Passive Sampling in Monitoring of New and Emerging Compounds – An Irish Perspective

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IRISH PASSIVE SAMPLING RESEARCH

Outline

- Project description
  - Background
  - Sampling sites
  - Analytes
  - Pharmaceuticals
  - Cypermethrin study
- Conclusions
- Future work

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

Target Analytes

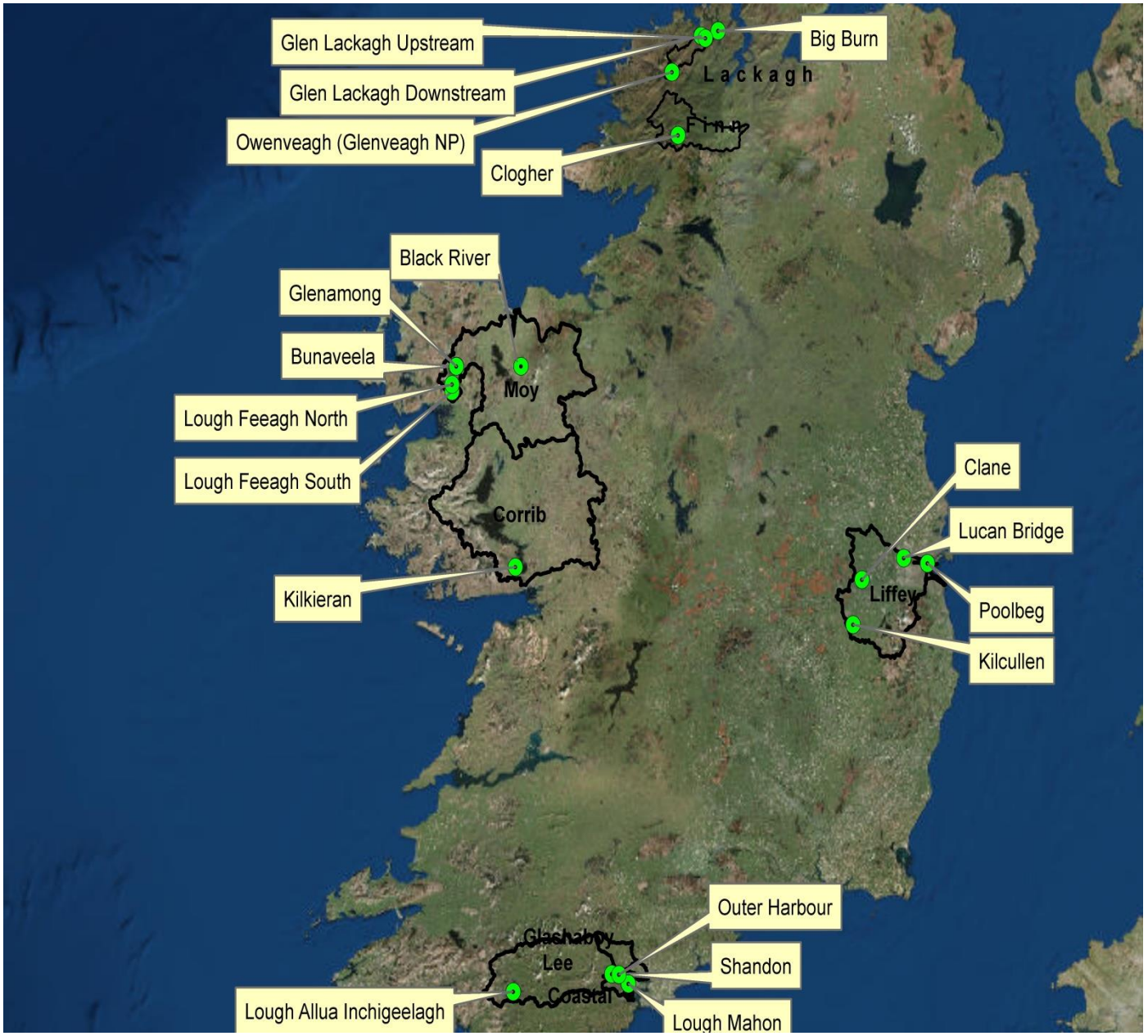
	EPA	Sampler type	Water	Biota
EDCs and pharmaceuticals	**Compound**	POCIS	Y	Y
	17b estradiol (E2)		Y	Y
	17a ethynyl estradiol (EE2)		Y	Y
	Diclofenac		Y	Y
	Alkylphenols		Y	Y
Organohalogens	HCB	PDMS	Y	Y
	Heptachlor		Y	Y
	Heptachlor epoxide		Y	Y
	HBCDD		Y	Y
	PCBs		Y	Y
	PBDEs		Y	Y
	HCBD		Y	Y
	Dioxins and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

