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Passive sampling of polar emerging contaminants in Irish catchments

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inspiring change

DCU | Water Institute

Outline

- Passive Sampling
  - Analytes
- Approach
  - Rationale
  - Catchment study
  - Sampling sites
- Cork catchment
- Conclusions

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 for biota monitoring
- 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

Passive Sampling

- Free flow of analyte molecules from sampled medium to collecting medium
  - only dissolved analytes, no energy source

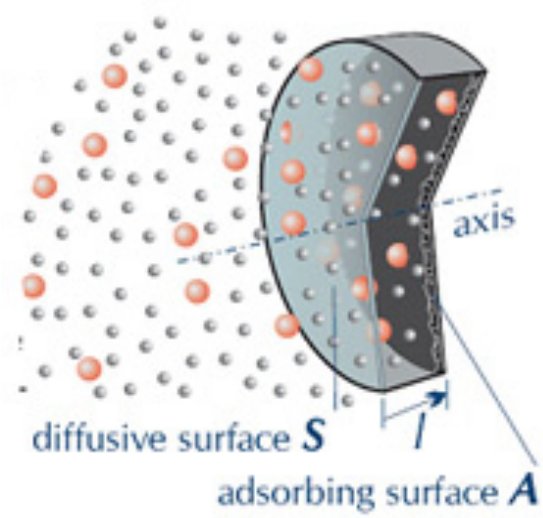


Fig. 1 – Passive sampling mechanism

Fig. 2 – Passive sampling device

Fig. 3 – Passive sampling devices

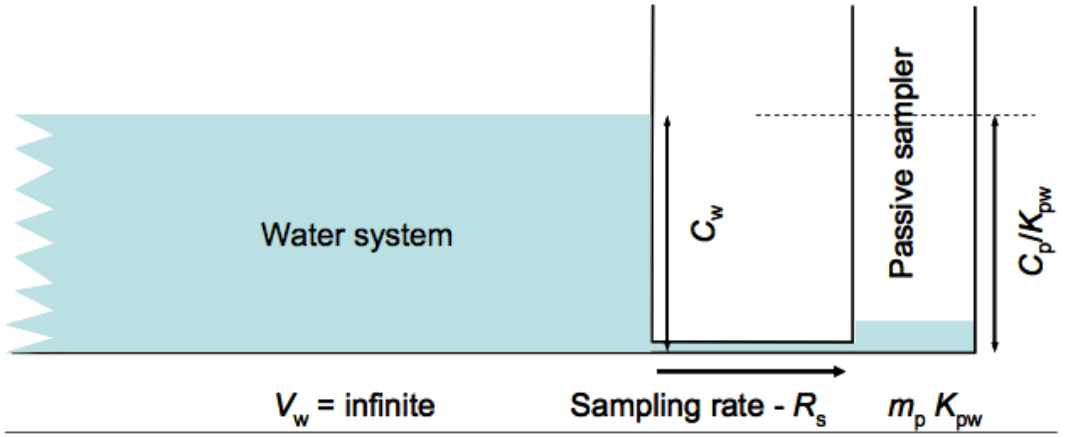
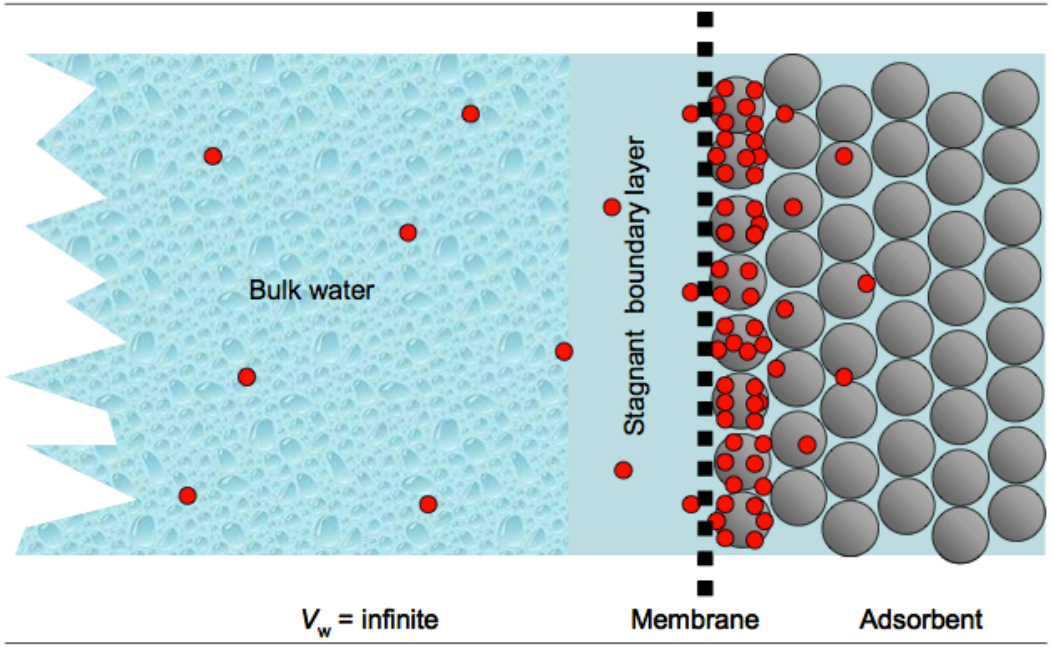


