Catchment approach to passive sampling of Irish waters

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Oceans'15

IRISH PASSIVE SAMPLING RESEARCH

Outline

- Project description
- Sampling sites
- Passive sampling
- Cork catchment
  - Overview
  - Results
  - Time trial
- Dublin catchment
  - Results
- Conclusions and outputs

Project description

- EPA funded 3 year project
- Role of PS as a screening and monitoring tool for new and emerging chemicals
- Role of PS as a surrogate to biota
- Qualitative/quantitative screening of selected substances in a number of Irish waters representative of different pressures
- Case studies on emerging compounds and pharmaceuticals using a catchment approach

Passive Sampling

- Determination of pollutants in aquatic environment
- Free flow of analyte molecules from sampled medium to collecting medium – only dissolved analytes, no energy source

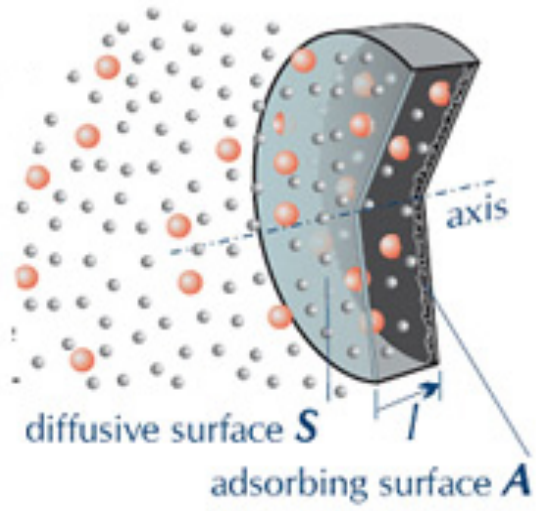


Fig. 1 – Passive sampling mechanism

Fig. 2 – Passive sampling device (interior)

Fig. 3 – Passive sampling devices

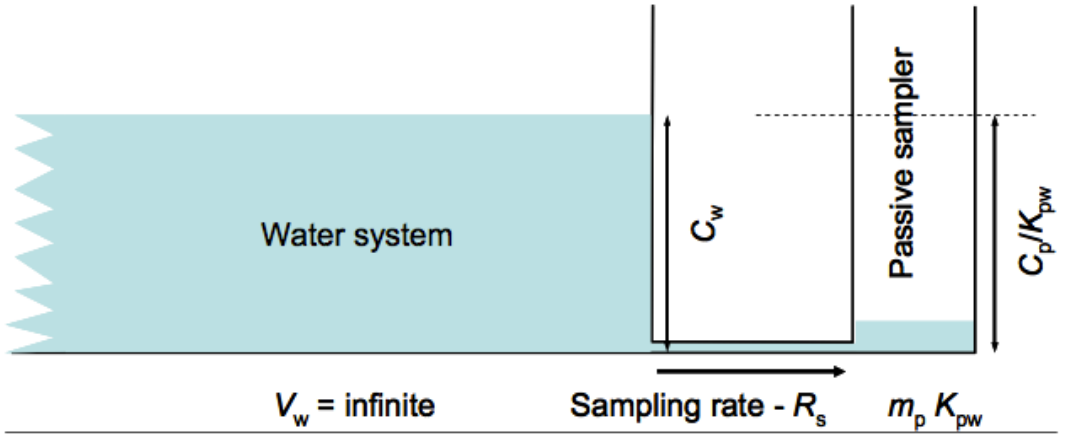
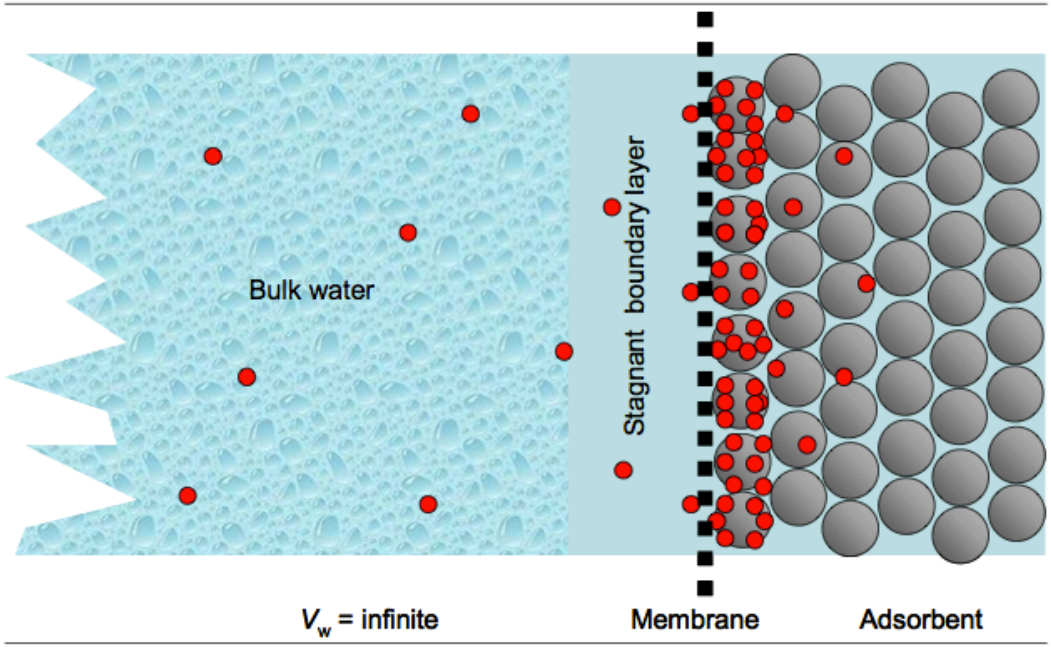


