Emerging contaminants in our water

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DCU
Ollscoil Chathair Bhaile Átha Cliath
Dublin City University

environmental protection agency

NATIONAL WATER EVENT 2019


UN Sustainable Development Goals
1 NO POVERTY
2 ZERO HUNGER
3 GOOD HEALTH AND WELL-BEING
4 QUALITY EDUCATION
5 GENDER EQUALITY
6 CLEAN WATER AND SANITATION
7 AFFORDABLE AND CLEAN ENERGY
8 DECENT WORK AND ECONOMIC GROWTH
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
10 REDUCED INEQUALITIES
11 SUSTAINABLE CITIES AND COMMUNITIES
12 RESPONSIBLE CONSUMPTION AND PRODUCTION
13 CLIMATE ACTION
14 LIFE BELOW WATER
15 LIFE ON LAND
16 PEACE, JUSTICE AND STRONG INSTITUTIONS
17 PARTNERSHIPS FOR THE GOALS
SUSTAINABLE DEVELOPMENT GOALS
Water JPI
Water is central to many of the UN SDGs

Every drop of water counts:

The **availability of affordable**, **clean water** represents the greatest global challenge of our time.

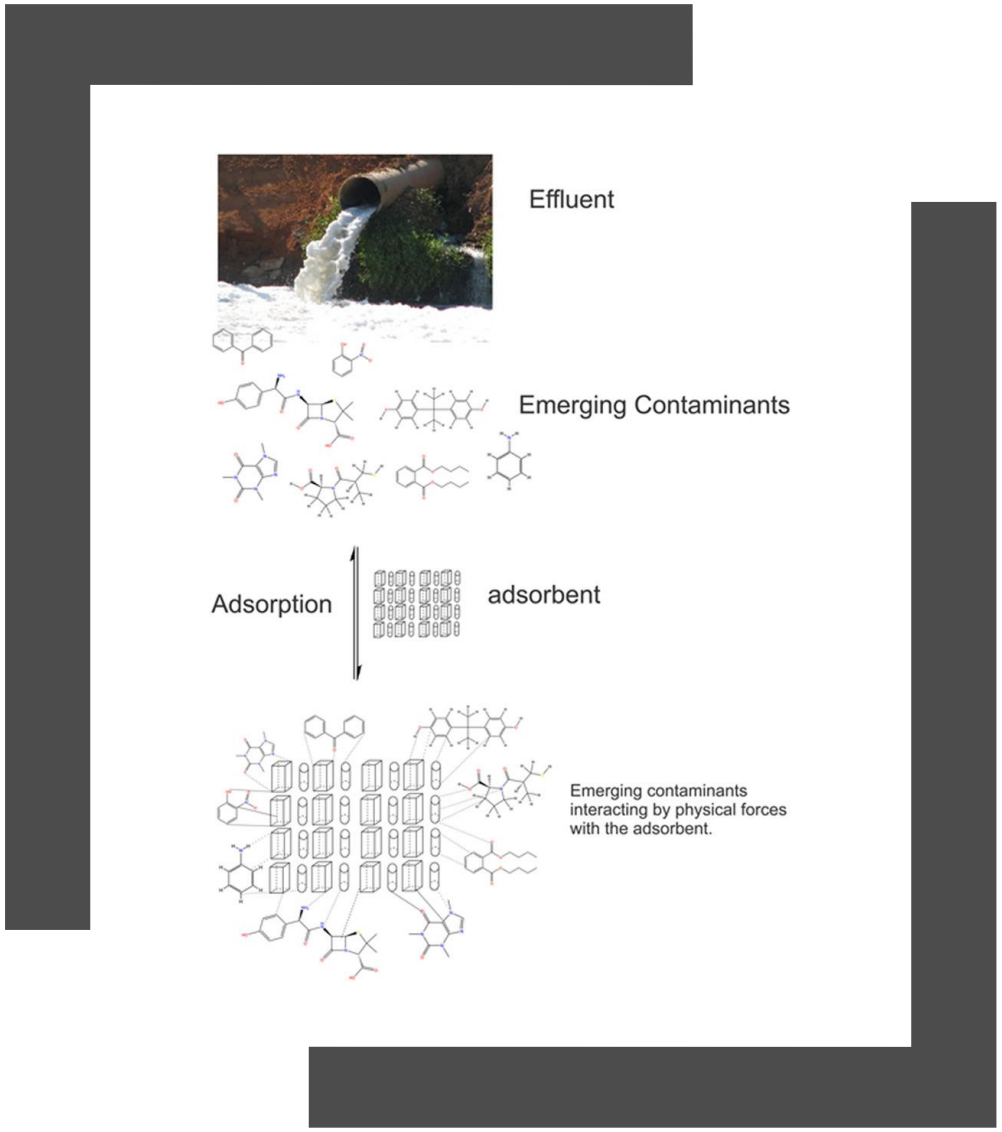
Throughout the journey **from source to sea** water management meets many challenges such as infrastructure failures, the need for treatment innovations

WaterIoT decision support tools could provide real value to the stakeholder.

The ultimate aim

To address challenges in the catchment, city/town, wastewater treatment plant, etc. all of which can be met by **distributed sensor networks** and **better information.**

Continual measurement is key to understanding sudden and gradual changes in chemical and biological quality of water, and for taking reactive remedial action in the case of contamination.



Emerging contaminants – what are they?

- Emerging contaminants (EC's) are pollutants of growing concern.
- They are mainly organic compounds such as: pesticides, pharmaceuticals and personal care products, hormones, plasticizers, food additives, wood preservatives, laundry detergents, surfactants, disinfectants, flame retardants, and
- other organic compounds that were found recently in natural wastewater stream generated by human and industrial activities.

Watch list – what is that?

JRC TECHNICAL REPORT

Development of the first Watch List under the Environmental Quality Standards Directive

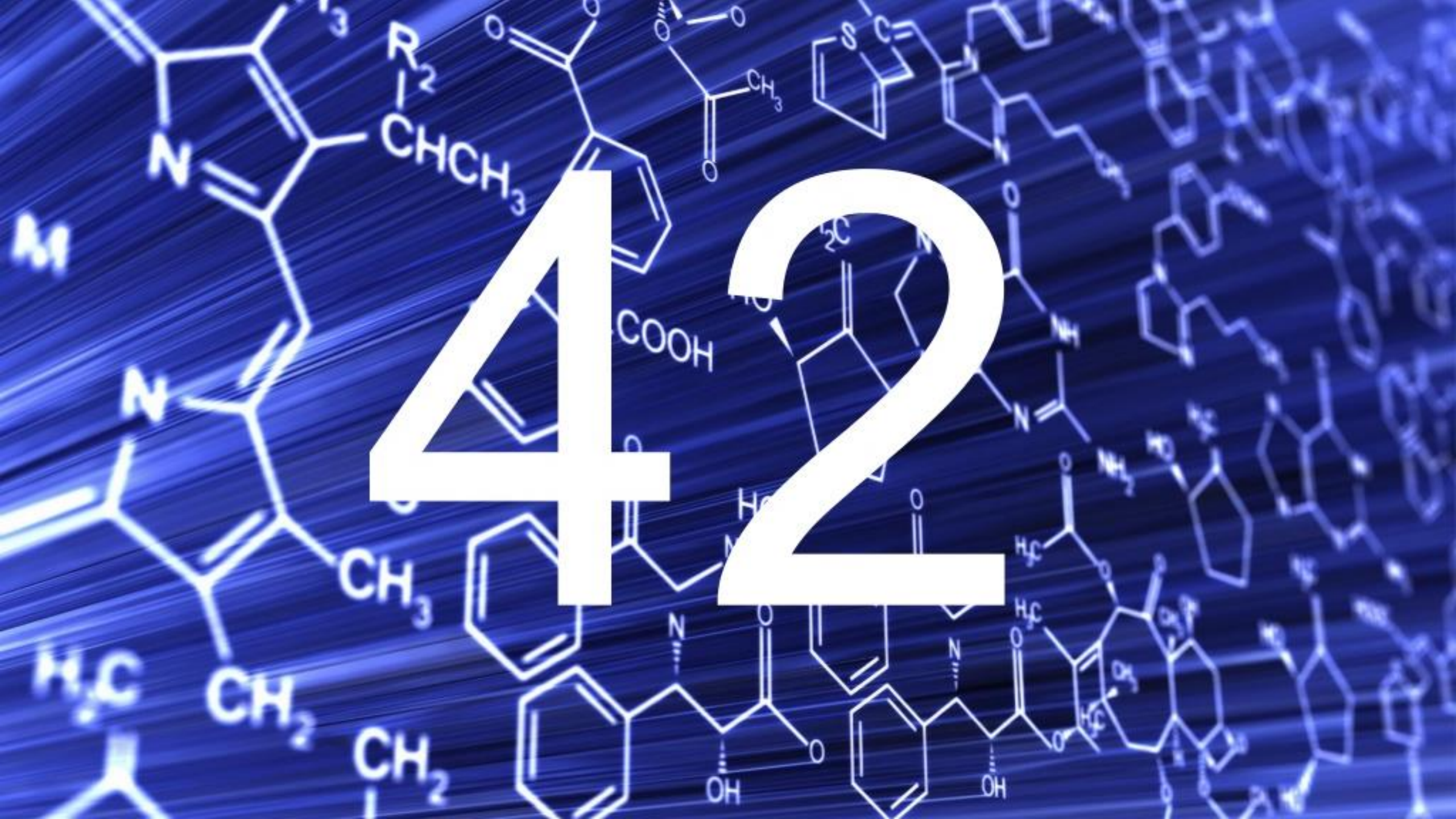
Directive 2008/105/EC, as amended by Directive 2013/39/EU, in the field of water policy

The main criteria for inclusion:

i) the substance is suspected of posing a significant risk to, or via, the aquatic environment, meaning there is reliable evidence of hazard and of a possible exposure to aquatic organisms and mammals, but

ii) there is not enough information to assess the EU-wide exposure for the substance, i.e. insufficient monitoring data or data of insufficient quality, nor sufficient modelled exposure data to decide whether to prioritise the substance.

