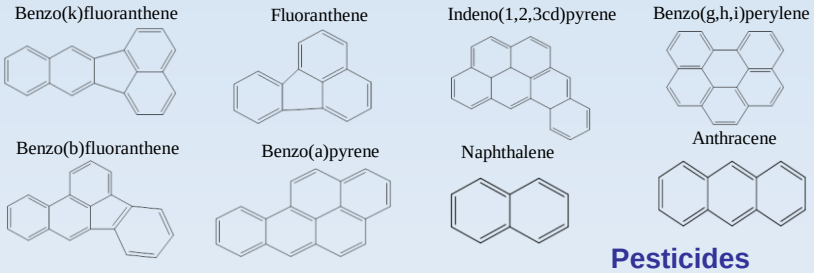
Priority and Hazardous Substances

Lisa Jones*[1], Antoin Lawlor[1], Michael Cahill[2], Brian Kinsella[2], Ken Forde[2], Ambrose Furey[2], Fiona Regan[1].
[1]NCSR, Dublin City University, Ireland.
[2] Cork Institute of Technology, Ireland.

Priority Pollutants

The EU Water Framework Directive (WFD) (2000/60/EC) was transposed into Irish law in 2003 as the European Communities (Water Policy) The level of priority substances present in water bodies is most commonly judged against set environmental quality standards (EQSs) . These standards dictate the maximum allowable concentrations (MAC EQS) or range of concentrations (Annual Average or AA EQS) of specific pollutants allowed to ensure compliance with the EC guidelines. The EU WFD was transposed into Irish Law in 2003 and as such these EQS values now form the basis of priority substance water monitoring in Ireland.

Polycyclic Aromatic Hydrocarbons (PAHs)



PAH	Mol. Wgt (g)	AA EQS (µg L^{-1})
Anthracene	178.23	0.1
Fluoranthene	202.25	0.1
Naphthalene	128.17	1.2
Benzo(a)pyrene	252.31	0.05
Benzo(b)fluoranthene	252.31	∑=0.03
Benzo(k)fluoranthene	252.31	
Benzo(g,h,i)perylene	276.33	∑=0.002
Indeno(1,2,3-cd)pyrene	276.33	

Pesticides

Pesticide	Mol. Wgt (g)	AA EQS (µg L^{-1})
Alachlor	269.77	0.3
Atrazine	215.68	0.6
Chlorfenvinhos	359.57	0.1
Brominated Diphenylethers	564.70	0.0002
Chlorpyrifos	350.59	0.03
Maneb	265.30	0.1
Diuron	390.54	0.2
Di(2-ethylhexyl) phthalate (DEHP)	233.09	1.3
Zineb	275.74	0.1
Hexachlorobenzene	284.80	0.01
Hexachlorobutadiene	260.76	0.1
Thiram	240.43	0.1
Isoproturon	206.28	0.3
(4-(para)-nonylphenol)	220.35	0.3
Para-tert-octylphenol	206.32	0.01
Pentachlorobenzene	250.34	0.0007
Pentachlorophenol	266.34	0.4

Pesticide	Mol. Wgt (g)	AA EQS (µg L^{-1})
Simazine	201.66	1
para-para-DDT	354.49	0.01
Aldrin	364.91	
Dieldrin	380.91	∑=0.005
Endrin	380.91	
Isodrin	364.91	
Trifluralin	335.28	
Epichlorohydrin	92.53	0.1
Mecoprop	214.65	0.02
Pirimiphos Methyl	305.30	0.05
Fenitrothion	277.20	0.01
Malathion	330.36	0.01
Epoxiconazole	329.76	0.1
Glyphosate	169.08	0.1
α -Endosulfan	406.93	0.0005
Hexachlorocyclohexane (Lindane)	290.83	0.002
Mancozeb	266.31	0.1

Volatile Organic Compounds (VOCs)

VOCs	Mol. Wgt (g)	AA EQS (µg L^{-1})
Benzene	78.11	8
1,2-Dichloroethane	98.96	10
Dichloromethane	84.93	20
Trichlorobenzenes	181.45	0.4
Trichloromethane	119.38	2.5
Carbontetrachloride	153.82	12
Tetrachloroethylene	165.83	10
Trichloroethylene	131.39	10