Target Analytes

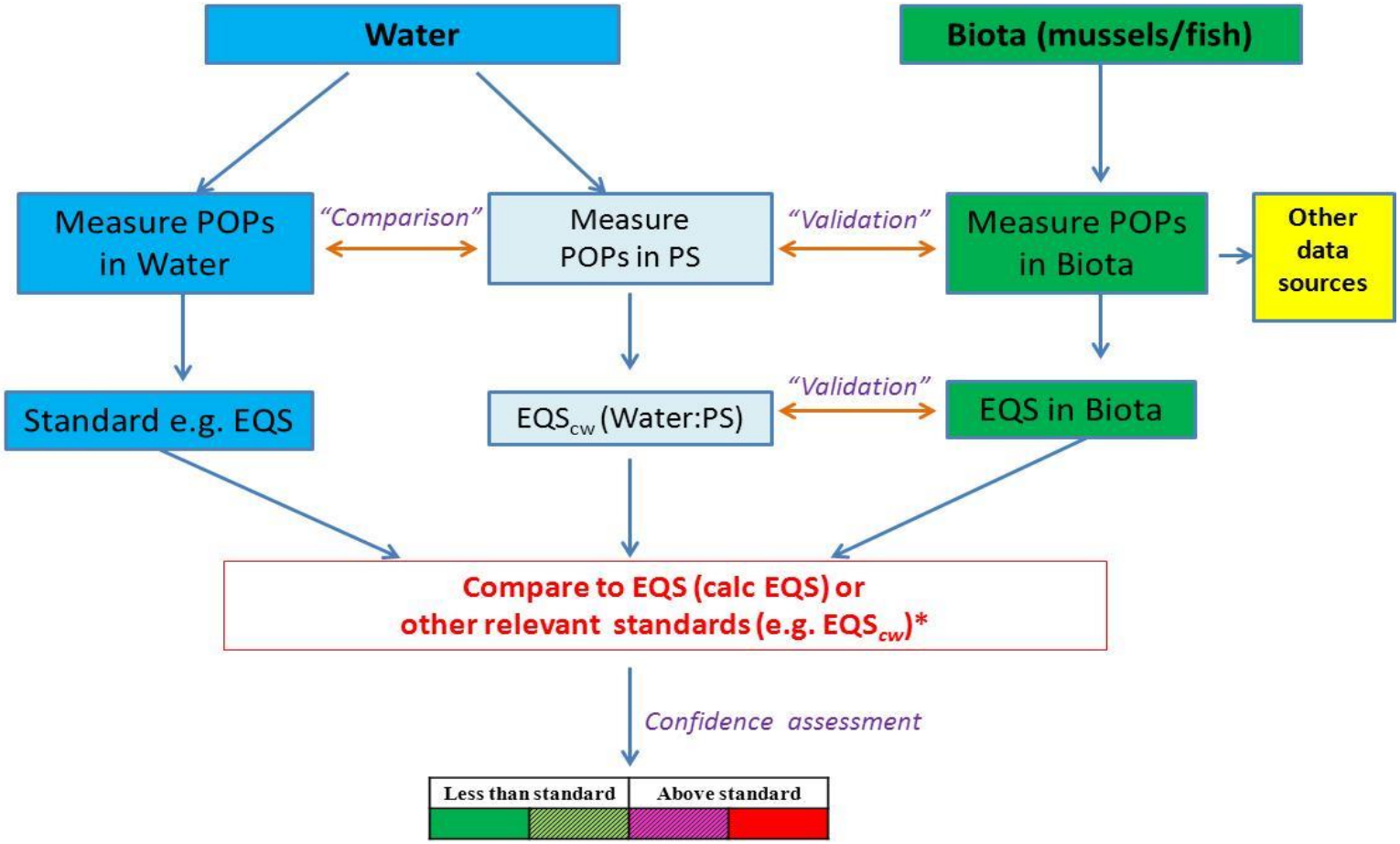
Compound group	Compound	Sampler type	Water	Biota
PAH	Naphthalene	PDMS	Y	Y
	Anthracene		Y	Y
	Fluoranthene		Y	Y
	Benzo-a-pyrene		Y	Y
	Benzo-b-fluoranthene		Y	Y
	Benzo-k-fluoranthene		Y	Y
	Indeno-1,2,3cd-pyrene		Y	Y
	Benzo-g,h,i-perylene		Y	Y
Pesticides	Aclonifen	POCIS	Y	Y
	Bifenox		Y	Y
	Cybutryn		Y	Y
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