Fig. 4 – Absorption passive sampling mechanism

Equilibrium is reached and time-weighted average is determined. Mainly for non-polar compounds.

Fig. 5 – Adsorption passive sampling mechanism

Kinetic regime is maintained and calculations are based on time-integrated measurements Mainly for polar analytes.



Ref: Smedes *et al.*, 2010

Passive Sampling

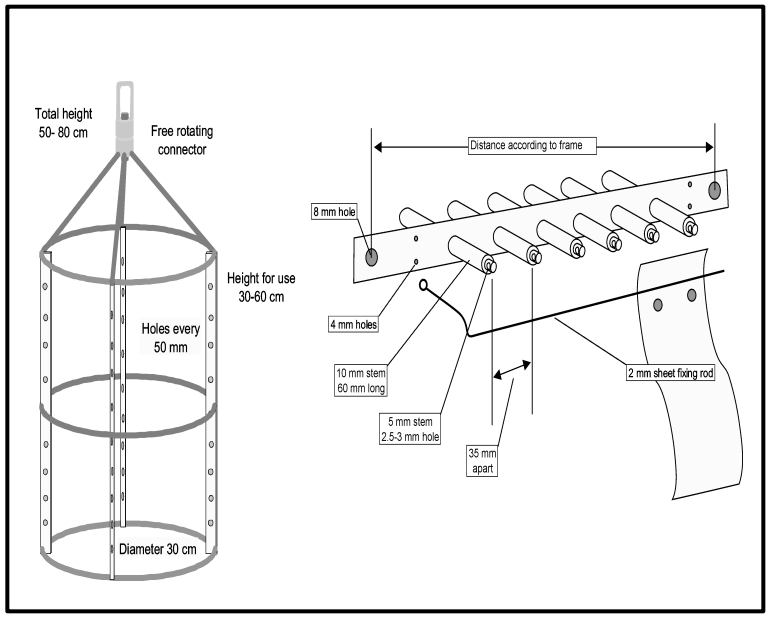
- Greater sensitivity than can be achieved by "traditional" spot-sampling
- Applicable to a wide variety of compounds
- Time-integrated sampling at low detection limits and in-situ extraction of analytes
- Ability to sample large volumes of water
- Ease of deployment and processing
- No external power input is required