Fig. 4 – Absorption passive sampling mechanism

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.



Advantages of 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

Target Analytes

	EPA	Sampler type	Water	Biota
EDCs and pharmaceuticals	**Compound**	POCIS	Y	Y
	17b estradiol (E2)		Y	Y
	17a ethynyl estradiol (EE2)		Y	Y
	Diclofenac		Y	Y
	Alkylphenols		Y	Y
Organohalogens	HCB	PDMS	Y	Y
	Heptachlor		Y	Y
	Heptachlor epoxide		Y	Y
	HBCDD		Y	Y
	PCBs		Y	Y
	PBDEs		Y	Y
	HCBD		Y	Y
	Dioxins and dioxin-like compounds		Y	Y
PFOS	PFOS	POCIS	Y	Y

Target Analytes

Compound group	Compound	Sampler type	Water	Biota
PAH	Naphthalene	PDMS	Y	Y
	Anthracene		Y	Y
	Fluoranthene		Y	Y
	Benzo-a-pyrene		Y	Y
	Benzo-b-fluoranthene		Y	Y
	Benzo-k-fluoranthene		Y	Y
	Indeno-1,2,3cd-pyrene		Y	Y
	Benzo-g,h,i-perylene		Y	Y
Pesticides	Aclonifen	POCIS	Y	Y
	Bifenox		Y	Y
	Cybutryn		Y	Y
	Terbutryn		Y	Y
	Quinoxyfen		Y	Y
	Dichlorvos	PDMS	Y	Y
	Dicofol		Y	Y
	Cypermethrin	SPMD/PDMS	Y	N

