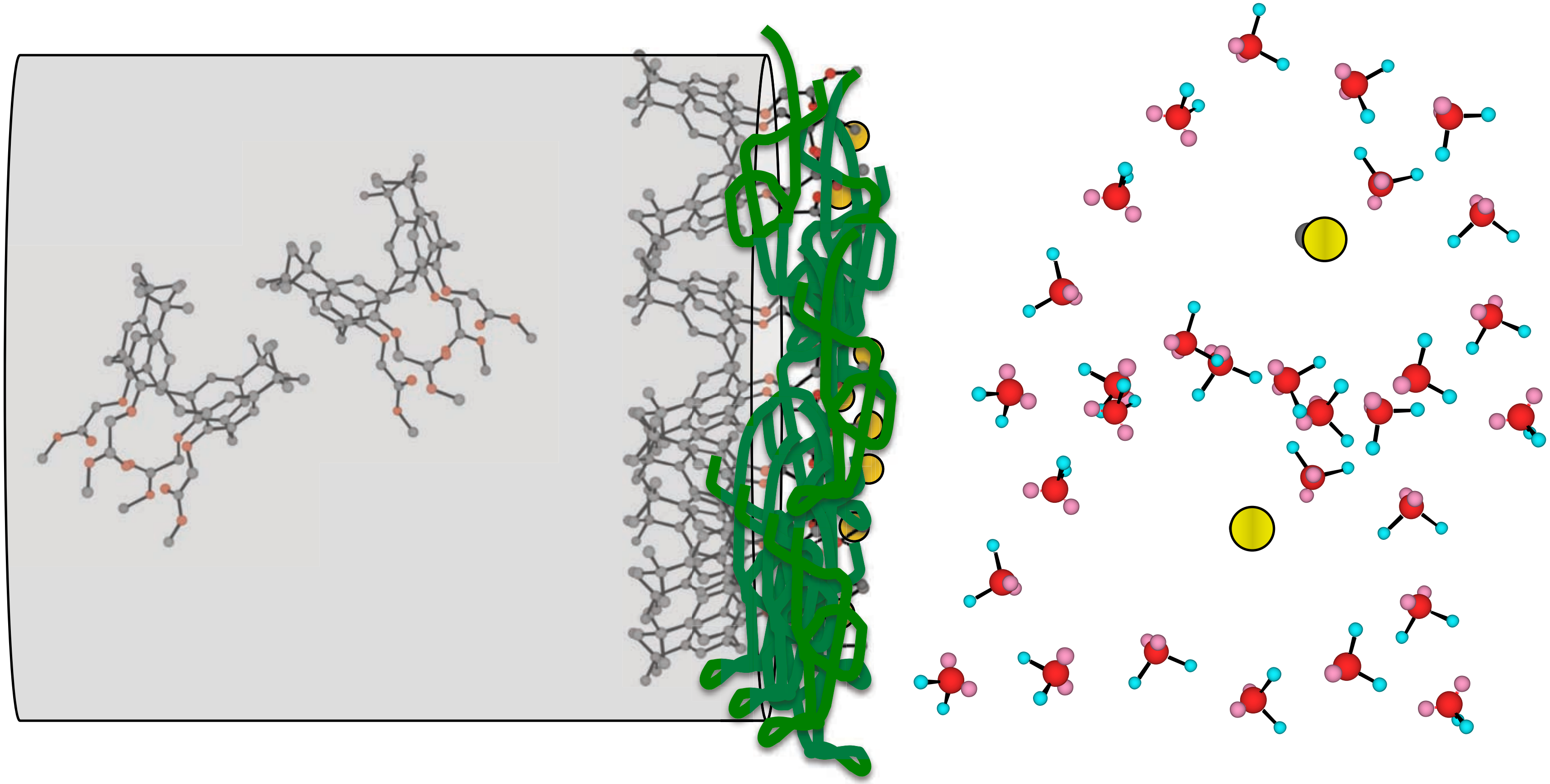
New electrode

- **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.

