

Application of passive sampling to the determination of cypermethrin in an Irish catchment

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Outline

- Catchment approach
- Passive sampling work
 - Polar pesticides
 - Cypermethrin study
- Conclusions



Project description

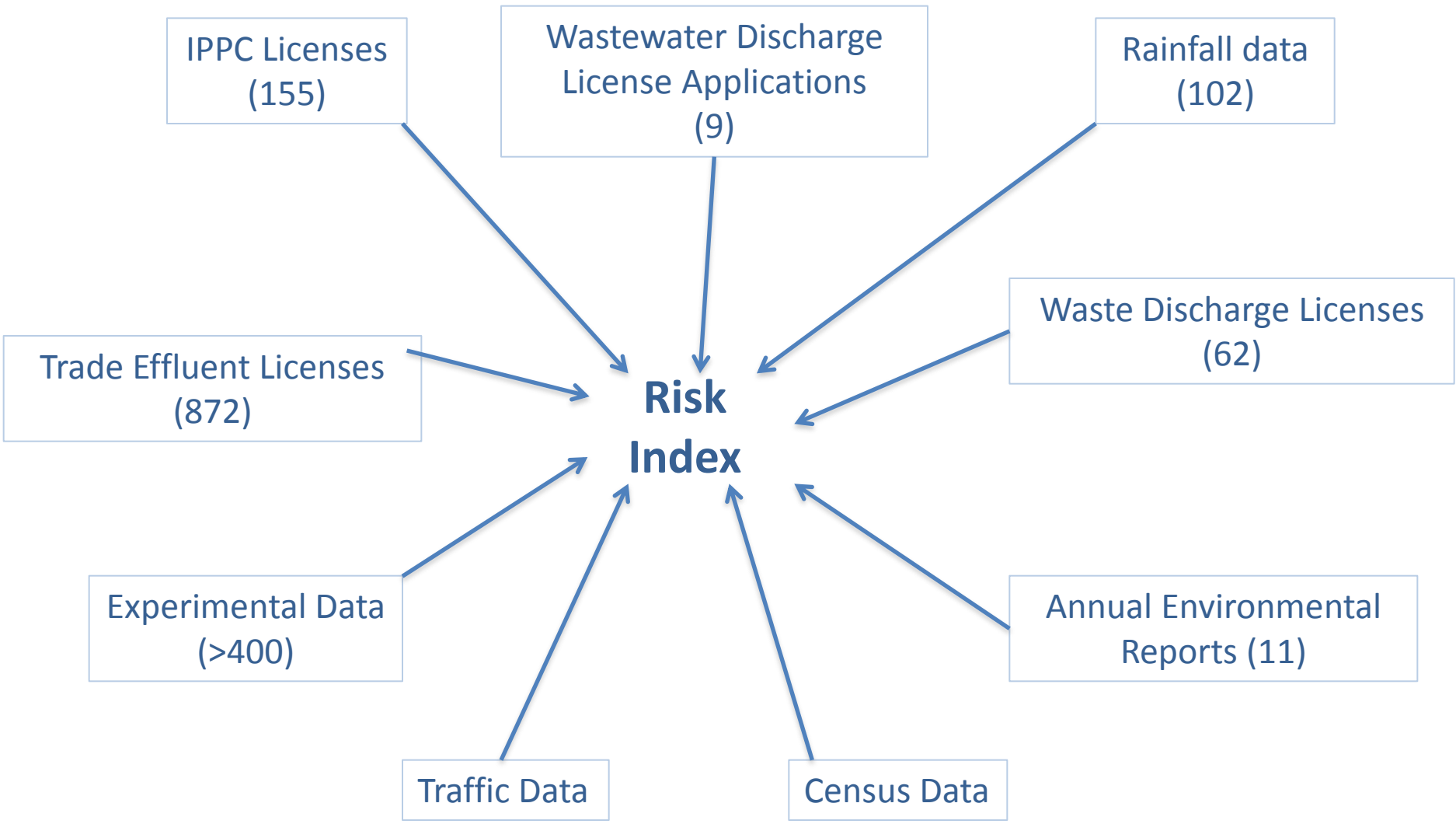
- EPA funded 3 year project
- Role of PS as a screening and monitoring tool for new and emerging chemicals
- Qualitative/quantitative screening of selected substances in a number of Irish waters representative of different pressures
- Case studies on emerging compounds, pesticides and pharmaceuticals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

