Cost effective sensing platform for the detection of phosphate in natural waters

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'Insight Centre for Data Analytics’

- Biggest single research investment ever by Science Foundation Ireland
- Biggest coordinated research programme in the history of the state
- Focused on ‘big data’

The Centre will receive funding of €58 million from the Department of Jobs, Enterprise and Innovation through SFI’s Research Centres Programme, along with a further contribution of €30 million from 30 industry partners. Insight represents a new approach to research and development in Ireland, by connecting the scientific research of Ireland’s leading data analytics researchers with the needs of industry and enterprise.
Create cost effective sensors that can obtain accurate, real-time information about environmental status (mainly related to water quality) from the highly local to global scale. This can only be realised through ‘deploy and forget’ models of use, in which the analytical platforms are:

i) capable of autonomous function for periods of months between servicing intervals;
ii) provide validated analytical data over this period,
iii) are relatively inexpensive to buy and maintain
Argo project – National Contributions

Argo

National contributions - 3904 Operational Floats
Latest location of operational floats (data distributed within the last 30 days)

ARGENTINA (2)  ECUADOR (1)  GREECE (8)  KENYA (1)
AUSTRALIA (370)  EUROPE (59)  INDIA (130)  MAURITIUS (1)
BRAZIL (6)  FINLAND (6)  IRELAND (10)  MEXICO (2)
CANADA (74)  FRANCE (319)  ITALY (70)  NETHERLANDS (26)
CHINA (116)  GERMANY (143)  JAPAN (171)  NEW ZEALAND (7)

NORWAY (10)  PERU (3)  POLAND (2)  KOREA, REPUBLIC OF (62)
UK (156)  USA (2142)

Accessed 19 June 2017; http://www.jcommops.org/board?t=Argo

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Argo project – Biogeochemical Sensors

Biogeochemical Argo

Sensor Types

- Operational Floats (284)
- Suspended particles (149)
- Downwelling irradiance (47)
- Nitrate (93)
- Chlorophyll a (150)
- pH (70)
- Oxygen (264)

Latest location of operational floats (data distributed within the last 30 days)

Accessed 19 June 2017; http://www.jcommops.org/board?t=Argo

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Argo project – Nitrate Sensing

Cost €60,000 per Sensor

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Nutrient Challenge

Nutrient Sensor Features

• Measure dissolved nitrate and/or phosphate
• Provide real-time data
• Easy to use
• Less than $5000 purchase price
• Unattended deployments for 3 months
• Highly accurate and precise

Winner - Systea S.P.A Analytical

• Colorimetric Chemistries
• Analysis of Phosphorus and Nitrogen ✓
• Deployable up to 60 days ✓
• Cost $30,000 ✗

http://www.systea.it/index.php?option=com_k2&view=item&layout=item&id=221&Itemid=176&lang=en
Title: Cost-effective sensors, interoperable with international existing ocean observing systems, to meet EU policies requirements

Total Budget: €6,074,497

Duration: 40 months

Consortium: 15 partners from seven different countries

(the COMMON SENSE consortium comprises six SMEs, five research development institutes, three universities and one foundation)
Develop innovative, cost-effective sensors that will increase the availability of standardised data on:

- **Eutrophication**
- Concentrations of heavy metals;
- Micro-plastic fraction within marine litter;
- Underwater noise;
- Parameters such as temperature and pressure.

Sensors will assess environmental conditions affecting marine ecosystems:

- Mitigating the anthropogenic impacts
- Climate change impacts
- Promoting basic research of marine science
European Legislation

COMMONSENSE and the Marine Framework Directive

Under the **Marine Strategy Framework Directive (MSFD)**, EU Member States are expected to assess the overall status of their marine environments and to put in place the necessary measures to achieve Good Environmental Status (GES) by 2020. Member States must implement cost-effective monitoring programmes in order to achieve MSFD monitoring objectives, as well as other European maritime and environmental policies such as the Common Fisheries Policy (CFP).

http://science.gu.se/digitalAssets/1322/1322948_nodularia-blooming_460px.jpg
Sensor Development

Develop Sensors for nutrients (nitrite, nitrate and phosphate) based on:

- Colorimetric chemical assays
- Rapid Fabrication and Prototyping
- Fluidic Control
- LED Based Microfluidic systems
- Wireless Communications

