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MEASURING CONTINUOUS CONCENTRATION OF MASS POLLUTANTS IN AQUATIC ENVIRONMENTS

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INNOVATE UK PROJECT: “MULTIMEMS”

- **Innovate UK** 3 year, £1.5m collaborative R&D project
  - start date: August 2014, Value: ~£1.5m
- **Environmental Monitoring Solutions Ltd** (Project Lead)
  - project management, market engagement and exploitation, guiding the practical design of instruments, and field trials
- **University of Sheffield**, and particularly the Kroto Institute
  - affinity chemistry, surface chemistry, mechanical MEMS design
- **INEX Ltd**
  - MEMS fabrication and MEMS chip packaging
- **Practical Control Ltd**
  - signal processing and production of the probe and associated software

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WHAT IS “MULTIMEMS”?

- MultiMEMS is a new sensor platform
- Based on coupling of:
  - polymeric compounds with affinity toward target substances
  - mass sensing technologies such as Quartz Crystal Microbalance (QCM)
- potential for sensing many different substances in real-time
  - we’re starting with phosphate and nitrate
- disruptive technology

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Why is MultiMEMS needed?

Why nutrients?

WHY DO WE NEED TO MONITOR? FUNDAMENTALLY

- to understand man's impact on the aquatic environment which sustains us
- effects of
  - agriculture (diffuse pollution)
  - urban runoff
  - abstraction
  - wastewater treatment works (difficult to remove chemicals)
  - sewer overflows

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WHY DO WE NEED TO MONITOR? LEGISLATIVELY

- to satisfy the requirements of the EU Water Framework Directive
- commits EU states to achieve good qualitative and quantitative status of all water bodies
- ***"Qualitative"***
  - chemical quality (maximum concentrations for specific water pollutants)
  - ecological quality
- ***"Good"***
  - definition is around the state of the water body before anthropogenic impact; returning it to its natural state
- evidence (monitoring) before and after remedial works

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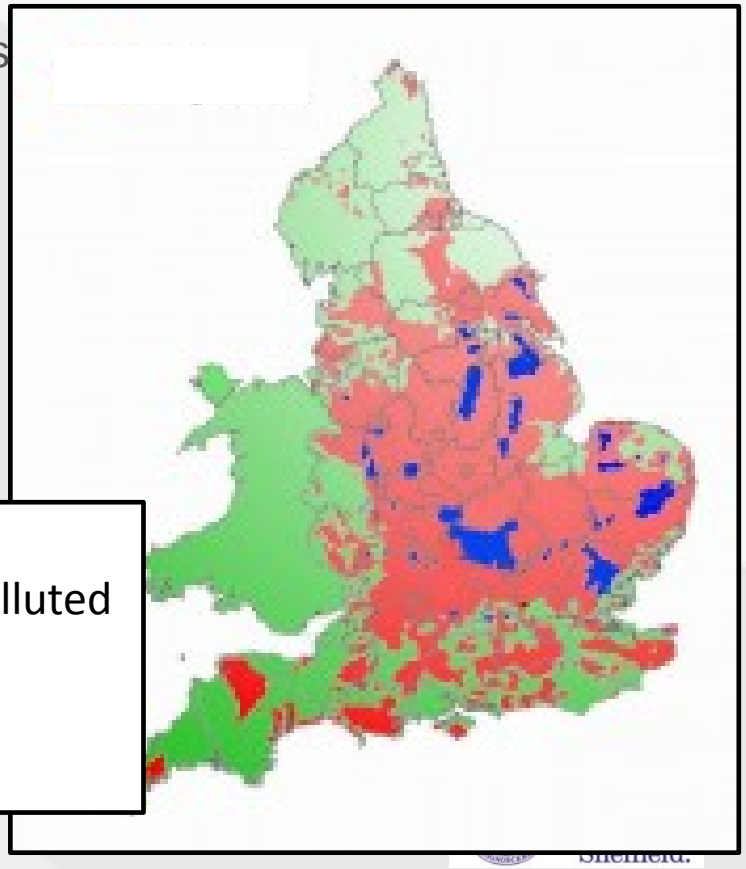
THE NEED FOR NUTRIENT MONITORING

- WFD focuses on anthropogenic impact
  - water-quality-wise, **THE IMPARTING OF NUTRIENTS ON WATER BODIES IS ARGUABLY MAN'S BIGGEST IMPACT**
    - impact of agri-runoff: need to optimise additives and methods
    - impact of wastewater treatment works outfalls: many chemicals are difficult to remove at low concentrations
- **Nitrates, phosphates, ammonia**
- Nutrient levels are very difficult to measure accurately in the field

Nitrate Vulnerable Zones (NVZ)

NVZs 1996

New NVZs



Nitrate Vulnerable Zones are areas of land that drain into nitrate polluted waters, or waters which could become polluted by nitrates. They were introduced in response to the EU mandate that all EU countries must reduce the nitrate in Drinking Water to a maximum of 50 mg/l.