- **100 000 chemicals in commerce**, 10 transformation products from each
- **20 million species**
- **22 000 billion exposure scenarios**, without considering
  - different concentrations,
  - simultaneous occurrence of chemicals,
  - any type of ecological interactions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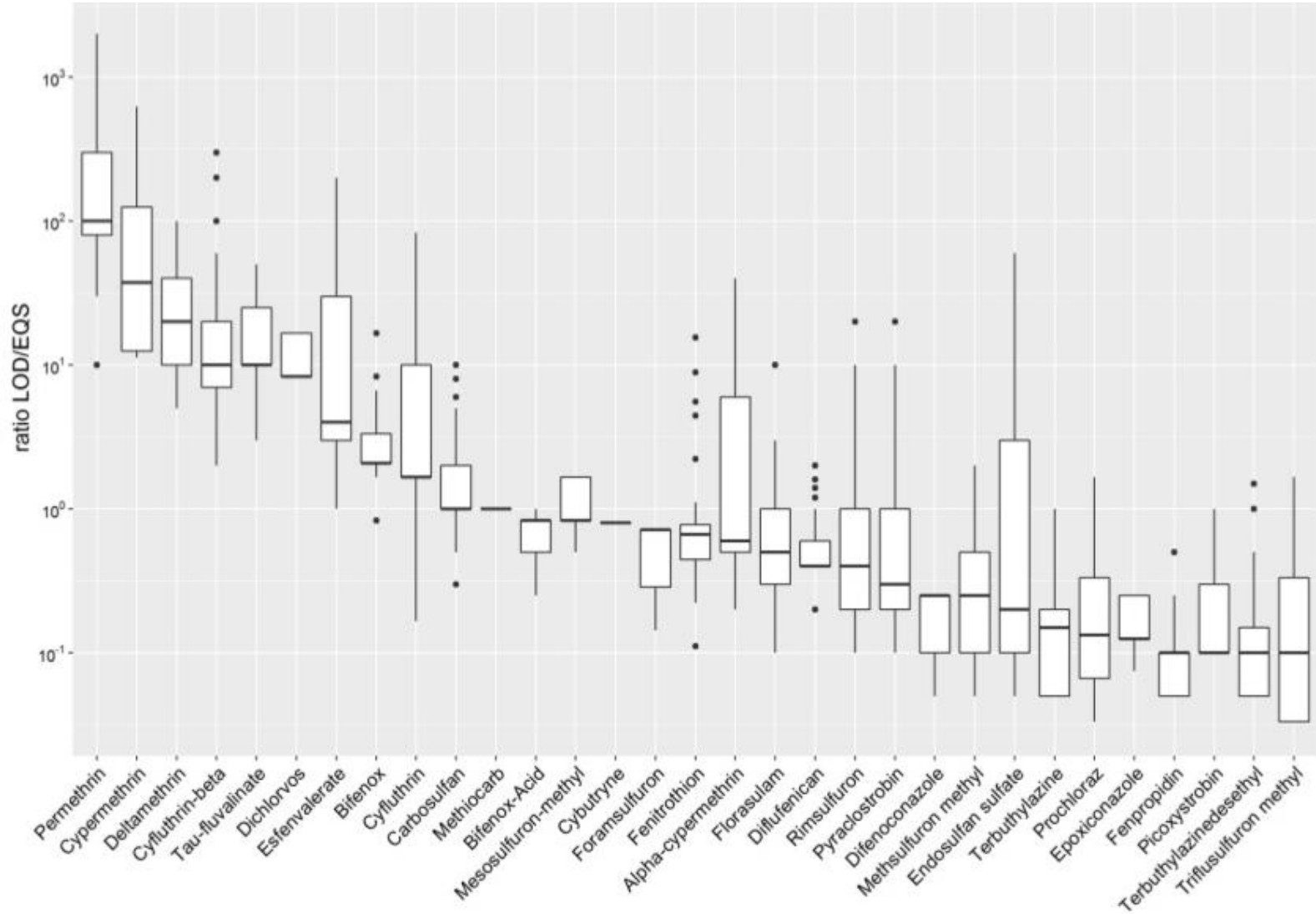
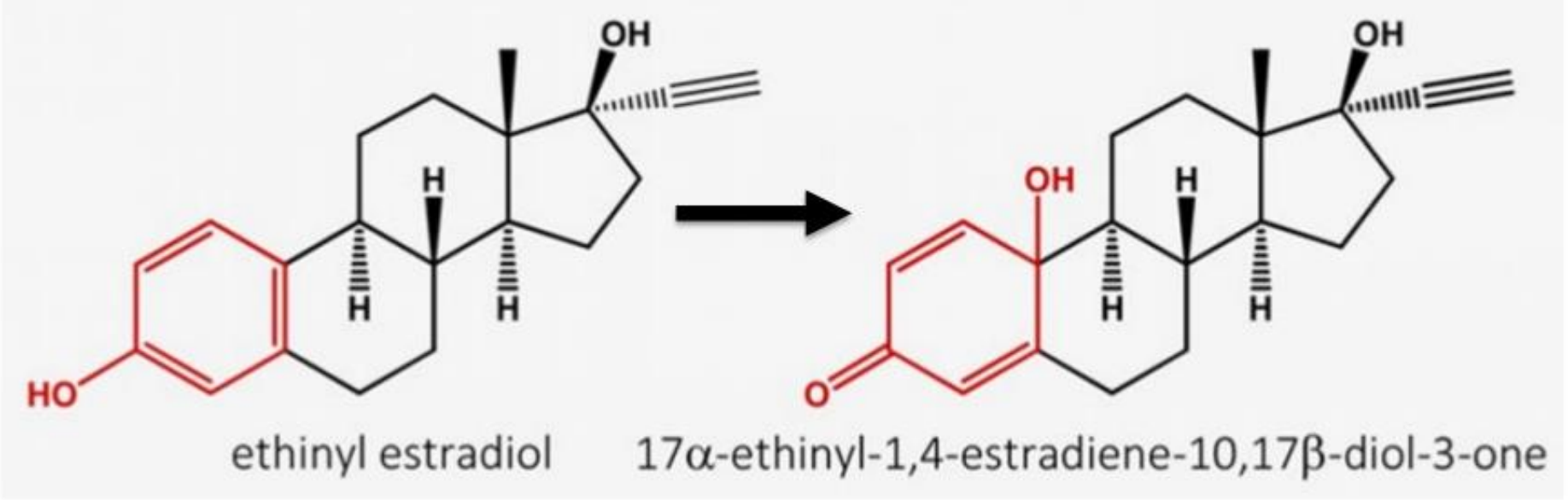
Analytical challenge



Gustavsson, et al. (2017) *Pesticide mixtures in the Swedish streams: Environmental risks, contributions of individual compounds and consequences of single-substance oriented risk mitigation*, Science of the Total Environment. 973–983.



Oxidation of Ethinylestradiol

Transformation product has a higher estrogenicity than the parent compound

Cwiertny, et al. (2014) 'Environmental designer drugs: When transformation may not eliminate risk', *Environmental Science and Technology*, 48(20), pp. 11737–11745.

Curren

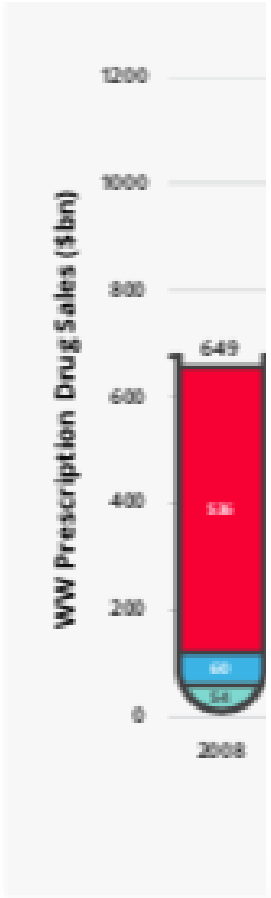
- Directive
- Challeng ıants

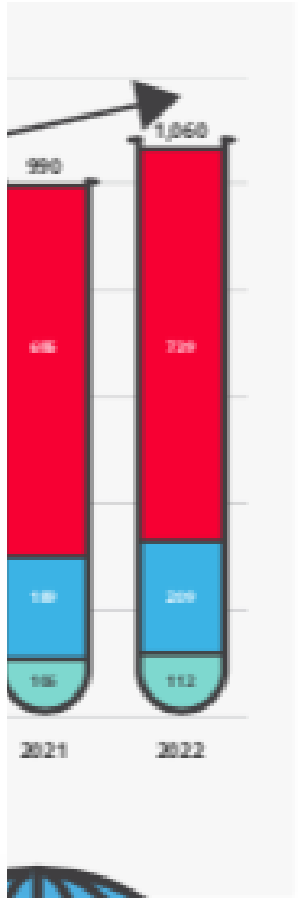
Figure 4. Top 15 prescription drug & OTC therapy categories by worldwide sales, 2016-2022

Therapy area	2016 WW sales (US$B)	Projected WW sales 2022 (US$B)
1. Oncology	93.7	192.2
2. Antidiabetics	43.6	57.9
3. Anti-rheumatics	53.3	55.4
4. Anti-virals	48.5	42.8
5. Vaccines	27.5	35.3
6. Bronchodilators	28.3	30.1
7. Sensory organs	20.2	28.3
8. Immunosuppressants	11.6	26.3
9. Anti-hypertensives	24.8	24.4
10. Anti-coagulants	14.1	23.2
11. MS therapies	21.6	21.7
12. Dermatologicals	10.5	19.9
13. Anti-fibrinolytics	11.6	17.1
14. Anti-hyperlipidaemics	13.8	13.4
15. Anti-bacteria	10.5	12.8
Top 15	434	601
Other	369	500
Total	803	1,100