Protocol for Passive Sampler Deployment

- ICES TIMES no. 52* for PDMS
- EA lab/NLS guidelines for POCIS

Record

- GPS co-ordinates
- Date and time of deployment
- Salinity
- Water temperature



PDMS sheet attachment*

POCIS canister**

*ICES TIMES no. 52. 2012. Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber

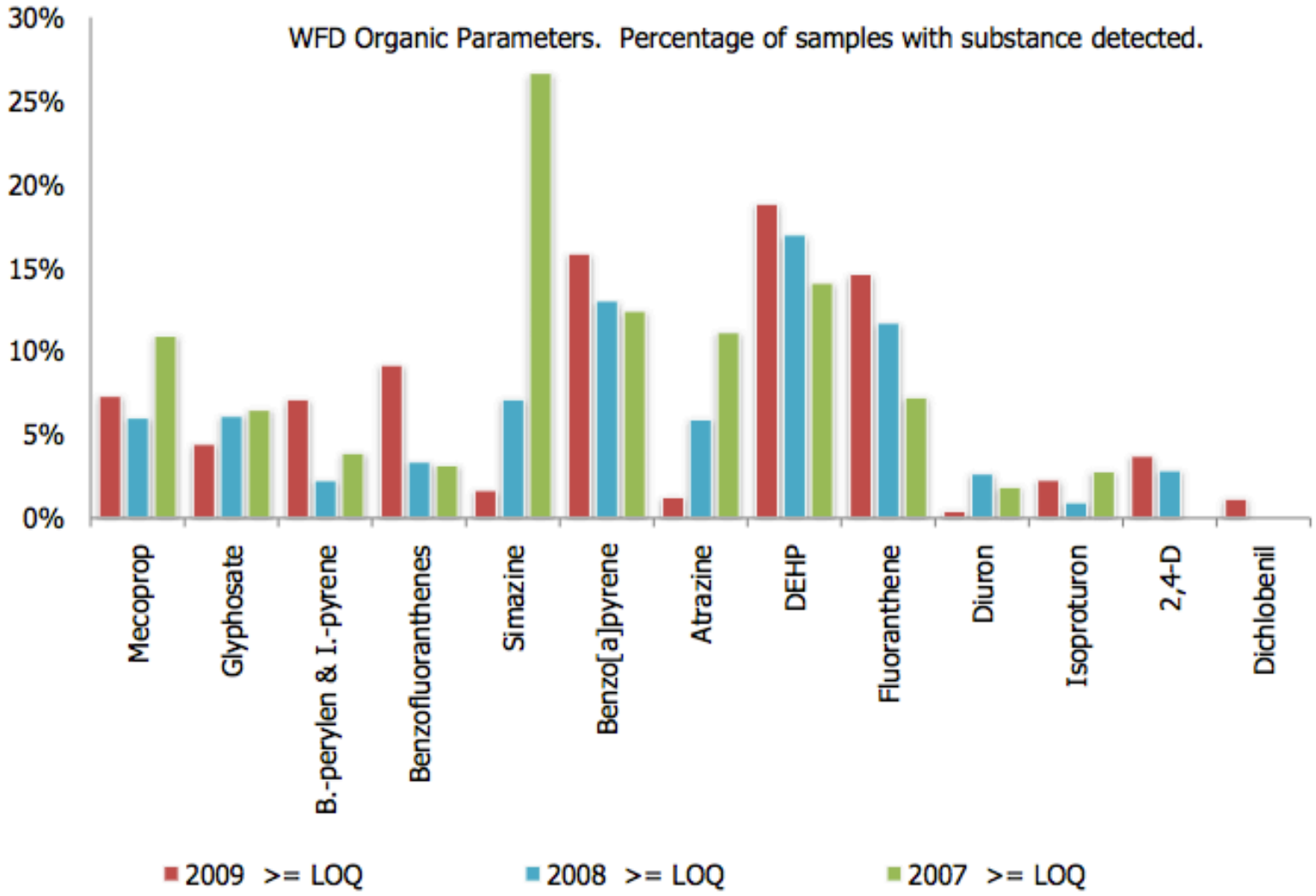
**Environmental Sampling Technologies lab: http://www.est-lab.com/pocis.php