Approach

Catchment Approach

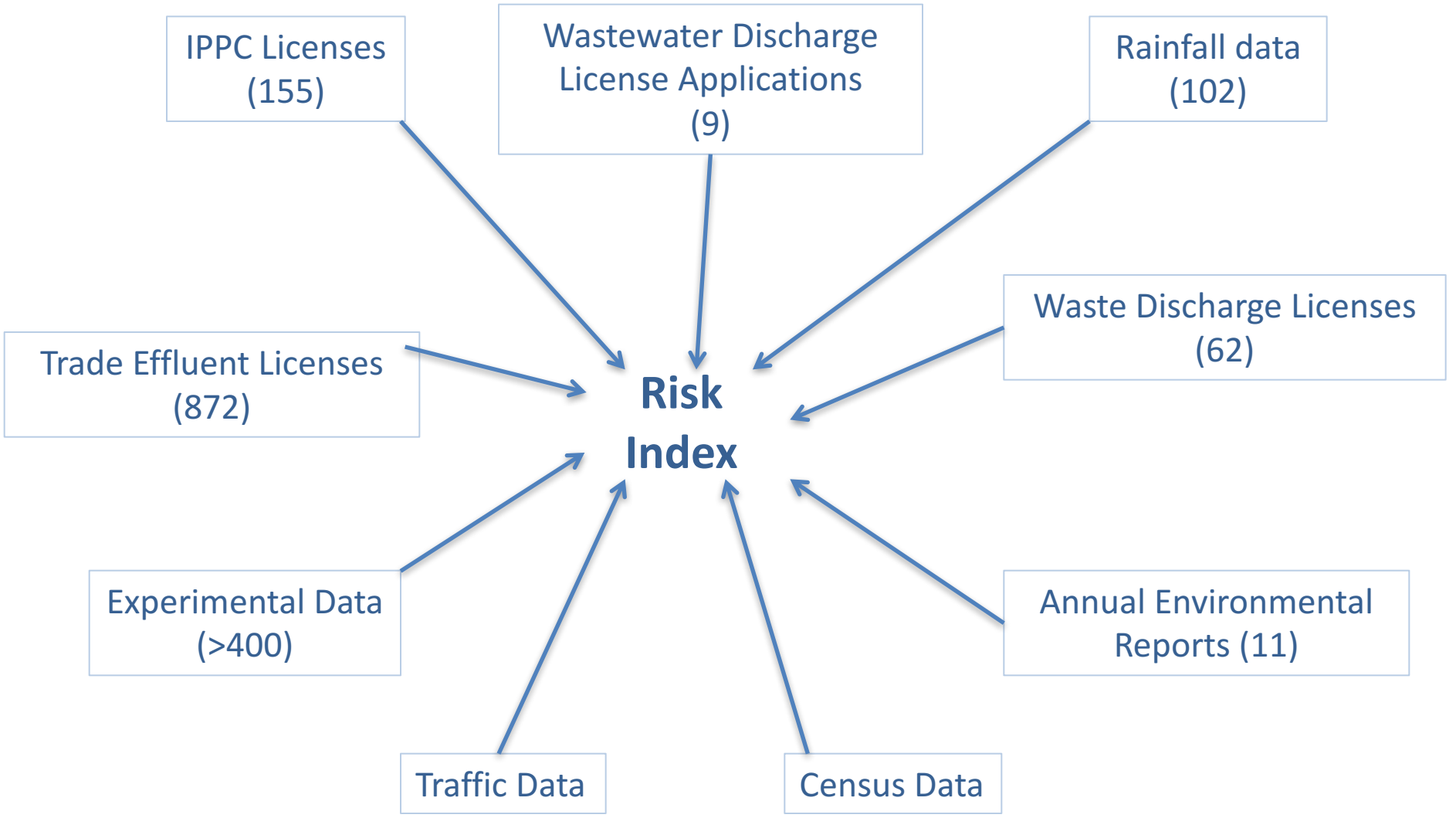
- The WFD introduced a comprehensive catchment based approach to water management
- Identify point sources and pathways of pollution
- More targeted approach to monitoring of emerging and priority compounds in water
- Potential role for the combination of catchment based approaches and focused water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

Priority pollutants in Wastewater

- Relate emission factors to occurrence
- Monitor priority pollutant levels in wastewater treatment plant effluents
- Relate levels detected to emission factors
  - Population equivalents, rainfall, traffic, etc.
- Create index of priority substance emissions from wastewater treatment plants