Why is MultiMEMS different?

CURRENT STATE OF THE ART FOR NUTRIENT MONITORING

- Cost
  - Expensive
  - Labour intensive
- Data
  - Low observability
  - Delayed
  - Inaccurate

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WATER QUALITY DATA COLLECTION*: STATE OF THE ART

Automatic Samplers and Labs

- Cumbersome
- Labour intensive
- Low observability

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WATER QUALITY DATA COLLECTION: STATE OF THE ART

Field Test Kits

- Colorimetry / spectrophotometry based
- Very cumbersome
- Labour intensive
- Low observability – single point
- High user skill and open to error and contamination

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WATER QUALITY DATA COLLECTION: STATE OF THE ART

Passive Samplers

- Chemical affinity
- Accumulation with time
- Multi-parameter
- Average over extended time periods (days/weeks)

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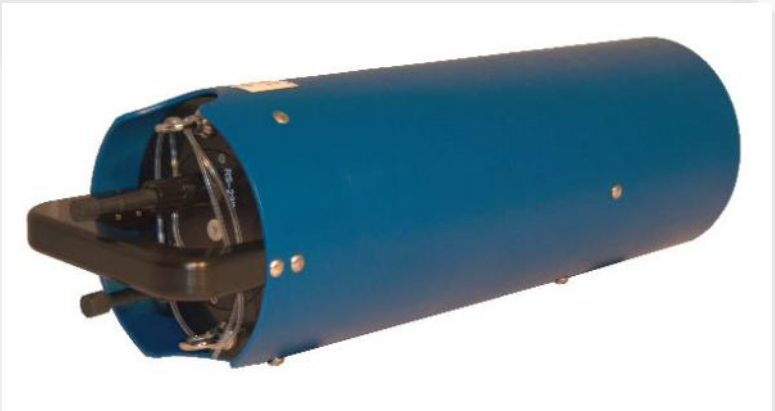
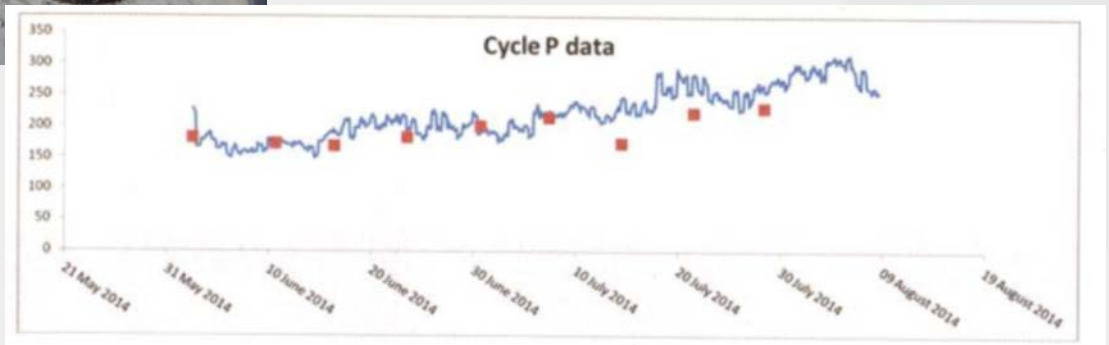
WATER QUALITY DATA COLLECTION: STATE OF THE ART





Process Buoy: Cycle P

- Phosphate
- On-board reagents
- Up to 1000 measurements
- Every 15 minutes
- Accurate
- Expensive

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WATER QUALITY DATA COLLECTION: STATE OF THE ART

Water Quality Instruments

- Limited parameters
  - pH, dissolved oxygen, pressure, temperature, turbidity, conductivity
- Very expensive and high maintenance

- ISEs for nitrates, ammonium
  - Indicative only
  - Very expensive and high maintenance
  - **No sensor for phosphate**