IRISH PERSPECTIVE

Status of Irish Water

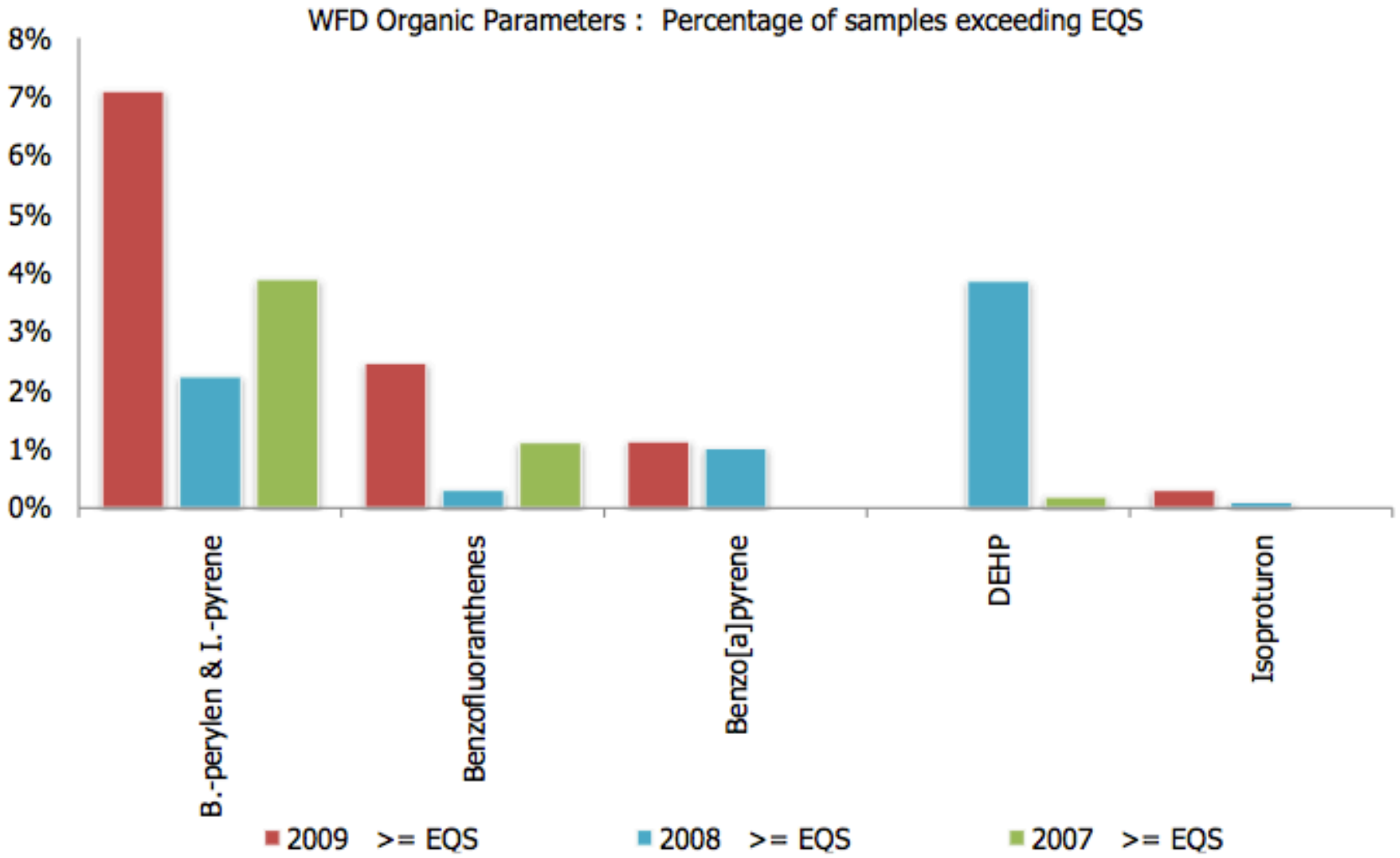
- 31 of the 41 WFD Priority Substances and 89 of the 161 relevant pollutants were detected in one or more samples. The most commonly detected compounds were metals and polycyclic aromatic hydrocarbon (PAH).

