Passive Sampling as a Screening Tool in Ireland for New and Emerging Chemicals

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Outline

- The Irish perspective

- Current status of Irish water bodies

- Past large-scale projects and results

- Proposed work on passive sampling in Ireland
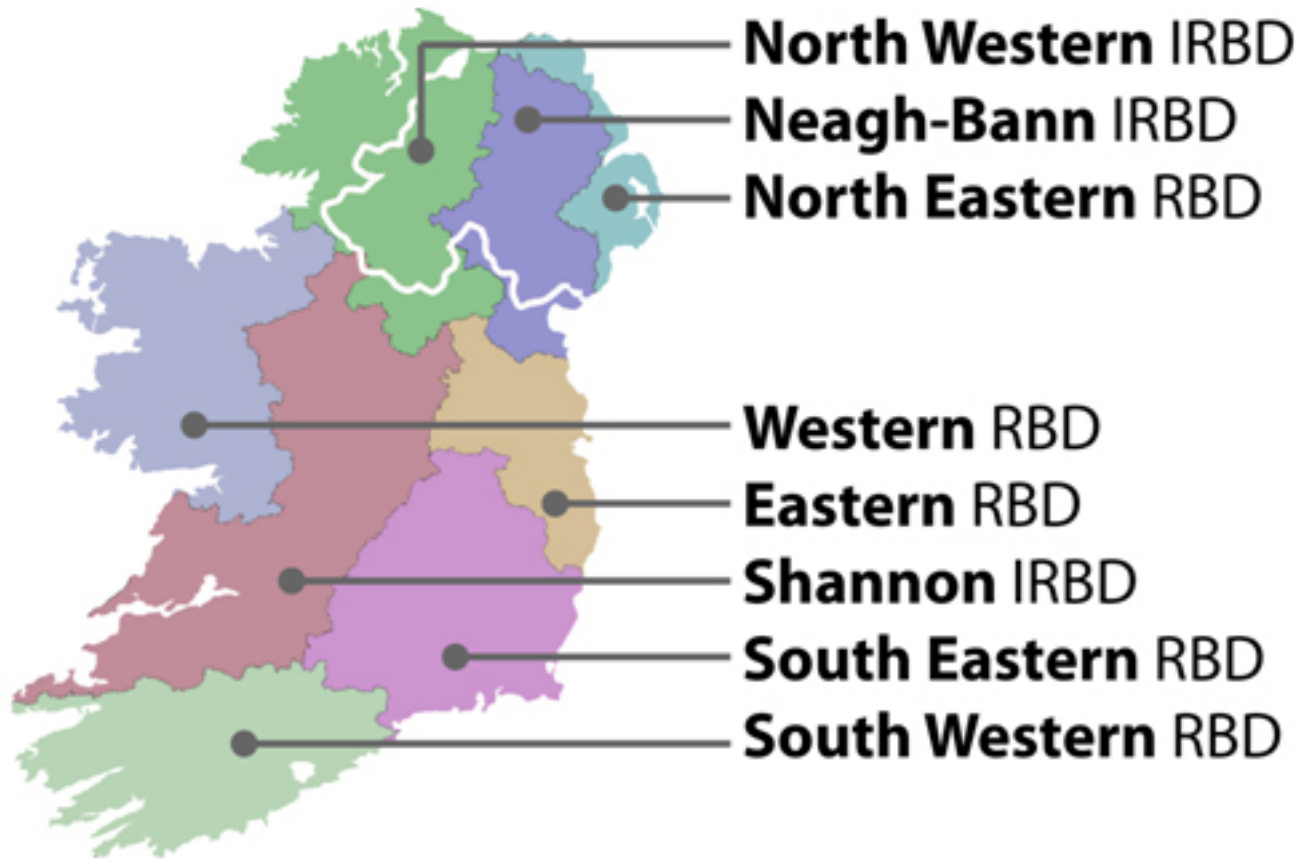
EU Directives

- Birds Directive (79/409/EEC) ;
- Drinking Water Directive (80/778/EEC) as amended by Directive (98/83/EC);
- Major Accidents (Seveso) Directive (96/82/EC);
- Environmental Impact Assessment Directive (85/337/EEC);
- Sewage Sludge Directive (86/278/EEC);
- **Urban Waste-water Treatment Directive** (91/271/EEC);
- Plant Protection Products Directive (91/414/EEC);
- Nitrates Directive (91/676/EEC);
- Habitats Directive (92/43/EEC);
- Integrated Pollution Prevention Control Directive (96/61/EC);
- **Water Framework Directive** (2000/60/EC);
- Bathing Water Directive (2006/7/EC) (repeals 76/160/EEC);
- Groundwater Directive (2006/118/EC);
- Floods Directive (2007/56/EC);
- **Marine Strategy Framework Directive** (2008/56/EC).

Irish Legislation

The WFD has been transposed into Irish law by means of five main Regulations:

- (**Water Policy**) Regulations, 2003 (S.I. No. 722 of 2003)

- Environmental Objectives (**Surface Waters**) Regulations, 2009 (S.I. No. 272 of 2009)

- Environmental Objectives (**Groundwater**) Regulations, 2010 (S.I. No. 9 of 2010)

- (**Good Agricultural Practice for Protection of Waters**) Regulations, 2010 (S.I. No. 610 of 2010)

- (Technical Specifications for the **Chemical Analysis and Monitoring of Water Status**) Regulations, 2011 (S.I. No. 489 of 2011)

Irish RBDs

WFD, MSFD and EQSD

- Main pieces of legislation

- Monitoring for compliance carried out by EPA, MI, Local Authorities and IFI

- Monitoring report published in 2010

- New proposed additions to EQS directive

- EA has already approved use of passive samplers and is investigating this further for WFD monitoring

Available Information in Ireland

- The EPA WFD surveillance monitoring programme for PS/PHS in rivers & lakes was undertaken between 2007 – 2009.

- The monitoring programme included 33 substances or group of substances on the WFD list as well as 28 relevant or specific pollutants selected for Ireland.

- Monitoring was undertaken at a number of sites at a frequency of 12 times per year once the programme commenced in mid 2007.

- In general the levels of priority pollutants were very low with very few exceedances being found (McGarrigle et al., 2010).

Status of Irish Water

- Of the lakes monitored, 140 (63%) were in high or good physico-chemical quality element status.

- Of the 2515 river sites surveyed in the 2007- 2009 period 953 were polluted or of less than good status.

- Total number of fish kills in surface freshwaters was 122; agriculture was suspected as being responsible for some 34 of these fish kills, with 28 due to sewage discharges and 15 to industry, with the balance attributable to 'other' (26) and 'unknown' (19) causes.

