Phthalates in the Environment: An Irish Perspective

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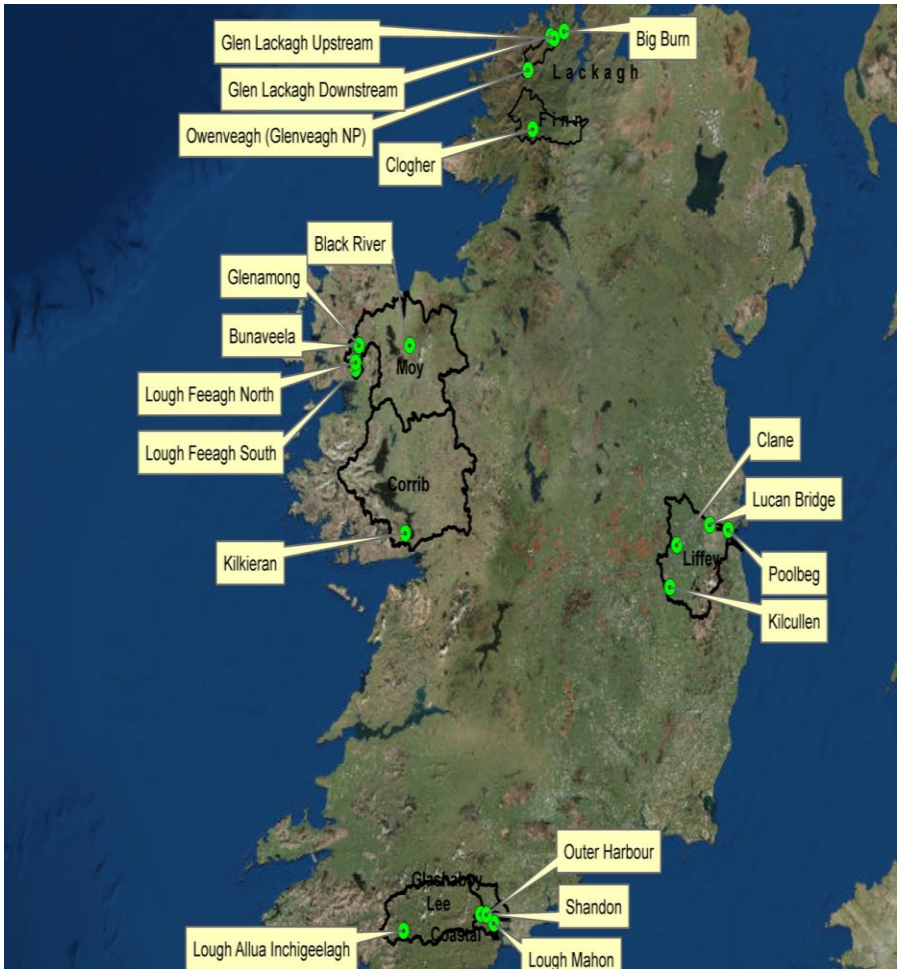
Overview

- Background
- Project overview
- Sampling rationale
- Method development
  - Sample preparation/extraction
  - Analysis
  - Quality control
  - Passive sampling
- Results
- Future work
- Social Media