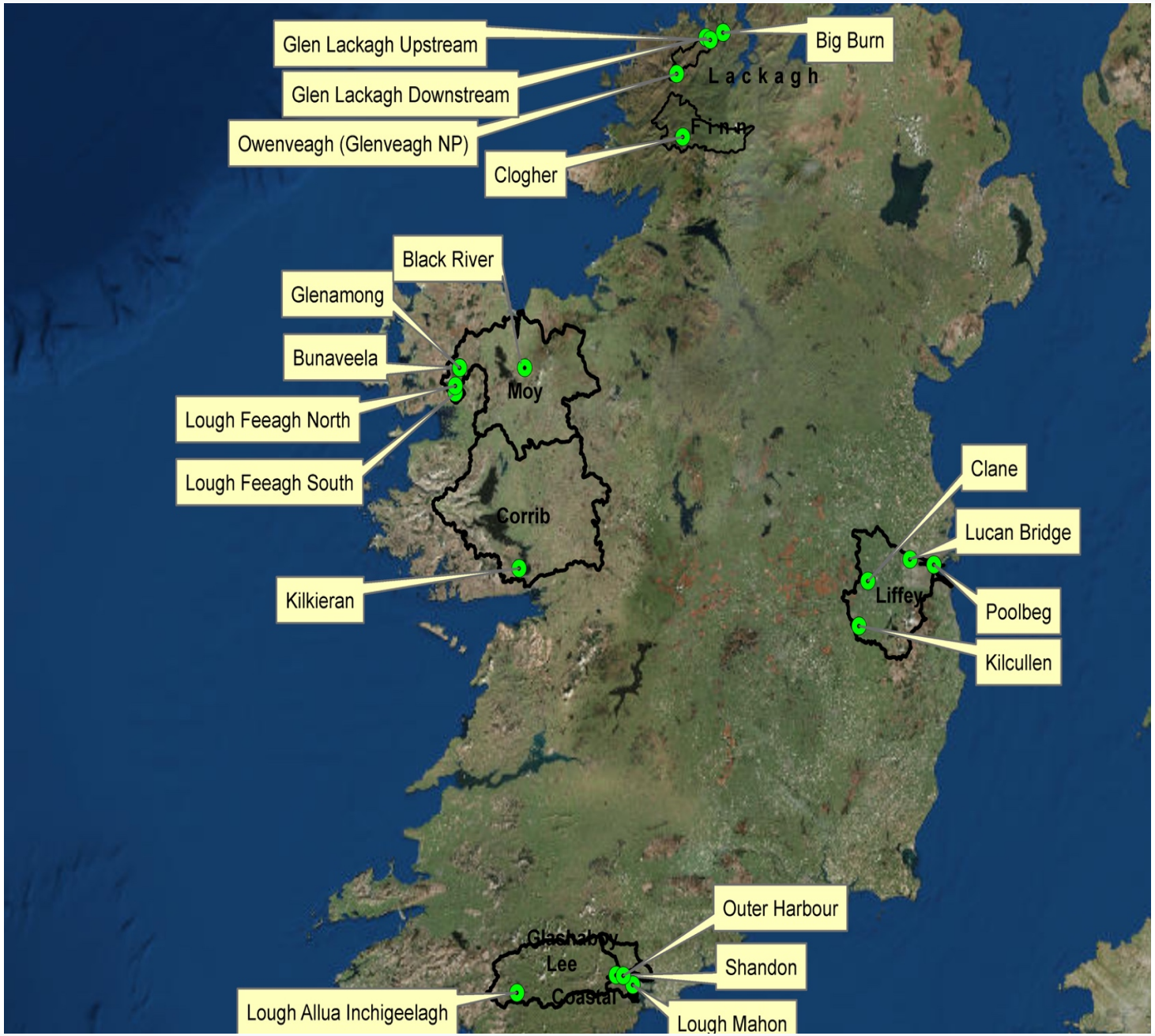
Emerging substances in Irish waters

	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


IPPC Licenses (155)
Wastewater Discharge License Applications (9)
Rainfall data (102)
Waste Discharge Licenses (62)
Trade Effluent Licenses (872)
Risk Index
Experimental Data (>400)
Annual Environmental Reports (11)
Traffic Data
Census Data

Target Monitoring Stations

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**		✓	✓	**EPA Benthic kick sampling**	
	Glen Lackagh 2	**Cypermethrin study**		✓	✓		


Glen Lackagh Upstream
Big Burn
Glen Lackagh Downstream
Lackagh
Owenveagh (Glenveagh NP)
Finn
Clogher
Black River
Glenamong
Bunaveela
Moy
Lough Feeagh North
Lough Feeagh South
Corrib
Clane
Lucan Bridge
Liffey
Kilkieran
Poolbeg
Kilcullen
Outer Harbour
Glashaboy
Lee
Shandon
Coastal
Lough Allua Inchigeelagh
Lough Mahon

Protocol for Passive Sampler Deployment - POCIS

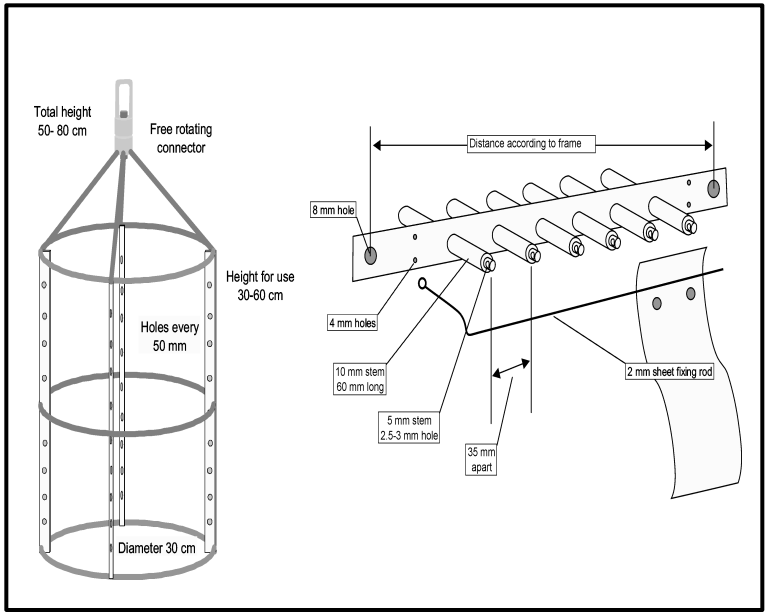
- EA lab/NLS guidelines for POCIS
- Sent in sealed canisters
- On site samplers and field blanks exposed to same conditions
- 4 week deployment time has been optimized

