

Priority and Hazardous Substances

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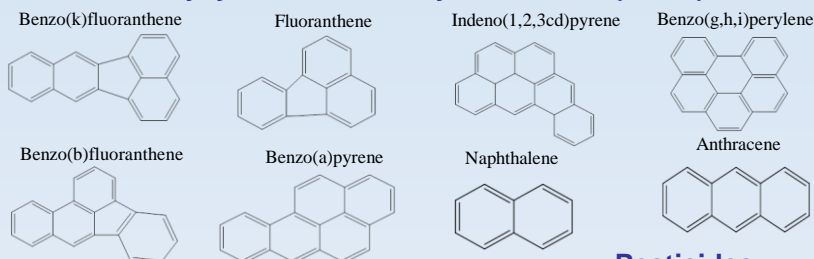
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Priority Pollutants

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 ($\mu\text{g L}^{-1}$)
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	$\Sigma=0.03$
Benzo(k)fluoranthene	252.31	$\Sigma=0.02$
Benzo(g,h,i)perylene	276.33	$\Sigma=0.02$
Indeno(1,2,3-cd)pyrene	276.33	

Pesticides

Pesticide	Mol. Wgt (g)	AA EQS ($\mu\text{g L}^{-1}$)	Pesticide	Mol. Wgt (g)	AA EQS ($\mu\text{g L}^{-1}$)
Alachlor	269.77	0.3	Simazine	201.66	1
Atrazine	215.68	0.6	para-para-DDT	354.49	0.01
Chlorfenvinhos	359.57	0.1	Aldrin	364.91	
Brominated Diphenylethers	564.70	0.0002	Dieldrin	380.91	$\Sigma=0.005$
Chlorpyrifos	350.59	0.03	Endrin	380.91	
Maneb	265.30	0.1	Isodrin	364.91	
Diuron	390.54	0.2	Trifluralin	335.28	
Di(2-ethylhexyl) phthalate (DEHP)	233.09	1.3	Epichlorohydrin	92.53	0.1
Zineb	275.74	0.1	Mecoprop	214.65	0.02
Hexachlorobenzene	284.80	0.01	Pirimiphos Methyl	305.30	0.05
Hexachlorobutadiene	260.76	0.1	Fenitrothion	277.20	0.01
Thiram	240.43	0.1	Malathion	330.36	0.01
Isoproturon	206.28	0.3	Epoxiconazole	329.76	0.1
(4-(para)-nonylphenol)	220.35	0.3	Glyphosate	169.08	0.1
Para-tert-octylphenol	206.32	0.01	α -Endosulfan	406.93	0.0005
Pentachlorobenzene	250.34	0.0007	Hexachlorocyclohexane (Lindane)	290.83	0.002
Pentachlorophenol	266.34	0.4	Mancozeb	266.31	0.1

Volatile Organic Compounds (VOCs)

VOCs	Mol. Wgt (g)	AA EQS ($\mu\text{g L}^{-1}$)
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 ($\mu\text{g L}^{-1}$)		Mol. Wgt (g)	AA EQS ($\mu\text{g L}^{-1}$)
Lead cmpds	207.20	7.2	Mercury cmpds	200.59	0.05
Nickel cmpds	58.69	20	Antimony	121.75	0.4
Fluoride	18.90	1000	Molybdenum	95.94	4.3
TBT cmpds	291.06	0.0002	Tin	118.69	0.2
Arsenic	74.92	1	Barium	137.34	1
Zinc	65.39	2.3	Boron	10.81	6.5
Copper	63.54	0.5	Vanadium	50.94	0.9
Chromium	52	0.3	Cobalt	58.93	0.2
Selenium	78.96	5.3	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.



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.



Legislation Controlling the Emission of Priority Pollutants

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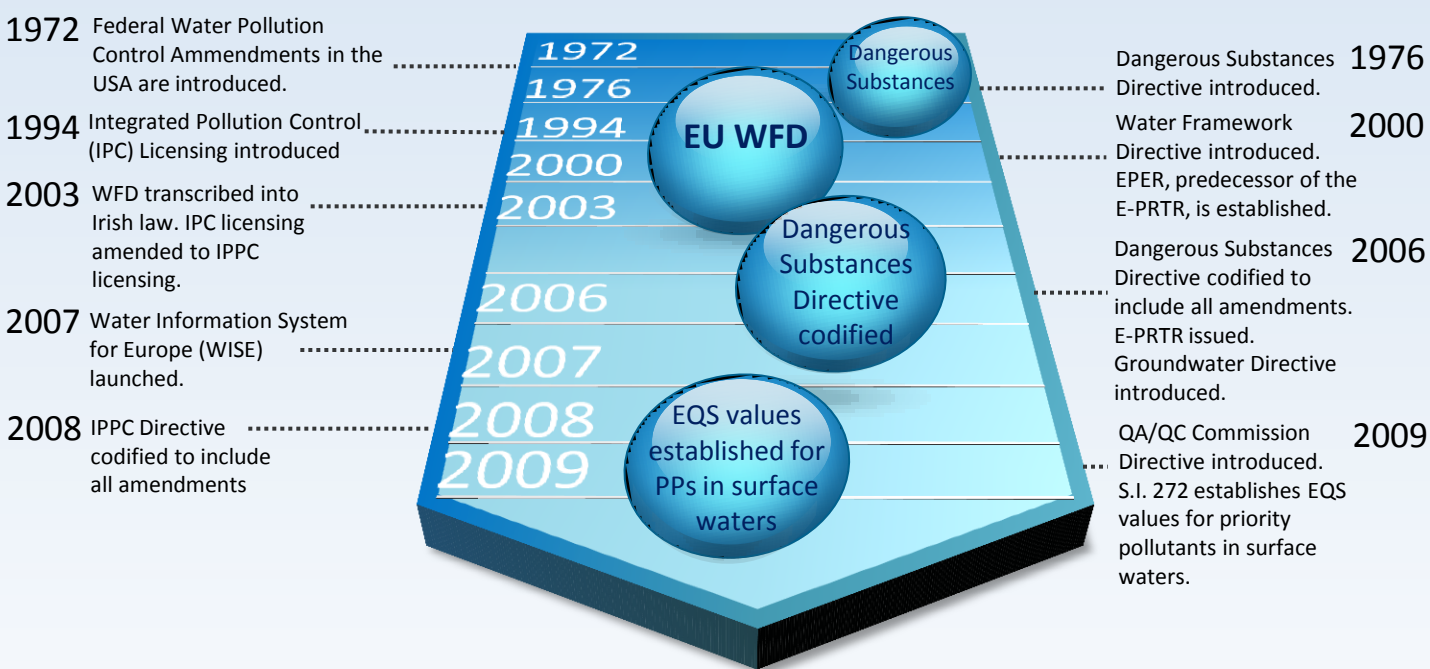
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The EU Water Framework Directive (2000/60/EC)

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.



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

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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.

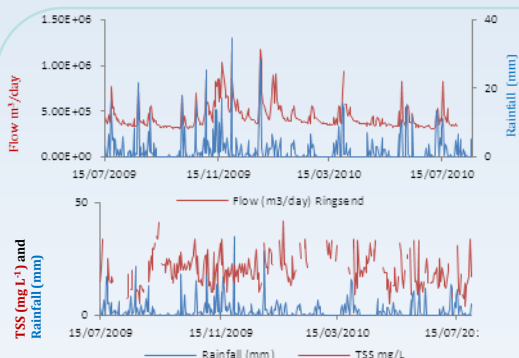
WWTP: Population Equivalent	Ringsend	Swords	Ballincollig	Bandon	Charleville	Fermoy	Mallow	Ringaskiddy
	1,900,000	50,000	26,000	20,000	15,000	20,000	18,000	97,556
Main contributions	Industrial and domestic		Domestic and agriculture					Domestic and Industrial
Level of treatment	Tertiary		Secondary					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.



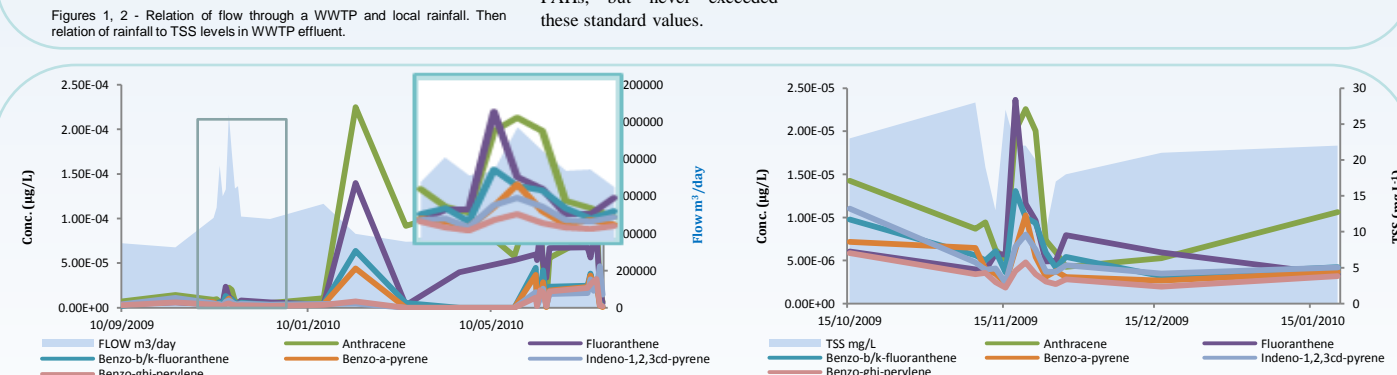
Results

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