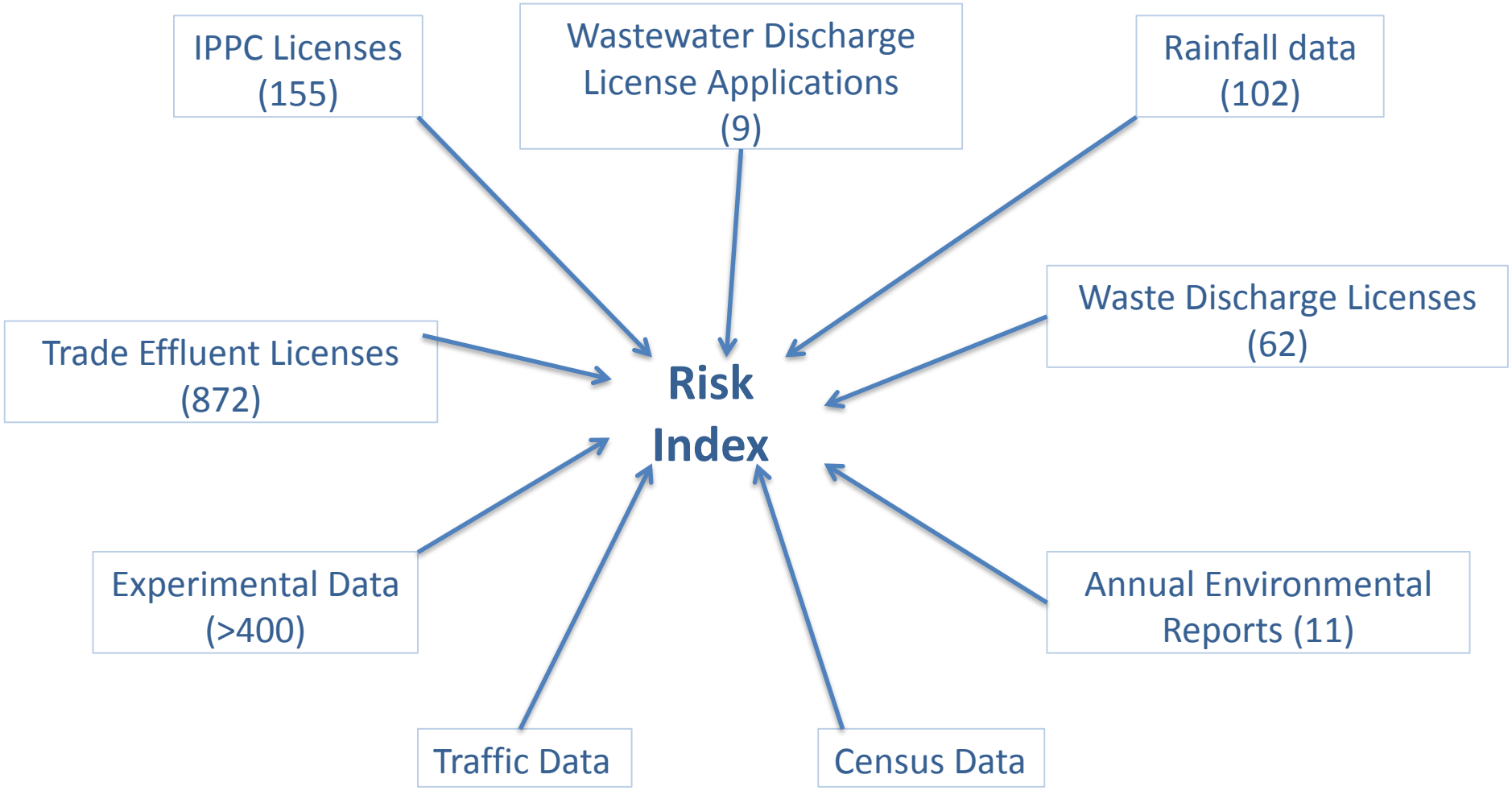
Background

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



Jones *et al*, *Catchment approach to passive sampling of Irish waters, IEEExplore,* ***2015.***



Relate levels detected to emission factors

- Population equivalents, rainfall, traffic, etc.

Jones *et al*, *Development of a risk index for use in water quality monitoring*, *Water Conservation Science and Engineering*, **2016**.