Source: EvaluatePharma, 2017

Figure 1. World





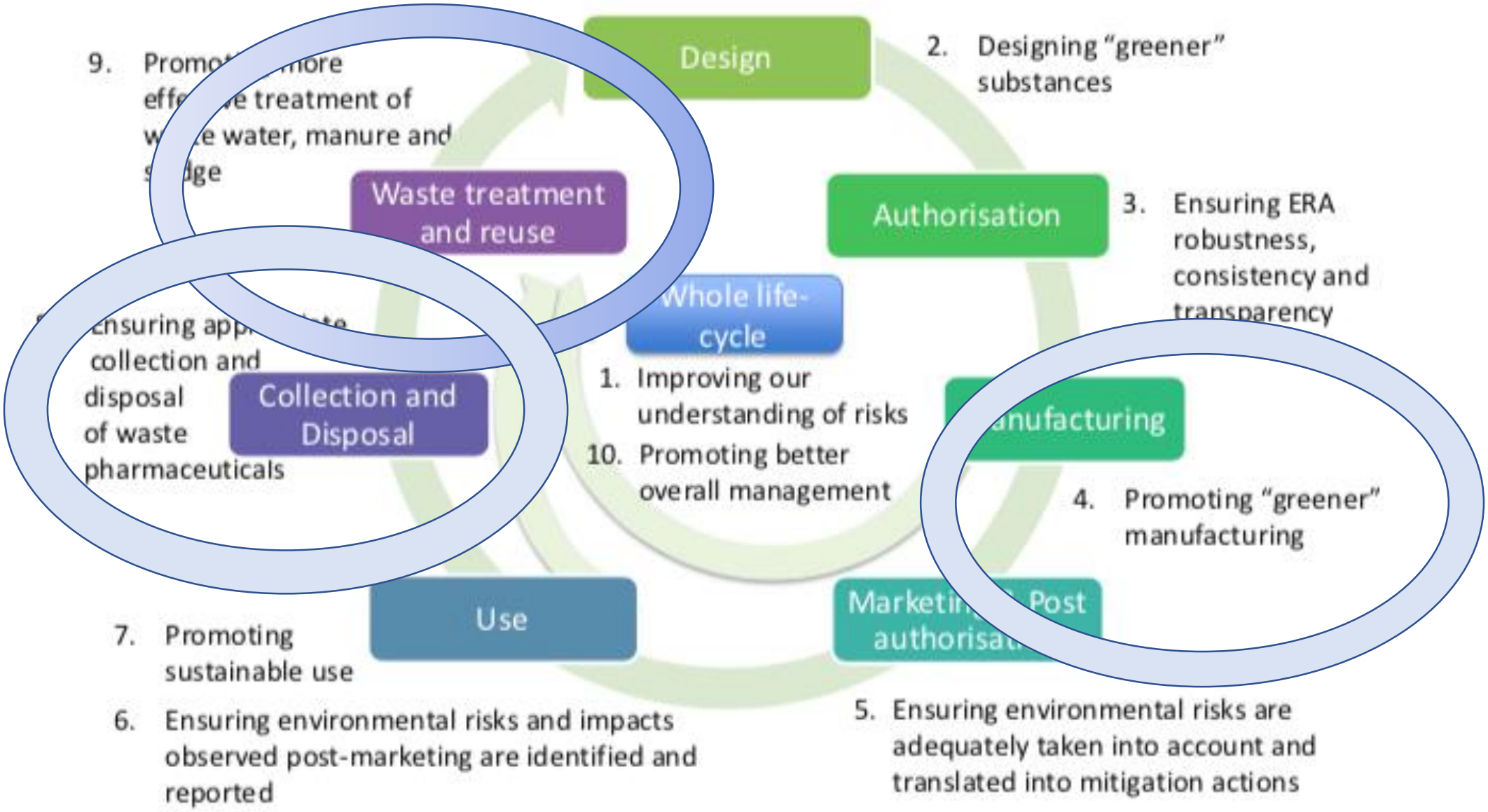
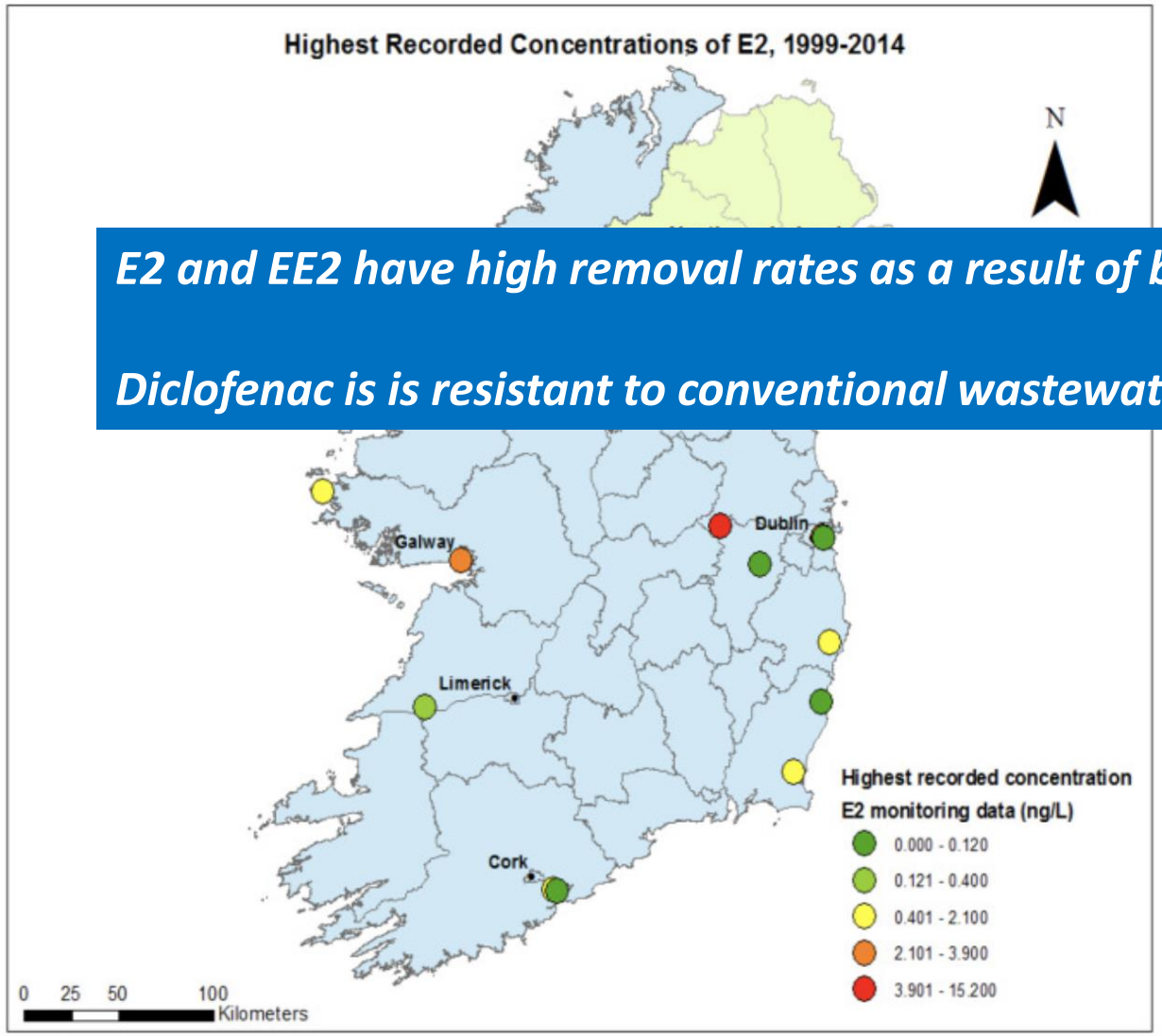
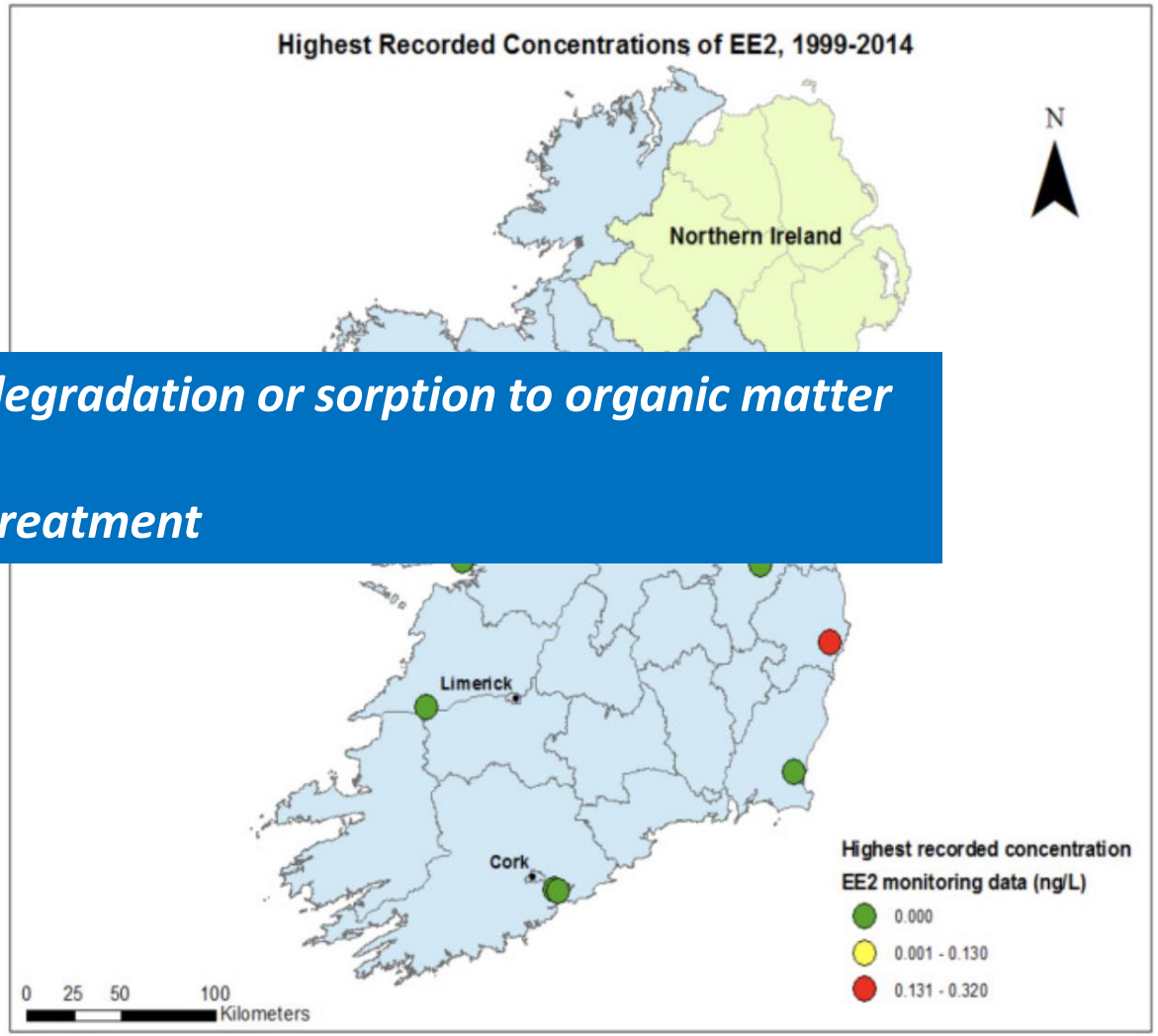


Figure 1: Ten main action areas across the life cycle of pharmaceuticals

Ireland and CECs – what do we know?





E2 and EE2 have high removal rates as a result of biodegradation or sorption to organic matter

Diclofenac is is resistant to conventional wastewater treatment

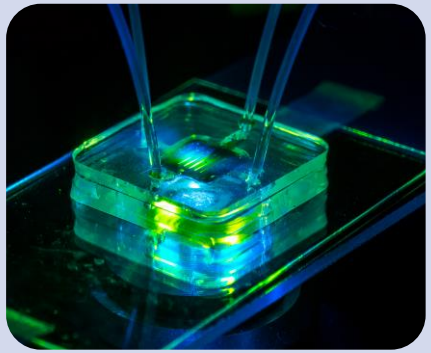
Tahar, A et al. Sci Total Environ (2018) 616-617:187

Development of environmental DECISION SUPPORT SYSTEMS

Decisions involve **problem formulation** as well as **solution generation**.

Emerging contaminants among the many pollutants in water

Sources of pollutants are many – and we need to monitor the change in water quality



Technology advances – integration of disciplines of biotechnology, chemistry, engineering, data

Information and decision support tools developed using integrated technologies with data analytics

EDSS→ Help to inform policy

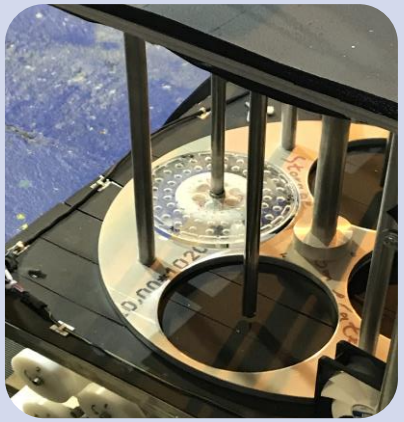
Leading to change in monitoring practice & improved management

Water Conserv Sci Eng
DOI 10.1007/s41101-016-0014-y

ORIGINAL PAPER

Development of a Risk Index for Use in Water Quality Monitoring

Lisa Jones[1] · David Styles[1] · Brian Kinsella[2] · Antoin Lawlor[1] · Ambrose Furey[2] · Fiona Regan[1]



Current Monitoring approach: Compliance, surveillance, investigative ➔ Levels of pollutants can vary temporally and spatially➔

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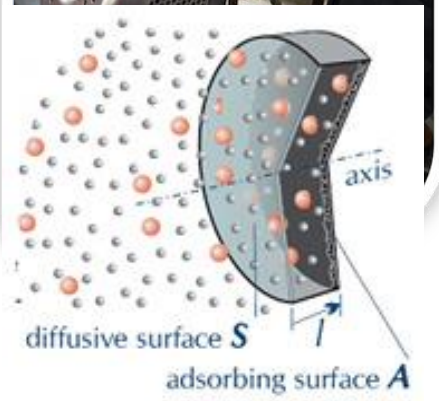
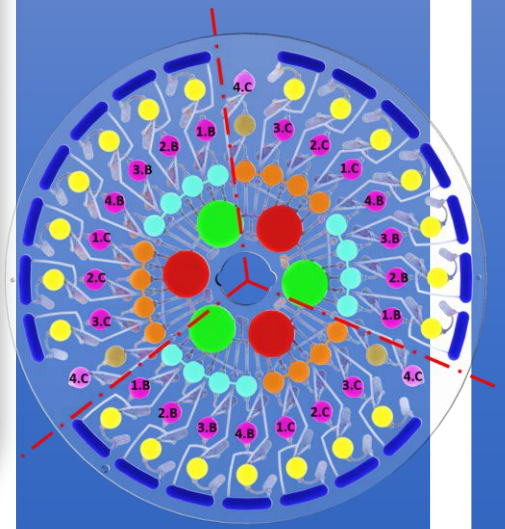