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

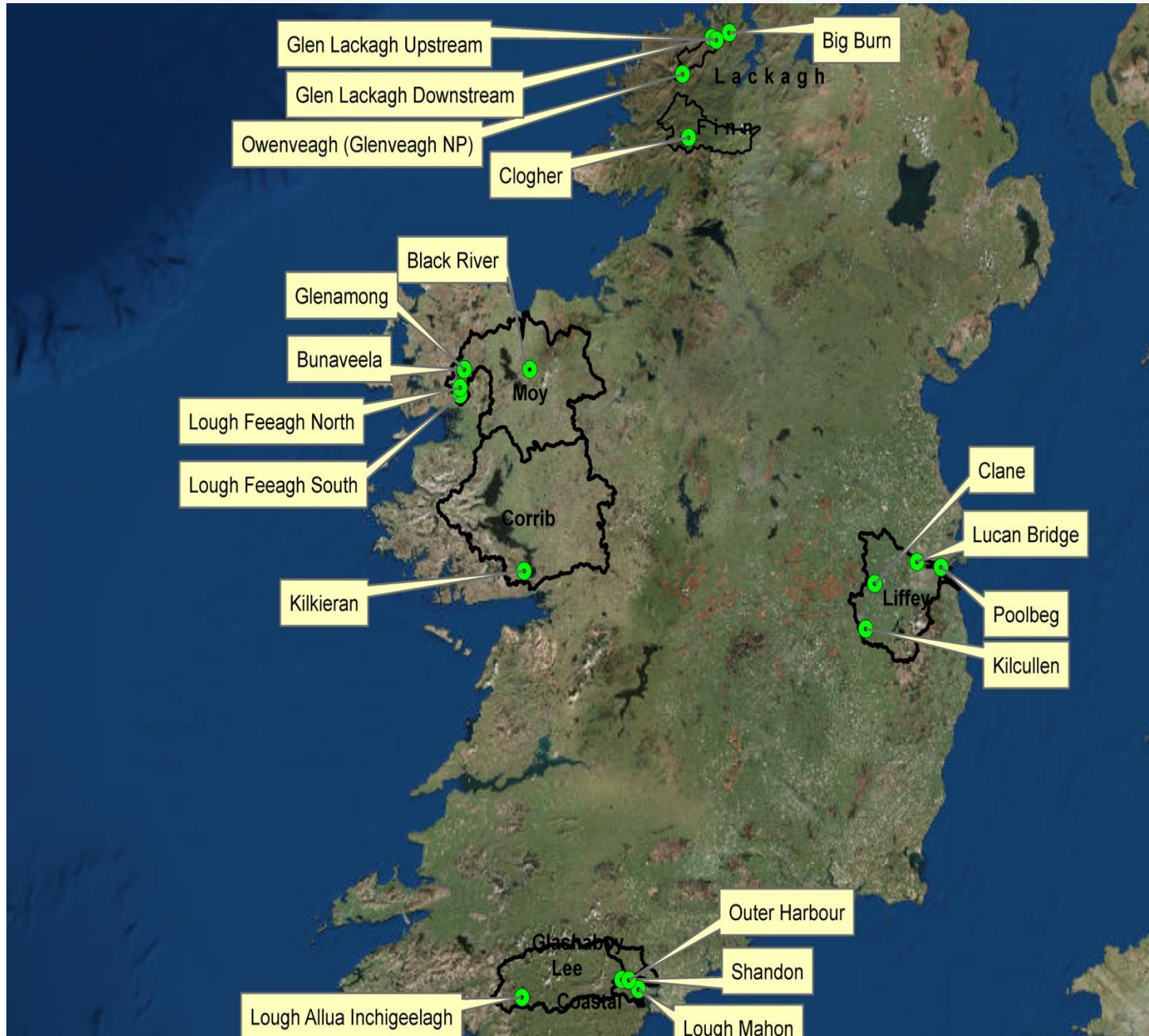


Catchment Approach

- 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

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		✓	✓		



Target Pesticides

Compound group	Compound	Sampler type	Water	Biota
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*	PDMS	Y	N