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	✓	✓		


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

Project approach to further incorporating PS into operational monitoring programmes



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

Protocol for Passive Sampler Deployment - POCIS

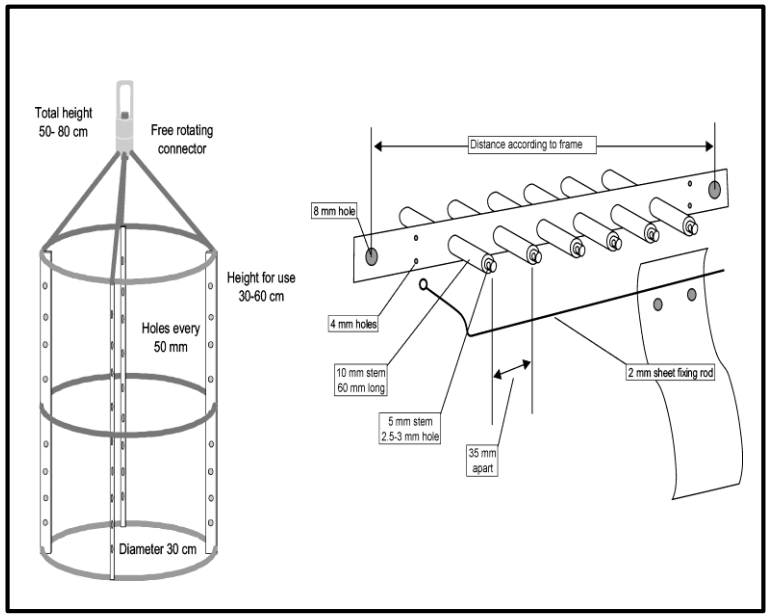
- EA lab/NLS guidelines for POCIS
- Sent in sealed canisters
- On site samplers and field blanks exposed to same conditions
- 4 week deployment time has been optimized

Protocol for Passive Sampler Deployment - PDMS

- ICES TIMES no. 52* for PDMS
- 5.5 x 9 cm rectangles
- Oligomers removed and PRCs spiked

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

Catchment Approach

- WFD: 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
- Combination of catchment based approaches and focused water and passive sampler analysis for surveillance and investigative monitoring

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

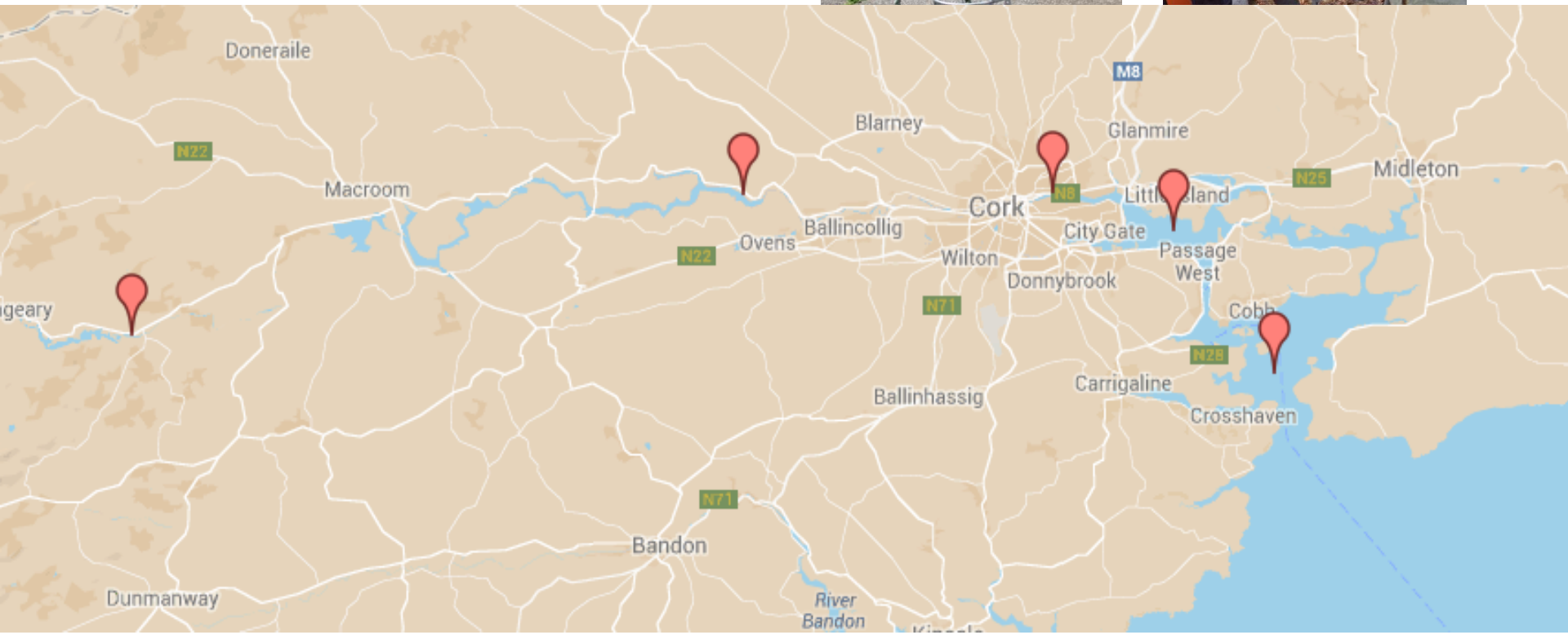
Passive sampling data from WFD sites (ng L^{-1})