- Day separation on 3-day 3-analyte disc
- Biological sample load reservoir
- Biological antibody mixing reservoir
- Chemical sample load reservoir
- Chemical antibody/peptide mixing reservoir
- Test reservoir
- Control reservoir
- Waste storage
- Chelex resin loaded reservoir (Control)
- Test Reservoir for Heavy metals only

1.B	Saxitoxin detection, and derivatives
2.B	Microcystin detection, and derivatives
3.B	Azaspiracid detection, and derivatives
4.B	Domoic acid detection, and derivatives
1.C	Naphthalene
2.C	PFOS
3.C	Camphechlor
4.C	All heavy metals

Journal of Environmental Monitoring

Cite this: *J. Environ. Monit.*, 2012, **14**, 3009

www.rsc.org/jem

PAPER

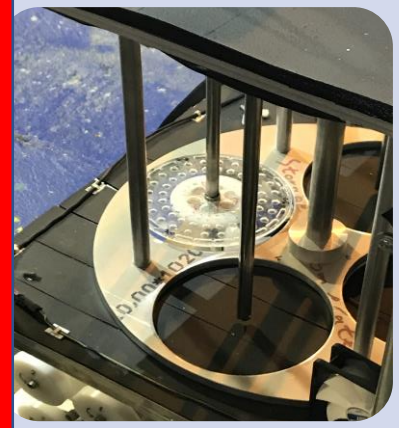
Monitoring the occurrence of PAHs in Irish wastewater effluent

Lisa Jones,*[a] Brian Kinsella,[b] Ambrose Furey[b] and Fiona Regan[a]

Received 26th July 2012, Accepted 14th September 2012
DOI: 10.1039/c2em30605k

Fig. 2 Comparison between detected levels of priority PAHs in waste water effluent and the flow through the plant at a Dublin WWTP, with a focus on the period of intensive sampling.

Are technology innovations meeting the needs?



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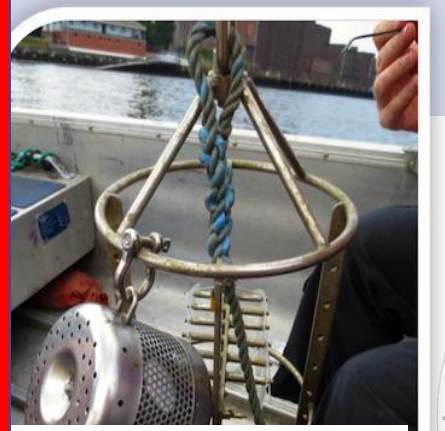
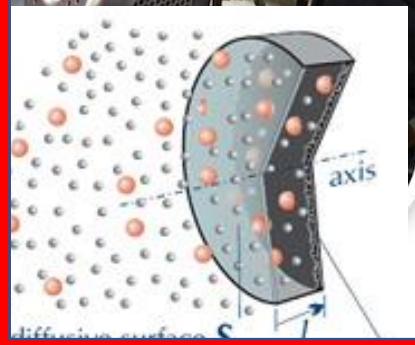
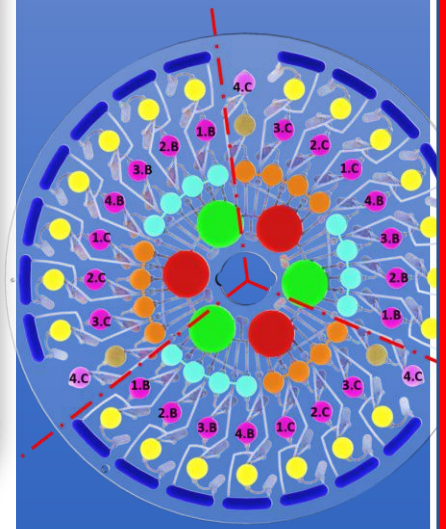
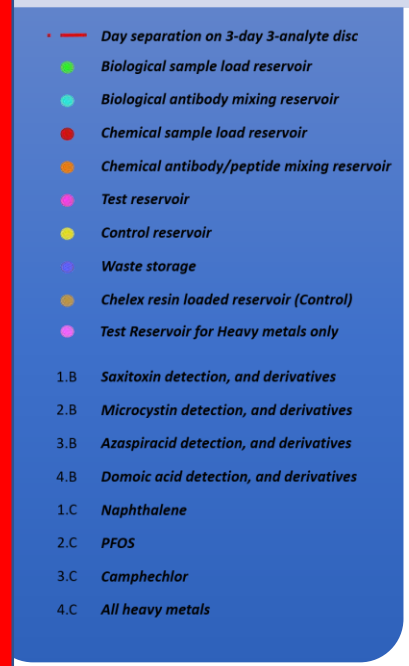


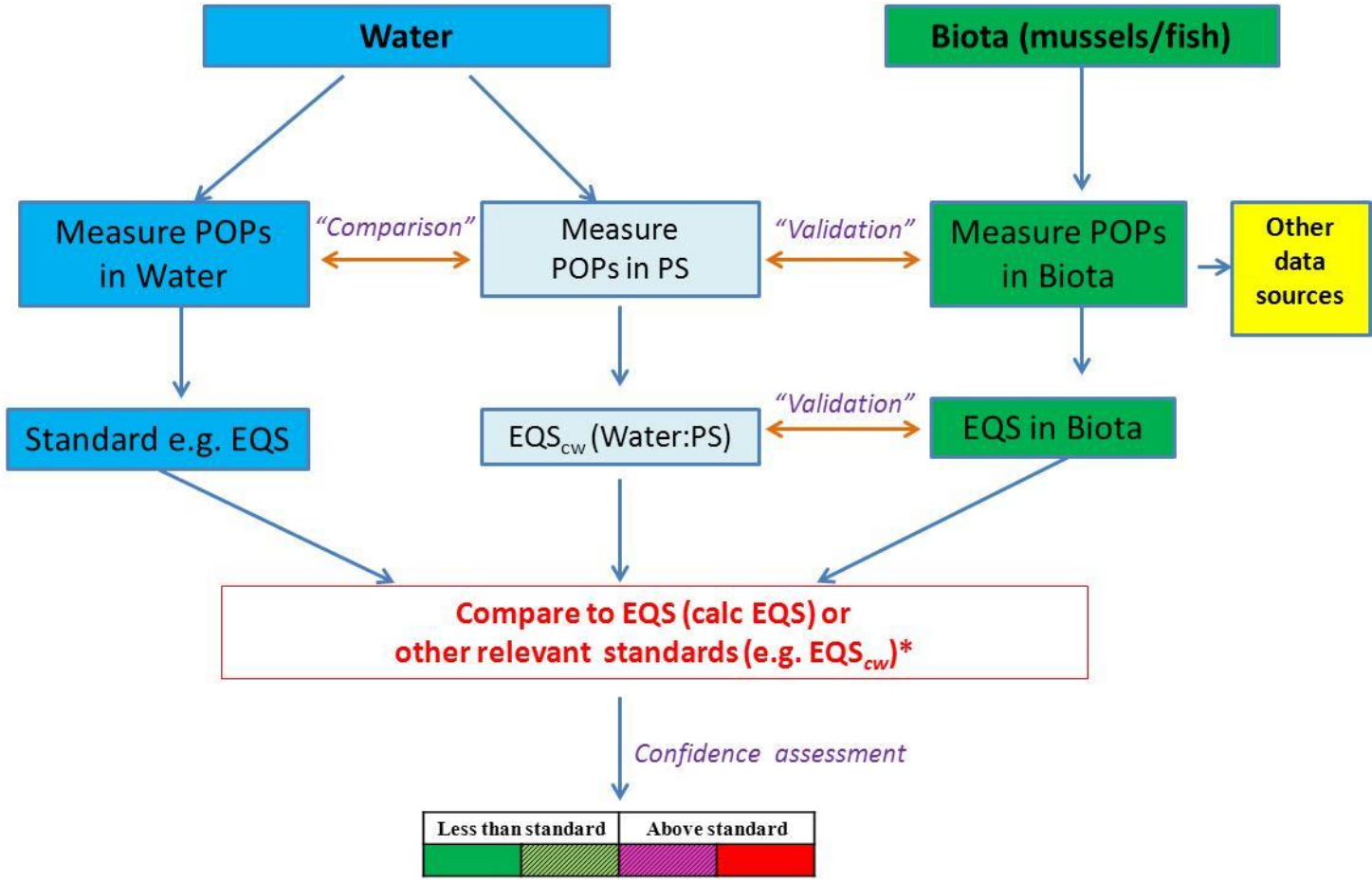






Passive sampling

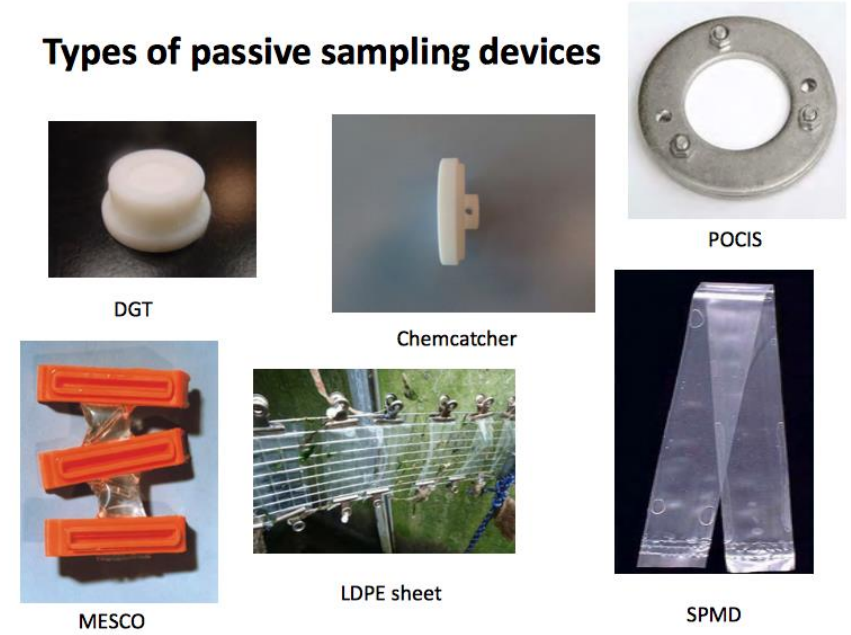
Summary of project approach to further incorporating PS into operational monitoring programmes.



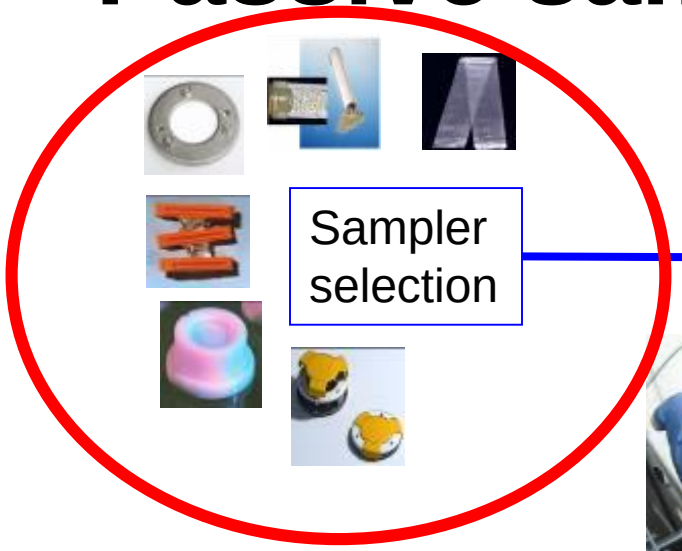
* *Based on the potential derivation of a passive sampling EQS equivalent* EQS*(PS).*

Passive Sampling

- Time weighted average concentration measurements;
- Screening for chemicals;
- Trend monitoring;
- A valuable tool in environmental assessment



Passive sampling



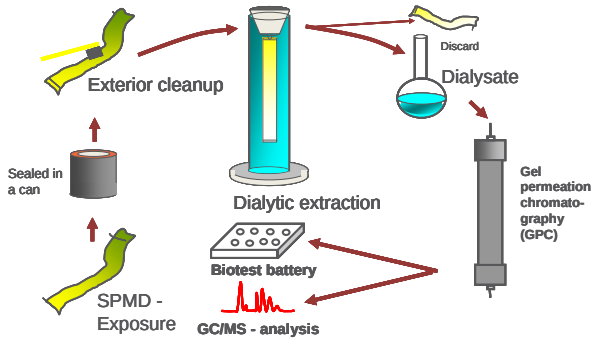
Sampler selection

Sampler deployment

Exposure for days-weeks

Sampler retrieval

Extraction and analysis



Calculation of water concentration C_w

Models

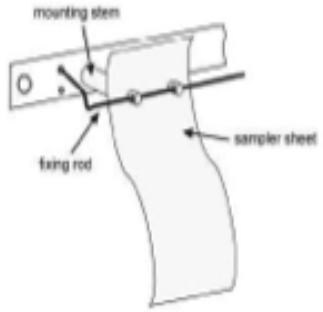
Calibration

Parameters

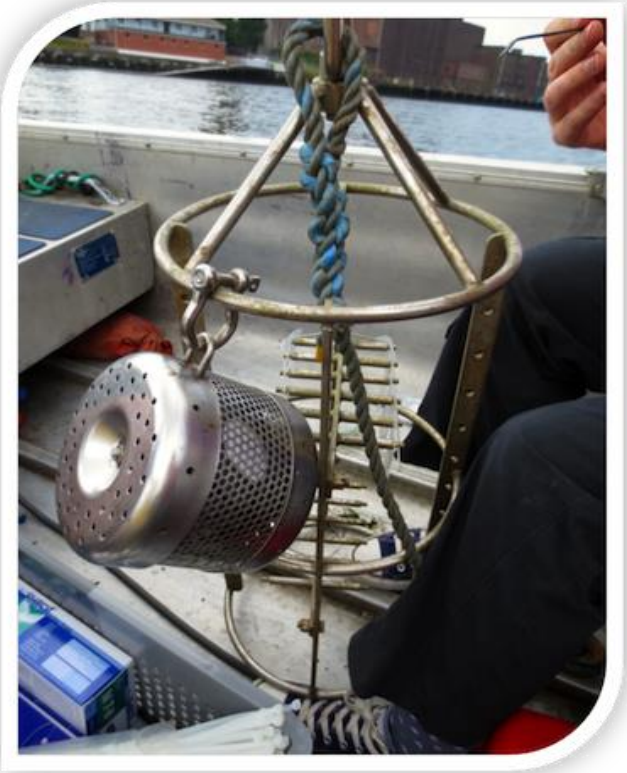
(sampling rates R_s, partition coefficients K_{sw})

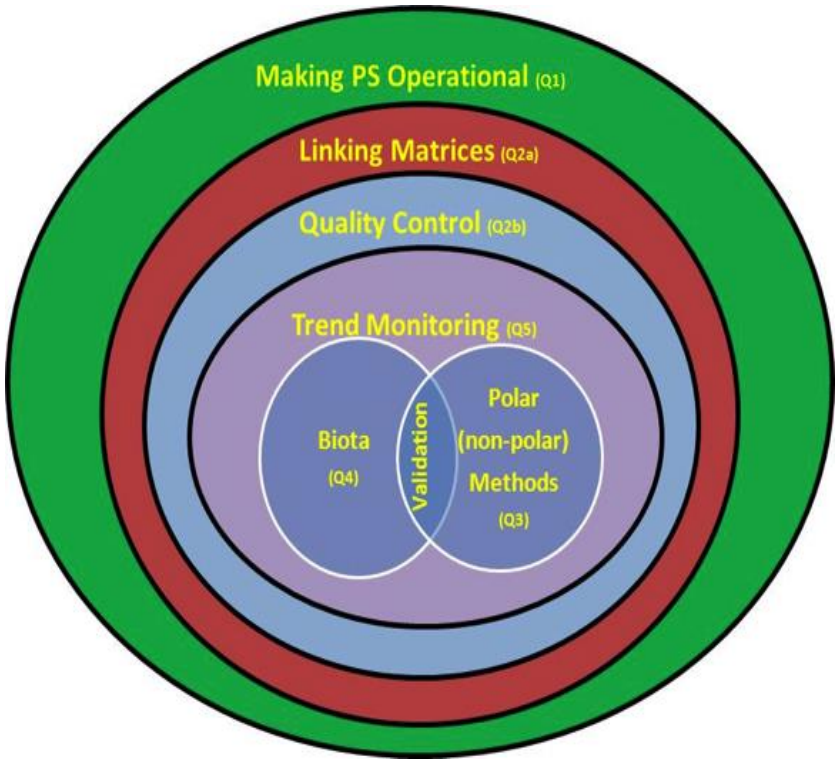
Sites selected for study in 2013

County	Site	Rationale	POCIS	PDMS	Water	Mussels	Fish (IFI)
Cork	Inchigeelagh	Upstream river	✓	✓	✓		✓
	Inniscarra	Downstream river	✓	✓	✓		✓
	Shandon	Riverine/transitional	✓	✓	✓		✓
	Lough Mahon	Riverine/transitional	✓	✓	✓	✓	
	Outer bay	Riverine/transitional	✓	✓	✓	✓	
Dublin	Poolbeg	High pressure coastal	✓	✓	✓	✓	
	Osberstown	Riverine/transitional	✓	✓	✓	✓	
	Lucan Bridge	Downstream river	✓	✓	✓		✓
	Kilcullen Bridge	Upstream river	✓	✓	✓		✓
Galway	Kilkieran Bay	Coastal reference	✓	✓	✓	✓	
Mayo	Burrishoole	Upstream river	✓	✓	✓		✓
Donegal*	Glen Lackagh 1	Cypermethrin study	SPMD	✓	✓	Benthic kick sampling	
	Glen Lackagh 2	Cypermethrin study	SPMD	✓	✓		



Cypermethrin study





	Matrix		Glen Lackagh U/S	Midstream A	Midstream B	Midstream C	Glen Lackagh D/S
Analyte		***Units***	**2014**				
Cypermethrin 29/4/14	Water	ng L^{-1}	**1.17**	NA	NA	NA	**1.08**
Cypermethrin 22/5/14		ng L^{-1}	**1.47**	**1.67**	**1.38**	**1.73**	**1.78**
Cypermethrin	PDMS	ng L^{-1}	**++**	NA	NA	NA	**+++**
Cypermethrin	SPMD	ng L^{-1}	<70	NA	NA	NA	<70

Cork POCIS and water estrogens

Upstream → **Downstream**

	Matrix		Lough Allua Inchigeelagh	Iniscarra	Shandon	Lough Mahon	Cork Outer Harbour
Analyte		***Units***			**2013**		
EE2	POCIS	ng L^{-1}	<0.2	**1.39**	<0.2	<0.2	<0.2
E2		ng L^{-1}	<0.5	<0.5	<0.5	**2.36**	**1.98**
EE2	Water	ng L^{-1}*	nd	nd	nd	nd	nd
E2		ng L^{-1}*	nd	nd	nd	nd	nd
Analyte		***Units***			**2014**		
E1	POCIS	ng L^{-1}	< 0.51	0.24	0.37	**0.48**	**0.37**
EE2		ng L^{-1}	< 0.12	< 0.04	< 0.04	< 0.04	**0.07**
E2		ng L^{-1}	< 0.13	< 0.04	< 0.04	**0.06**	**0.09**
E1	Water	ng L^{-1}*	nd	**0.41**	nd	**0.41**	**0.54**
EE2		ng L^{-1}*	nd	nd	nd	nd	nd
E2		ng L^{-1}*	nd	nd	nd	nd	nd

*LOD water samples by LC-MS/MS: E1: 0.07 ng L^{-1} E2: 0.07 ng L^{-1}, EE2, 0.11 ng L^{-1}. 5 L sample n = 2
Effective sampling rates POCIS (ng/sampler/day)*: E1: 0.39, E2: 0.46, EE2: 0.235

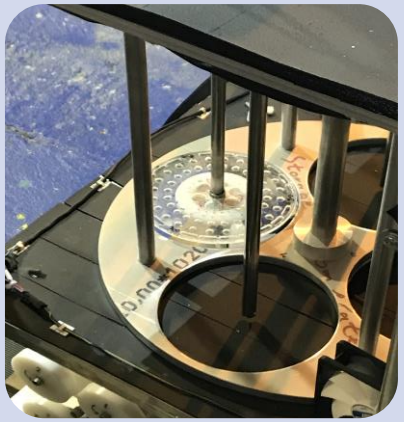
Dublin Bay PAHs

Analyte	Estimated Water Concentrations (ng L^{-1}) SPMD
Acenaphthene	<1.19
Acenaphthylene	<1.47
Anthracene	<0.84
Benzo(a)anthracene	<0.63
Benzo(a)pyrene	<0.74
Benzo(b)fluoranthene	<0.61
Benzo(ghi)perylene	<1.00
Benzo(k)fluoranthene	<0.69
Chrysene	0.84
Dibenzo(a,h)anthracene	<0.80
Fluoranthene	2.25
Fluorene	<0.98
Indeno(1,2,3-cd)pyrene	<0.91
Naphthalene	<5.73
Phenanthrene	1.04
Pyrene	3.73

New project underway

Reason for detecting:	Chemical	Class	Contaminant of emerging concern (CEC)
WFD watchlist	diclofenac	anti-inflammato	low level
WFD watchlist	17-Beta-estradiol (E2	hormone, EDC	low level
WFD watchlist	17-Alpha-ethinylestradiol (EE	hormone, EDC	low level
WFD watchlist	Oxadiazon	herbicide	pesticide
WFD watchlist	Methiocarb	insecticide	pesticide
WFD watchlist	2,6-ditert-butyl-4-methylphenol	antioxidant used	Personal care and cosmetic products
WFD watchlist	Tri-allate	herbicide	pesticide
WFD watchlist	Neonicotinoids (Imidacloprid, Thiacloprid, Thiamethoxam,	insecticide	pesticide
WFD watchlist	Makrolide antibiotics (Erythromycin, Clarithromycin,	antibiotics	low level pharmaceuticals
WFD watchlist	2-Ethylhexyl 4-methoxycinnamate	sunscreen agent	Personal care and cosmetic products
Water reports	Atrazine		pesticide
Water reports	Simazine		pesticide
Water reports	Di(2ethylhexyl)-phthalate (DE	plasticiser	PCCP ??
RBMP 2017-202	Mecoprop (methylchlorophenoxypropionic aci		pesticide
RBMP 2017-202	2-methyl-4-chlorophenoxyace	herbicide	pesticide
RBMP 2017-202	2,4-dichlorophenoxyacetic acid		pesticide
2010-2012 wate	Glyphosphate		pesticide
2010-2012 wate	cypermethrin		pesticide
	UV filters??		PCCPs

Are technology innovations meeting the needs?



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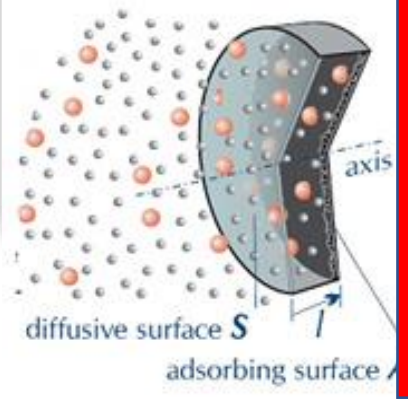
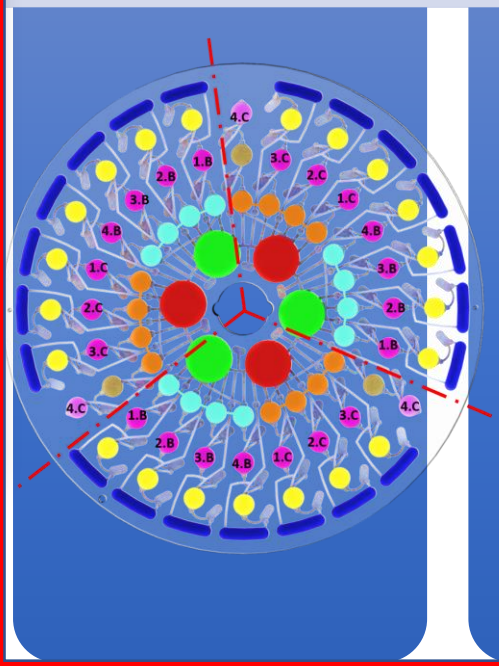
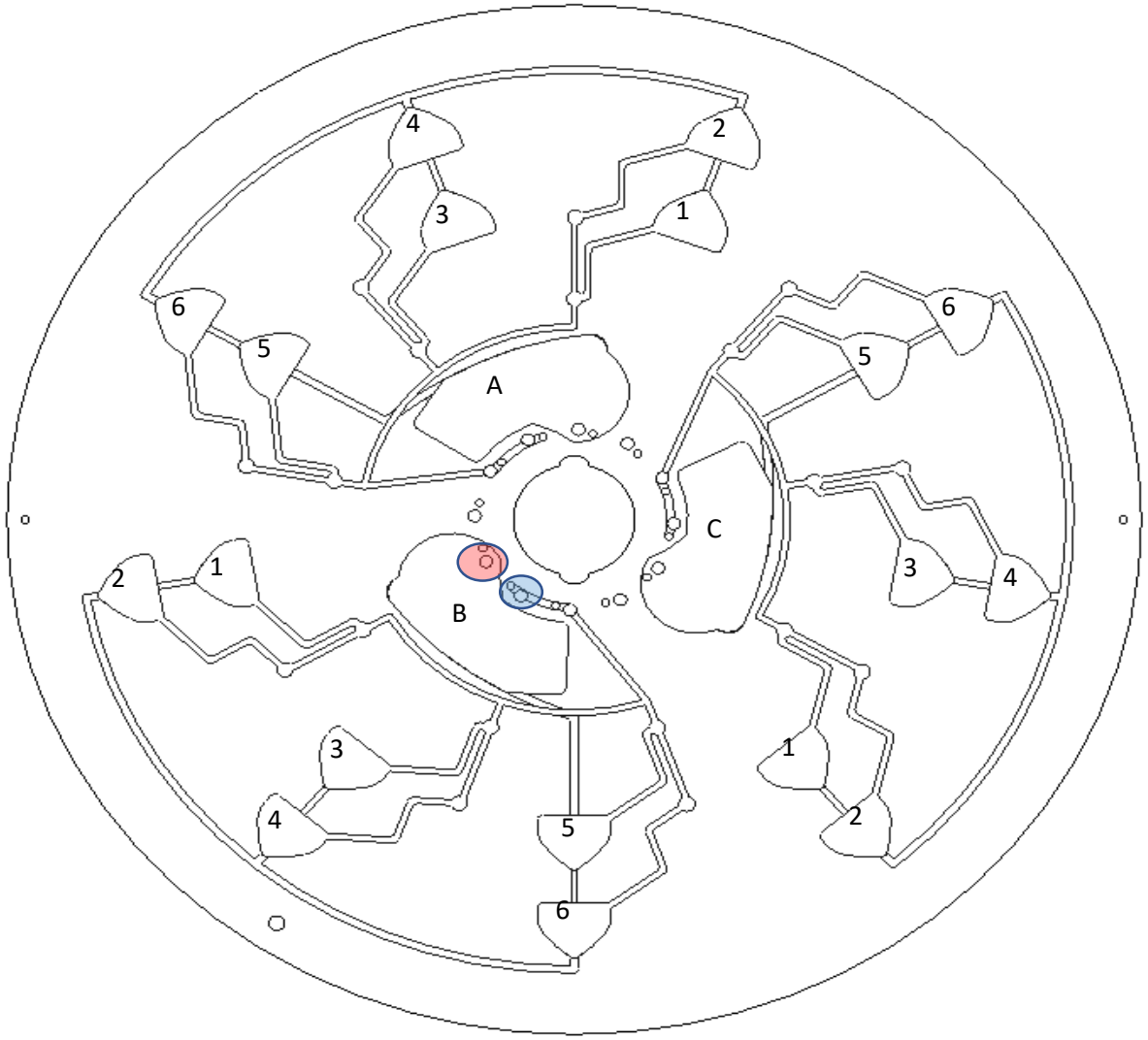


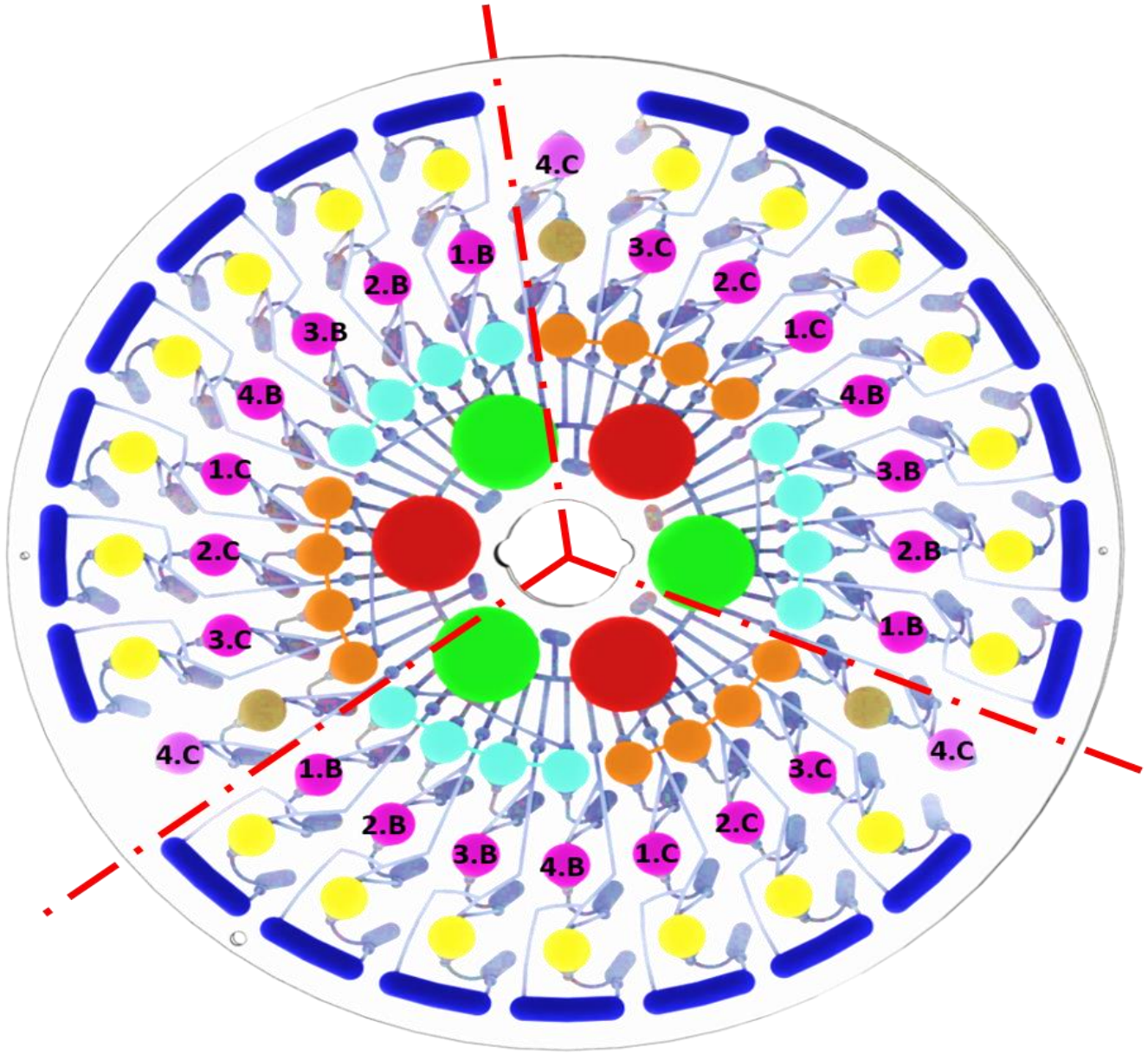


Biosensors:

- Immunoassays → increased in popularity
- Antibodies routinely used for analyte identification
- They are highly sensitive
- Attempts to miniaturize the detection systems and to develop *in-situ* monitoring systems have been made
- A lateral flow ‘dipstick’ style assay for toxins developed
- EU FP7 project Mariabox – Oceans of Tomorrow call → algal toxin monitoring and micro-pollutant detection.

Sensor Platforms




4.C
1.B
3.C
2.B
2.C
3.B
1.C
4.B
4.B
1.C
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3.C
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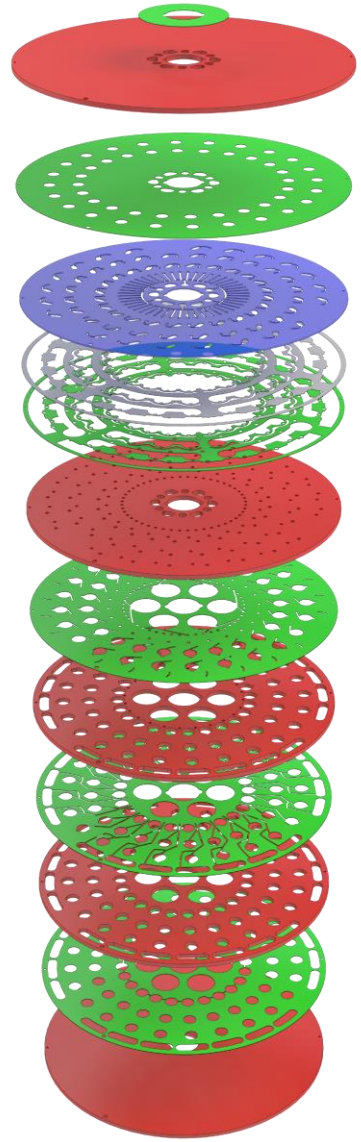
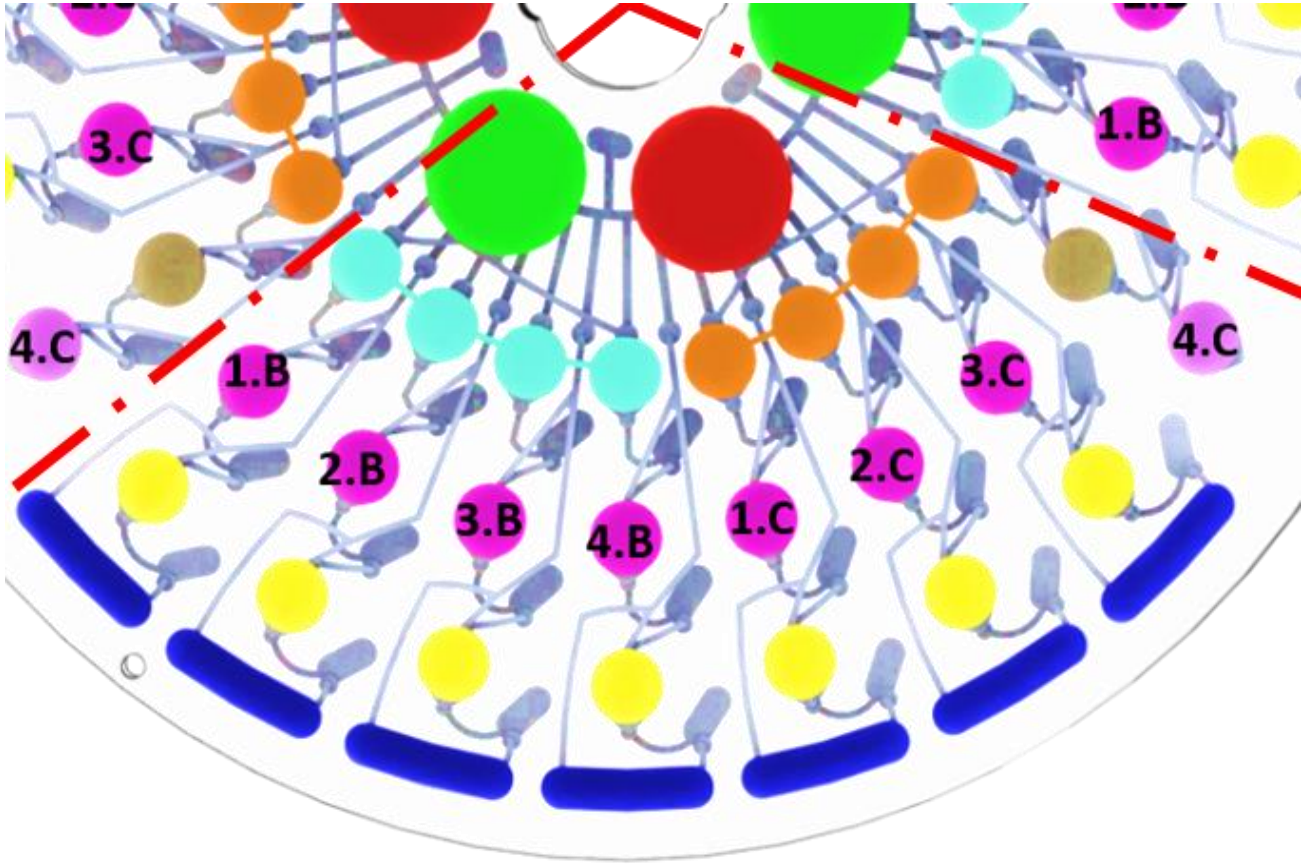
1.B
3.C
2.B
2.C
3.B
4.B
1.C