Metals/Trace Elements

	Mol. Wgt (g)	AA EQS (µg L^{-1})
Lead cmpds	207.20	7.2
Nickel cmpds	58.69	20
Fluoride	18.90	1000
TBT cmpds	291.06	0.0002
Arsenic	74.92	1
Zinc	65.39	2.3
Copper	63.54	0.5
Chromium	52	0.3
Selenium	78.96	5.3

	Mol. Wgt (g)	AA EQS (µg L^{-1})
Mercury cmpds	200.59	0.05
Antimony	121.75	0.4
Molybdenum	95.94	4.3
Tin	118.69	0.2
Barium	137.34	1
Boron	10.81	6.5
Vanadium	50.94	0.9
Cobalt	58.93	0.2
Cadmium	112.41	0.2

Note: The AA EQS values listed above apply to freshwater systems. MAC EQS values were not available for all compounds listed.

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Legislation Controlling the Emission of Priority Pollutants

Lisa Jones*[1], Antoin Lawlor[1], Michael Cahill[2], Brian Kinsella[2], Ken Forde[2], Ambrose Furey[2], Fiona Regan[1].
[1]NCSR, Dublin City University, Ireland.
[2] Cork Institute of Technology, Ireland.

The EU Water Framework Directive (2000/60/EC)

Although many efforts have been made in the area of environmental policy, a significant step towards a cleaner environment was taken in October 2000 as the European Parliament established the Water Framework Directive (WFD). This document acts as a single piece of legislation which covers rivers, lakes, groundwater and transitional (estuarine) and coastal waters. The main objective of this directive is to attain 'good' status in water bodies that are below 'good' status at present, as well as to retain 'good' or better status where it currently exists, by 2015.The WFD was transposed into Irish law in 2003 as the European Communities (Water Policy) Regulations 2003 (S.I. 722 of 2003) and is the principal piece of legislation governing water quality in Ireland. Under this legislation water bodies in Ireland were divided into 7 River Basin Districts (RBD's), which are river catchments or groups of catchments, which must be monitored.

The WFD aims to 'achieve the elimination of priority hazardous substances and contribute to achieving concentrations in the marine environment near background values for naturally occurring substances' with a list of priority hazardous substances being defined and established by an amendment to the WFD in 2001.

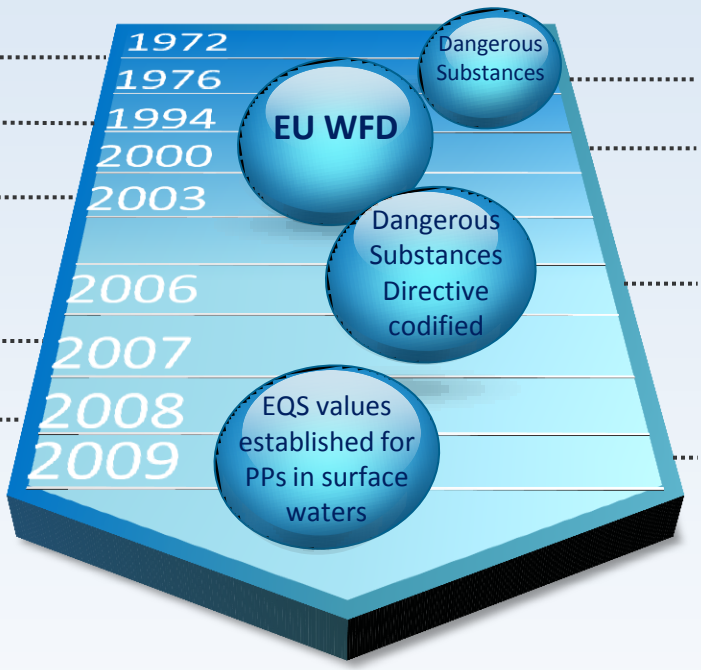
1972 Federal Water Pollution Control Ammendments in the USA are introduced.

1994 Integrated Pollution Control (IPC) Licensing introduced

2003 WFD transcribed into Irish law. IPC licensing amended to IPPC licensing.

2007 Water Information System for Europe (WISE) launched.

2008 IPPC Directive codified to include all amendments



1976 Dangerous Substances Directive introduced.

2000 Water Framework Directive introduced. EPER, predecessor of the E-PRTR, is established.

2006 Dangerous Substances Directive codified to include all amendments. E-PRTR issued. Groundwater Directive introduced.

2009 QA/QC Commission Directive introduced. S.I. 272 establishes EQS values for priority pollutants in surface waters.

Dangerous Substances Directive 76/464/EEC and 2006/11/EC

This Directive lays down rules for protection against, and prevention of, pollution resulting from the discharge of certain substances into the aquatic environment. It applies to inland surface water, territorial waters and internal coastal waters. Two lists of dangerous substances have been compiled to combat pollution: discharge of substances in list I must be eliminated; while discharge of substances in list II must be reduced. Pursuant to Annex IX of the WFD, quality objectives and emission limit values are established by the "daughter directives" of Directive 2006/11/EC. Moreover, emission limit values for pollutants must be based on the best available techniques in line with Article 10 of the WFD. All discharges of substances included in list I require prior authorisation by the competent authority in the Member State concerned. For the substances on list II, the Member States adopt and implement programmes to preserve and improve water quality. All discharges are subject to prior authorisation by the competent authority in the Member State concerned that lays down the emission standards.

The Member States draw up an inventory of the discharges into the waters covered by this Directive and may take more severe measures than those laid down by Community legislation to reduce or eliminate pollution caused by dangerous substances. Before 22 December 2012, Member States may carry out surveillance and notification pursuant to Articles 5, 8 and 15 of the Water Framework Directive.

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Monitoring and Modelling the Occurrence of Priority Substances in Wastewater

***Lisa Jones**, Antoin Lawlor,Fiona Regan.*
[1]NCSR, Dublin City University, Ireland.
lisa.a.jones@gmail.com

Introduction

In 2000 the Water Framework Directive (WFD), 2000/60/EC, was introduced and a group of 66 chemicals, including pesticides, polycyclic aromatic hydrocarbons, and metals were listed as chosen priority pollutants. The levels of these priority pollutants in the environment are regulated by set environmental quality standards (EQSs) and are affected by a number of emission factors including anthropogenic activities, population equivalents, and weather. In order for these EQSs to be enforced, regular monitoring of all water bodies must be carried out, a process which is both costly and time consuming. We have developed a model defining emission levels relating to priority pollutants occurrence in the environment. This is based on information collected from local authorities, Met Eireann and pollutant levels in waste water treatment plant (WWTP) effluents.

This study involved the analysis of samples from 8 WWTPs in both Cork and Dublin, Ireland, for priority pollutants, Table 1. These sites were chosen for their varying population equivalents, geographic locations, and main contributions, in order to make the final model of emission factors as comprehensive as possible.

Table 1 – Comparison of WWTPs included in this study, with the largest sites; Ringsend and Swords, located in County Dublin, and the rest of the sites located in County Cork.

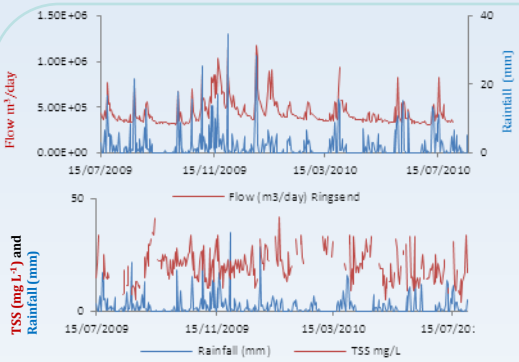
WWTP:	Ringsend	Swords	Ballincollig	Bandon	Charleville	Fermoy	Mallow	Ringaskiddy
Population Equivalent	1,900,000	50,000	26,000	20,000	15,000	20,000	18,000	97,556
Main contributions	Industrial and domestic	Domestic and agriculture						Domestic and Industrial
Level of treatment	Tertiary	Secondary						None
Type of sample	Grab	Composite	Grab					Composite

Over the sampling plan 71 samples were collected over an 18 month period with intensive sampling for several weeks of the summer and winter.

Wastewater effluent was the chosen medium for this study for a because it is:

A major point-source input to surface waters
Responsible for localised EQS exceedances
Often upstream of drinking water abstraction
Controllable.

Data on emission factors was collected to populate our model and map the patterns between these emission factors and the occurrence of our priority pollutants.



Figures 1, 2 - Relation of flow through a WWTP and local rainfall. Then relation of rainfall to TSS levels in WWTP effluent.

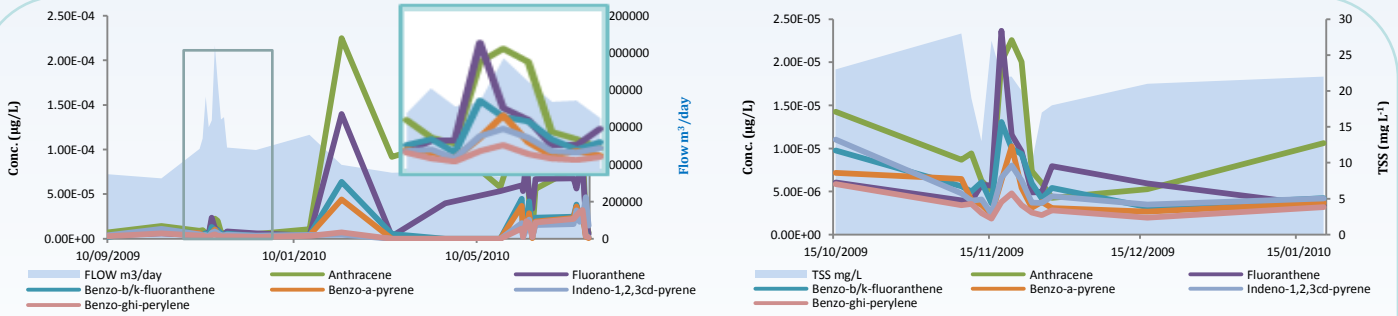
Results

Figures 1 and 2 show the relation between rainfall and flow through the WWTP, and then rainfall and total suspended solids (TSS) through the WWTP.

Table 2 summarises the results for one group of PPs over the sampling timeframe., compared to the Annual Average EQS (AA EQS) level. All samples tested positive for PAHs, but never exceeded these standard values.

Table 2 – Summary of results for one group of the priority pollutants, the PAHs.

Parameter	AA EQS (µg L^{-1})	LOD SPE-GCMS (µg L^{-1})	Frequency (N=71)	Range	
				Min	Max
Naphthalene	1.2	0.0001	48	1.07 x 10^{-4}	0.035
Anthracene	0.1	0.0005	27	6.30 x 10^{-4}	0.013
Fluoranthene	0.1	0.0001	28	1.40 x 10^{-4}	0.0086
Benzo-b/k-fluoranthene	Σ=0.003	0.0001	29	1.20 x 10^{-4}	0.0044
Benzo-a-pyrene	0.05	0.0005	19	5.50 x 10^{-4}	0.0036
Indeno-1,2,3cd-pyrene	Σ=0.002	0.0005	35	1.55 x 10^{-4}	0.0025
Benzo-ghi-perylene		0.0005	20	5.90 x 10^{-4}	0.0032



Figures 3,4 - Relation of flow through a WWTP and PAH concentration, with the insert highlighting the value of intensive sampling data. Relation of PAH concentration to total suspended solids levels in WWTP effluent.

Compared rainfall levels and TSS levels to PP levels in the WWTP effluent (Figures 3 and 4). Increased rainfall can bring forward stale sewage in a flushing effect. PPs in wastewater greatly increase, sometimes 10 – 100 fold when compared to dry weather levels. This specifically affects PAHs with regard to road-runoff, with PAHs being released from motor vehicles as particulates which settle on the roads and are washed into the sewers during periods of rainfall.

Increased rainfall and thus increased TSS content increased the PAH levels, but we can see that the more water soluble PAHs (e.g. anthracene) increased more than the less water soluble PAHs (e.g. benzo-ghi-perylene) as they were likely adsorbed onto the solid material.

Conclusions

This study serves to inform targeted priority substance monitoring, highlighting the importance of high intensive sample collection, especially with regard to valuable temporal variation data, and the value of creating an index of emission factors relating to priority substance occurrence in the environment.

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