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

Jones *et al*, *Monitoring Water Framework Directive Priority Substances in Wastewater, The Column, 2012.*

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

Jones *et al*, *Monitoring the occurrence of PAHs in Irish Wastewater Effluent, J. Environ. Monit.*, **2012**.
Jones *et al*, *Monitoring the occurrence of heavy metals in Irish Wastewater Effluent*, Analytical Letters, **2016**

Emerging contaminants in Ireland 2013/2014

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	POCIS	ng L^{-1}	<0.04	<0.04	<0.04	**0.06**	**0.05**
EE2	Water	ng L^{-1}*	nd	nd	nd	nd	nd
E2	Water	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	POCIS	ng L^{-1}	<0.04	<0.04	**0.07**	<0.04	<0.12
EE2	Water	ng L^{-1}*	nd	nd	nd	nd	nd
E2	Water	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})

Jones *et al*, *Passive sampling of polar emerging contaminants in Irish catchments*, **2017**.

Emerging contaminants in Ireland 2013/2014

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

Jones *et al*, *A robust analytical method for the determination of pesticide residues in wastewater*, *Analytical Methods*, **2017**.

Phthalates

Phthalates

- Phthalates are a class of widely used industrial compounds used as plasticizers especially in PVC (polyvinyl chloride)
- Various types of phthalates
  - Range from one carbon to seventeen carbons
  - PVC plasticizers generally range from 4-13 carbons
- Accounts for 80–90 percent of the world plasticizer consumption
- Exposure:
  - Anything plastic; ‘New car smell’; toys; cosmetics; leather; cables; products with vinyl;
  - fatty items like cheese and meat from food packaging;
  - medical tubing/bags.

Harmful effects

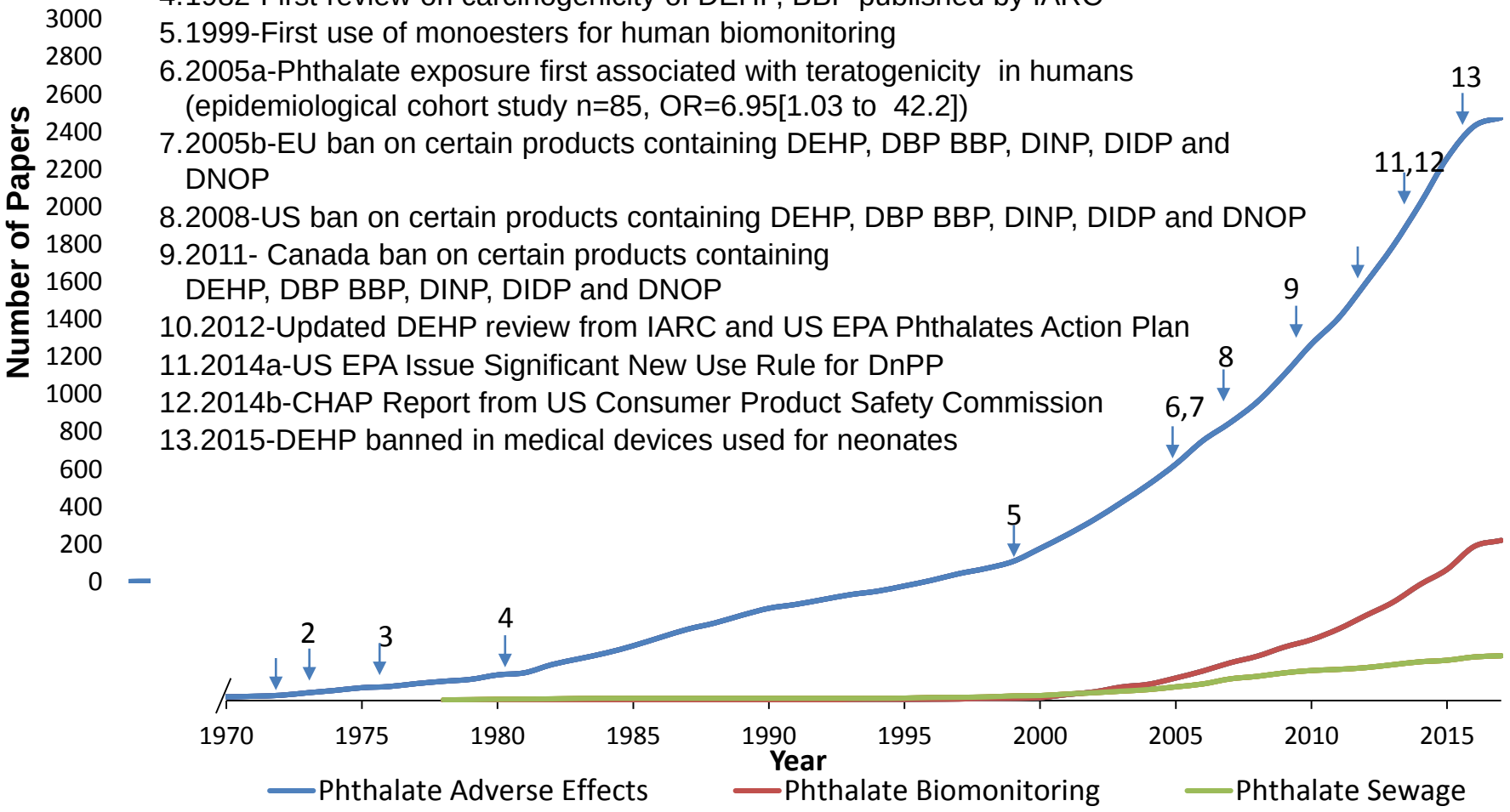
- Male reproductive development is acutely sensitive to some phthalates
- DBP & DEHP produced dramatic changes in male sexual characteristics when exposure took place *in utero*, at levels far beneath those of previous toxicological concern
- Males
  - Hypospadias (anomaly of the urethra)
  - Damage of Sertoli cells caused by a metabolite of DEHP, monoethylhexyl phthalate (MEHP)
  - Low sperm count
  - Reductions in semen quality
  - DNA damage to sperm
- Females
  - Premature breast development
- Premature birth
- Carcinogenic

Phthalates in legislation

- Classed as EDCs, governed by:
  - Water Framework Directive (2000)
  - REACH Regulation (2006)
  - Regulation on Plant Protection Products (2009)
  - Regulation on Cosmetics (2009)
  - Regulation on Biocidal Products (2012)
  - Phthalates Directive 2005/84/EC

Phthalate research and legislation

1. 1972-Teratogenicity of phthalates first studied (rat model)
2. 1973-Monesters as phthalate metabolites first (rat model)
3. 1978-Monoesters as phthalate metabolites first studied (humans)
4. 1982-First review on carcinogenicity of DEHP, BBP published by IARC
5. 1999-First use of monoesters for human biomonitoring
6. 2005a-Phthalate exposure first associated with teratogenicity in humans (epidemiological cohort study n=85, OR=6.95[1.03 to 42.2])
7. 2005b-EU ban on certain products containing DEHP, DBP BBP, DINP, DIDP and DNOP
8. 2008-US ban on certain products containing DEHP, DBP BBP, DINP, DIDP and DNOP
9. 2011- Canada ban on certain products containing DEHP, DBP BBP, DINP, DIDP and DNOP
10. 2012-Updated DEHP review from IARC and US EPA Phthalates Action Plan
11. 2014a-US EPA Issue Significant New Use Rule for DnPP
12. 2014b-CHAP Report from US Consumer Product Safety Commission
13. 2015-DEHP banned in medical devices used for neonates



Phthalates in Ireland

- Very limited study of occurrence of phthalates in the Irish environment has been undertaken.
- DBP, DEHP, DINP and DIDP assessed for a variety of solid matrices including sediments, sludges and leachate soils
  - Irish Midlands Shannon Catchment region during the winter of **2004/5;**
  - river sediment levels of up to 24.4 mg kg^{-1} phthalate were found;
  - leachate sediments and in sludge values of up to 49.8 mg kg^{-1} and 174 mg kg^{-1} were quantified;
  - water samples from the Shannon river basin DEHP was found to occur at levels of 0.77–92.84 µg/L.

Project Description

Project Description

- Monitoring and analysis of 11 priority phthalates;
  - assess the potential sources and environmental fate
- Passive sampling (PS) and standard sampling techniques to evaluate these compounds;
  - surface water, wastewater, treated wastewater, municipal solid waste, compostable waste and dry recyclables, sludge, landfill leachate, and soil;
- Sewage as a biomarker for human health;
- Investigate potential sources, environmental fate, sampling and analysis of these compounds;
- Investigate potential for incorporating PS, grab sampling and sewage biomarker monitoring in future compliance, monitoring and exposure/risks for human health.

Sampling Rationale

County	Rationale
Dublin	Small scale WWTP
Dublin	Medium scale WWTP
Dublin	Large scale WWTP; industrial, urban inputs.
Dublin	Surface water catchment
Dublin and Wicklow	Soil catchment
Dublin	Landfill
Dublin	Recycling plant

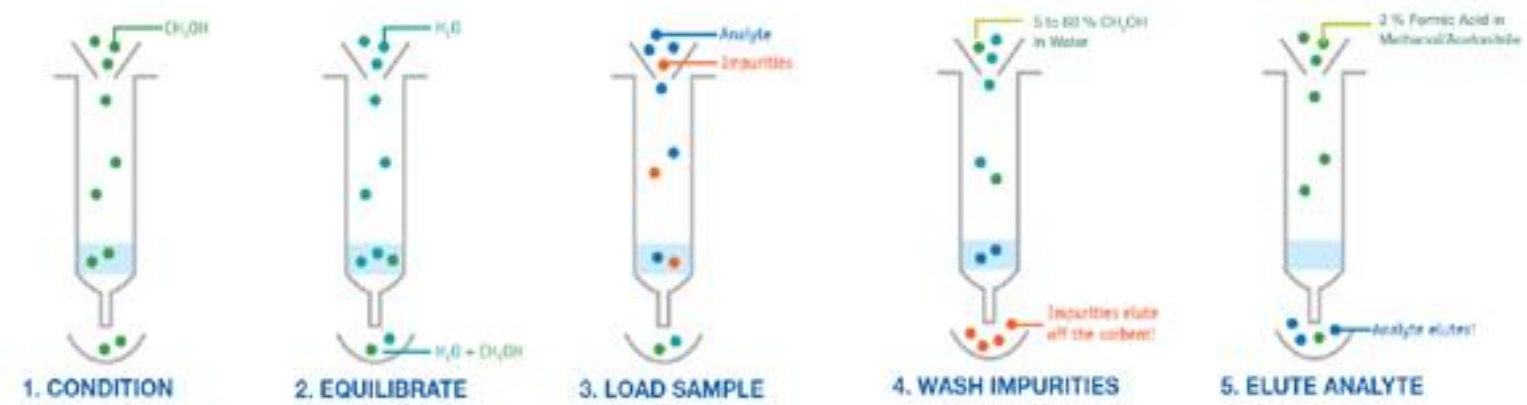
Method Development

Method Development - Extraction

Solid Phase Extraction (SPE): water, leachate, sludge (after pre-prep)