1.B ***Saxitoxin detection, and derivatives***

2.B ***Microcystin detection, and derivatives***

3.B ***Azaspiracid detection, and derivatives***

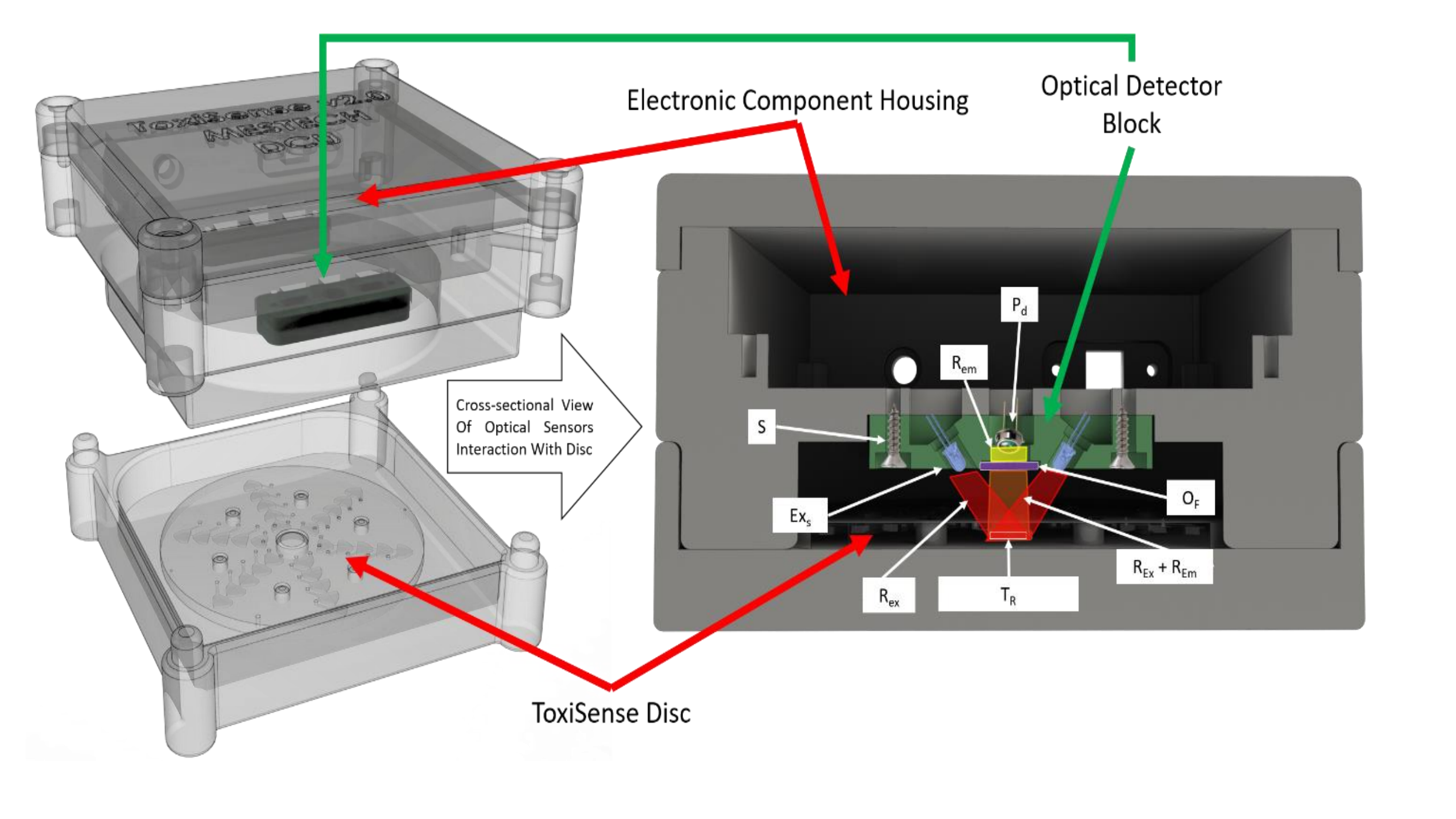
4.B ***Domoic acid detection, and derivatives***

1.C ***Naphthalene***

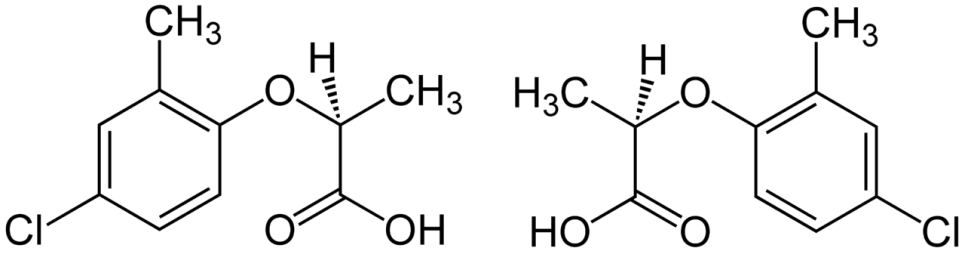
2.C ***PFOS***

3.C ***Camphechlor***

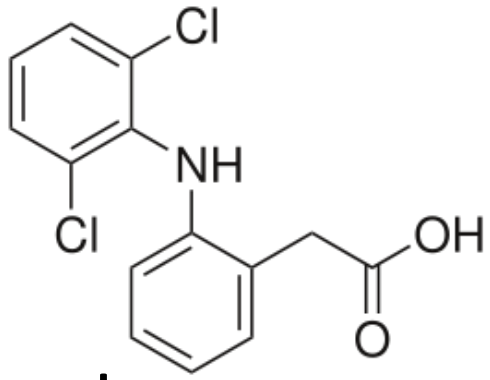
4.C ***All heavy metals***


Electronic Component Housing
Optical Detector Block
Cross-sectional View Of Optical Sensors Interaction With Disc
P_d
R_{em}
S
Ex_s
O_F
$R_{Ex} + R_{Em}$
R_{ex}
T_R
ToxiSense Disc