Prior to Integration

- Individual Component testing and Validation
- Validation of Colorimetric Assays
Nutrient System Schematic

8 Pumps, 12 valves, 5 Microfluidic Chips

Nutrient Sensing
Nitrite Reagents
High → Low
Nitrate Reagents
High → Low
Phosphate Reagents
High → Low
Ammonia Reagents
High → Low

3/2 Valves
Piezo Pumps
2/2 Valves
Mixing chip
LED
Photo Detector
Waste

Heating Element

Non Return Valve

Heavy Metal Sensing
Reagent (HCL or Nitric Acid)
Mixing chip
C-Bi electrode
Peristaltic Pumps
Waste

Pump
Inlet
Reservoir
Non Return Valve
Outlet
System Overview

Electronics for Autonomous operation, Detection and Data Transmittance
System Overview

Microfluidic Chip, Photodiode and LED

Sample and Reagent Bags

Waste Collection Bag

Battery Compartment
Prioritised due to

- Increasingly high demand for monitoring
- Typically the limiting nutrient in freshwater ecosystems
- Non-renewable resource – increasing attention on recovery from waste

Yellow method (vanadomolybdophosphoric acid)

- Simple colorimetric method – Single reagent 1:1 ratio
- Highly stable reagent (>1 year in solution)
- Fast reaction time
- Absorbance-based detection using UV-LED (375nm) and photodiode
Colorimetric Chemical Assay’s
Phosphate Analysis in Artificial Seawater

- Sample Number: \( n = 10 \)
- Wavelength: 375 nm
- Limit of Detection: 0.05\(\mu M\) \(\text{PO}_4^{3-}\)

\[ R^2 = 0.999 \]
Rapid Prototyping

Solid Works Design

3D Render

3D Printing

Laser Ablation
Rapid Prototyped Components

Use of 3D Printing, Laser Ablation and Micro milling techniques for rapid Prototyping

- Parts quickly and easily manufactured in house
- Reduces manufacturing time
- Reduces cost

Manufactured part

3D Render

Cuvette Holder with Led Alignment

Piezo Pump Mountings

Microfluidic Optical Chip
Fluidic Handling – Piezo Pumps

Takasago Piezoelectric Pump

Workings of the diaphragm pump

Initial Pump Flow rates

Pumps run at a frequency of 10Hz, Duty Cycle 50% and signal supply voltage of 2.5v

Pump Calibrations 1:1

Low Calibration Standard

High Calibration Standard

Sample
Fluidic Handling - Inlet System

Inlet pump intakes approximately 210ml of representative sample from the environment using a 12V diaphragm pump.

Passive drainage system allows excess sample to drain in 12 minutes using a flow restricting outflow.
Membrane Characterisation

Durapore 0.45μM

Nikon D3300 DSLR

Hitachi S-300n Scanning Electron Microscope
Membrane Characterisation - Diatoms

Coccolithophore – 3 Days Growth

Coccolithophore – 7 Days Growth

Paribellus

Thalassiosira
Microfluidic Detection

Overview:
• Complete integration of Fluidic Handling within a microfluidic chip.
• Manufactured using Micro milling and Laser cutting.
• Serpentine channel for Sample and Reagent Mixing.
• Minimal Fluid Volume per assay.
• Optical Detection on chip.

Detection on Chip Validated against Spectrophotometer when integrated into bench top system and Autonomous System
Phosphate detection on-chip

Absorbance

Concentration Phosphate \( \text{PO}_4^{3-} \) (μM)

Sample  Reagent  Waste

Phosphate (0-5μM)

\[
y = 0.0343x - 0.0006 \\
R^2 = 0.9953
\]

\[
y = 0.0346x - 0.0026 \\
R^2 = 0.9977
\]

Photodiode

2cm Path length

3D Render

Manufactured Chip

Photodiode

LED

Photodiode

Spectrometer

CS System

Phosphate detection on-chip
CS Nutrient Sensor

**Generation 1**
- Benchtop prototype
- Integrated electronics
- Optical detection
- Deployed November 2016

**Generation 2**
- Integrated fluidics
- Sample inlet
- On chip detection
- Sampling Rate every 2 hours
- Battery powered
- Deployed Ny-Alseund June 2016
- 6ml reagent per assay

**Generation 3**
- Integrated fluidics
- Sample inlet
- On chip detection
- Sampling Rate every 1 hour
- Battery powered
- Wireless communication
- Deployed Milan WWTP
- 1.3ml reagent per assay
Water samples were collected for nutrient and heavy metal analysis, over 95 samples analysed onboard for Nitrite and Nitrate. Samples not analysed were stored at -22°C for subsequent analysis.