Protocol for Passive Sampler Deployment

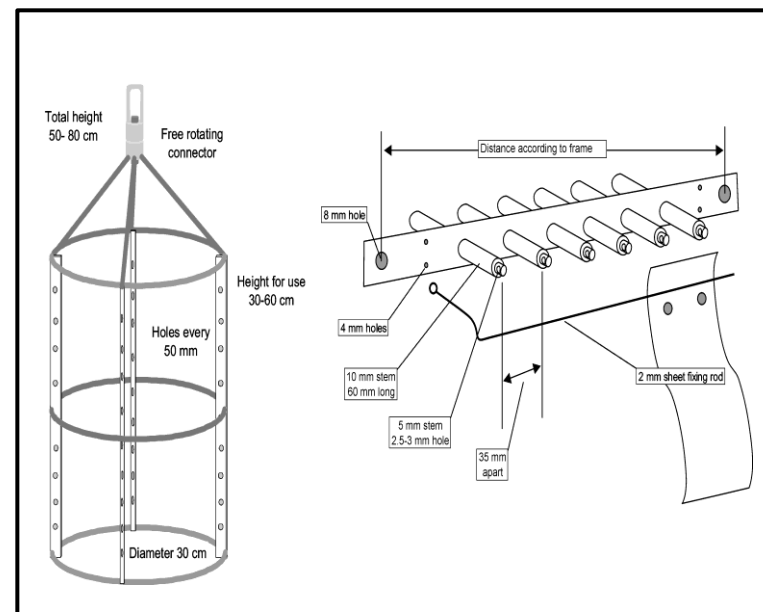
- ICES TIMES no. 52* for PDMS
- EA lab/NLS guidelines for POCIS

Record:

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

*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>



PDMS sheet attachment*



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 CH₃OH: 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

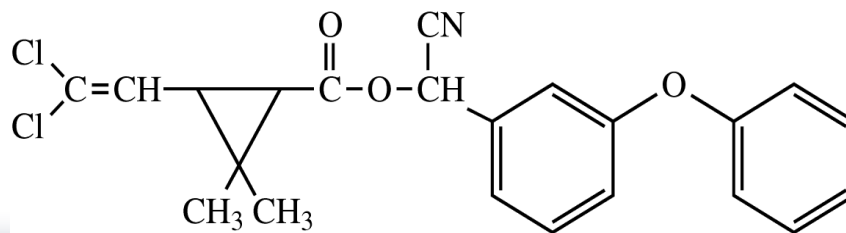
Pesticides Occurrence in Water

Pesticide	Target EQS	Freq.	Max Detected
	$\mu\text{g L}^{-1}$	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
Quinoxifen	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



Census of agriculture

Coilte

DEFRA

Teagasc

Department of Veterinary
Medicine

Department of Agriculture

Cypermethrin

In 2004 approx. 2,274 kg
was used on arable crops
in Ireland.

Is an active compound in
15 veterinary medicines.

18 products listed on
the Dept. of Agriculture
Food and the Marine
register.

4.6 tonnes of products were
imported for use as
agrochemicals in 2012.