Irish Rivers



(EPA Water Quality Report, 2010)

Irish Rivers



(EPA Water Quality Report, 2010)

Overview of Irish agencies with potential information relating to priority substances in Irish waters

	EPA	RBDs	DAFF	LAs	Other (14 Agencies)
Surface water	✓	✓		✓	4 others
Groundwater	✓	✓		✓	4 others
Landfill	✓			✓	
Mining	✓				
Stormwater/runoff					1 other
WWTPs	✓			✓	
Industry	✓		✓	✓	
Agriculture			✓	✓	2 others
Forestry			✓		2 others
Legislation	✓	✓	✓	✓	4 others
Domestic households					1 other
Airports				✓	
Aquaculture			✓		2 others

PROJECT OVERVIEW

Target Monitoring Stations

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

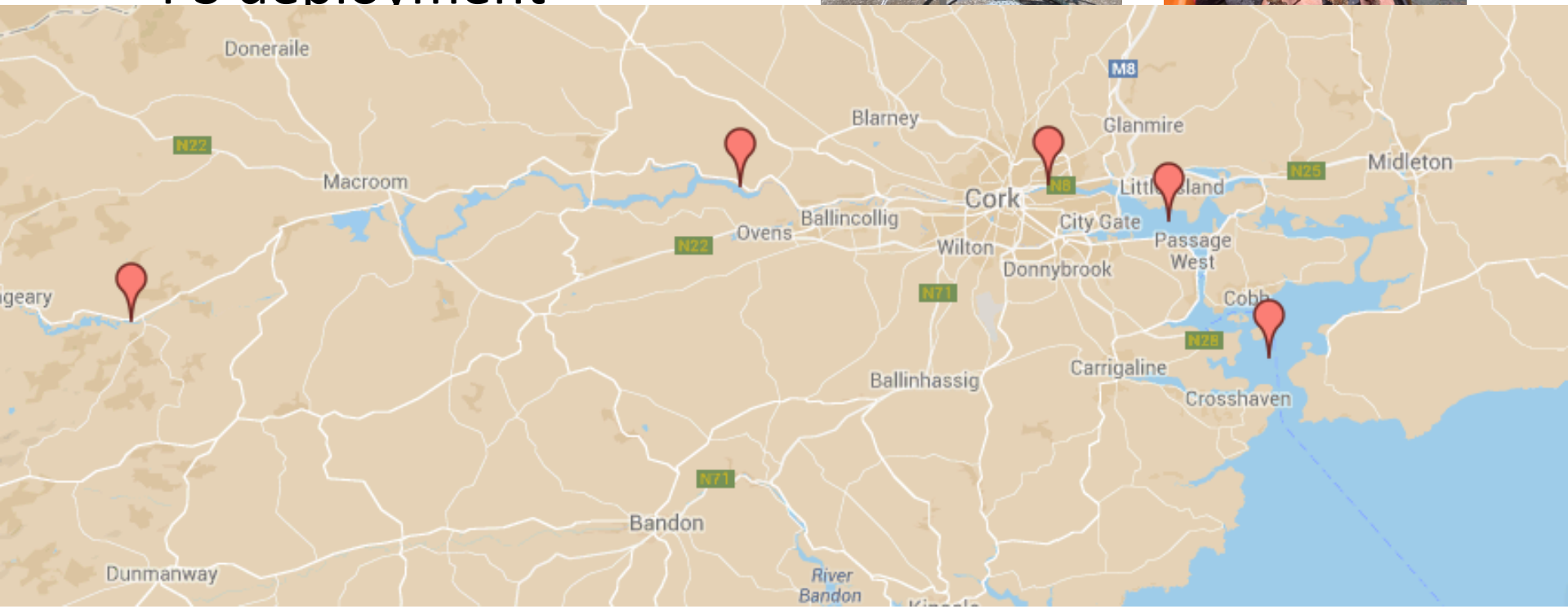
Catchment Approach

- The WFD introduced a comprehensive catchment based approach to water management
- Identify point sources and pathways of pollution
- More targeted approach to monitoring of emerging and priority compounds in water
- Potential role for the combination of catchment based approaches and focused water and passive sampler analysis for the surveillance monitoring