Strata-X Teflon cartridges

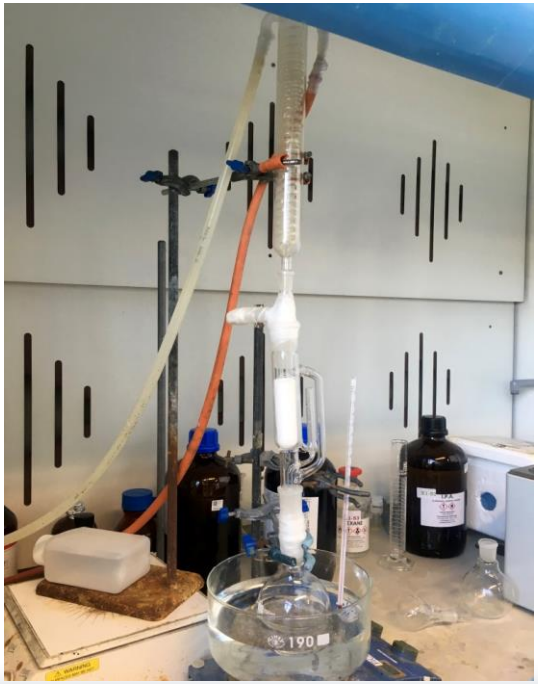
- Condition: 20 mL of ACN
- Equilibrate: 20 mL of water
- Load: Sample (*500 mL – 1 L of sample and matrix very slowly*)
- Wash: 20 mL of (40:60) Methanol:Water
- Dry: 10 min under full vacuum
- Elute: 20 mL of ACN



Extraction

Soxhlet Extraction (SE): solids, plastics

- 1 g of material
- Place in round bottom flask and add 100 mL DCM
- Assemble SE apparatus
- Bring to 40 ^{o}C and maintain for 16 h

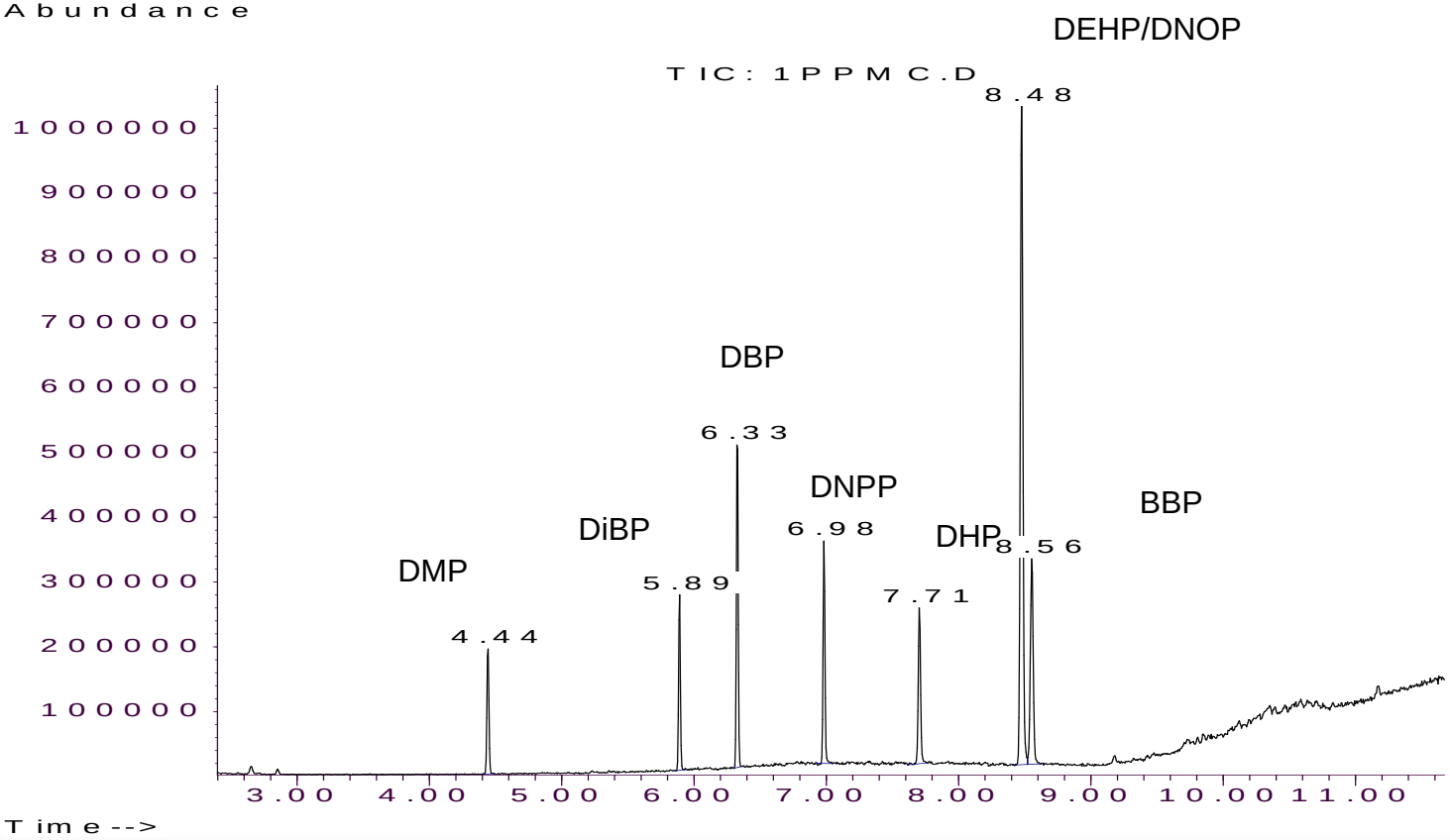


GC-MS

System: Agilent GC-MSD

Method:

- Column: Zebron ZB-50, GC Cap. Column 30 m x 0.25 mm x 0.25 µm
- Mobile Phase: 135 ºC to 275 ºC @ 25 ºC/min for 3.5 min to 340 ºC @ 35 ºC/min for 1 min; flow rate: 1 mL/min



LC-MS

System: Agilent LC with Bruker HCT MS

Method 1 + 2:

- Column: Kinetex 2.6 µm Biphenyl 100 Å, LC Column 50 x 3.0 mm
  Kinetex 2.6 µm EVO C18 100 Å, LC Column 50 x 3.0 mm
- Mobile Phase: Gradient; diWater:MeOH, flow rate: 0.4 mL/min
- Research collaboration Agilent
  - 6470 Triple Quad
  - Transferring methods

Quality Control

- Phthalate-free materials
- Stringent glassware preparation
- Limit possible contamination at each stage
- Blanks – field, solvent, vial rinse, mobile phase, etc.
- Calibration
- Clean room

Passive Sampling

Passive Sampling

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

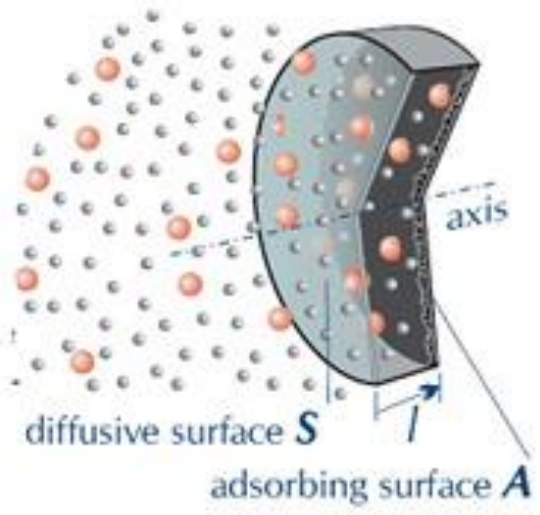


Fig. 1 – Passive sampling mechanism

Fig. 2 – Passive sampling device

Fig. 3 – Passive sampling devices

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
- Membrane based passive sampling devices have previously been deployed successfully for a number of the phthalates in this study, including DMP, BBP, DEHP, DNDP and DBP

Jones *et al*, *Emerging priority substances in the aquatic environment: A role for Passive Sampling in supporting WFD monitoring and compliance* , **2015.**.

Results

Results – Cheese wrappers

- 3 types of cheese packaging: Brie, Cheddar, Gouda.
- Phthalates being detected: DMP, DiBP, DEHP.
- Soxhlet Extraction
- GC-MS analysis
- Compared to current EU regulations.
  - EU Regulation No 10/2011 on 'Plastic Materials and Articles Intended to Come into Contact with Food'.
  - States that for high-fat food packaging, DiBP and DEHP must make up no more than 0.1% of the total composition.

Results

Material	Average RT (min)	Compound	Average Area (mAU)	Concentration (ppm)	Composition %
Brie	5.026 +/- 0.002	DMP	138.2	0.077	0.008
Brie	6.296 +/- 0.002	DiBP	1450.5	0.225	0.023
Brie	8.917 +/- 0.002	DEHP	1378.2	0.354	0.035

Material	Average RT (min)	Compound	Average Area (mAu)	Concentration (ppm)	Composition %
Cheddar	5.026 +/- 0.002	DMP	11570.4	6.481	**0.648**
Cheddar	6.296 +/- 0.002	DiBP	16247.2	1.978	**0.198**
Cheddar	8.917 +/- 0.002	DEHP	16385.7	2.230	**0.223**

Material	Average RT (min)	Compound	Average Area (mAU)	Concentration (ppm)	Composition %
Gouda	5.026 +/- 0.002	DMP	67103.3	37.585	**3.759**
Gouda	6.296 +/- 0.002	DiBP	14756.0	1.801	**0.180**
Gouda	8.917 +/- 0.002	DEHP	23538.5	3.124	**0.312**

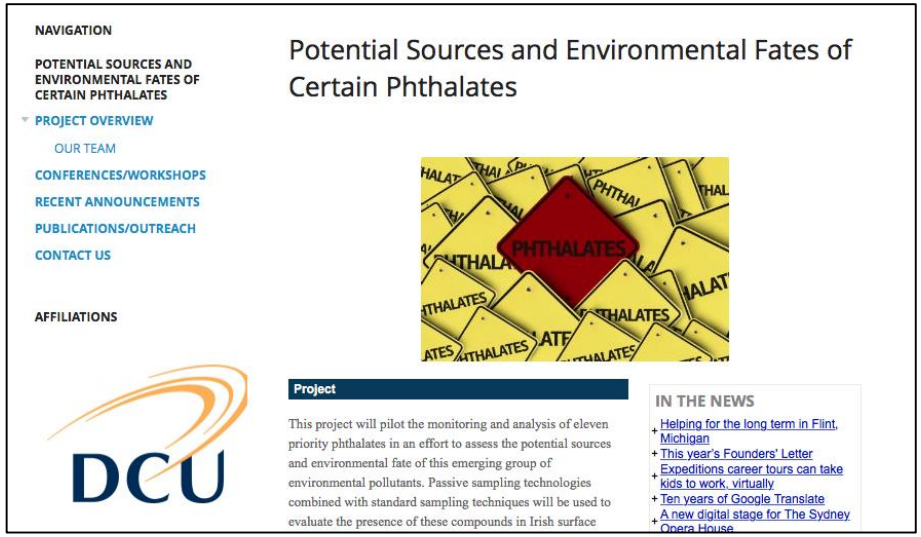
Future Work

Future work…

- Ongoing sample collection and analysis;
- Uptake study on passive sampling materials;
- Evaluation of sewage biomarkers as indicators of consumption, exposure and health effects from phthalates;
- Development of recommendations and guidelines for monitoring of phthalates in water, wastewater, waste, sludge, landfill leachate and soil;
- Assessment of threats posed by phthalates to human health and the environment.

Social Media

- Twitter: @phthalatesDCU and @DCUWater
- Website: https://sites.google.com/site/phthalatesireland/
- www.dcuwater.ie
- Email: phthalatesireland@gmail.com



Acknowledgements

Thank you for your attention!

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.