	UBΣ PAH	UB Σ 7PCBs	UB Σ PBDEs	α-HCH	γ-HCH	HCB	UB Σ 7OCs
Mutton Island	6.13	120	n.a	1.77	1.35	0.12	6.10
Dublin Port	32.6	843	n.a	1.74	10.4	n.d	20.2
Bantry Bay	8.86	54.6	n.a	0.73	2.22	0.03	6.45
Omey Island	3.18	371	n.a	0.51	0.09	n.d	0.89
Cork 1	31.8	858	n.a	5.52	6.17	0.2	18.2
Cork 2	27.1	824	n.a	5.39	6.09	0.2	17.6
Wexford Harbour	28.2	126	n.a	4.87	6.09	0.06	13.8
Shannon	30.8	158	n.a	8.12	6.12	0.12	15.2
NWA Seaboard	4.08	44.5	0.004	2.38	2.61	n.d	4.99
Gweebarra Bay	9.18	76.9	0.010	<0.01	0.03	n.d	0.56
Erne Estuary	34.6	126	0.016	5.02	3.99	n.d	10.1
Furnace Lough	7.23	50.1	0.009	4.02	3.47	n.d	7.51
Kilkieiran	9.08	11.4	0.010	0.13	0.04	n.d	0.25
Lower Shannon	22.8	51.3	0.013	2.60	2.94	n.d	8.72
Upper Shannon	30.5	139	0.038	4.18	3.66	n.d	12.8
Limerick Dock	38.9	304	0.064	7.62	4.70	n.d	13.4
Upper Blackwater	27.2	69.5	n.a	2.04	3.01	n.d	6.29
New Ross	38.6	252	0.067	1.83	2.74	n.d	4.75
Upper Barrow	34.3	64.2	0.052	6.74	4.34	n.d	11.5
Nore Estuary	34.5	71.5	0.085	3.62	2.58	n.d	10.5
Upper Slaney	22.0	114	0.083	1.74	0.78	n.d	4.20

Cork Catchment

Cork 2013-2014

- Methodology
  - LC-MS/MS
  - GC-MS/MS



Catchment approach in Lee catchment , Cork

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	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})