PHARMACEUTICALS STUDY

Cork 2013-2014

- Method development
  - LC-MS/MS
  - GC-MS/MS
- PS deployment



Catchment approach in Lee catchment , Cork

Cork POCIS and water oestrogens

Upstream → **Downstream**

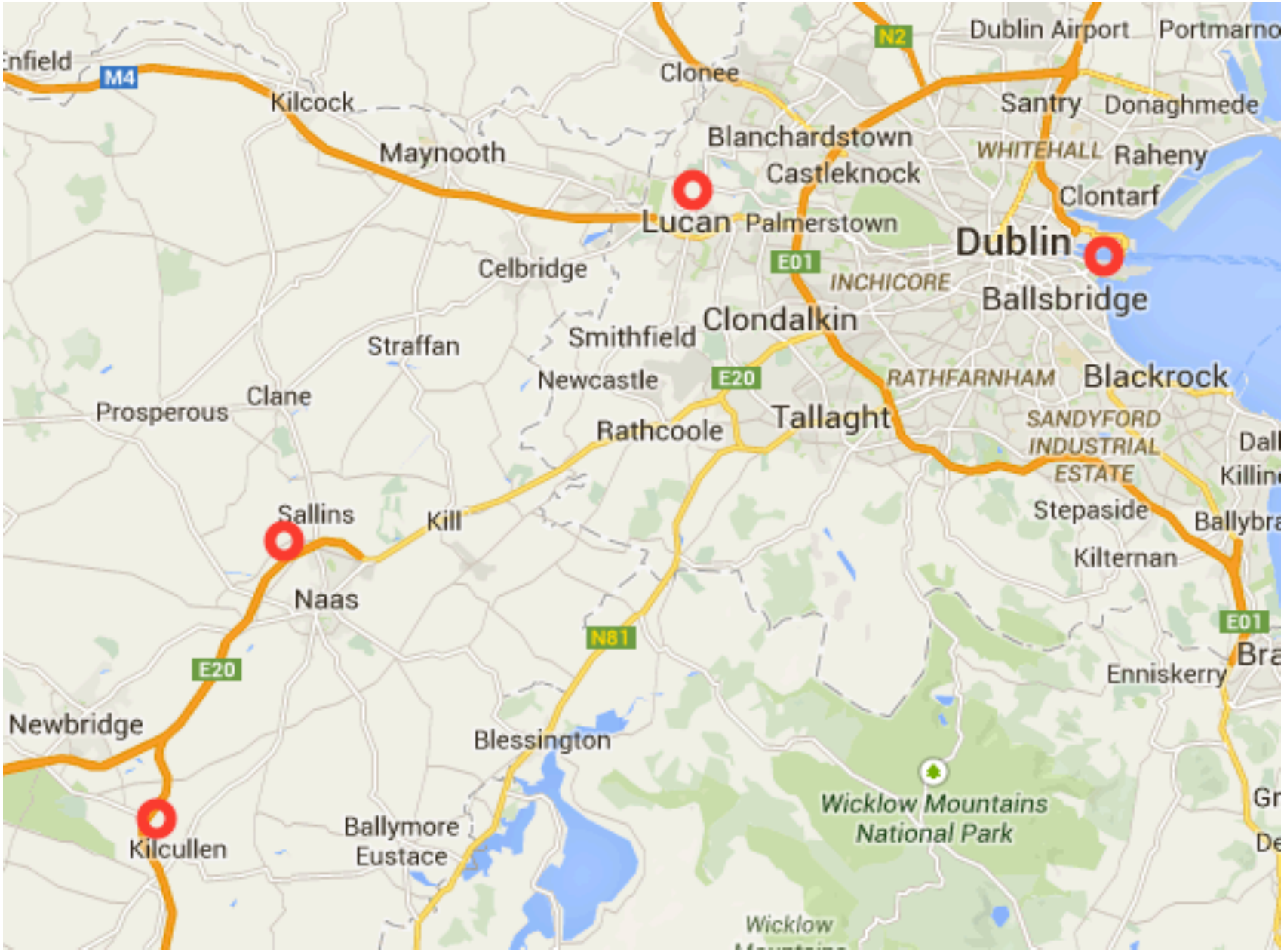
	Matrix		Lough Allua Inchigeelagh	Iniscarra	Shandon	Lough Mahon	Cork Outer Harbour
Analyte		***Units***	**2013**				
EE2	POCIS	ng L^{-1}	<0.2	**1.39**	<0.2	<0.2	<0.2
E2		ng L^{-1}	<0.5	<0.5	<0.5	**2.36**	**1.98**
EE2	Water	ng L^{-1}*	nd	nd	nd	nd	nd
E2		ng L^{-1}*	nd	nd	nd	nd	nd
Analyte		***Units***	**2014**				
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