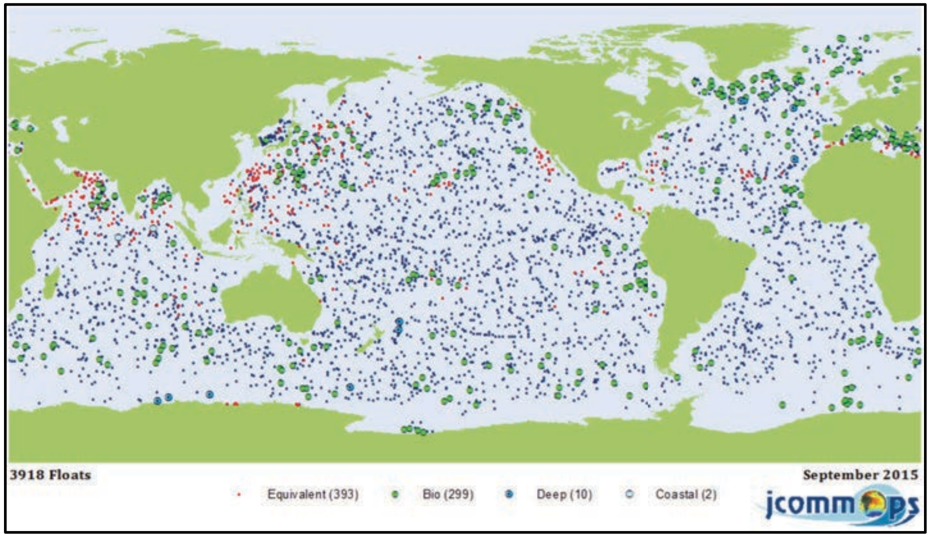
Osberstown – 3 week deployment

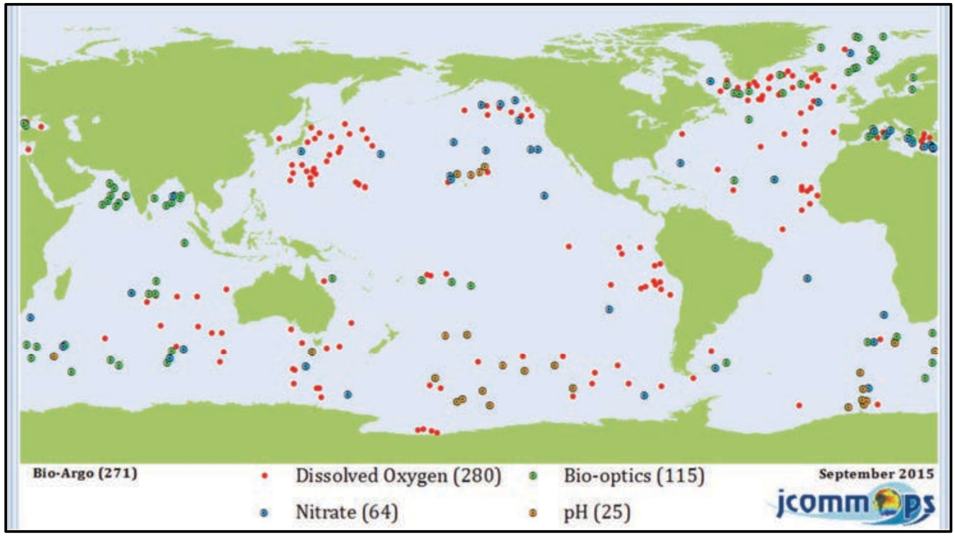
Control of membrane interfacial exchange & binding processes



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

Argo Project (accessed March 20 2016)





- **Ca. 4,000 (3918) floats: temperature and salinity**
- **Bio/Chem: Nitrate (64), DO (280), Bio-optics (115), pH (25)**

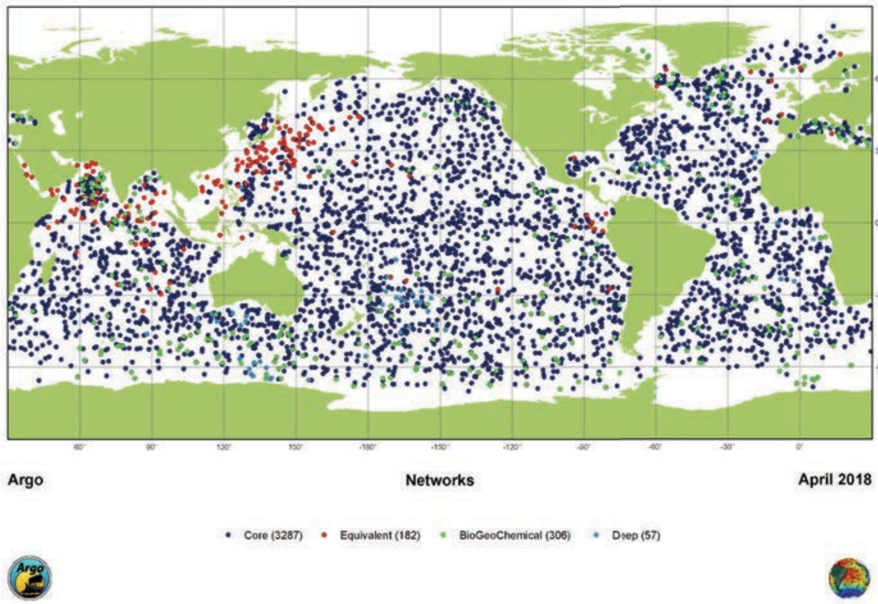
DO is by Clark Cell (Sea Bird Electronics) or Dynamic fluorescence quenching (Aanderaa)

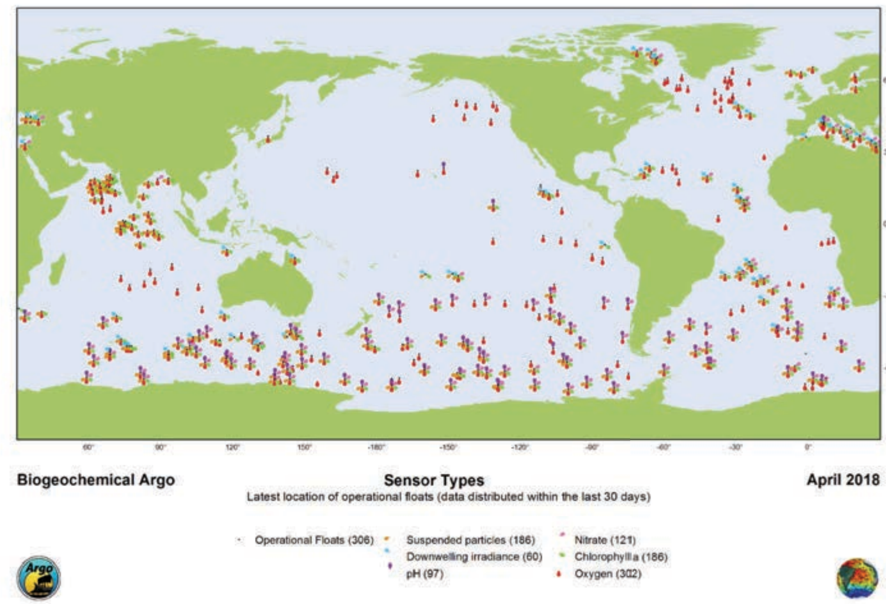
@€60K ea!