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

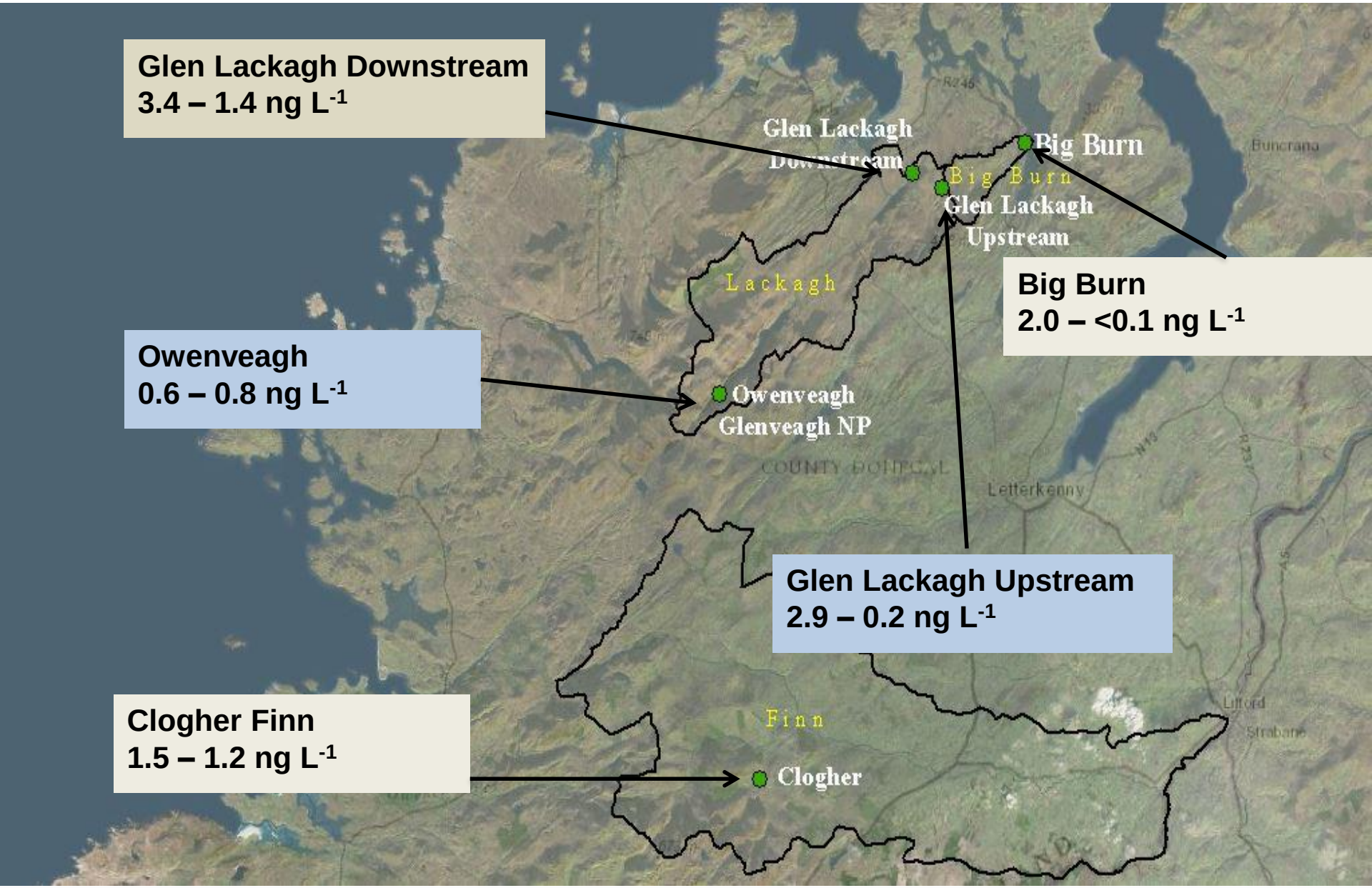
Cypermethrin study

- 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
  - Based on previous benthic kick sampling (q values)
  - Integration of chemistry and biology

Cypermethrin study

	Matrix		Glen Lackagh Upstream	Glen Lackagh midstream A*	Glen Lackagh midstream B	Glen Lackagh midstream C	Glen Lackagh Bridge*
		Units	**2014**				
April	Water	ng L^{-1}	**1.17**	**-**	**-**	**-**	**1.08**
May	Water	ng L^{-1}	**1.47**	**1.67**	**1.38**	**1.73**	**1.78**
	SPMD	ng L^{-1}	<70	-	-	-	<70
	PDMS		++	-	-	-	+++

EQS: 0.08 ng L^{-1}



3 Sensitive/potentially impacted sites 2 Control sites

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:
  - PS 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.

Future work

- Investigating potential sources and environmental fates of 11 phthalates
- Wastewater, surface water, soil, sludge, recycled materials, leachate, passive sampling
- Poster 11 for more information

@phthalatesDCU

@irishwaterstudy

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Thank you for your attention!