- 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).
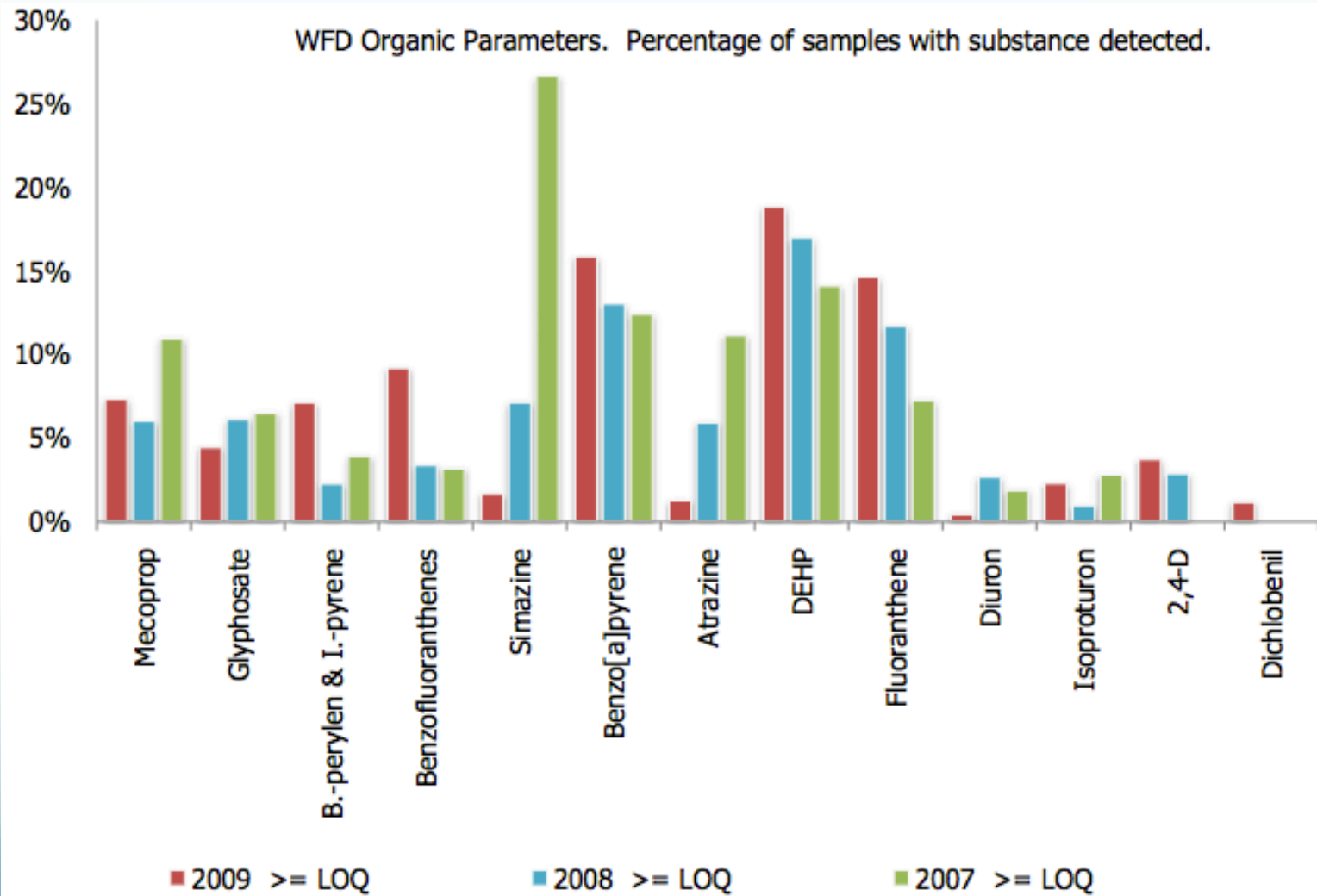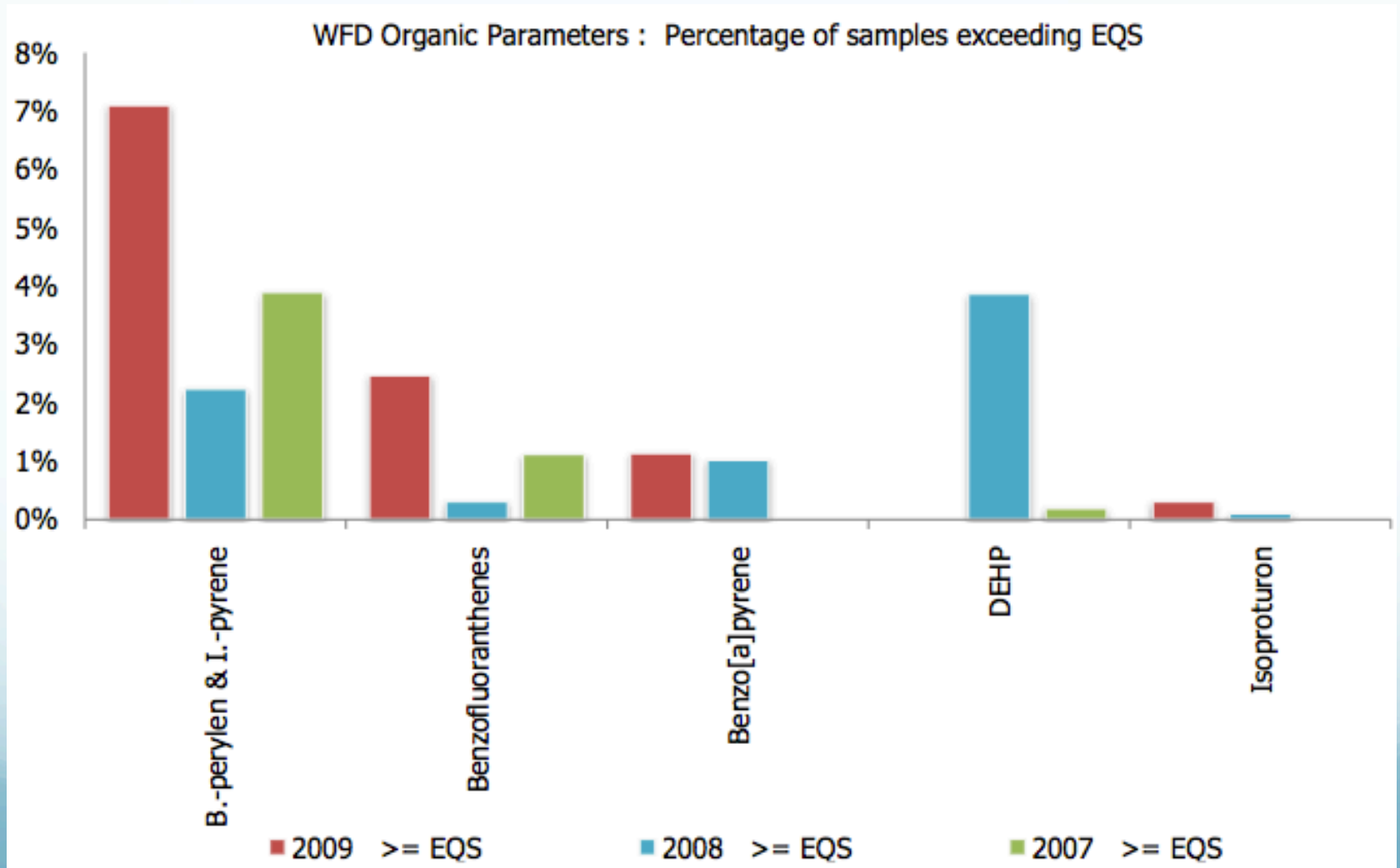
Irish Lakes
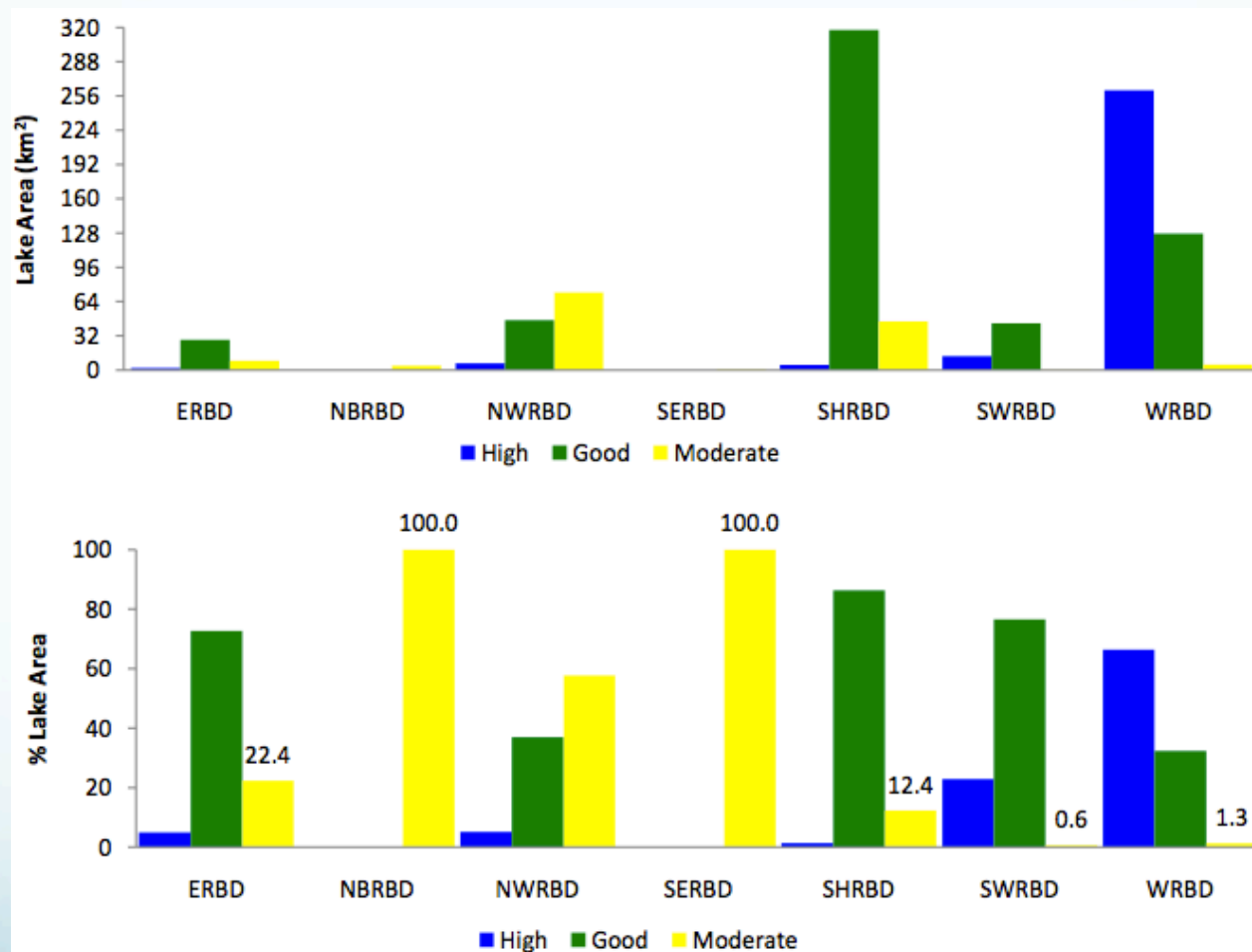
WFD Physico-chemical Status: The area (top) and percentage area of lake (bottom) examined assigned to each physico-chemical status category in each RBD. (EPA Water Quality Report, 2008)

Irish Rivers

WFD Organic Parameters. Percentage of samples with substance detected.

Legend: ■ 2009 >= LOQ   ■ 2008 >= LOQ   ■ 2007 >= LOQ

Categories: Mecoprop, Glyphosate, B.-perylen & I.-pyrene, Benzofluoranthenes, Simazine, Benzo[a]pyrene, Atrazine, DEHP, Fluoranthene, Diuron, Isoproturon, 2,4-D, Dichlobenil

(EPA Water Quality Report, 2008)

Irish Rivers

WFD Organic Parameters : Percentage of samples exceeding EQS

2009 >= EQS   2008 >= EQS   2007 >= EQS

(EPA Water Quality Report, 2008)

Irish Wastewater

Met the effluent quality and sampling standards

Failed to meet the effluent quality and/or sampling standards

Failed to meet the effluent quality standards due to lack of secondary treatment

70%

23%

7%

Compliance of all larger urban areas (n=165) in 2011 with the effluent quality (BOD, COD & TSS) and sampling standards in the Urban Waste Water Treatment Directive.

(EPA Water Quality Report, 2008)

Results of Irish Research on Priority Substance Occurrence

Project title: Development of a Risk-based Model for use in Water Quality Monitoring

Funding: ~€300,000 Irish EPA

Partners: DCU, Cork IT, Fingal Co. Co, Cork Co. Co.

Start and end dates: June 2008-Sept. 2012

Development of a Risk-based model

- Nine agglomerations, ranging in size, physical characteristics, industrial contributions, treatment levels;

- Over 400 samples collected;

- Data collated on potential sources (e.g. industry) and risk factors (e.g. combined drainage) for each catchment;

- WWTP removal efficiencies data;

- Investigated meteorological or physico-chemical parameters and PS conc. / loads;

- Devised risk index for high PS in effluent (across catchments, over time).

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
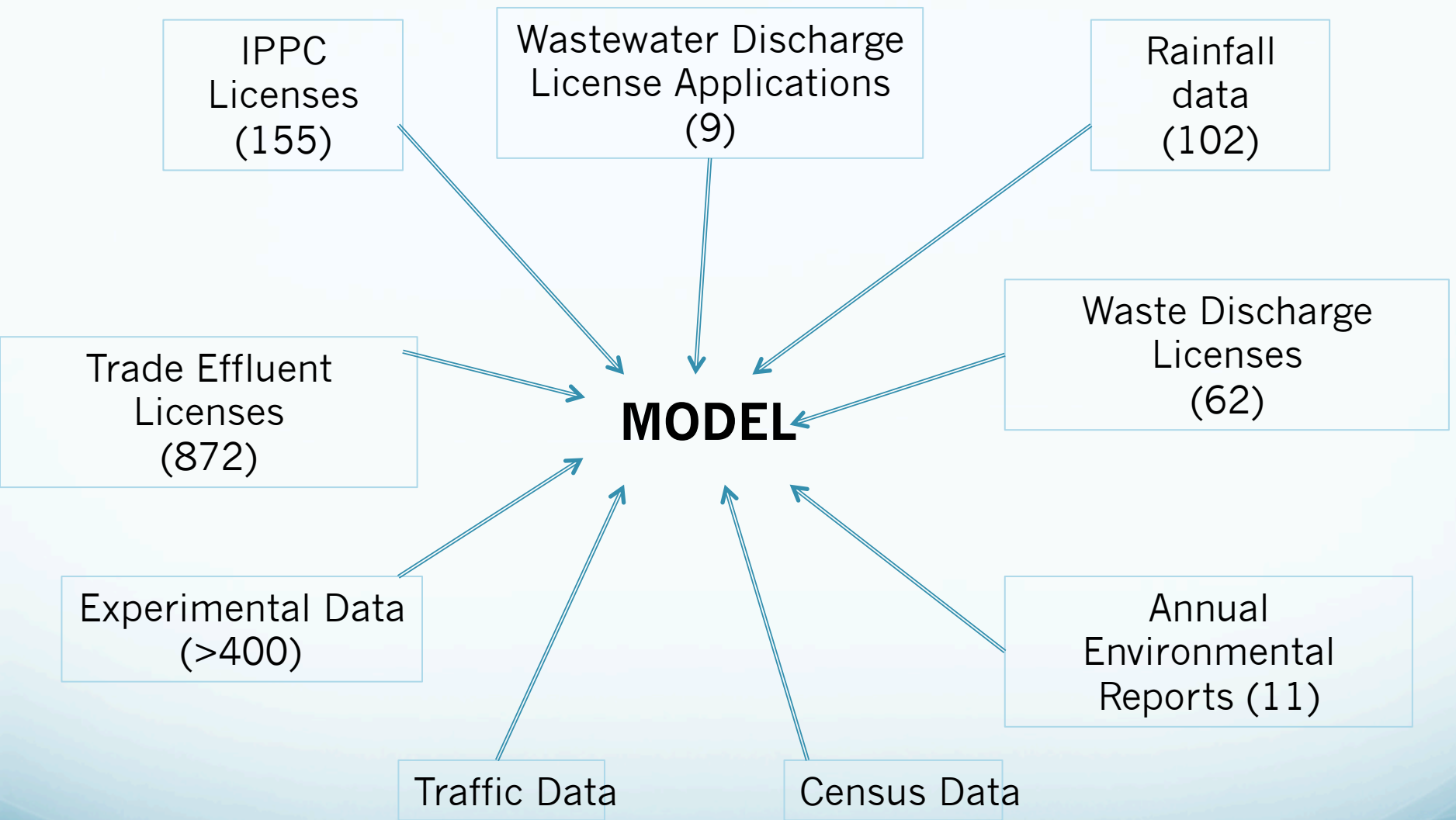
Parameter	Target EQS	Freq. n=34	Range		Percentile		
	$\mu g\ L^{-1}$		Min.	Max.	50	75	90
Boron		34	8.00^{E+01}	2.52^{E+02}	1.32^{E+02}	1.67^{E+02}	1.95^{E+02}
Vanadium		12	1.06^{E+00}	2.88^{E+00}	1.63^{E+00}	1.88^{E+00}	1.98^{E+00}
Chromium	0.6-4.7	23	1.10^{E+00}	1.24^{E+01}	1.82^{E+00}	2.89^{E+00}	5.38_{E+00}
Cobalt		5	1.04^{E+00}	2.36^{E+00}	2.03^{E+00}	2.04^{E+00}	2.23^{E+00}
Nickel	20	34	1.88^{E+00}	4.45^{E+01}	3.50^{E+00}	4.66^{E+00}	8.53^{E+00}
Copper	5.0-30	34	4.25^{E+00}	1.24^{E+02}	1.58^{E+01}	2.69^{E+01}	3.90^{E+01}
Zinc	8-100	34	2.48^{E+01}	6.86^{E+02}	5.73^{E+01}	8.86^{E+01}	1.23^{E+02}
Arsenic	20-25	32	1.01^{E+00}	3.81^{E+00}	1.53^{E+00}	1.99^{E+00}	2.50^{E+00}
Selenium		12	1.01^{E+00}	2.86^{E+00}	1.25^{E+00}	1.50^{E+00}	2.01^{E+00}
Molybdenum		34	1.68^{E+00}	1.11^{E+01}	3.04^{E+00}	4.36^{E+00}	6.54^{E+00}
Cadmium	0.08-0.25						
Tin	0.0002	20	1.02^{E+00}	5.94^{E+00}	1.48^{E+00}	1.83^{E+00}	3.15^{E+00}
Antimony		10	1.02^{E+00}	1.77^{E+00}	1.31^{E+00}	1.66^{E+00}	1.77^{E+00}
Barium		34	9.66^{E+00}	6.88^{E+01}	1.84^{E+01}	2.45^{E+01}	3.18^{E+01}
Lead	7.2	19	1.01^{E+00}	6.71^{E+00}	1.83^{E+00}	3.19^{E+00}	5.73^{E+00}