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*

*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

Analysis

- 1 L water samples (n=3)
- Sampler deployments 4-6 weeks (POCIS/PDMS)
- SPE – Strata-X with elution using DCM
- HPLC-MS/MS
  - Applied Biosystems 3200 Q-TRAP was used. The mobile phases were deionised water (A) and 0.025 % TEA in 95:5 CH_3OH: acetone (B) flowing at 300 µL per minute with a gradient as follows: 0 to 0.5 min (5 to 20 % B), 0.5 to 1 min (20 to 40 % B), 1 to 12 min (40 to 80 % B), 12 to 14 min (80 % B) and 14 to 14.5 min (80 to 5 % B) with analysis as per the Environment Agency Blue Book 220

Cork Catchment

Target Monitoring Stations

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	✓	✓	EPA Benthic kick sampling	
	Glen Lackagh 2	Cypermethrin study	SPMD	✓	✓		

Cork oestrogen results

Upstream → **Downstream**

	Matrix		Lough Allua Inchigeelagh	Iniscarra	Shandon	Lough Mahon	Cork Outer Harbour
Analyte		***Units***	**2013**				
EE2	POCIS	ng L^{-1}	<0.04	***0.06***	<0.04	<0.04	<0.04
E2		ng L^{-1}	<0.04	<0.04	<0.04	**0.06**	**0.05**
EE2	Water	ng L^{-1}*	nd	nd	nd	nd	nd
E2		ng L^{-1}*	nd	nd	nd	nd	nd
Analyte		***Units***	**2014**				
EE2	POCIS	ng L^{-1}	<0.04	***0.06***	***0.09***	<0.04	<0.13
E2		ng L^{-1}	<0.04	<0.04	**0.07**	<0.04	<0.12
EE2	Water	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
EQS: EE2 (0.007 ng L^{-1}) E2 (0.08 ng L^{-1})

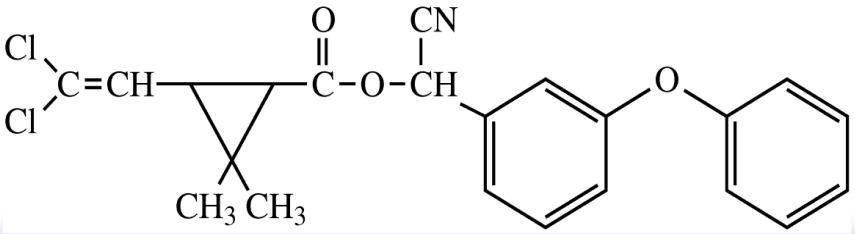
Pesticides Occurrence in Water

Pesticide	Target EQS	Freq.	Max Detected
	μg L^{-1}	N = 25	
Aclonifen	0.12	4	0.2×10^{-5}
Bifenox	0.012	4	3.8×10^{-6}
Cybutryn	0.0025	10	0.6×10^{-5}
Dichlorvos	0.0006	12	3.2×10^{-6}
Dicofol	0.0013	0	0
Heptachlor	0.0000002	0	0
Heptachlor epoxide		0	0
Quinoxyfen	0.15	15	6.4×10^{-6}
Terbutryn	0.065	8	1.3×10^{-6}