See https://picasaweb.google.com/JCOMMOPS/ArgoMaps?authuser=0&feat=embedwebsite

'calibration of the DO measurements by the SBE sensor remains an important issue for the future', Argo report 'Processing Argo OXYGEN data at the DAC level', September 6, 2009, V. Thierry, D. Gilbert, T. Kobayashi

Argo Project (accessed May 2018)



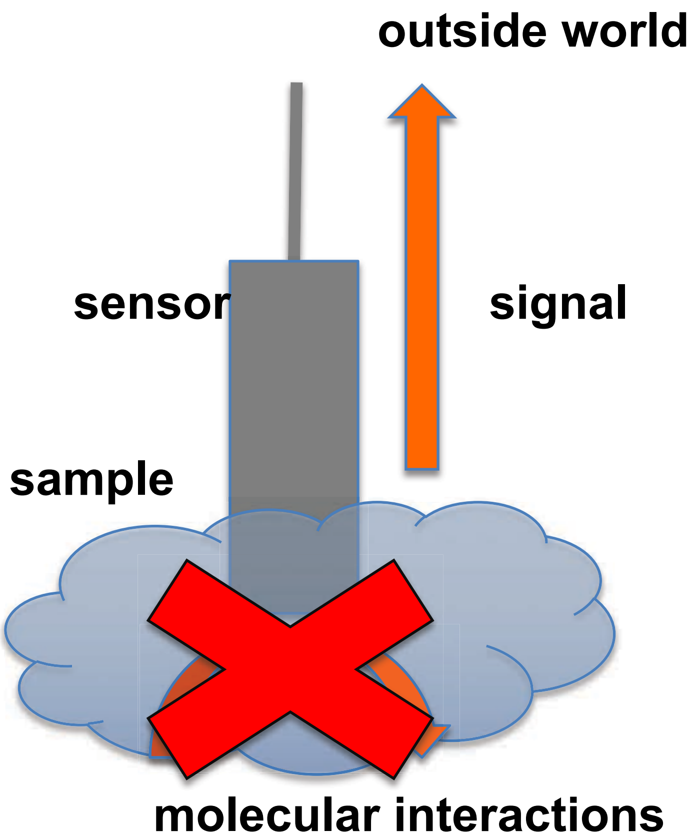


Argo (2000). Argo float data and metadata from Global Data Assembly Centre (Argo GDAC) http://doi.org/10.17882/42182

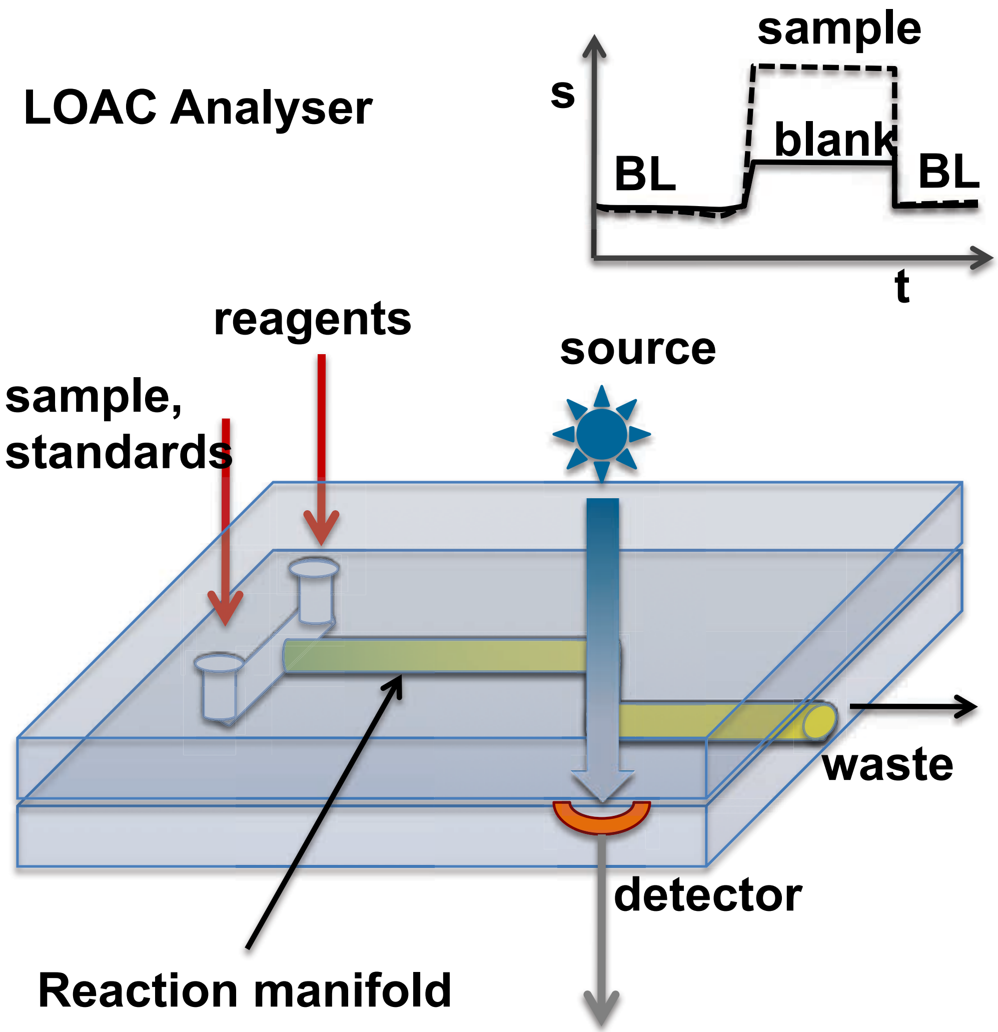
Core: 3287 Biochemical:306
Suspended particles: 186; Nitrate: 121 Chlorophyll: 186 pH: 97 DO: 302

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

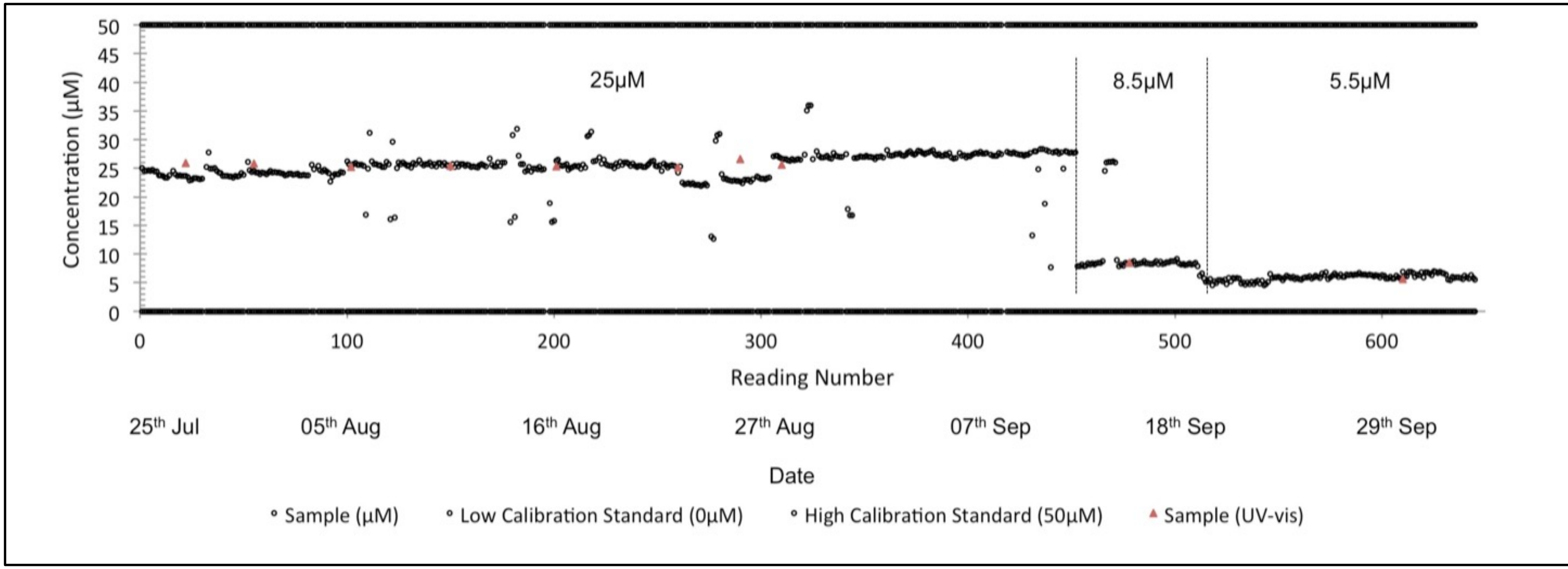
(KH_2PO_4)

↓

$(NH_4)_3PO_4.NH_4VO_3.16MoO_3$

- 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!!!!

Laboratory Validation of Nutrient Platform



1941 Measurements over 78 Days
Testing Continued until the 1st of December

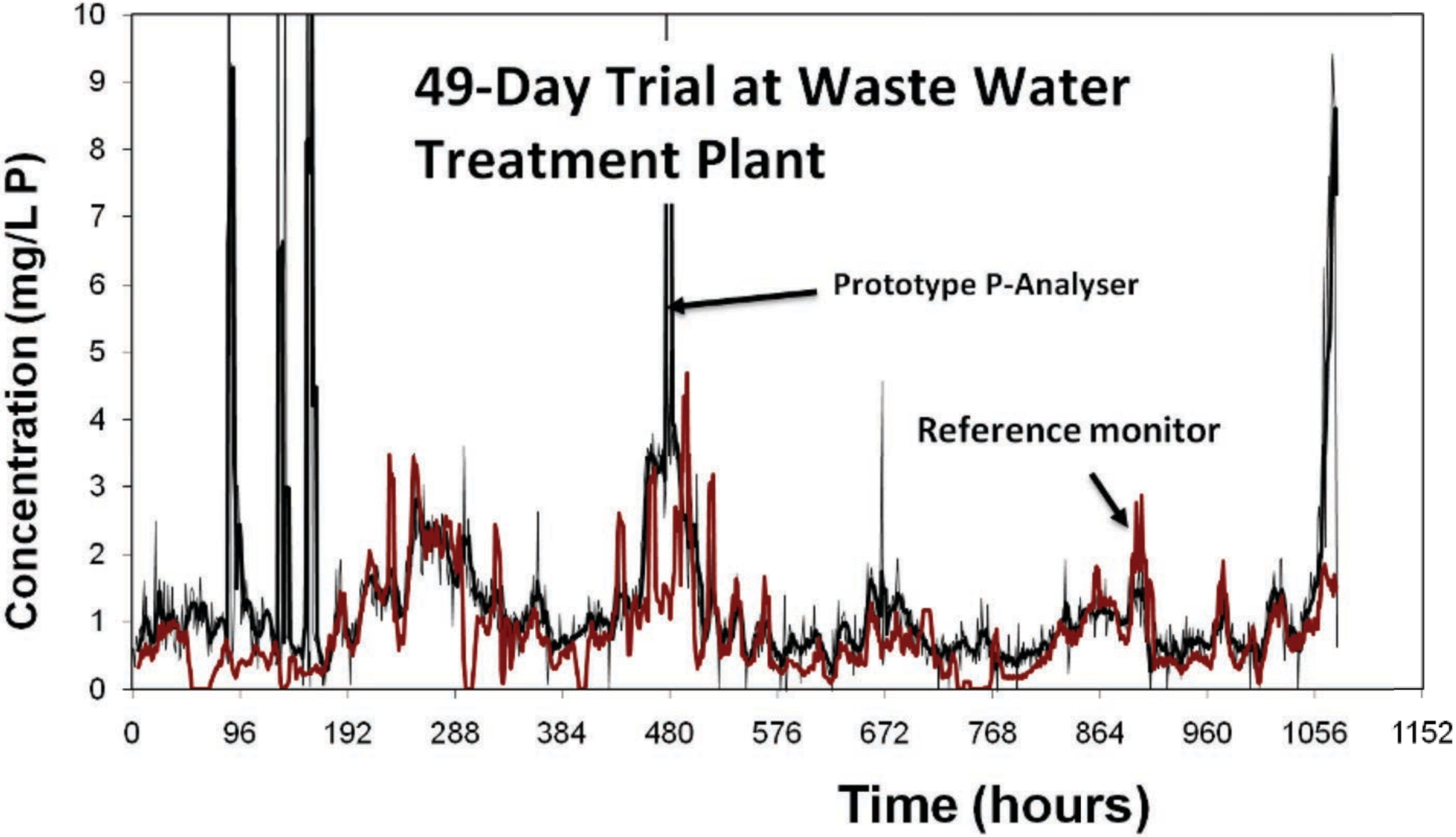
Nutrient Sensor (µM)	Standard Deviation (µM)
5.93 (n=139)	0.56
8.4 (n=71)	0.27
25.35 (n=408)	2.77

Prototype Testing – Generation 3

Milano San Rocco WWTP

Available Sampling Points:
1. Output water after Sand Filtration
2. Output water after the Clarifier
3. Activated Sludge (Biological Tank)
4. Input Water

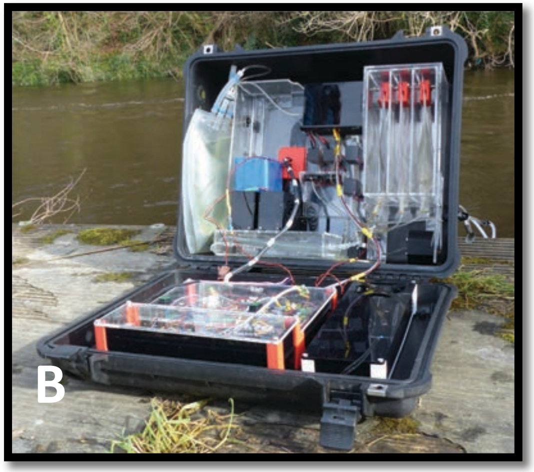
Autonomous Chemical Analyser



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

- **Sensor deployed on the River Liffey for 28 days (21/02/2018 – 19/03/2018)**
- **Measurements of Phosphate (PO_4^{3-}) detected every 3 hours**
- **Environmental Temperature, Rainfall and Water level recorded**



Beast from the East: Status Red snow alert in place until Friday

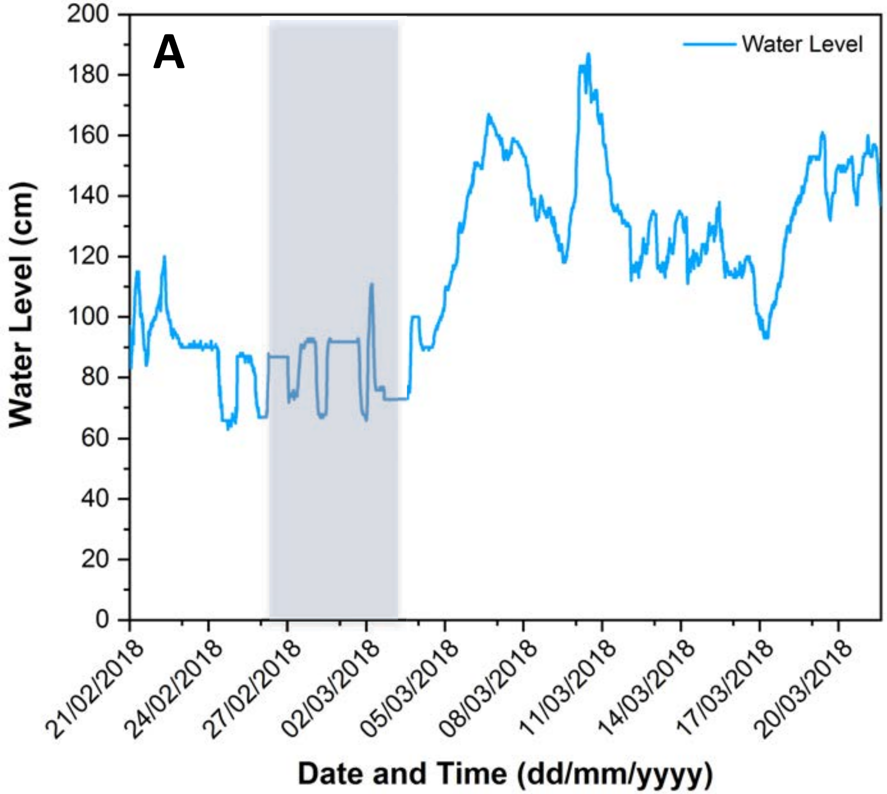
Varadkar says people 'should not venture out of doors' while the red level warning is in place

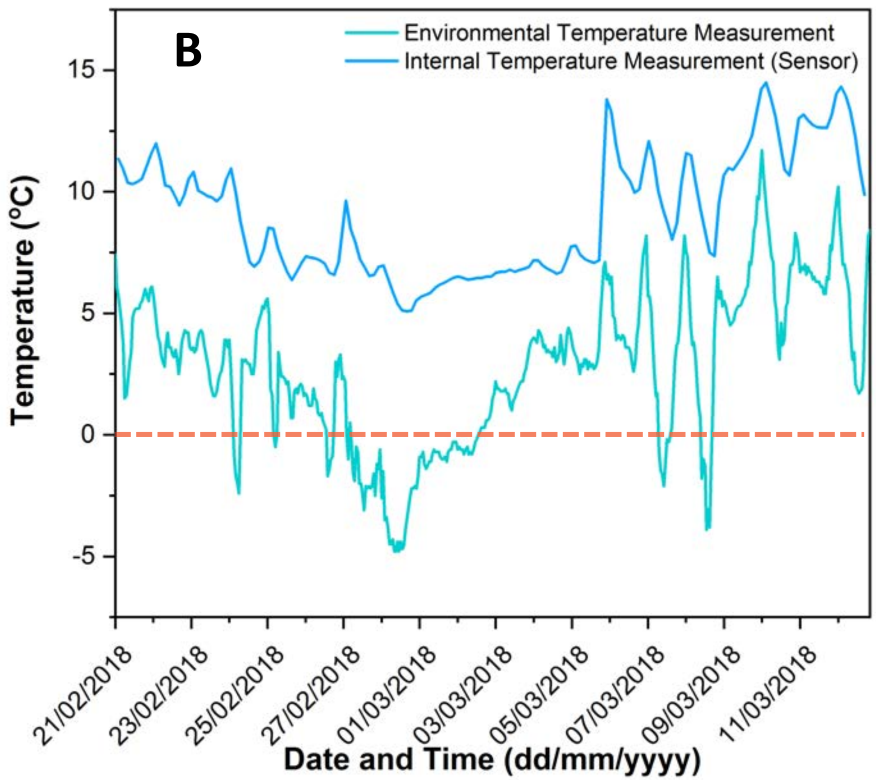
Wed, Feb 28, 2018, 06:29 | Updated: Wed, Feb 28, 2018, 21:05

D

A. **Deployment Location**
B. **Sensor Deployed**
C. **Sensor Deployed by depth gauge**
D. **Temperatures reach -4.5°C**

River Liffey Deployment, Palmerstown, Dublin

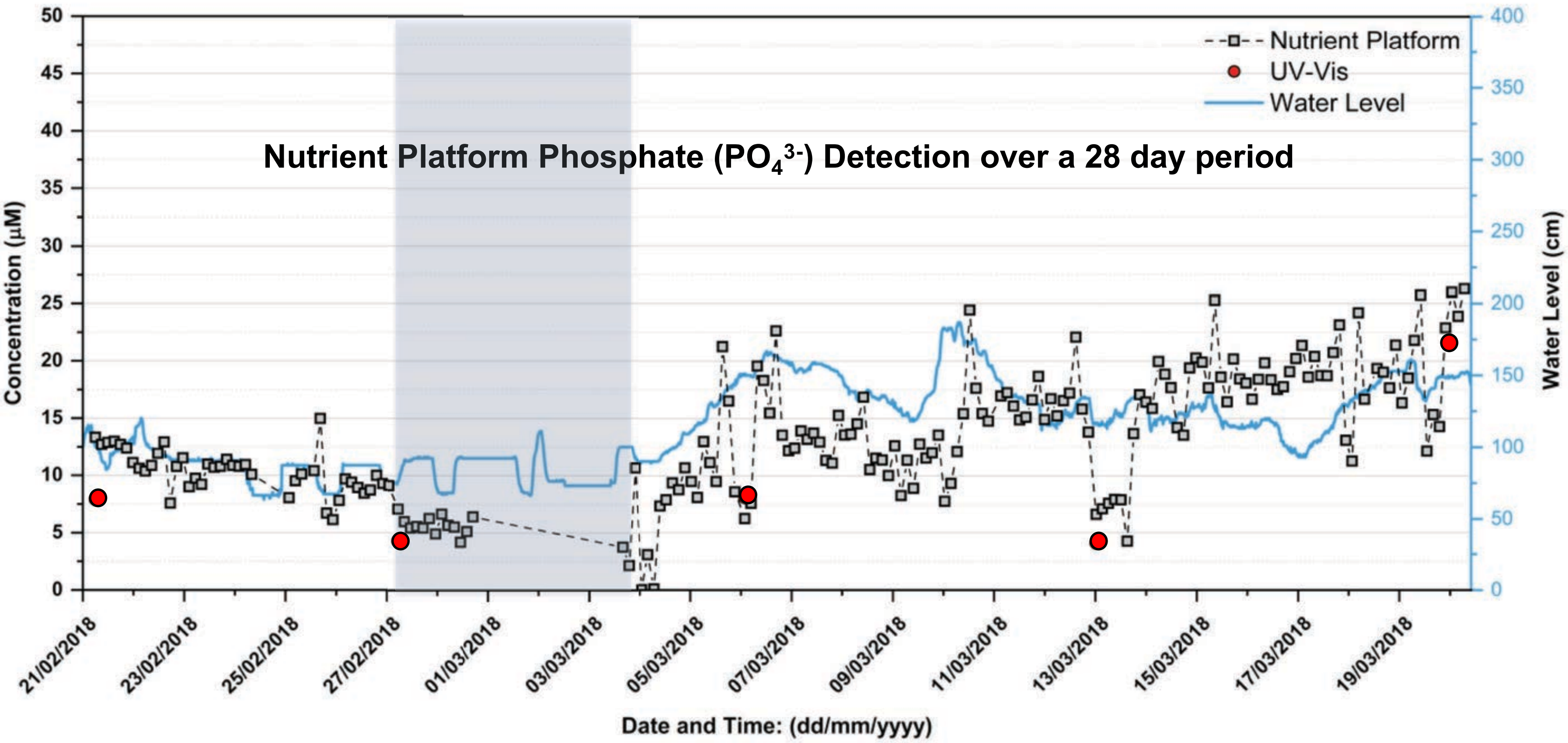




A. Water levels controlled by Leixlip Dam. Increasing water levels from the 5th Mar due to snow melt.

B. External vs Internal Temperature External lows of -4.5^{o}C. Internal lows of 5^{o}C.

River Liffey Deployment, Palmerstown, Dublin



636 measurements over 28 days recorded

Achieving Scale-Up

Challenge

- Drive down costs;
  - Purchase
  - Ownership/maintenance

Solution

- Lower production costs
- Improve reliability – longer service interval

Impact of 3d Printing

Minimum thickness

- Assembled chip 4.25 mm
- 3D Printed Chip 1.58 mm

Assembled Chip

Printed Chip

Advantages:

- No Assembly
- No Bonding necessary
- Integrated barbs (1/16”)
- Chip thickness reduced by 63%
- Automated manufacturing

Rendered Chip

Printed Chip

From Multi-Part to Single Part Fluidic Chips

7 Parts : 3 days
~€50/chip

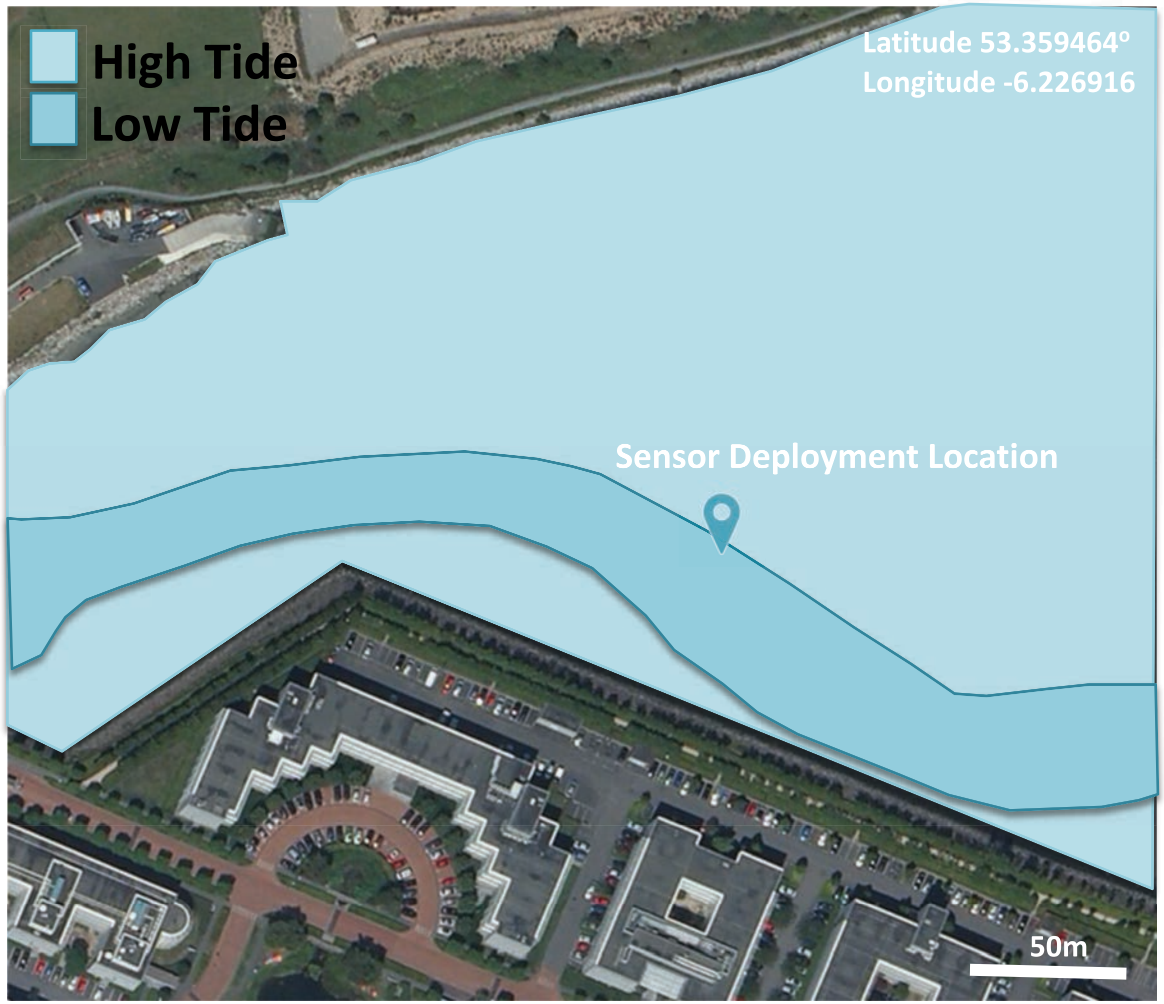
3 Parts : 1 day

1 Part : 1 hour
~€1/chip

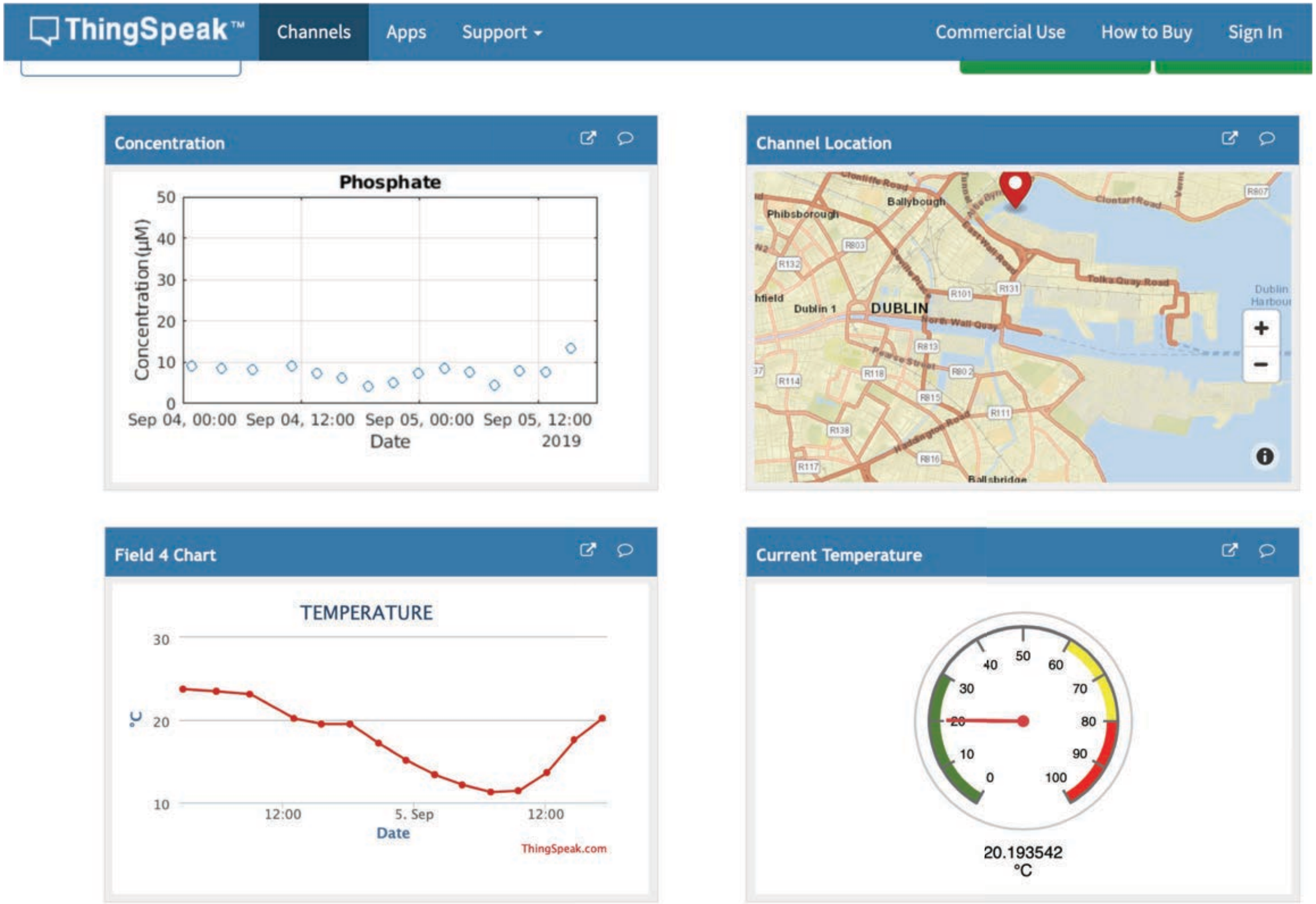
With Laurent Malaquin (LAAS-CNRS)


High Tide


Low Tide

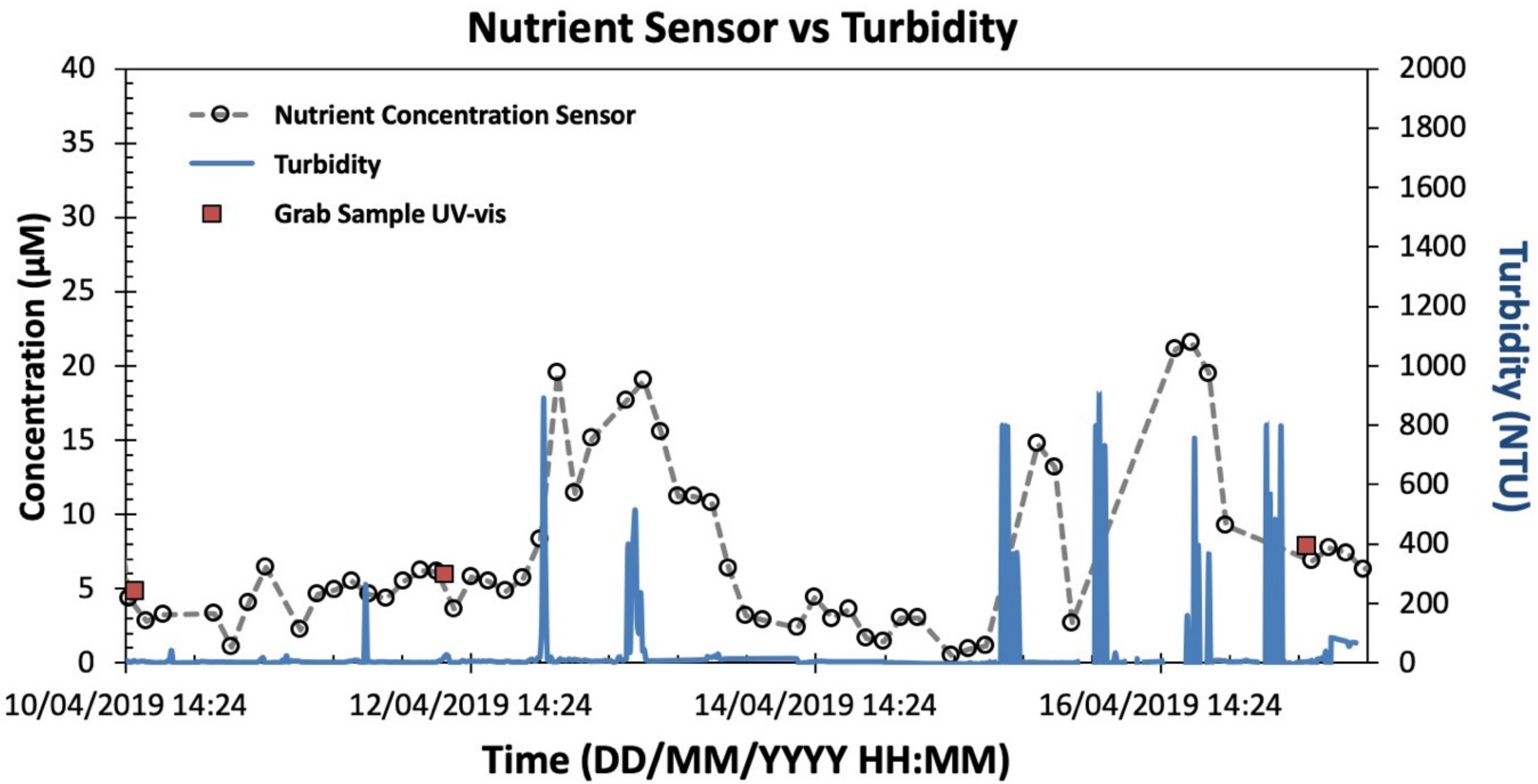

High Tide
Low Tide
Latitude 53.359464º
Longitude -6.226916
Sensor Deployment Location
50m

3D Printed Chip – Live Feed



https://thingspeak.com/channels/786279

Nutrients and Turbidity



Correlation between Nutrient concentration (PO_4^{3-}) and Turbidity spikes

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

THE IRISH TIMES

Tuesday 3rd September 2019

Beach near Dublin's wastewater plant blanketed in noxious material

'No evidence of sewage discharge,' on scenic Shelly Banks strand, says Dublin City Council

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
- H2020: Holifab Project

Jean Louis Viovy (Fluigent) , Mark Bowkett (TE Laboratories), Laurent Malaquin (LAAS)

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
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Thanks for the invitation!