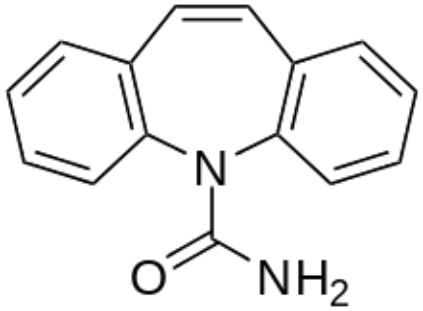
Mecoprop

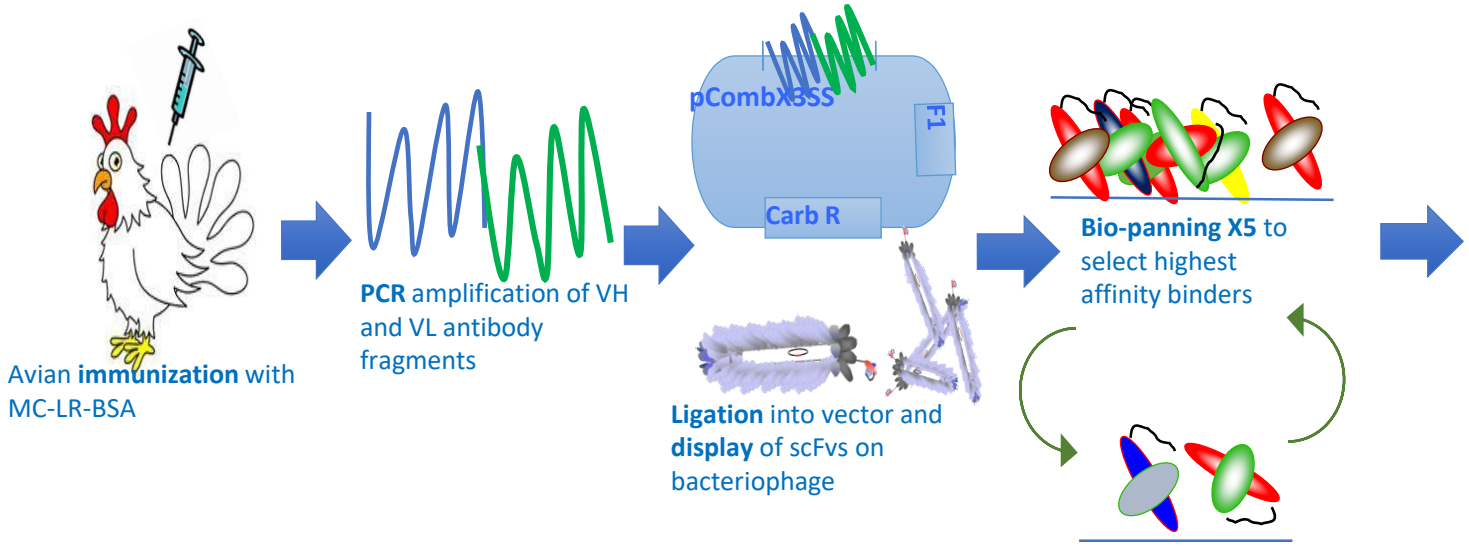


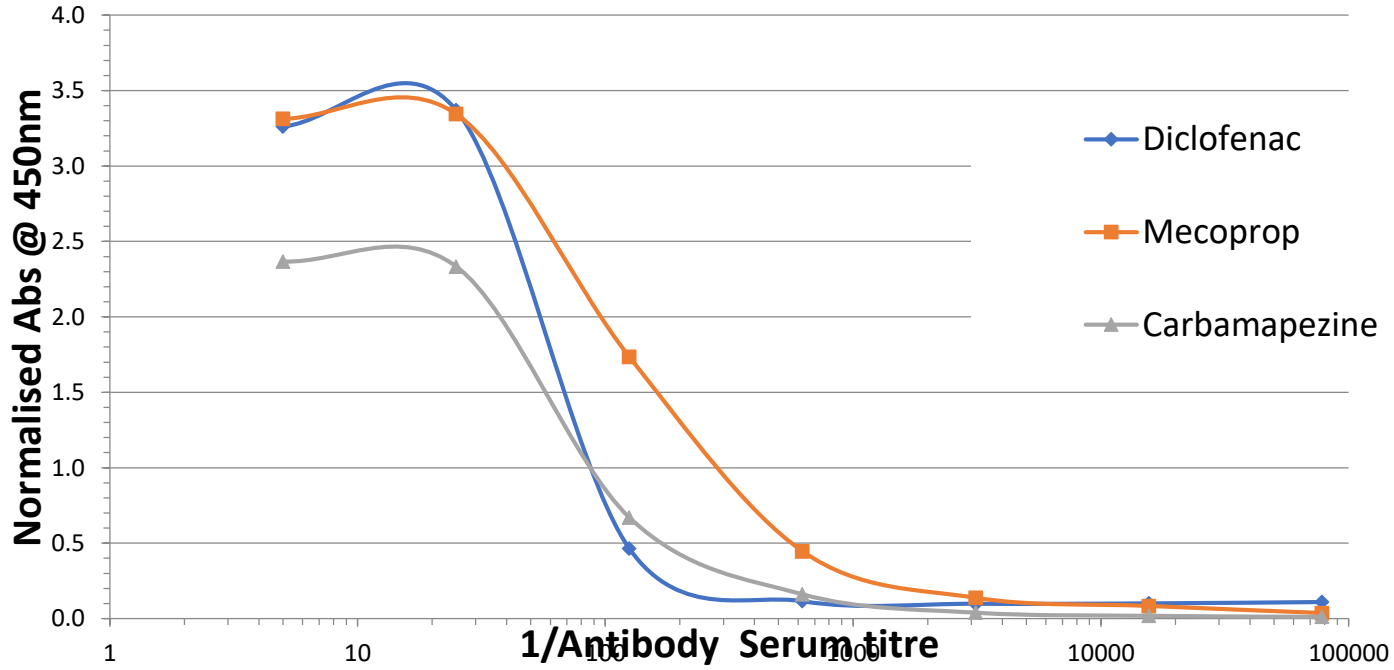
Diclofenac



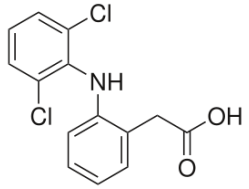
Carbamezapine







Technologies for emerging contaminant monitoring



Watch List chemicals

Industries

Continuing need to develop real-time monitoring platforms

Polar and non-polar organics

- Traditional separation methods
- Compliance monitoring - EQS

- Longer-term monitoring
- Trend monitoring
- Passive sampling

- Sensor platform development
- Single and multi-analyte systems
- Integration of technologies

Emerging chemicals of concern

Environmental pollutants (toxins, pharmaceuticals)

Is there a role for surrogate monitoring to show trends?

A single sample

4-6 weeks

Up-to a year autonomously

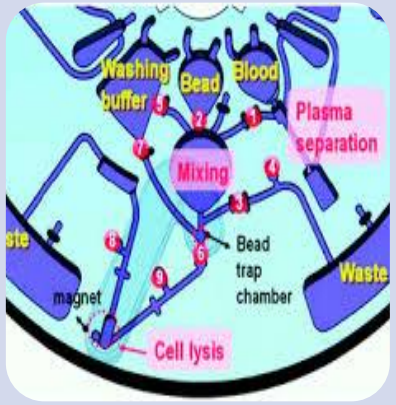
Spot sampling

Longer-term monitoring of trends

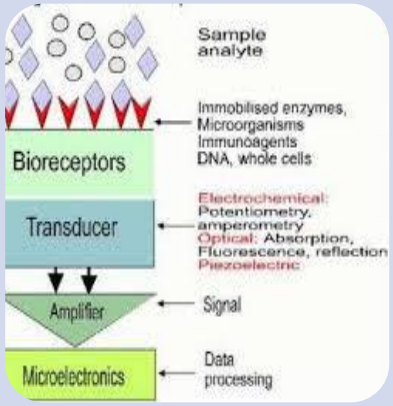
Continuous real-time monitoring of certain parameters

Key Messages

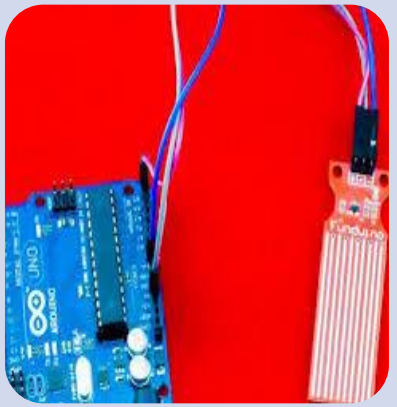
Informed decision making in response to the need to manage & protect water



Be open to **new ways of monitoring** water for emerging contaminants of concern



Novel technology can play a role and we need to see significant investment in capacity and research



Integrate technology with data analytics – work with stakeholder to understand the problem

Better approach to management of a scarce & valuable resource

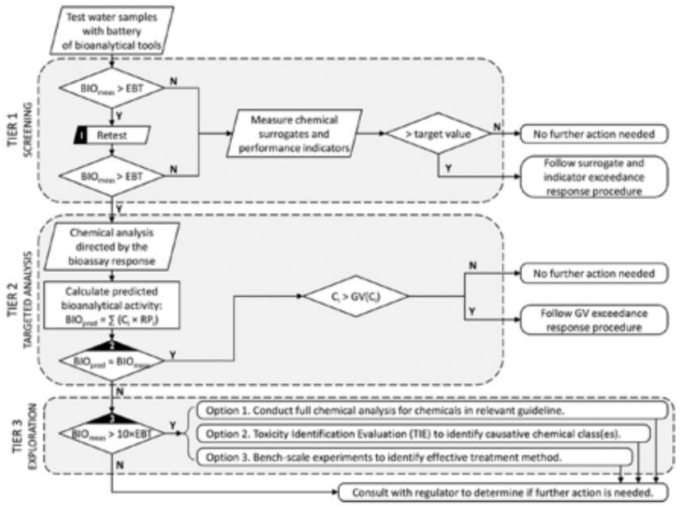


Figure 3. Framework to apply bioanalytical tools in water quality monitoring (Leusch and Snyder 2015).

Wernersson *et al. Environmental Sciences Europe* (2015) 27:7
DOI 10.1186/s12302-015-0039-4

Environmental Sciences Europe
a SpringerOpen Journal

RESEARCH Open Access

The European technical report on aquatic effect-based monitoring tools under the water framework directive

Ann-Sofie Wernersson[1], Mario Carere[2*], Chiara Maggi[3], Petr Tusil[4], Premysl Soldan[4], Alice James[5], Wilfried Sanchez[5],

STATE OF THE SCIENCE REPORT

GLOBAL WATER RESEARCH COALITION

IN VITRO BIOASSAYS: CURRENT STATUS AND FUTURE APPLICATION FOR WATER MANAGEMENT

Lead agent: Global Water Research Coalition

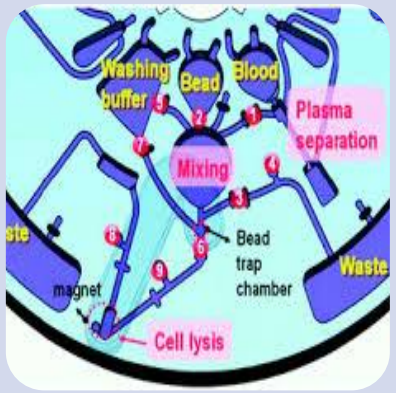
Prepared by: Shane A. Snyder and Frederic D.L. Leusch

AUGUST 2018

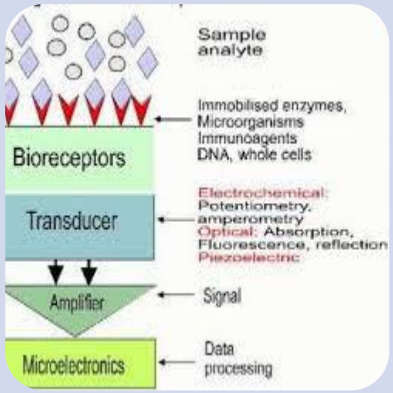
Future trends: Effect Based Biomonitoring

Key Messages - Technologies Informing Policy

Investigative and trend monitoring - improving water bodies over time with real-time systems

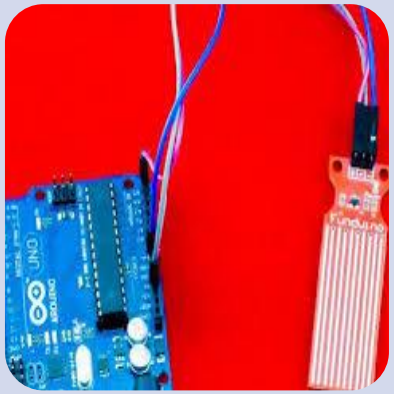


Capacity building in the technology & engineering space essential for future



Risk-based approaches to monitoring not every contaminant

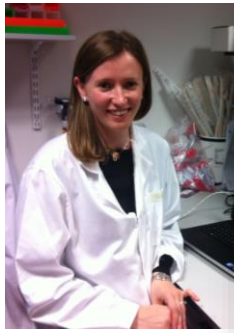
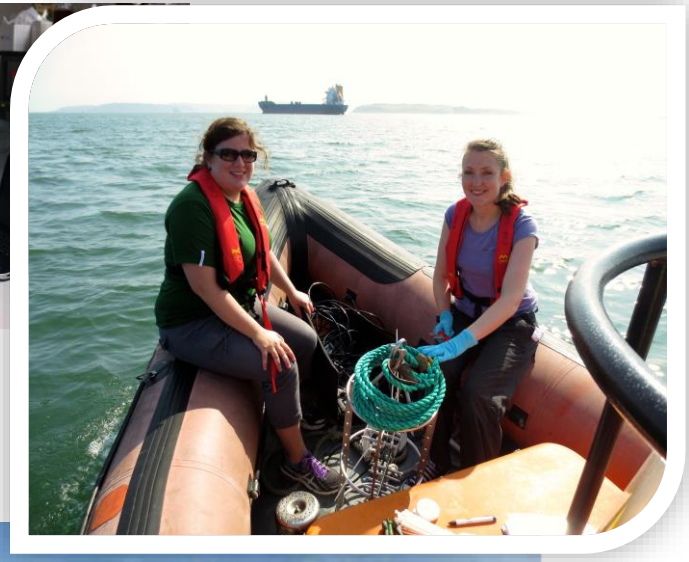
(40 new chemicals every hour)



New capabilities & innovations that can be translated

Improved, faster response for public information



DCU
Ollscoil Chathair
Bhaile Átha Cliath
Dublin City University

Thank you

Water JPI
Maria BOX
SEVENTH FRAMEWORK PROGRAMME
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National Centre for Sensor Research
Iascach Intíre Éireann
Inland Fisheries Ireland
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SeaChange
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SSTI
Strategy for Science, Technology and Innovation
epa
Environmental Protection Agency
BACKDROP