Cypermethrin Study

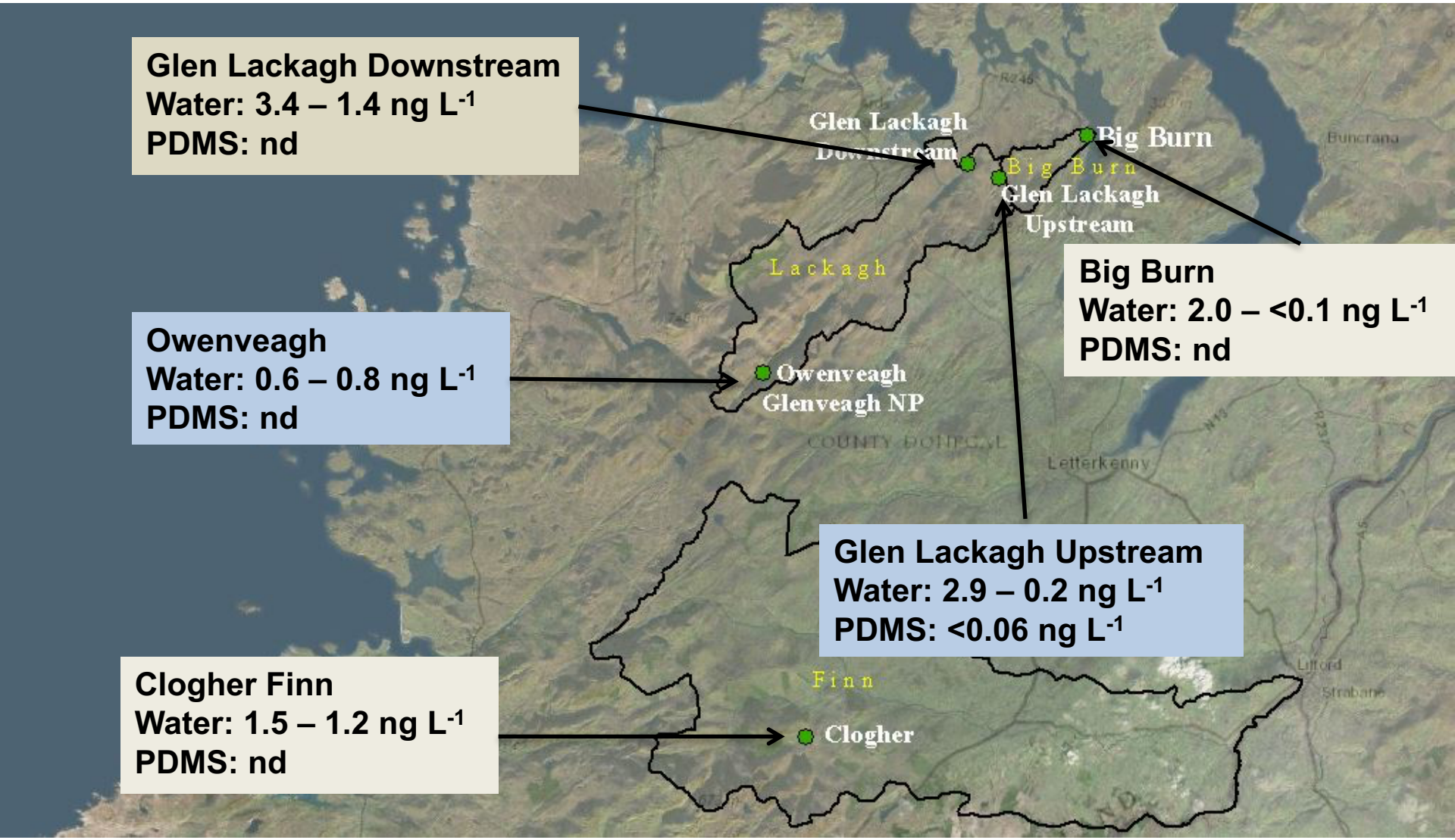
Cypermethrin study

- Persistent pyrethroid insecticide.
- Cypermethrin kills invertebrates and although it has a short half-life (<2 weeks) it can have lasting effects.
- Sites selected based on pressures from agriculture, forestry and aquaculture.
- Large dataset of usage and occurrence reports has been compiled



Cypermethrin study

- Aim to study the effects of upstream activity and the occurrence of cypermethrin using passive sampling.
- NIEA and UK EA began surveillance monitoring in 2013.
- EPA advised on site selection in Donegal:
  - Upstream and downstream sites in Glen Lackagh



3 Sensitive/potentially impacted sites 2 Control sites

EQS: 0.08 ng L^{-1}

Conclusions

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

The Way Forward

- It is proposed that:
  - PSM could become part of a larger strategy for monitoring;
  - There is a role for PS in a risk-based screening approach to operational monitoring;
  - PS is applicable in trend monitoring (feeding into risk based assessments);
  - There is a need to develop a plan defining how to implement PS for the purposes of trend monitoring.

Project Media

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

Acknowledgements

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Thank you for your attention!