*field data collectio

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MULTIMEMS: OBJECTIVES

- **Continuous measurement**
  - high observability
  - real-time data
  - accurate data
  - sensors integratable with current telemetry platforms
- **Cost**
  - aim is for technology to be comparable in cost to pH, DO, ISEs and so on
- **Increased understanding of environmental impacts, e.g. agricultural runoff**
- **The first step in addressing environmental impacts**

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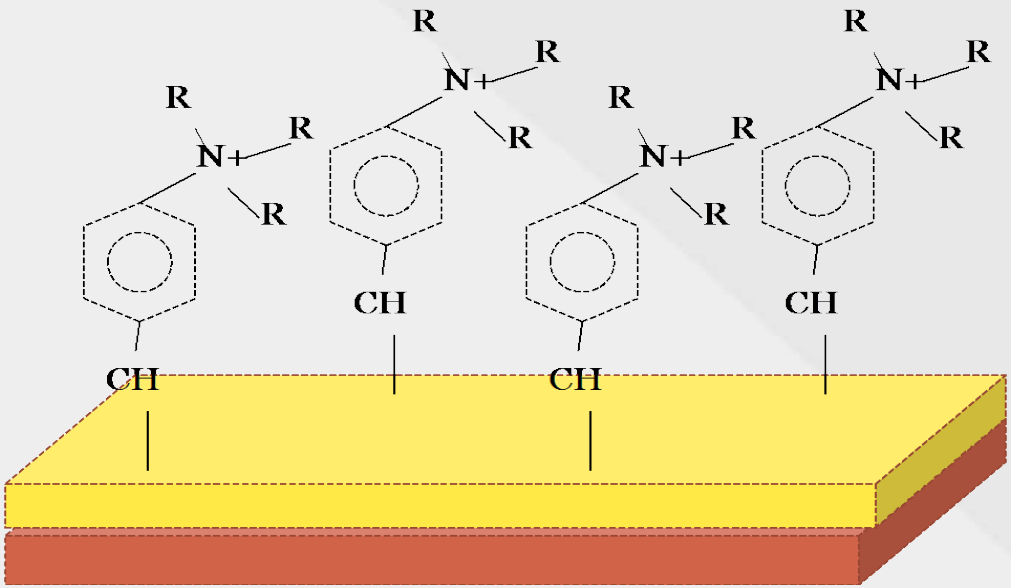
CHEMISTRY

CONCEPTUAL MODEL OF FUNCTIONALISED POLYMER

- Common backbone
- Using library approach
- Multiple functionalities



POLYMER CHARACTERISTICS

- Selective towards phosphate: major interference from sulphate has been avoided
- Sensitive:
  - LOD: 0.150 mg PO_4^{3-} L^{-1} 1
  - LOQ: 0.250 mg PO_4^{3-} L^{-}
- Simple synthetic route: polystyrene based synthesis
- Other interferences: no other ions have been found to interfere during phosphate detection

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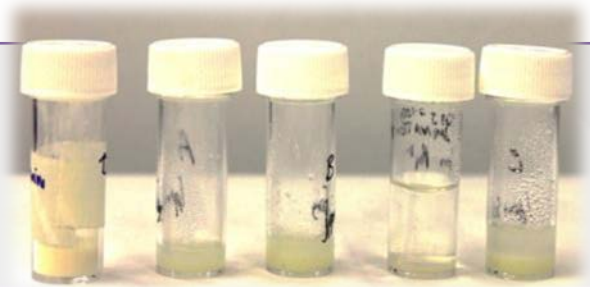
PHOSPHATE REMOVAL FROM WATER USING POLYMER COMPOUNDS – BATCH EXPERIMENTS

PO_4^{3-} standard (mg L^{-1})	PO_4^{3-} standard after contact with polymer (mg L^{-1})	% PO_4^{3-} removed from solution
1	0.015 ± 0.001	98.5
2.5	0.008 ± 0.001	99.7
5	0.11 ± 0.007	97.7
50	5.22 ± 0.008	89.5



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CONCLUSIONS

- The development of MultiMEMS provides a route to detect analytes in water, particularly phosphate.
- The concept is being extended to other compounds, specifically nitrate and can be adapted to sulphate. The possibility of constructing a sensor for pesticides is also being explored.
- The functionalised polymers are prepared using common synthetic techniques, facilitating scaling up processes.
- Interferences from other compounds present in water, especially solids or large organic matter compounds may not be avoided from main functionalities but can be overcome using multiple affinity groups on surface or using other polymer features to improve the performance of the sensor.

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