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

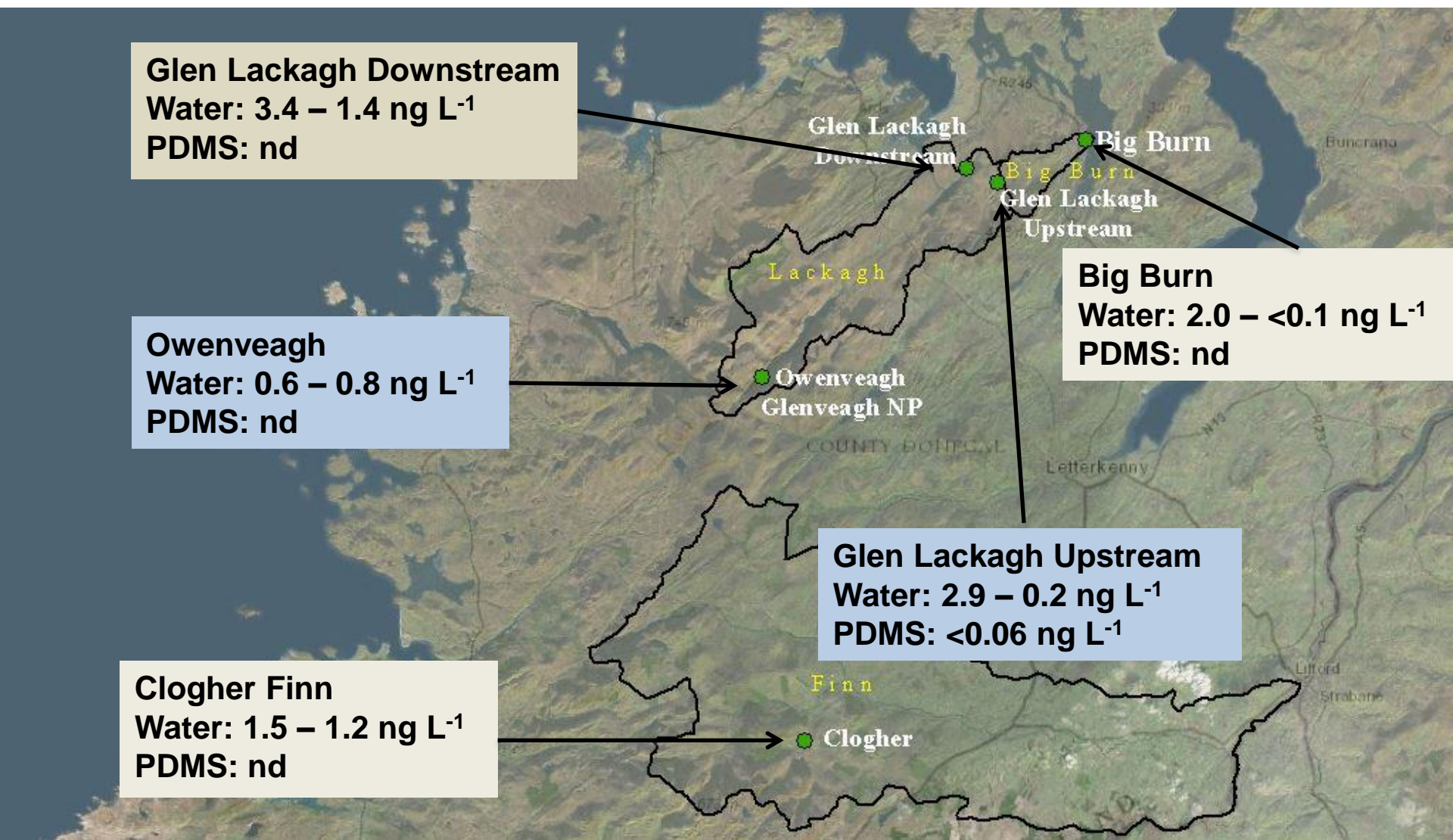
Glen Lackagh Downstream
Water: 3.4 – 1.4 ng L⁻¹
PDMS: nd

Owenveagh
Water: 0.6 – 0.8 ng L⁻¹
PDMS: nd

Big Burn
Water: 2.0 – <0.1 ng L⁻¹
PDMS: nd

Glen Lackagh Upstream
Water: 2.9 – 0.2 ng L⁻¹
PDMS: <0.06 ng L⁻¹

Clogher Finn
Water: 1.5 – 1.2 ng L⁻¹
PDMS: nd



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>

The screenshot shows the homepage of the Irish Passive Sampling Research website. The header features the title "IRISH PASSIVE SAMPLING RESEARCH" in large blue letters, with the IPSPR logo below it. A search bar is located to the right of the logo. On the left side, there is a navigation menu with categories: "Navigation" (Home, Conferences/Workshops), "Contact Us", "NEWS", "Project Team", "Publications", "Sitemap", and "Affiliations". The main content area is titled "Home" and includes an "About" section with text about the project's funding and purpose, and an "Acknowledgements" section. On the right side, there is a "Twitter Feed" widget displaying two tweets from @IrishPSresearch.

IRISH PASSIVE SAMPLING RESEARCH

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IRISH PASSIVE SAMPLING RESEARCH

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About

This project is a large-scale, Irish EPA funded, investigation into the role of passive sampling in the screening and monitoring of new and emerging chemicals in freshwater.

Acknowledgements

This project is funded by the EPA as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007-2013. This programme is financed by the Irish Government under the National Development Plan 2007-2013. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency, which has the statutory function of co-ordinating and promoting environmental research.

Twitter Feed

Passive Sampling
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IrishPSresearch Check out the details of the upcoming ATWARM international conference - Water: The Greatest Global Challenge - here!
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IrishPSresearch This years International Passive Sampling Workshop and Symposium will take place in Bordeaux - check it out! psw.eu/2013/
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Acknowledgements

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Thank you for your attention!



National Development Plan 2007 - 2013