Key Observations

Site	PAHs		PESTICIDES		METALS		VOCs	
	DWF	WWF	DWF	WWF	DWF	WWF	DWF	WWF
BG	0.09	0.15	0.02	0.04	0.05	0.66	0.03	0.93
BN	0.8	0.37	0.65	1.31	0.44	1.17	0.3	0.8
CE	1.9	0.09	1.75	3.5	1.39	2.32	0.6	1.23
CY	0.26	0.19	0.31	2.64	0.11	1.06	0.17	1.6
FY	0.48	0.05	0.38	0.77	0.26	0.69	0.28	0.58
MW	0.35	0.06	0.3	0.59	0.27	0.53	0.13	0.26
RY	3.79	0.82	1.6	7.1	1.44	5.55	2.56	6.71
RD	0.06	0.21	0.03	1.3	0.04	1.72	0.03	2.34
SD	0.06	0.03	0.01	0.08	0.04	0.29	0.04	0.21

Key Observations

- Management needs to be streamlined
  - Information sharing
  - Licensing control

- Unlicensed sources

- Compile complete dataset

- Standardisation of methods and procedures

- Need to investigate other sampling techniques – passive sampling

New Passive Sampling Project

Project Outline

- Partners: DCU, MI, IFI, UK EA, TE Labs

- Duration: Feb. 2013 – Feb. 2016

- Deployment locations: 9 sites

- Deployment schedule: July and November 2013

- Type of samplers: POCIS and PDMS

- Analytes: EDCs, Pharmaceuticals, PAHs, Organohalogens, PFOS, Brominated flame retardants and Pesticides

Project Aims

- To test the use of passive sampling technologies and biota analysis in surface water monitoring of priority substances in Ireland;

- Qualitative/quantitative screening of selected substances in a number of Irish waters representative of different pressures;

- A broad qualitative GCMS screening for other substances in surface waters;

- Screening study of certain pharmaceutical substances in Irish surface waters;

Passive Sampling Experience

- 2005-2006: ICES (OSPAR) Passive sampling initiative in Dublin and Galway
Concurrent EPA funded MSc. (PDMS only)

- 2007-2010: EPA funded PS project with DIT (PDMS/SPMD)

- 2008-2012: EPA MI Sea Change-funded project (PDMS/POCIS)
"Biological effects and chemical measurements in Irish marine waters"
Concurrent EPA funded PhD:
"Novel passive sampling materials for the determination of priority pollutants in surface waters"

- 2012-ongoing: WFD PDMS deployments (16 sites) PDMS

Target Analytes

Compound group	Compound	Sampler type	Water	Biota
EDCs and pharmaceuticals	17b estradiol (E2)	POCIS	Y	N
	17a ethynyl estradiol (EE2)		Y	N
	diclofenac		Y	N
	alkylphenols		Y	N
Organohalogens	HCB*	PDMS	N	Y
	heptachlor**		N	Y
	heptachlor epoxide**		N	Y
	HBCDD**		N	Y
	PCBs		Y	Y
	PBDEs**		Y	Y
	HCBD*		N	Y
	Dioxins and dioxin-like compounds		Y	Y
PFOS	PFOS**	POCIS	Y	Y

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	N
	Bifenox		Y	N
	Cybutryn		Y	N
	Terbutryn		Y	N
	quinoxyfen		Y	N
	Dichlorvos	PDMS	Y	Y
	Dicofol**		Y	Y
	Cypermethrin	POCIS and PDMS	Y	N

Sampling Rationale

- 1 coastal station west coast reference,

- 1 high pressure coastal,

- 1 riverine/transitional station,

- 2 freshwater river stations down stream from point discharges (wwtp),

- 2 downstream river stations representing diffuse/ agricultural pressures,

- 2 upstream river stations respresenting diffuse pollution (sheep farming, forestry)

Sampling Sites

| County	Site number	Site	Rationale
Cork	1	Gougane barra	Upstream river station (diffuse)
	2	Inniscarra	Downstream river station diffuse/ agricultural pressures
	3	Lough Mahon	Riverine/transitional station
	4	Outer bay lighthouse	Riverine/transitional station
Dublin	5	Poolbeg	High pressure coastal
	6	Liffey	Riverine/transitional, downstream from WWTP
Galway	7	Kilkieran Bay	Coastal reference station
Mayo	8	Burrishoole	Upstream river station (diffuse)
Donegal	9	River Finn	Cypermethrin study

Passive Samplers
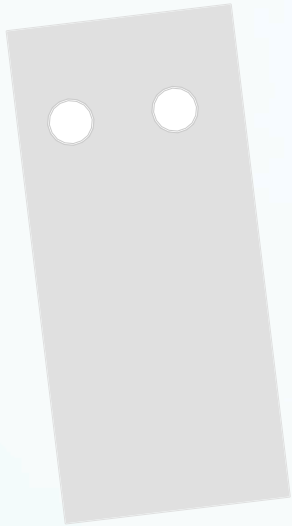
PDMS/SPMD
Hydrophobic
compounds
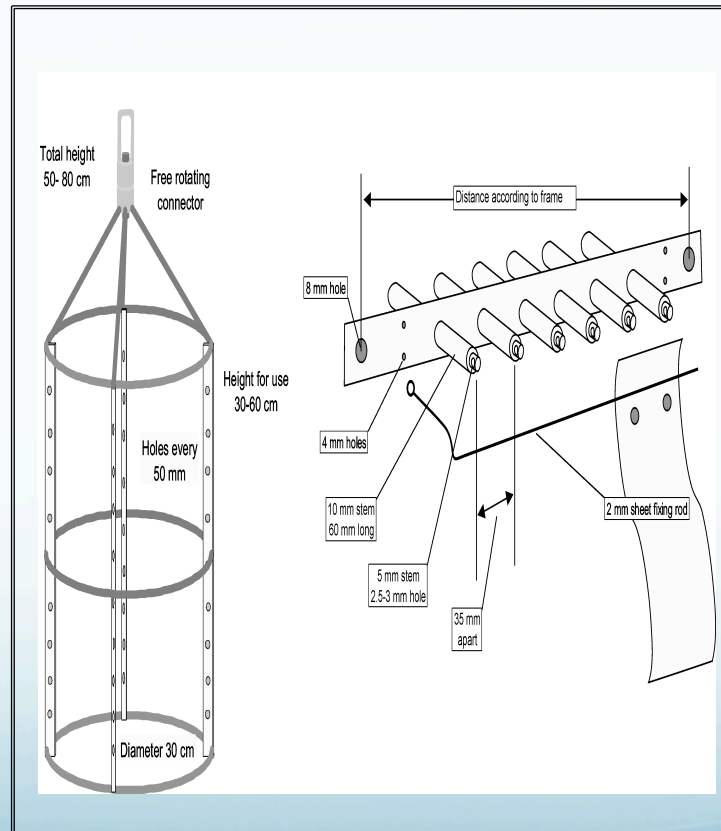
Deployment
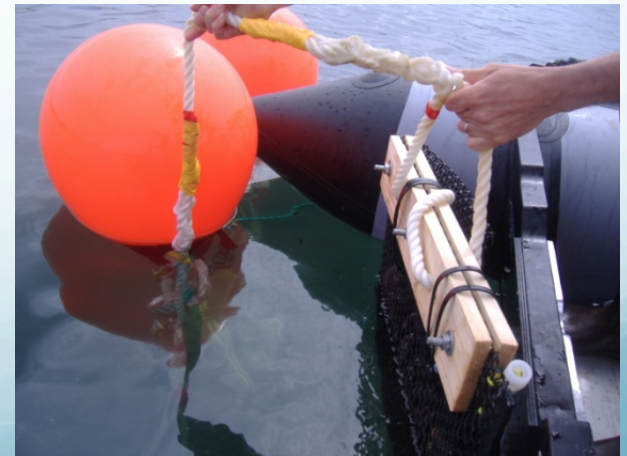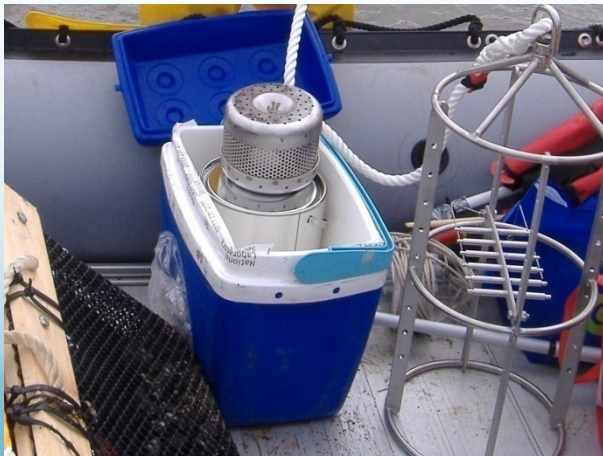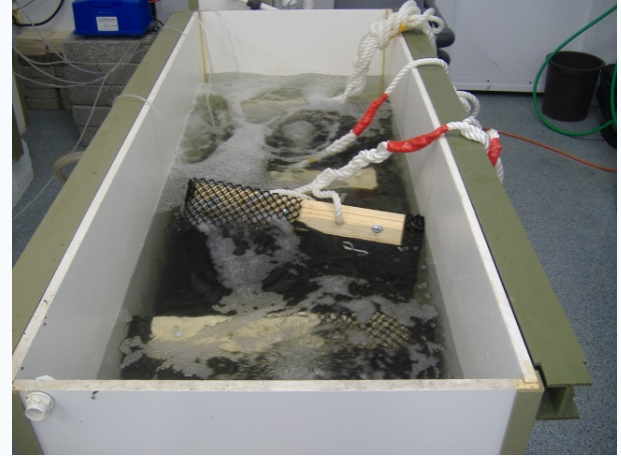
Passive Sampler Deployment
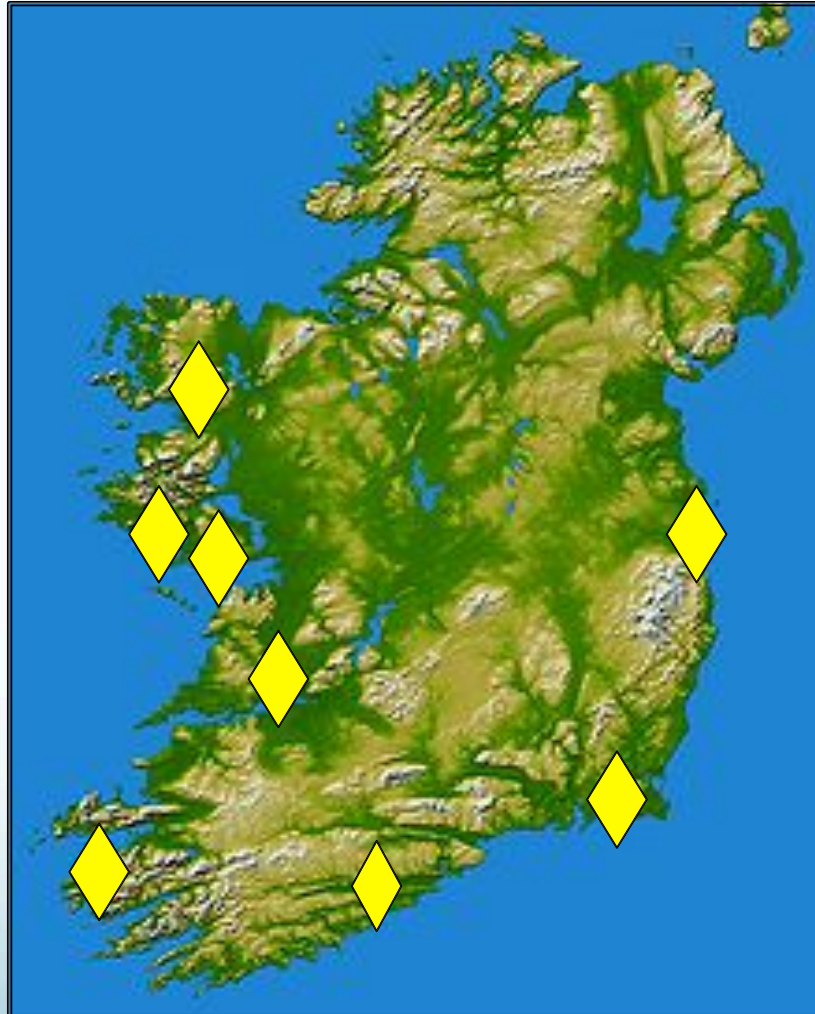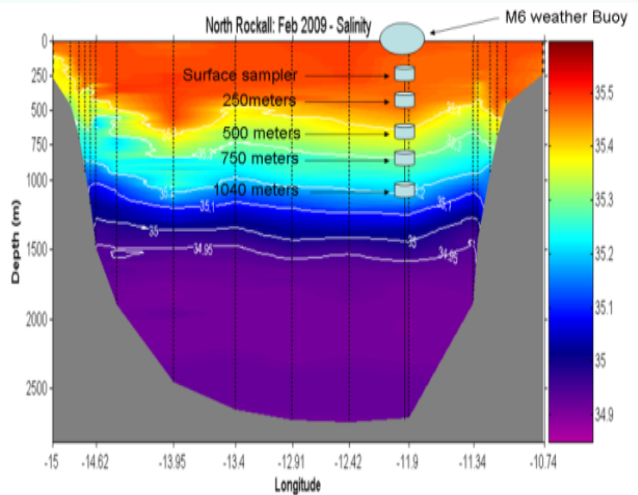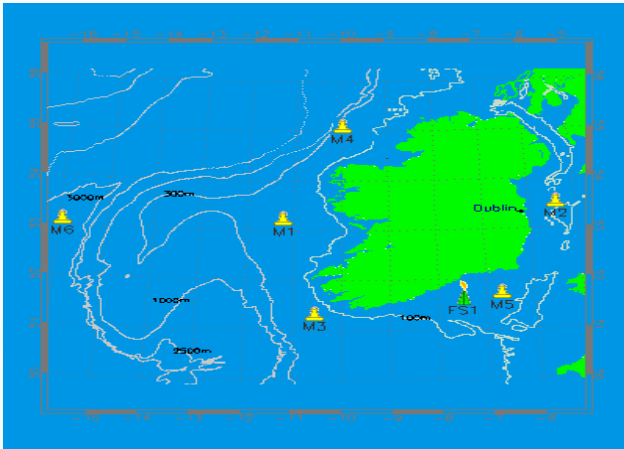
Passive sampling results to date:

- Passive samplers were successfully deployed to identify for the first time the presence in the water column of PCDD/Fs and dimethoxylated octachlorodiphenyl ether (diMeOoctaCDE)
  - (impurities found in pentachlorophenol (PCP) production).

- Principal component analysis (PCA) identified similarities between PCDD/F profiles in technical PCP mixtures and environmental samples from the Burrishoole region.

Hydrophobic Compound Determination (ng L^{-1})

	Galway	Dublin Bay	Bantry	Cork (1)	Cork (2)	Wexford	Shannon	Omey Is
*Naphthalene**	3.41	4.83	27.7	2.40	4.71	2.25	8.01	3.58
Acenaphthylene	1.18	1.68	0.46	0.79	0.67	0.62	0.62	0.12
Acenaphthene	1.01	3.41	0.53	3.50	2.60	4.14	1.14	0.14
Flourene	2.60	6.46	2.40	12.1	9.9	3.00	4.74	0.74
Phenanthrene	8.53	13.6	3.29	38.7	40.0	6.81	20.8	2.29
Anthracene	0.33	3.11	0.24	2.34	3.47	2.35	1.49	0.12
Flouranthene	6.31	34.8	1.96	42.2	42.8	21.8	28.7	2.18
Pyrene	3.92	41.6	0.90	26.7	27.6	15.2	18.9	0.46
Chrysene	0.54	10.5	0.14	4.56	4.62	7.87	2.61	0.13
Benzo(a)anthracene	1.56	16.1	0.61	11.5	12.0	15.8	8.63	0.27
Benzo(b)flouranthene	0.66	9.39	0.34	7.82	7.93	12.0	2.22	0.13
Benzo(k)flouranthene	0.59	5.63	0.39	7.82	7.50	10.5	2.22	0.14
Benzo(a)pyrene	0.26	7.04	0.09	2.84	2.59	2.55	0.68	0.09
Indeno(1,2,3-cd)pyrene	0.43	2.05	0.13	4.92	3.69	2.56	0.59	0.06
Dibenzo(a,h)anthracene	0.29	0.81	0.03	1.14	0.57	0.54	0.06	0.02
Benzo(g,h,i)perylene	0.30	2.61	0.08	4.01	3.25	2.05	0.57	0.03
∑PAH	31.9	164	39.3	173	174	110	102	10.5
S7PCBs**	<52.7	<96.8	<45.7	<43.6	<41.2	<43.4	<40.6	<57.2
HCB**	9.01	6.14	0.38	3.17	3.21	1.20	3.17	1.20
PPDDE	4.20	2.97	2.59	0.84	3.55	14.1	3.92	2.08

Polar Compound Determination

Location	Matrix	Matrix	POCIS (Screening) E1	POCIS (Screening) E2	POCIS (Screening) EE2	Water E1	Water E2	Water EE2	Tissue E1	Tissue E2	Tissue EE2	Tissue NP	Tissue OP
Cork	Shellfish(n=2)	Mussels							nd	nd	nd	nd	nd
	POCIS (n=2)	POCIS	4.12–5.18	0.12–0.49	<0.40								
	Fish (n=6)*	Dab							nd	nd	nd	nd	nd
	Sediment	Sediment											
Dublin Bay	Shellfish (n=12)	Mussels							nd	nd	nd	nd	nd
	Shellfish	Mussels							nd	nd	nd	nd	
	POCIS (n=4)	POCIS	3.59-8.45	0.69-3.8	<0.10								
	Water (n=5)	Water				0.76-1.11	nd-0.13	nd					
	Sediment	Sediment											
	Fish (n=4)	Dab + plaice							nd	nd	nd	nd	nd
Shannon	Shellfish (n=1)	Mussels							nd	nd	nd	nd	nd
	POCIS (n=1)	POCIS	<1.0	<0.30	<0.10								
	Fish (n=3)*	Dab							nd	nd	nd	nd	nd
Wexford	Shellfish (n=2)	Mussels							nd	nd	nd	nd	nd
	POCIS	POCIS	6.5	1.61	<0.40								
	Fish (n=2)*	Dab							nd	nd	nd	nd	nd
	Sediment	Sediment											

Passive Sampler Results

Estrone (E1) ng per device[6]				
Location	July T=1	August T=2	Sept T=3	Oct T=4
Dublin Bay	8.5	6.3	4.7	3.6
Mutton Island	15.3	6.9	7.6	N/a
Omey Island	6.4	N/a	N/a	3.01

17β Estradiol (E2) ng per device[6]				
Location	July T=1	August T=2	Sept T=3	Oct T=4
Dublin Bay	3.8	2.9	1.1	0.7
Mutton Island	3.9	2.1	1.2	N/a
Omey Island	2.1	N/a	N/a	0.48
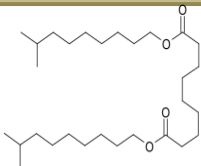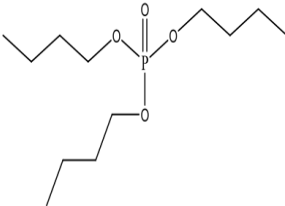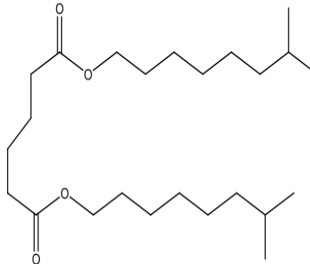
Proposed Project Outputs

- Recommendations and guidelines for the use of passive samplers in future monitoring of surface waters in Ireland;

- Recommendations and guidelines for biota monitoring, including species/tissue selection, in future monitoring for chemical status in Ireland;

- Develop novel passive sampling materials.

Novel Passive Sampling Material Design & Testing
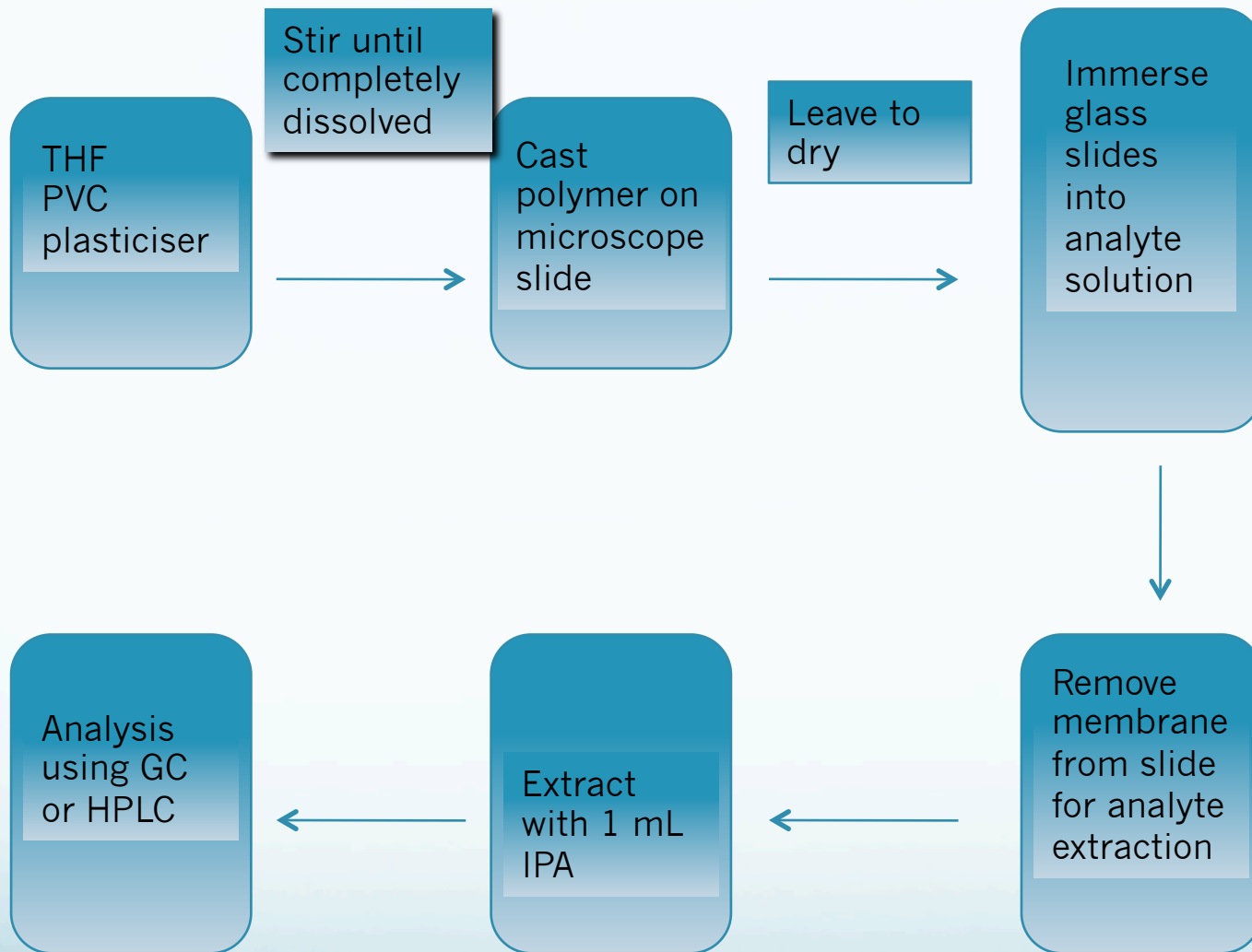
Tuning of passive sampling material

	Plasticiser A	Plasticiser B	Plasticiser C
Structure			
Molecular Formula	$C_{29}H_{56}O_4$	$C_{12}H_{27}O_4P$	$C_{24}H_{46}O_4$
Molecular Weight $(gmol^{-1})$	468.75	266.36	398.62
Density (gcm^{-3})	0.91	0.98	0.92
Log K_{ow}	11.45	4.27	9.16

IR-ATR measurement of enrichment of priority pollutants

Aims:

To establish diffusion rates of analytes in novel PS materials;

Predict enrichment of priority pollutants.

Method is suitable because of fast measurement capability

Atrazine
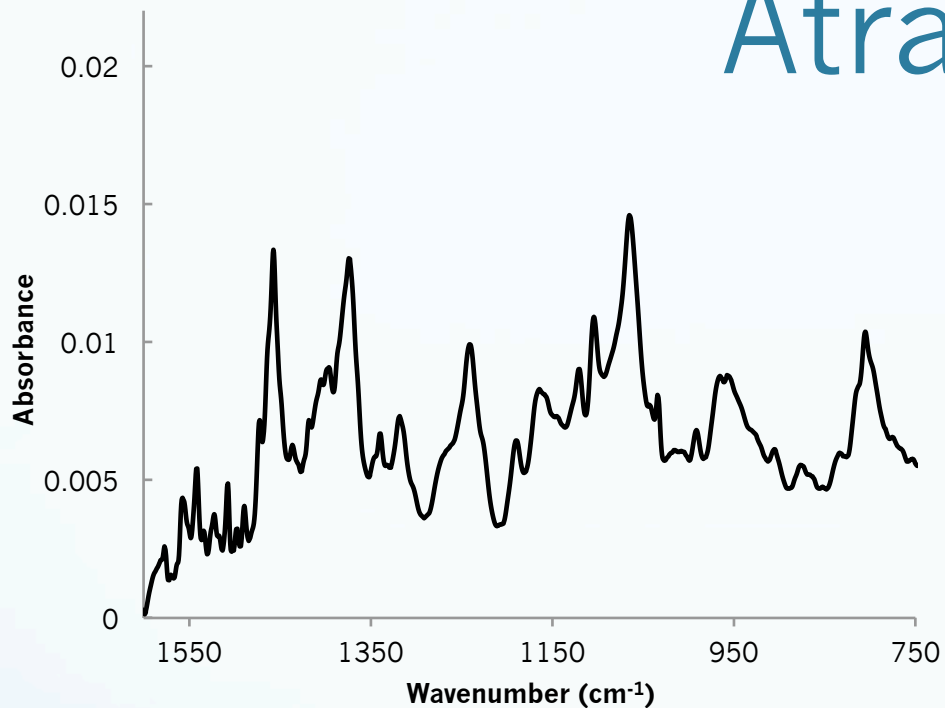
Literature	Experimental	Identification
806	806	C-Cl stretch
1244	1242	in plane C-H bending
1304	1310	C-N stretch
1550	1541	C=C aromatic stretch
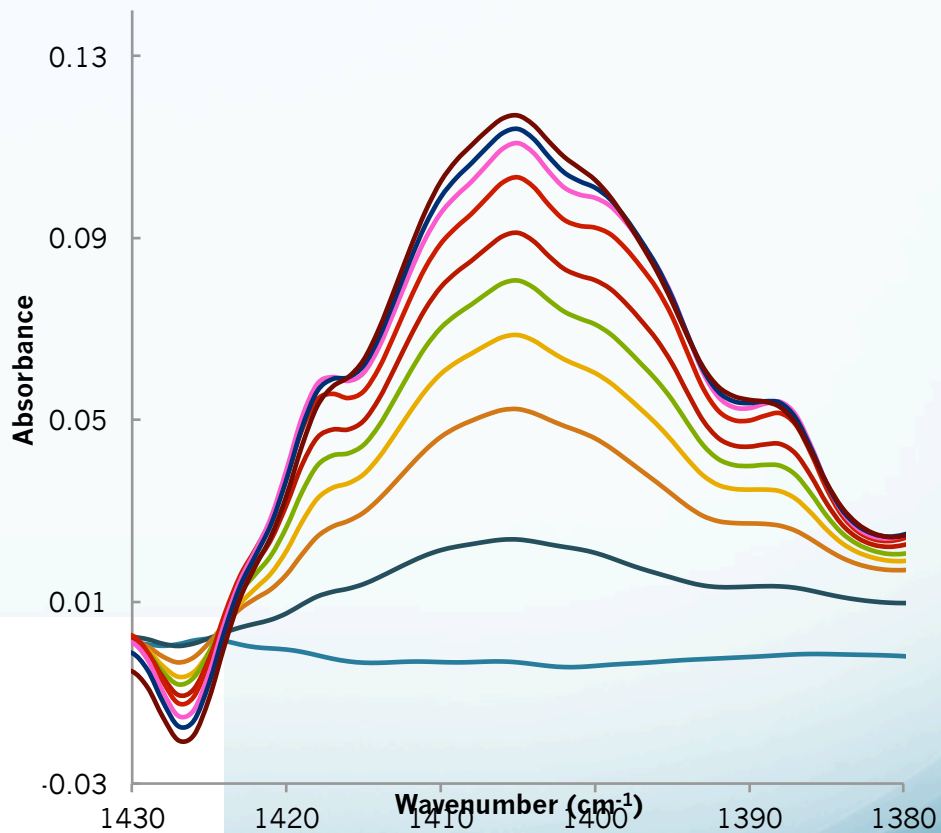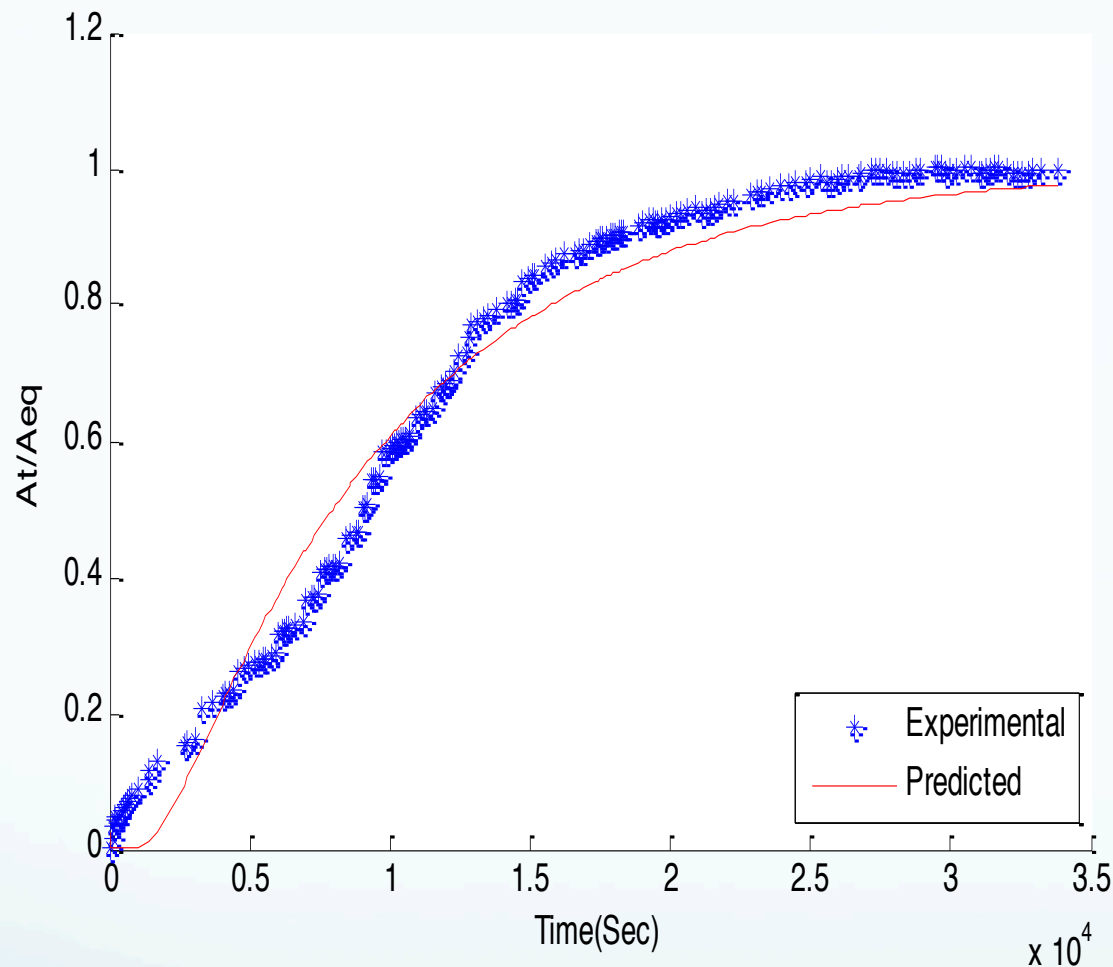
Atrazine diffusion into a 44.22 μm novel passive sampling polymer film.

Wavelength monitored 1408 cm^{-1} attributed to the –C-H bending present in the molecule.

Dieldrin
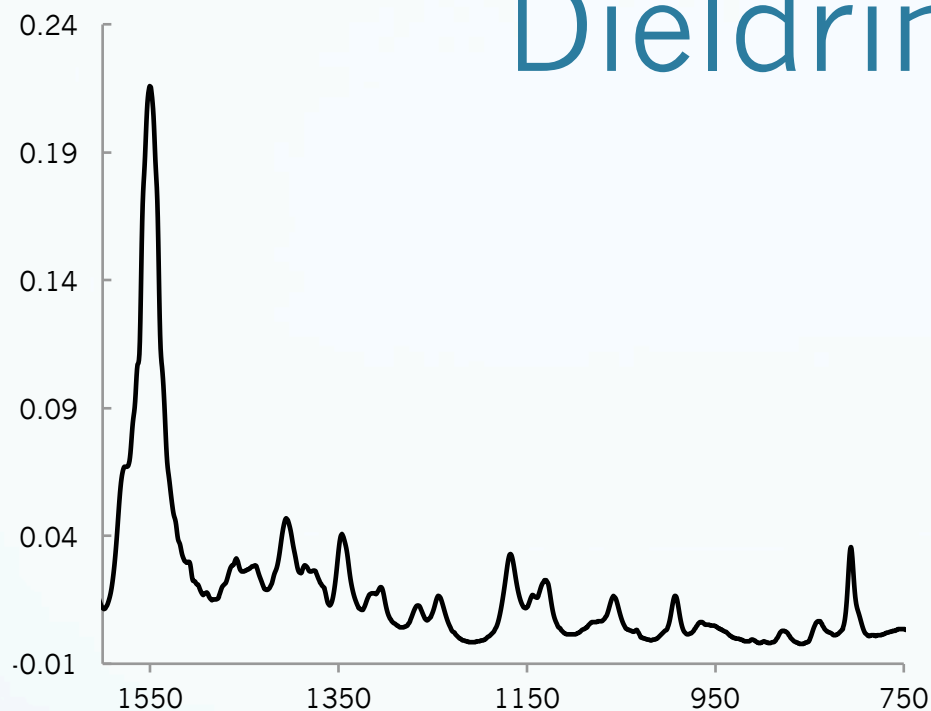
| Literature	Experimental	Identification
840	839	Epoxide group
1050	1058	C-C Skeleton vibration cyclohexane ring
1128	1130	C-O-C (saturated aliphatic ester)
1345	1346	C-H Bending
1439	1445	$-CH_2$ deformation
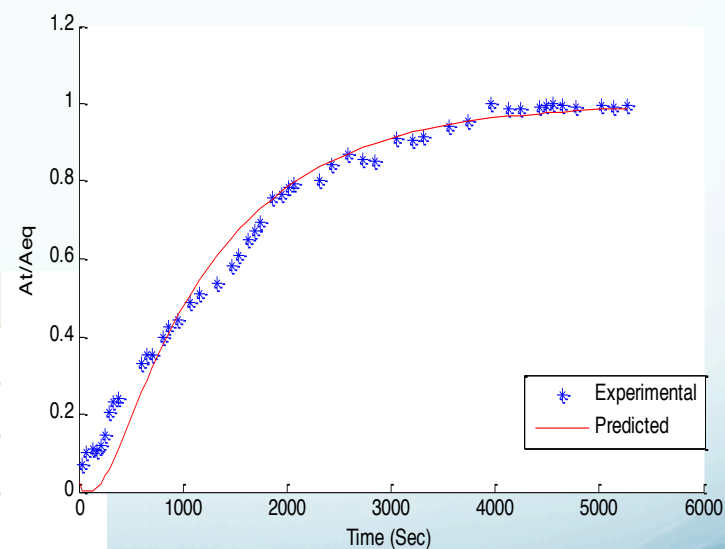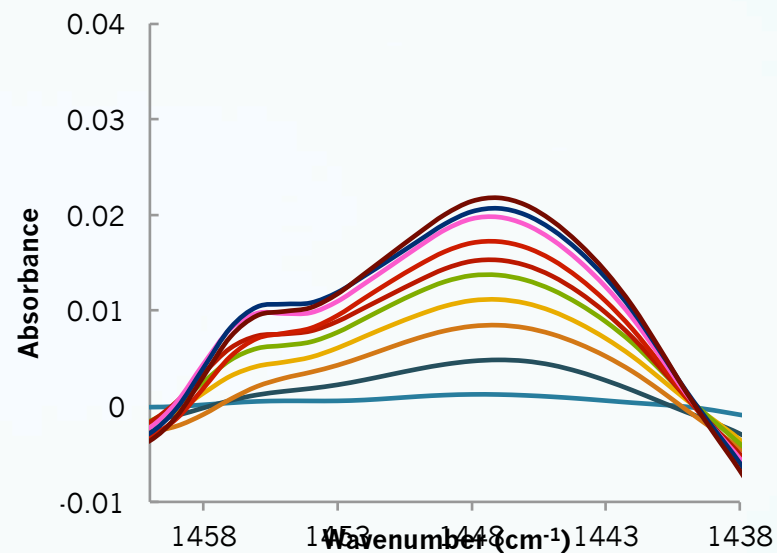
Dieldrin diffusion into a 44.22 μ m Polymer film. Wavelength monitored 1447 cm^{-1}–CH2 deformation present in the molecule.

Diffusion coefficients (cm^2s^{-1}) for the analytes

	Log K_{ow}	D (cm^2s^{-1})
Atrazine	2.61	1.42×10^{-9}
Aldrin	6.1	3.13×10^{-9}
Alachlor	3.5	1.90×10^{-9}
Anthracene	4.54	2.95×10^{-9}
Naphthalene	3.3	3.54×10^{-9}
Benzo k fluoranthene	5.6	4.73×10^{-9}
Dieldrin	5.4	5.90×10^{-9}

Enrichment of multiple analytes
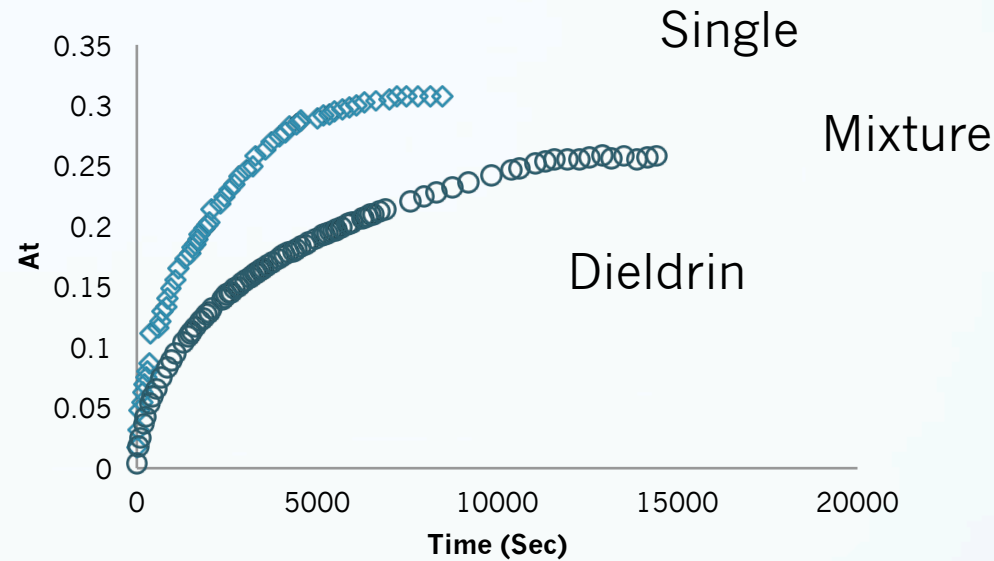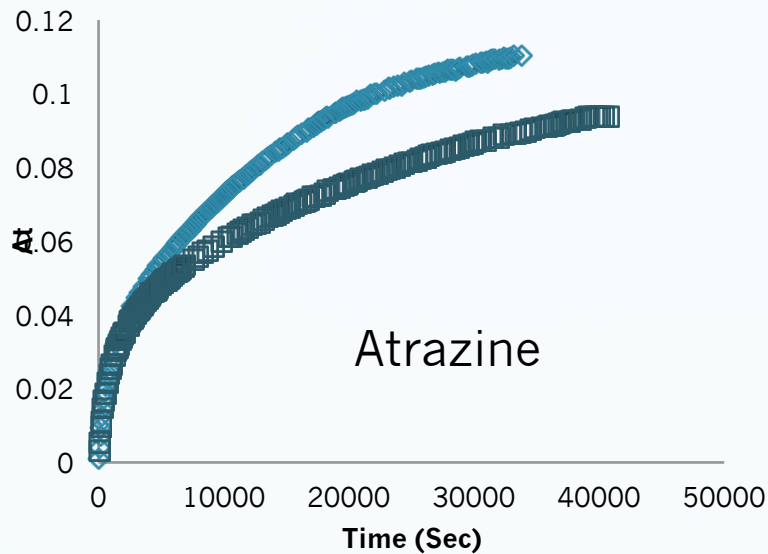
		Diffusion Coefficient (cm^2sec^{-1})		Absorbance at T_{100}	
Analyte	Structure	Single Component	Multi Component	Single Component	Multi Component
Atrazine		1.416×10^{-9}	1.123×10^{-9}	0.1102	0.0937
Dieldrin		5.898×10^{-9}	3.047×10^{-9}	0.3069	0.2581

Summary of Materials Development

- Use of ATR-IR useful in determining diffusion rates of analytes and identifying suitable PS materials:

- Tuning materials towards analytes of choice shows promise:

- Much work needed using off-the-shelf systems in monitoring and in developing selective materials;

- Parallel biota studies necessary.

Passive sampler deployment & Biofouling

Lough Hyne and Ringsend

Conclusions

- Need for structured investigation of passive sampling techniques in Ireland run in parallel with grab and biota sampling;

- Emission factors and pressures must be taken into account.

Project in Social Media

- Project blog:
  http://passivesampling.wordpress.com

- Twitter account:
  @IrishPSresearch

- Project website:
  https://sites.google.com/site/irishpassivesampling/

Thank you for your attention!

Acknowledgements