Results: POCIS
Temporal aspects

- Due to issues with variability of environmental conditions in the field it was necessary to evaulate deployment duration for POCIS
- 4 week deployment has been deemed the optimal timeframe for POCIS deployment

		Shandon Boat Club		
Analyte	***Estimated Water Conc.***	**2 Weeks**	**4 Weeks**	**6 Weeks**
17alpha ethynylestradiol (EE2)	ng L^{-1}	< 0.09	0.07	< 0.04
17beta estradiol (E2)	ng L^{-1}	< 0.10	0.09	0.08
Estrone (E1)	ng L^{-1}	< 0.39	0.37	0.29


M4
Kilcock
Maynooth
Clonee
N2
Dublin Airport
Portmarnock
Santry
Donaghmede
Blanchardstown
Castleknock
WHITEHALL
Raheny
Clontarf
Lucan
Palmerstown
Dublin
E01
INCHICORE
Ballsbridge
Celbridge
Clondalkin
Smithfield
Straffan
Newcastle
E20
RATHFARNHAM
Blackrock
Clane
Prosperous
Rathcoole
Tallaght
SANDYFORD
INDUSTRIAL
ESTATE
Stepaside
Sallins
Kill
Naas
Kilternan
N81
E01
Enniskerry
E20
Newbridge
Blessington
Wicklow Mountains
National Park
Kilcullen
Ballymore
Eustace
Wicklow

Results: Estrogens in water

Analyte	E1 ng L^{-1}	E2 ng L^{-1}	EE2 ng L^{-1}
Kilcullen T0	<0.07	nd	nd
Kilcullen T1	nd	nd	nd
Osberstown T0	nd	0.33	nd
Osberstown T1	nd	nd	nd
Lucan Bridge T0	0.33	0.43	nd
Lucan Bridge T1	nd	nd	nd
Poolbeg T0	nd	<0.07	nd
Poolbeg T1	1.92	0.23	nd

T0 = Time zero, T1 = one month after sampler deployment
LOD water samples by LC-MS/MS: E1: 0.07 ng/L E2: 0.07 ng/L, EE2, 0.11 ng/L. 5 L sample n = 2

Environmental challenges and solutions

- PS addresses challenges of detecting at low EQS
  - Dissolved vs total water concentration remains an issue

- Time-integrated measurements

- Easy to deploy and analyse
  - Simpler matrix
  - Lack of confounding biological factors
  - Suitable for “temporal” trend monitoring (and for surveillance/ screening) and for co-deployment with biota

- Ongoing development of modelling and partition coefficients will drive capabilities

Outputs from research

- Comprehensive review of PS as a support to WFD monitoring
- Assessment of PS as surrogate to biota
- Assessment of priority pollutants in Irish catchments
- Recommendations for use of PS as a screening/monitoring tool

Project Media

- Twitter: @irishPSresearch
- Website: https://sites.google.com/site/irishpassivesampling/home

Acknowledgements

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NDP
National Development Plan 2007 - 2013

SSTI
Funded as part of the Strategy for Science, Technology and Innovation

epa
Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil