In-Situ Sensing of Water Quality Parameters Using Low-Cost Autonomous Analysers: Opportunities and Challenges

Dermot Diamond (Margaret McCaul)

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Invited Lecture Presented at

The University of Granada

October 11th, 2023

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.

450+ Researchers

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220+ Industry Partners

8 Research Institutions

https://www.insight-centre.org/

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.

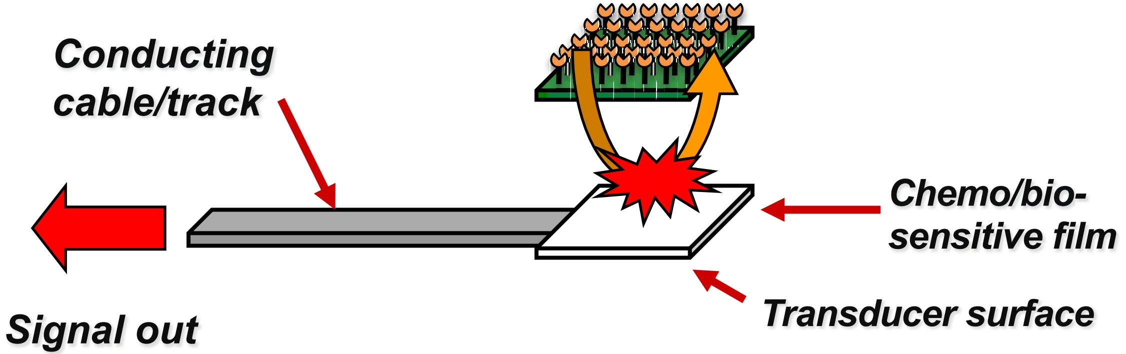
Digital communications networks are at the heart of modern society. The digitalization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions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

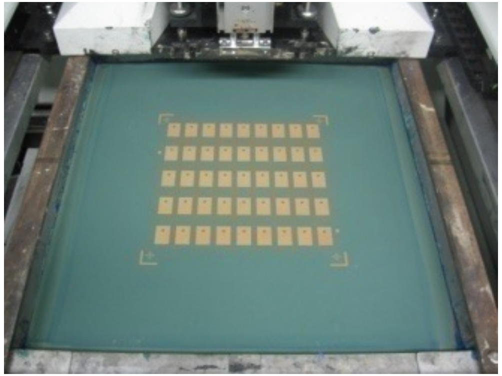


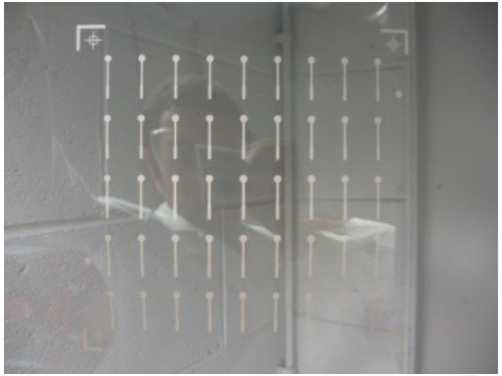
Chemo/Bio-sensing involves selective **BINDING** & **TRANSDUCTION** on the device surface; this also implies the target analyte MUST meet the device surface (**LOCATION** & **MOVEMENT**). It provides a signal observable in the macroscopic world (**COMMUNICATION**)

Mass production of SCISEs and SCREs

(Alek Radu and Salzitsa Anastasova)

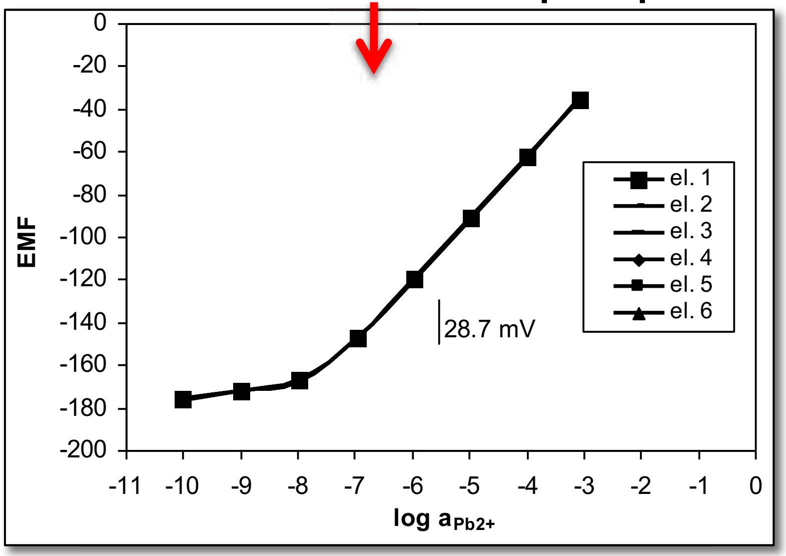
- Using Screen Printer DEK 248 silver paste was printed on plastic sheets.
- Next, carbon was printed twice, with 15 minutes of curing in oven at 200ºC between successive prints.
- After finishing carbon, the insulating layer was printed and UV-cured.
- Conducting polymer Poly (3-octylthiophene) (10^{-2} 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!

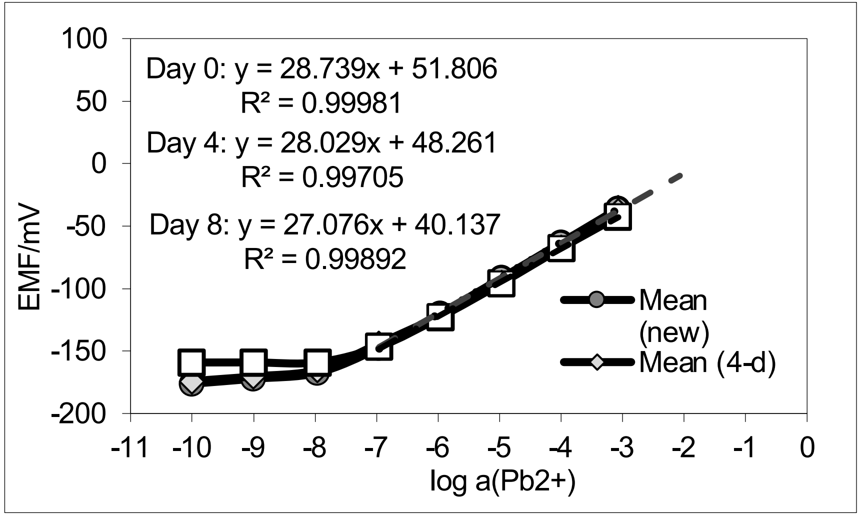


electrode number	Baseline, mV Day0	Slope, mV Day0	LOD Day0	Eo/mV Day0
1	-176.11	28.75	-8.00	53.87
2	-176.08	28.75	-8.00	53.90
3	-176.40	28.75	-7.95	52.14
4	-176.23	28.74	-7.90	50.83
5	-176.13	28.72	-7.92	51.32
6	-176.16	28.74	-8.00	53.73
Mean	-176.18	28.74	-7.96	52.63
SD	0.12	0.01	0.04	1.38

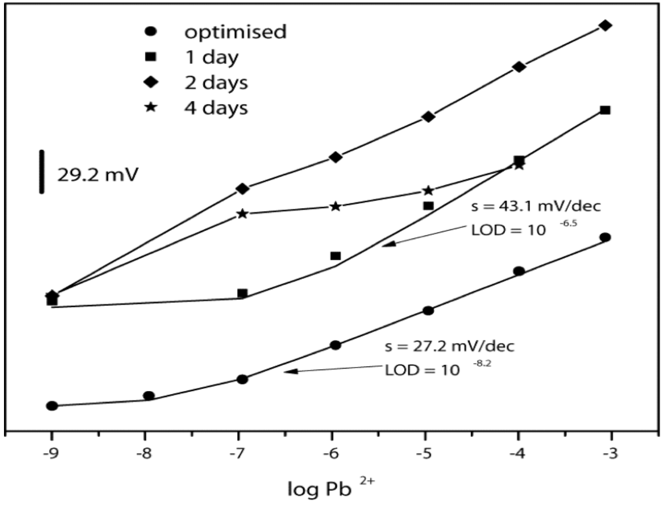
Screen Printed fabrication, **electrochemical deposition of Conducting Polymer (PEDOT)**, manual deposition of sensing layer.

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: Pb^{2+} in River Water



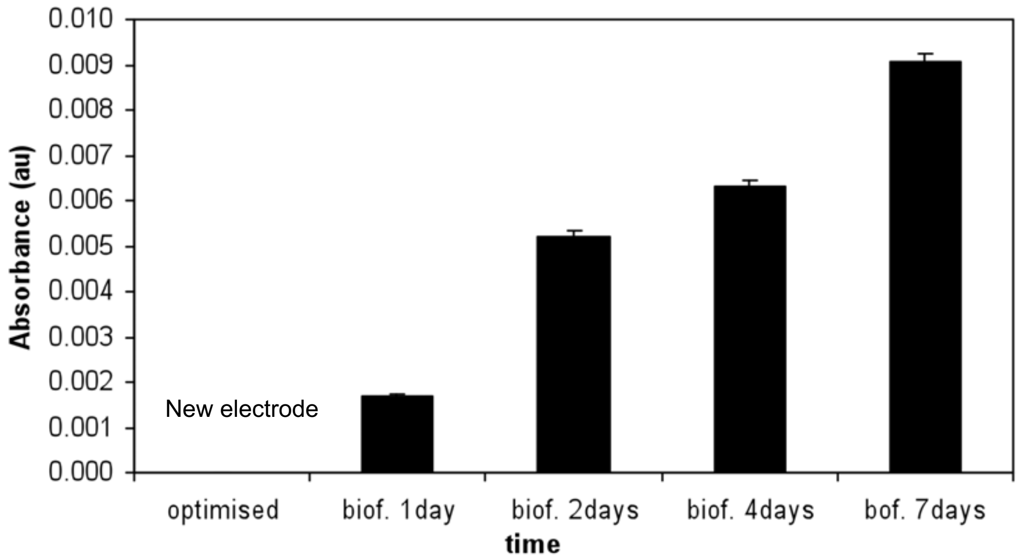
stored in 10^{-9}M Pb^{2+}, pH=4, in the lab



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

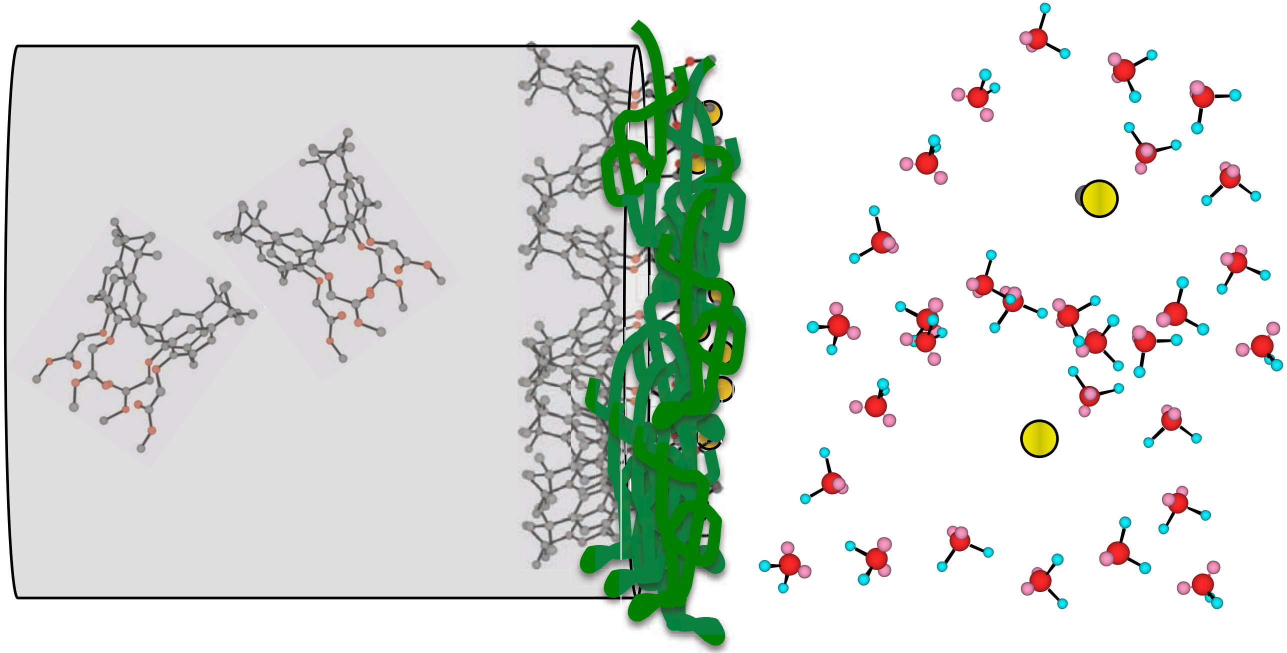


- **Electrodes exposed to local river water (Tolka)**
- **'Slime test' shows biofilm formation happens almost immediately and grows rapidly**

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.

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!!

Remote (Continuous) Water Monitoring 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

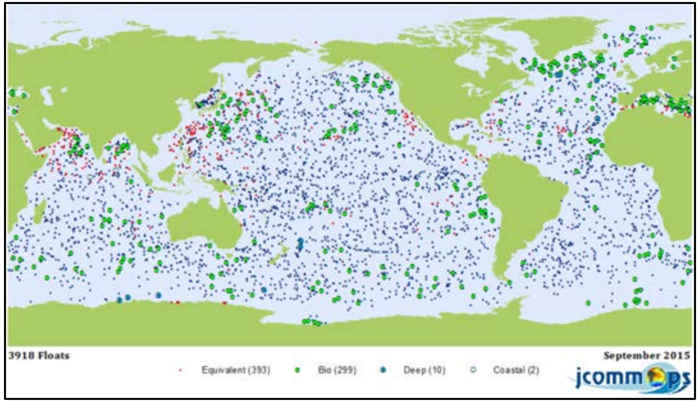
Marine Water

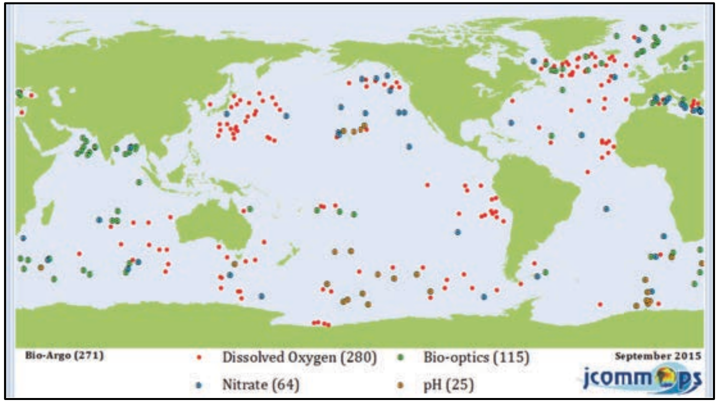
Challenging conditions

Remote locations & Limited infrastructure

Concentrations tend to be lower and tighter in range

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-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".**

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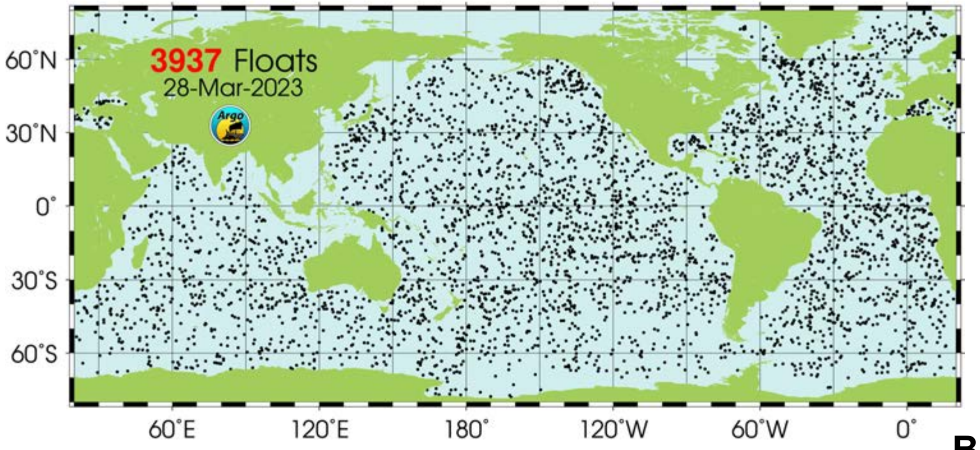

Core: ca. 4,000 floats (March 2023)

BioGeoChemical (BGC) Sensors: 522 ~ 13%

Chlorophyll: 308
Suspended particles: 308
pH: 268
DO: 514
Nitrate: 241
Full BGC Floats: 32 (<1%)

BCG are optical measurements except DO (Clark Cell) and pH (ISFET)

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)

'Calibration of the DO measurements by the SBE-IDO sensor remains an important issue for the future',
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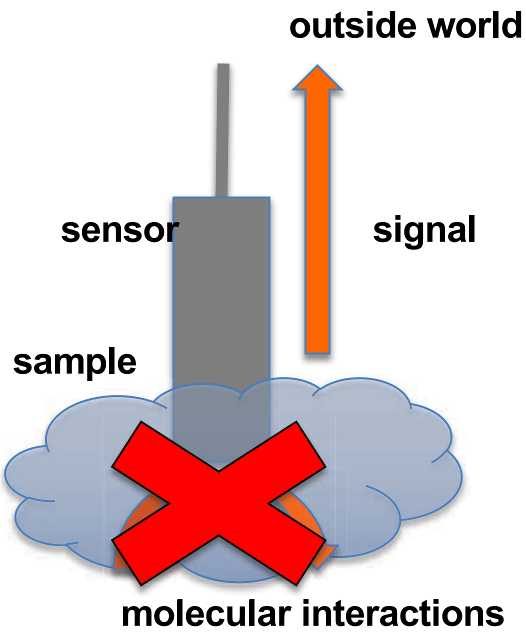
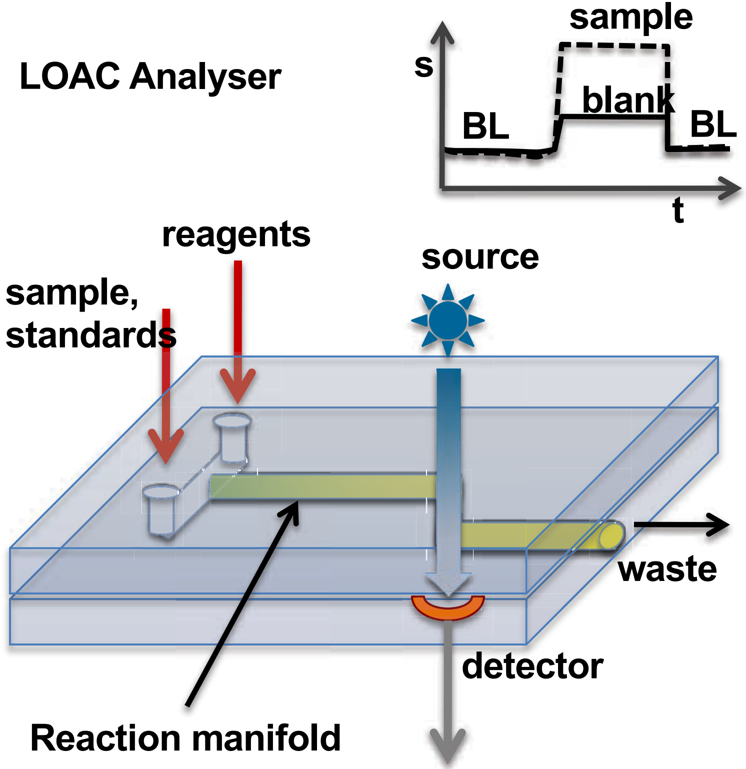
Direct Sensing vs. Reagent Based LOAC/ufluidics





Phosphate: The Yellow Method

Mixture (Reagent)

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

+

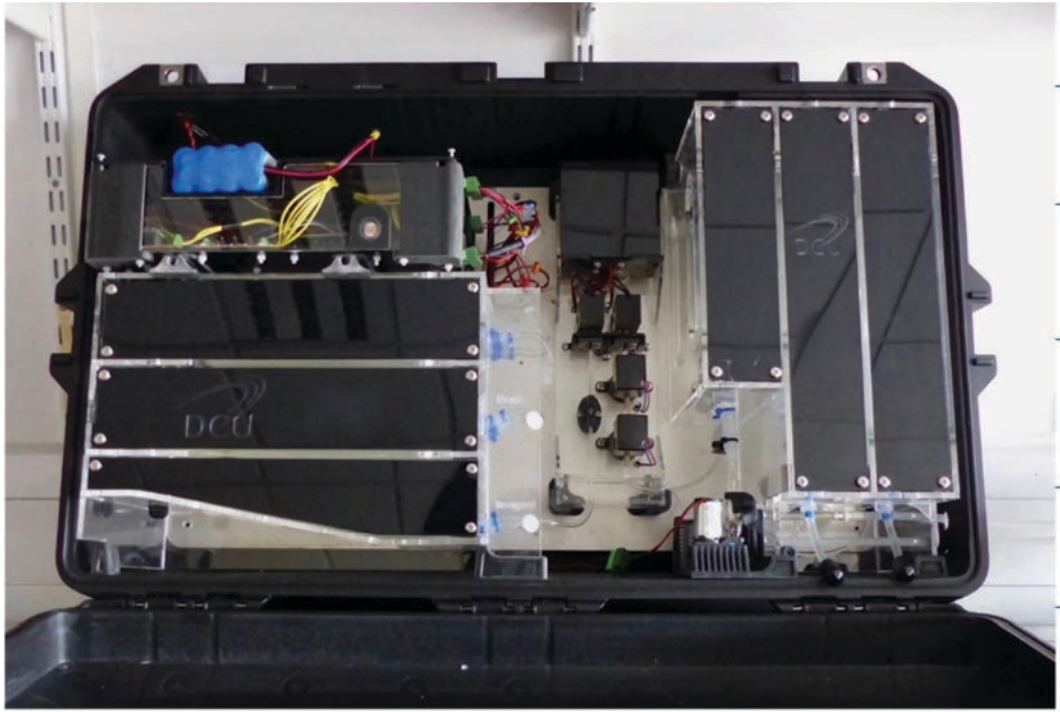
Sample

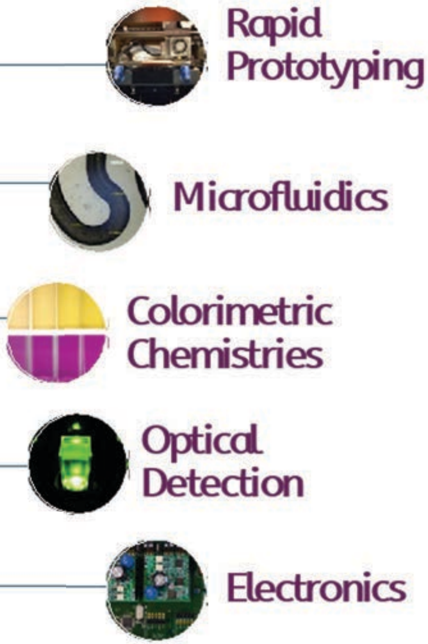
(KH_2PO_4)

$$(NH_4)_3PO_4.NH_4VO_3.16MoO_3$$

- 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!!!!

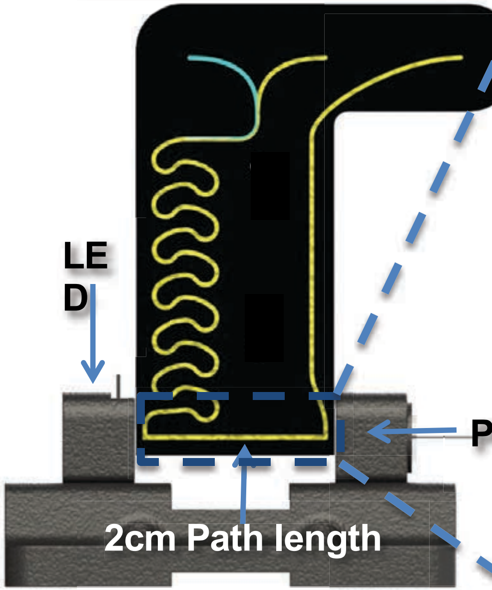
Phosphate Prototype Sensor



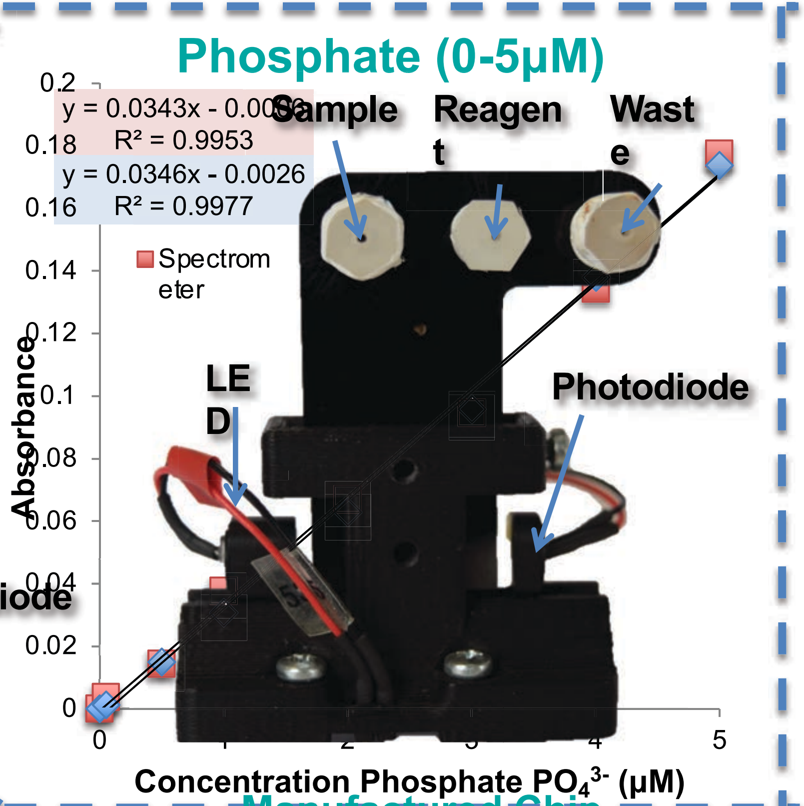


Reading on Chip

Phosphate detection on-chip

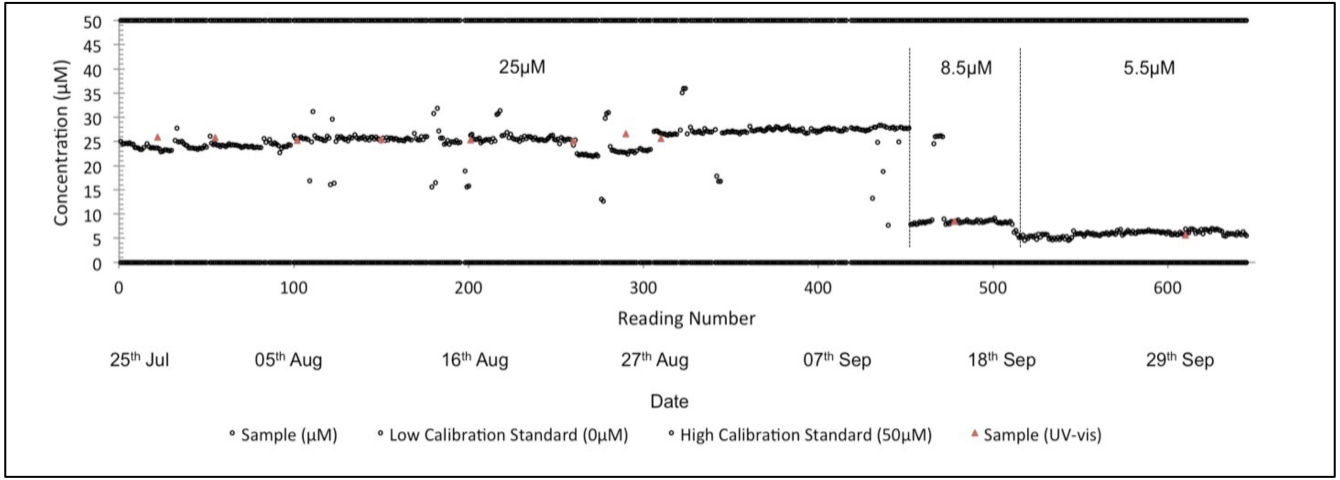


3D Render



Manufactured Chip

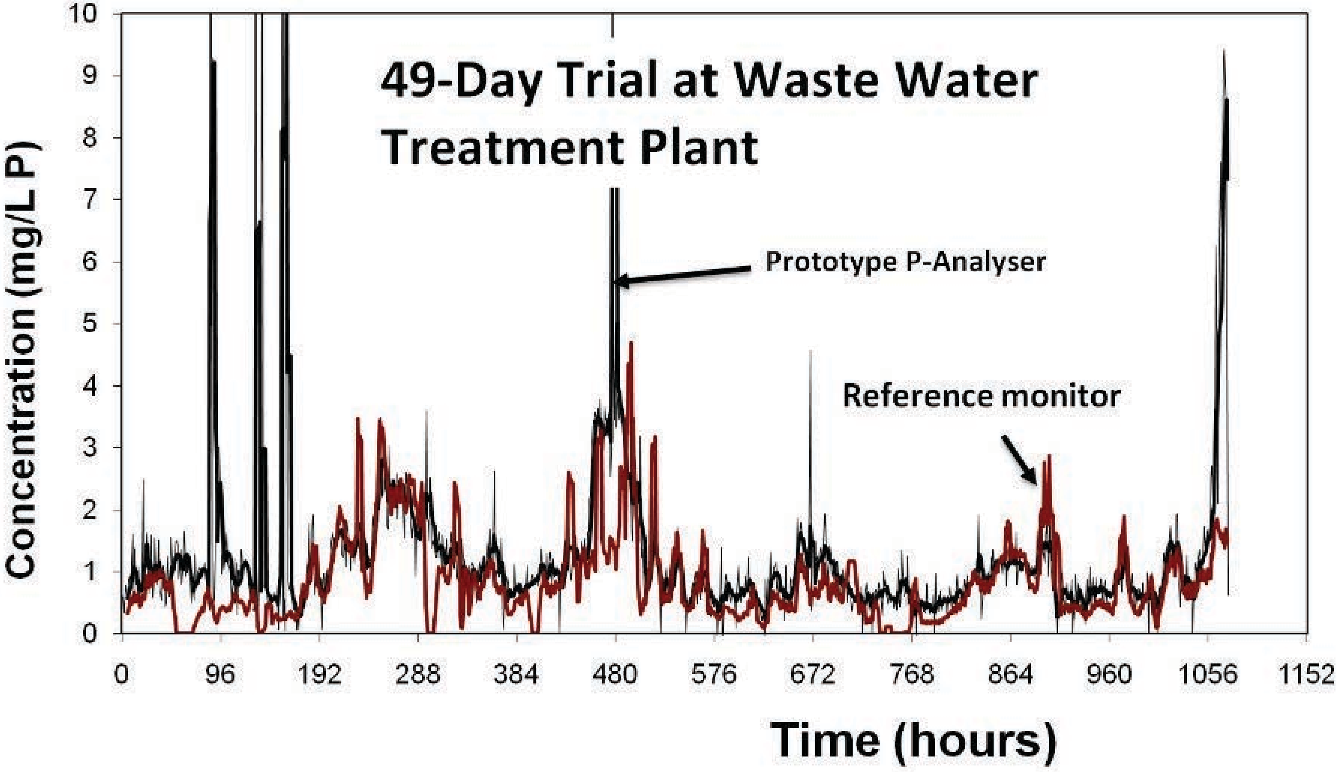
Laboratory Validation of Nutrient Platform



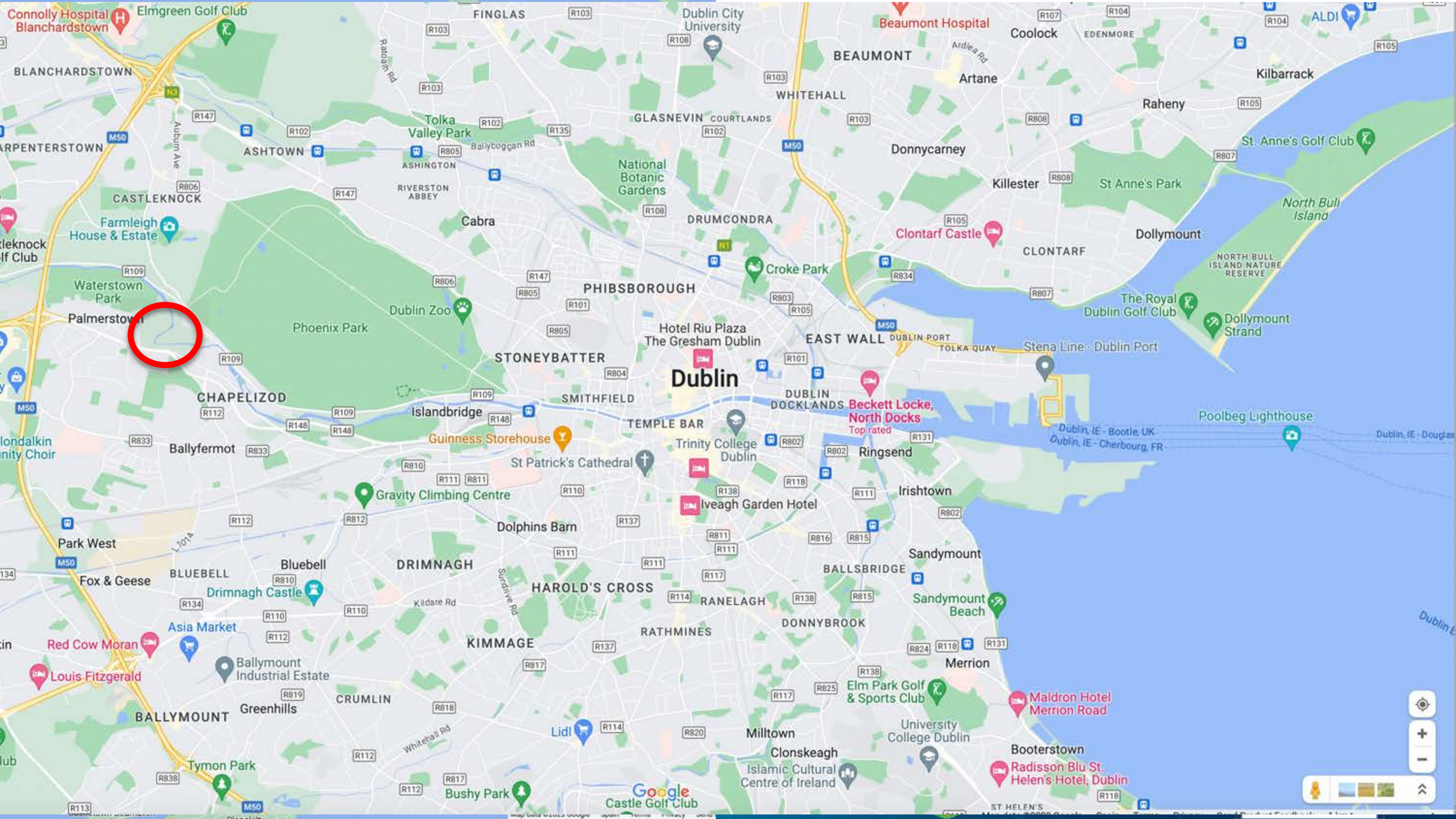
1941 Measurements over 78 Days
Testing Continued until the 1st of December

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

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.



Connolly Hospital Blanchardstown
Elmgreen Golf Club
FINGLAS
Dublin City University
Beaumont Hospital
Coolock
EDENMORE
ALDI
BLANCHARDSTOWN
BEAUMONT
Artane
Kilbarrack
WHITEHALL
Raheny
Tolka Valley Park
GLASNEVIN
COURTLANDS
ASHTOWN
ASHINGTON
Donnycarney
St. Anne's Golf Club
National Botanic Gardens
Killester
St Anne's Park
CASTLEKNOCK
RIVERSTON ABBEY
North Bull Island
Farmleigh House & Estate
Cabra
DRUMCONDRA
Clontarf Castle
Dollymount
CLONTARF
Croke Park
NORTH BULL ISLAND NATURE RESERVE
Waterstown Park
PHIBSBOROUGH
The Royal Dublin Golf Club
Palmerstown
Dublin Zoo
Dollymount Strand
Phoenix Park
Hotel Riu Plaza The Gresham Dublin
EAST WALL
DUBLIN PORT
TOLKA QUAY
Stena Line - Dublin Port
STONEYBATTER
Dublin
CHAPELIZOD
SMITHFIELD
DUBLIN DOCKLANDS
Beckett Locke, North Docks
Top rated
Poolbeg Lighthouse
Islandbridge
TEMPLE BAR
Guinness Storehouse
Trinity College Dublin
Ringsend
Ballyfermot
St Patrick's Cathedral
Gravity Climbing Centre
Irishtown
Iveagh Garden Hotel
Dolphins Barn
Park West
Sandymount
Bluebell
DRIMNAGH
BALLSBRIDGE
Fox & Geese
BLUEBELL
Drimnagh Castle
HAROLD'S CROSS
RANELAGH
Sandymount Beach
Asia Market
DONNYBROOK
Red Cow Moran
KIMMAGE
RATHMINES
Merrion
Louis Fitzgerald
Ballymount Industrial Estate
Elm Park Golf & Sports Club
Maldron Hotel Merrion Road
CRUMLIN
BALLYMOUNT
Greenhills
University College Dublin
Milltown
Lidl
Booterstown
Clonskeagh
Tymon Park
Islamic Cultural Centre of Ireland
Radisson Blu St. Helen's Hotel, Dublin
Bushy Park
Google
Castle Golf Club

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

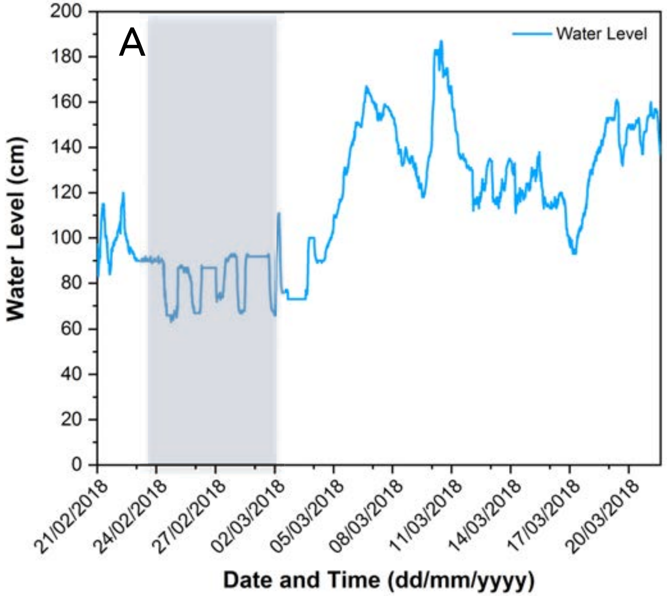
Varadkar says people 'should not venture out of doors' while the red level warning is in place

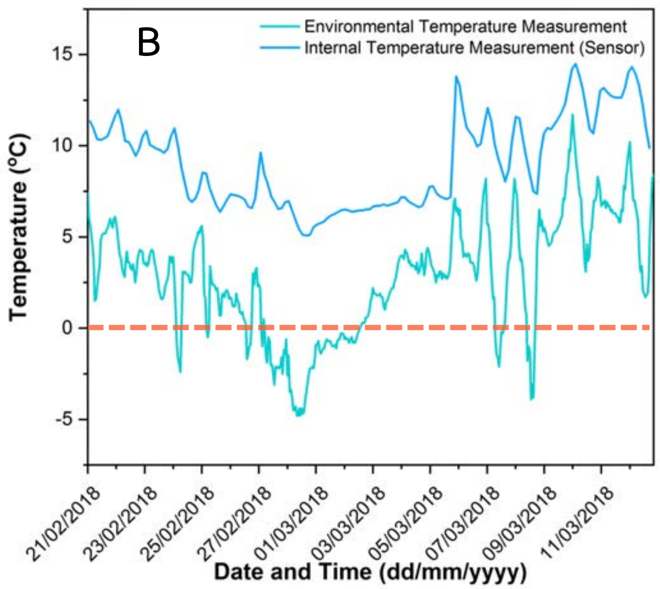
Wed, Feb 28, 2018, 06:29 | Updated: Wed, Feb 28, 2018, 21:05

A. Deployment Location
B. Sensor Prepared for Deployment
C. Temperatures reach -4.5°C

https://www.irishtimes.com/news/environment/beast-from-the-east-status-red-snow-alert-in-place-until-friday-1.3408511

River Liffey Deployment, Palmerstown, Dublin

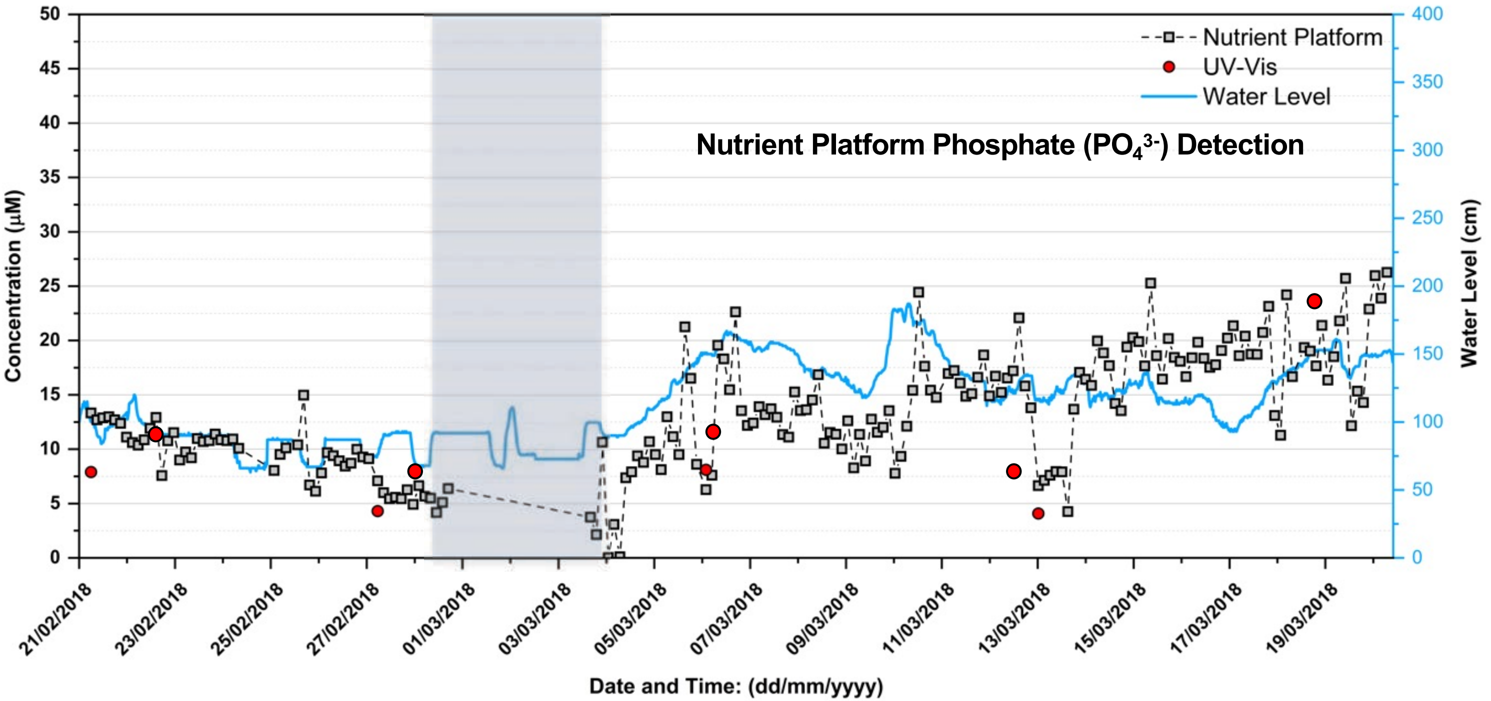




A. Water levels controlled by Leixlip Dam. Increasing water levels from the 5th Mar due to snow melt.

B. External vs Internal Temperature
External lows of -4.5°C.
Internal lows of 5°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

Advantages:

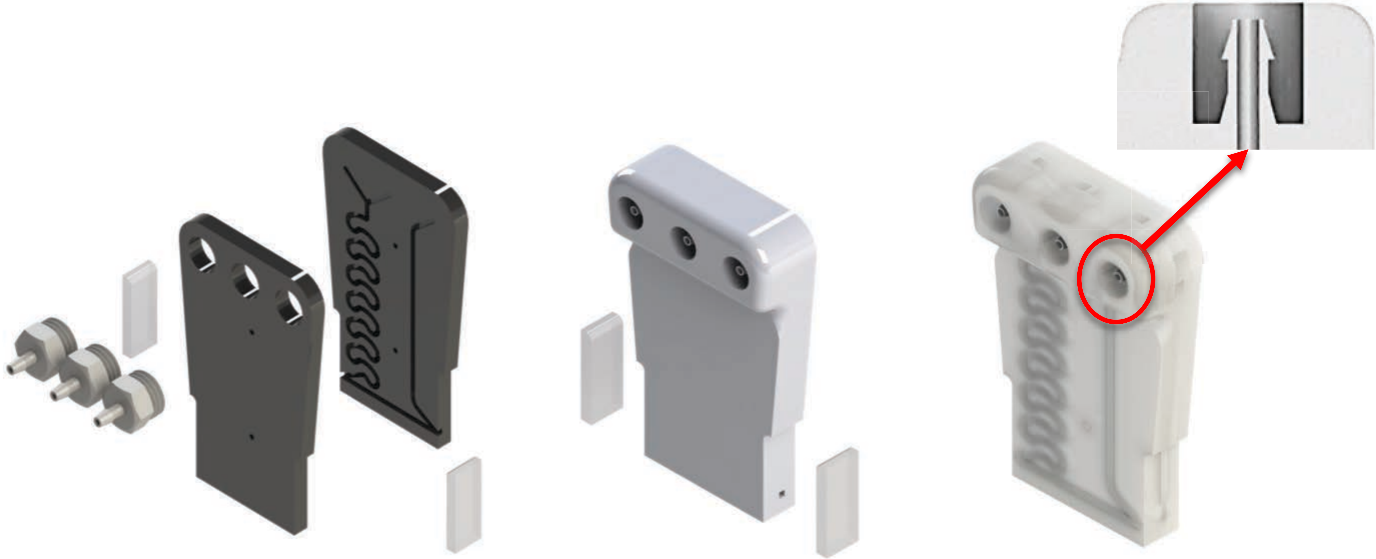
- **No Assembly**
- **No Bonding necessary**
- **Integrated barbs (1/16”)**
- **Chip thickness reduced by 63%**
- **Automated manufacturing**

Assembled Chip **Printed Chip**

Rendered Chip

Printed Chip

From Multi-Part to Single Part Fluidic Chips



7 Parts : 3 days

~€50/chip

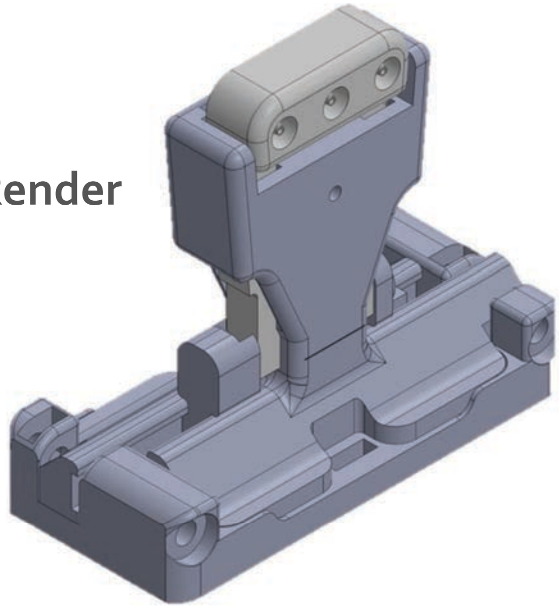
3 Parts : 1 day

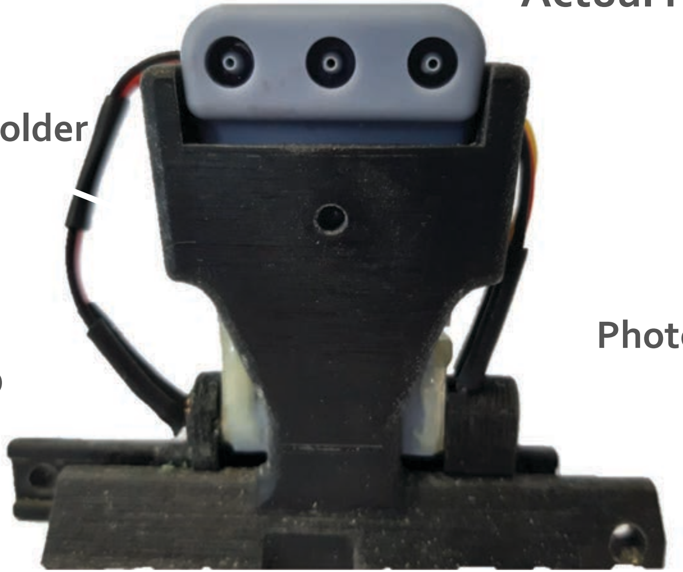
1 Part : 1 hour

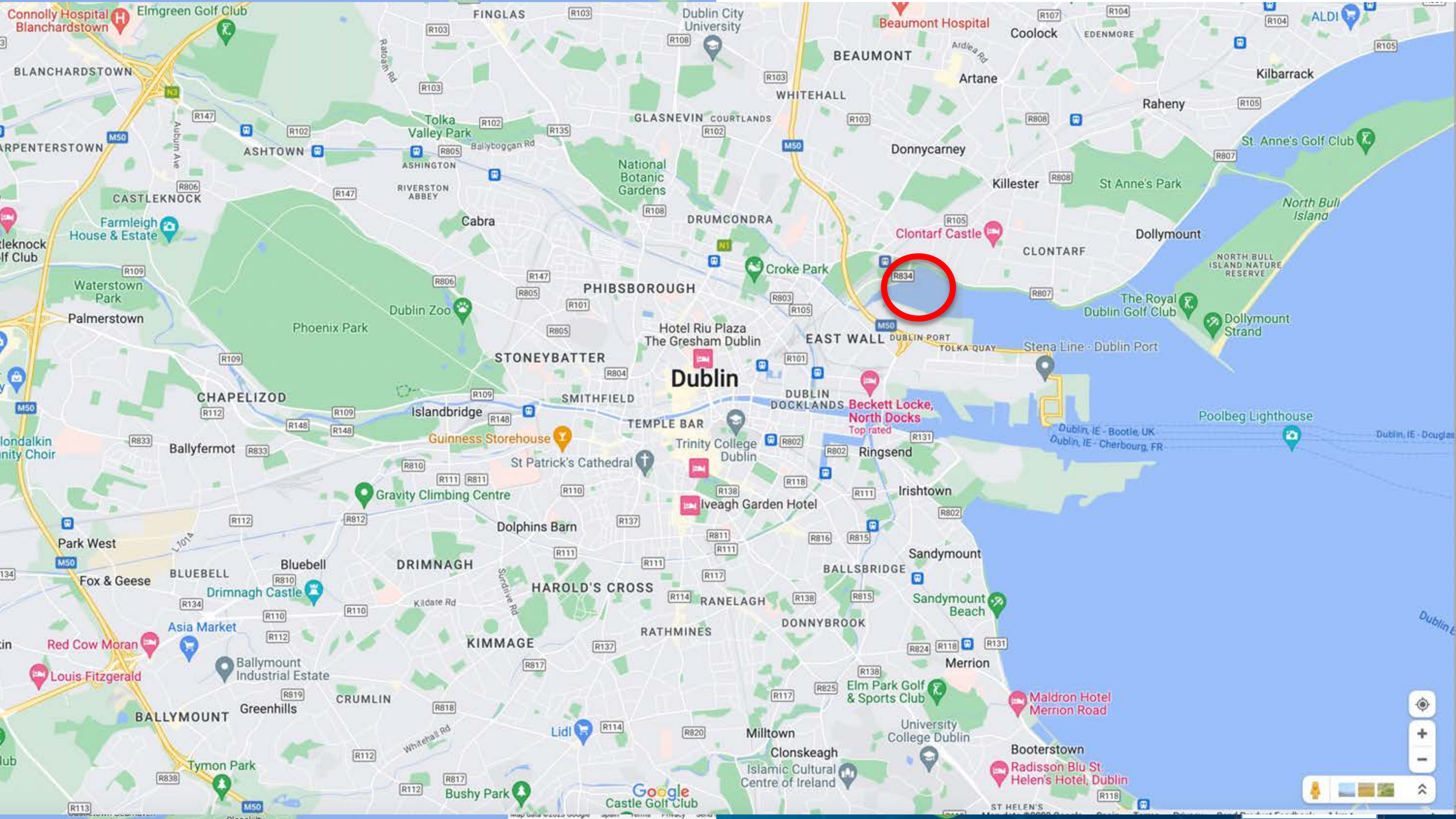
~€1/chip

With Laurent Malaquin (LAAS-CNRS, Toulouse)

Fluidic Chip







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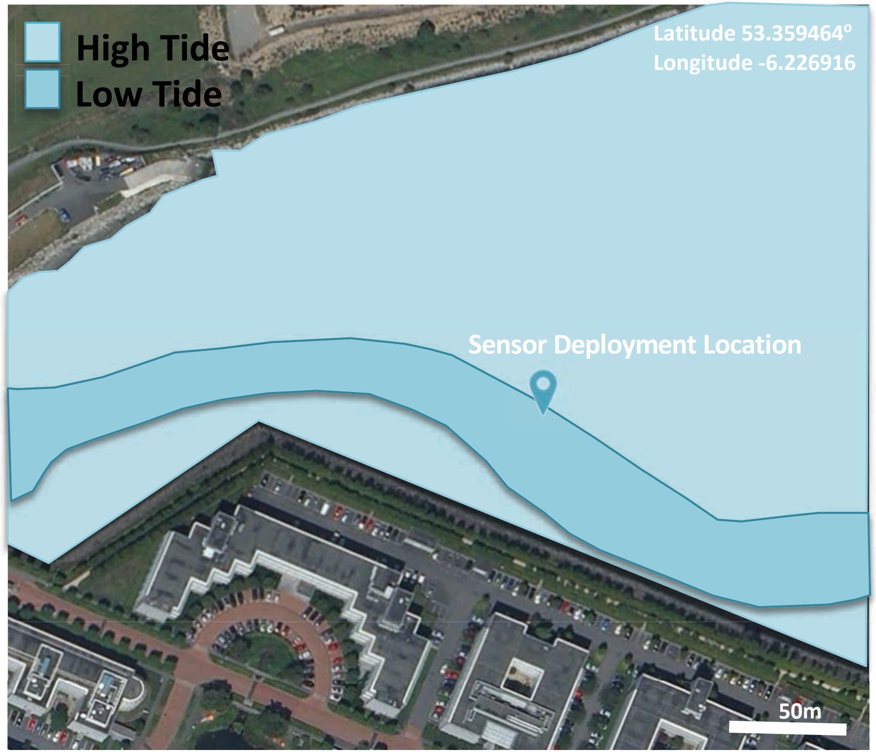
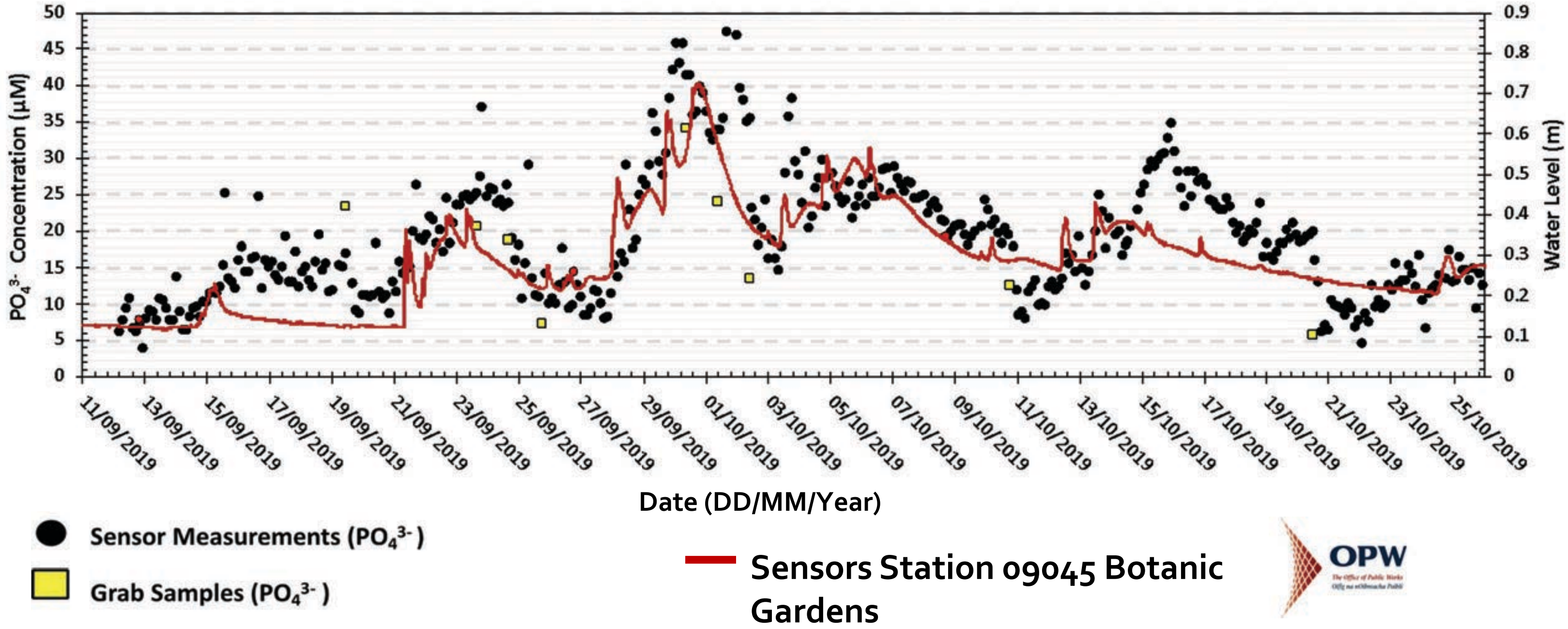
The Royal Dublin Golf Club
Palmerstown
Dublin Zoo
Dollymount Strand
Phoenix Park
Hotel Riu Plaza The Gresham Dublin
EAST WALL
DUBLIN PORT
TOLKA QUAY
Stena Line - Dublin Port
STONEYBATTER
Dublin
CHAPELIZOD
SMITHFIELD
DUBLIN DOCKLANDS
Beckett Locke, North Docks
Top rated
Poolbeg Lighthouse
Islandbridge
TEMPLE BAR
Dublin, IE - Bootle, UK
Dublin, IE - Cherbourg, FR
Dublin, IE - Douglas
Guinness Storehouse
Trinity College Dublin
Ringsend
Ballyfermot
St Patrick's Cathedral
Irishtown
Gravity Climbing Centre
Iveagh Garden Hotel
Dolphins Barn
Park West
Sandymount
BALLSBRIDGE
Bluebell
DRIMNAGH
Fox & Geese
BLUEBELL
HAROLD'S CROSS
Drimnagh Castle
RANELAGH
Sandymount Beach
Kildare Rd
Asia Market
DONNYBROOK
RATHMINES
Red Cow Moran
KIMMAGE
Ballymount Industrial Estate
Merrion
Louis Fitzgerald
CRUMLIN
Elm Park Golf & Sports Club
Maldron Hotel Merrion Road
BALLYMOUNT
Greenhills
University College Dublin
Milltown
Booterstown
Clonskeagh
Islamic Cultural Centre of Ireland
Radisson Blu St. Helen's Hotel, Dublin
Tymon Park
Lidl
Bushy Park
Castle Golf Club
Google

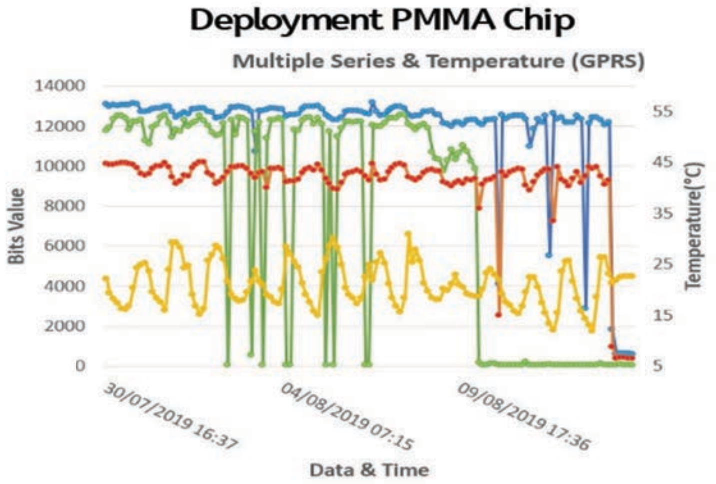
Dublin Bay (Estuarine) Deployment

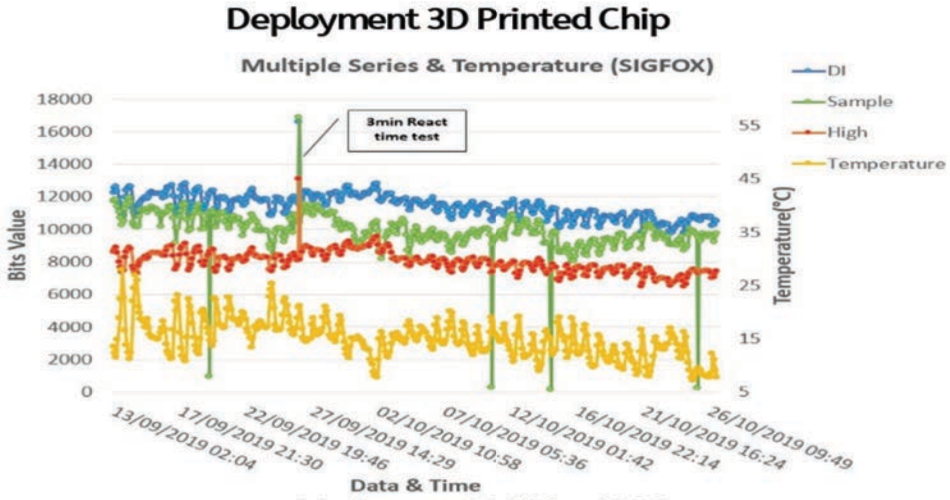


In-Situ Sensor Measurements



Multi-Part Chip vs. 3D Printed Chip





15-day deployment = 140x3 = 420 readings

24 failed readings observed (DI, High, Sample)

Failure rate = 5.71%

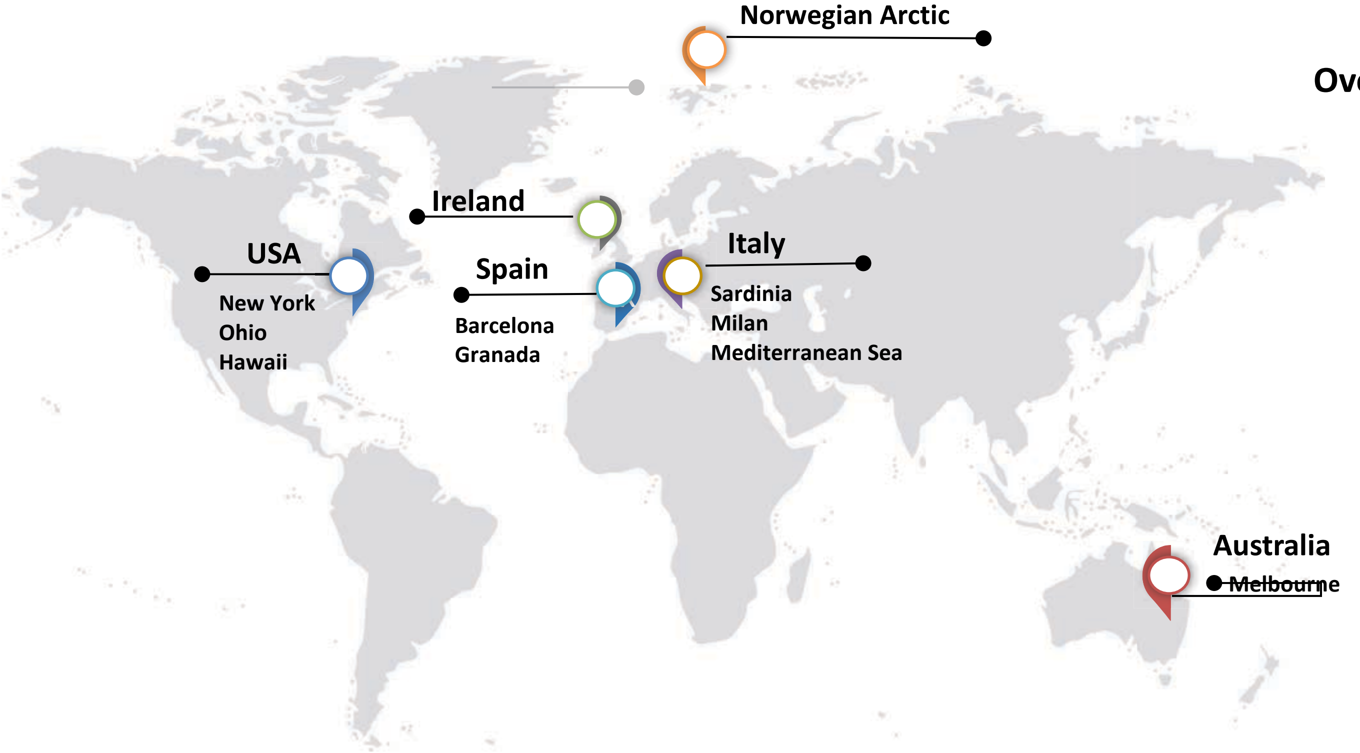
44-day deployment = 411x3 = 1,233 readings

4 failed readings observed (Sample)

Failure rate = 0.32%

Data failure rate is improved by a factor of x18!

Development and De-Risking through Deployment



Over 20 Different Deployments in 6 Different Countries


LGSONIC
DCU
Ollscoil Chathair
Bhaile Átha Cliath
Dublin City University
LG SONIC

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

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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

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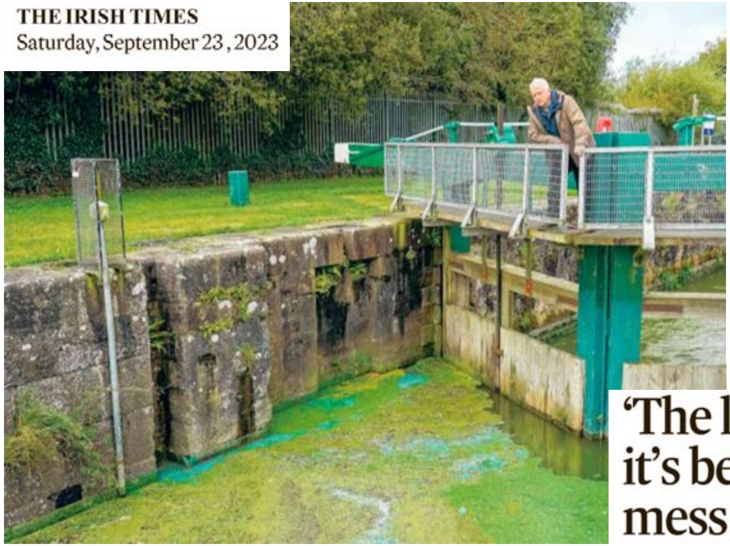

Freya McClements
Northern Editor

The largest freshwater lake in Ireland is being contaminated by a spread of poisonous algae

'The lough isn't just dying, it's been killed': The clotted mess choking Lough Neagh

Conclusions

- Demand for long-term ‘continuous’ monitoring of remote environmental waters is increasing and will continue to grow.
- Regular calibration imposes the need for an integrated 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.....

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Questions??