Interlaboratory validation

- CNR-Italy All stations (48)
- DCU All stations (48)
- TelLab 10 stations

- Approximately 400 samples analysis CNR, DCU, 50 TelLabs
- Parameters: Phosphate, Nitrite, Nitrate
- DCU – CS bench-top system and UV-Vis
- Approximately 1200 measurements
A) Phosphate  B) Nitrate and  C) Nitrite concentrations at along a depth profile from 0 to 166m at station 432.

D) Phosphate concentrations at along a depth profile from 0 to 3500m at station Geostar
Prototype Testing – Generation 2
Deployed Ny-Alseund June 2016

Deployment team

Acquiring Sample

Lab Validation
Prototype Testing – Generation 2
Deployed Ny-Alseund June 2016

Laboratory Testing in Ny-Alesund
• System Validation prior to deployment
• Sample was taken from 10 liters of artificial seawater spiked with a known concentration of each nutrient
• Subsamples were taken and measured using the CS bench top system

Validation at Artic Base

CS Bench-top nutrient Sensor
In-situ Measurements

- Kongsfjorden Fjord, Svalbard
- Sample Plan stations from A-B-C
- CNR Italy measuring CTD at each station

CS Deployable system acquiring samples on board the MS Teisten beneath the of Kongsvegen glacier
A) Phosphate, Nitrite and Nitrate concentrations at along a depth profile from 0 to 75m at station 023

B) Phosphate  
C) Nitrite and  
D) Nitrate concentrations at along a depth profile from 0 to 75m at station 023
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
Available Sampling Points:
1. Output water after Sand Filtration
2. Output water after the Clarifier
3. Activated Sludge (Biological Tank)
4. Input Water

Output water after the Clarifier:
Typical Parameters
• Low detectable Nitrites
• 5mg/L Nitrates
• 1.5mg/L Phosphates
• 10mg/L Suspended Solids
Results Obtained from Output after the Clarifier

Autonomous System Readings

15 Readings from the 4th to the 5th of May

Absorbance

High Calibration Standard (50μm)
Low Calibration Standard (0μm)
Environmental Sample

Time (Hour:Minute:Second)

0 0.2 0.4 0.6 0.8 1 1.2
12:00:00 14:24:00 16:48:00 19:12:00 00:00:00 02:24:00 04:48:00 07:12:00 09:36:00 12:00:00 14:24:00

High Calibration Standard
Environmental Sample
Low Calibration Standard

4th May 5th May
Results Obtained from Output after the Clarifier

Phosphate $\text{PO}_4^{3-}$

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Concentration ($\mu$M) vs. Time (Hour:Minute:Second)

- **High Calibration Standard**
- **Low Calibration Standard**
- **Environmental Sample**

0 20 40 60 80 100 120 140

12:00:00 14:24:00 16:48:00 19:12:00 21:36:00 00:00:00 02:24:00 04:48:00 07:12:00 09:36:00 12:00:00 14:24:00

4th May 5th May

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**Environmental Sample**

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**High Calibration Standard**

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**Low Calibration Standard**
System Monitoring

Internal System Temperatures

Temperature (°C) vs Time (Hour:Minute:Second)

- Battery Temperature 1
- Battery Temperature 2
- Environmental Temperature

Temperature (°C):
- 0
- 5
- 10
- 15
- 20
- 25
- 30
- 35

Time (Hour:Minute:Second):
- 14:24:00
- 19:12:00
- 00:00:00
- 04:48:00
- 09:36:00
- 14:24:00
- 19:12:00
- 00:00:00
- 04:48:00
- 09:36:00
- 14:24:00
System Monitoring

Internal light during testing

Case opened during testing

Internal Light During Deployment
Inlet System- Durapore 0.45μM

- Approximately 5.25L sampled during deployment.

- Sample was taken for 2 ½ minutes every 2 hours.
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