

# Determination of Priority Substances in Wastewater using SPE, LCMS and GCMS

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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.

This study involved the analysis of samples from 8 WWTPs in both Cork and Dublin, Ireland, for priority pollutants, Table 1.

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	

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.

## Methods

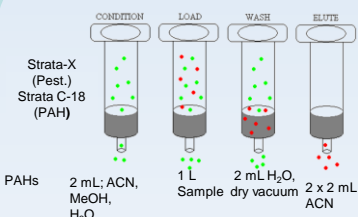


Figure 1 - SPE methods used for extraction, gives preconcentration factor of x1000

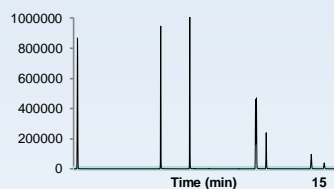


Figure 2 - Separation of PAHs; a) naphthalene, b) anthracene, c) fluoranthene, d + e) benzo-b- and benzo-k-fluoranthene, f) benzo-a-pyrene, g) benzo-ghi-perylene and h) indeno-123 cd-pyrene

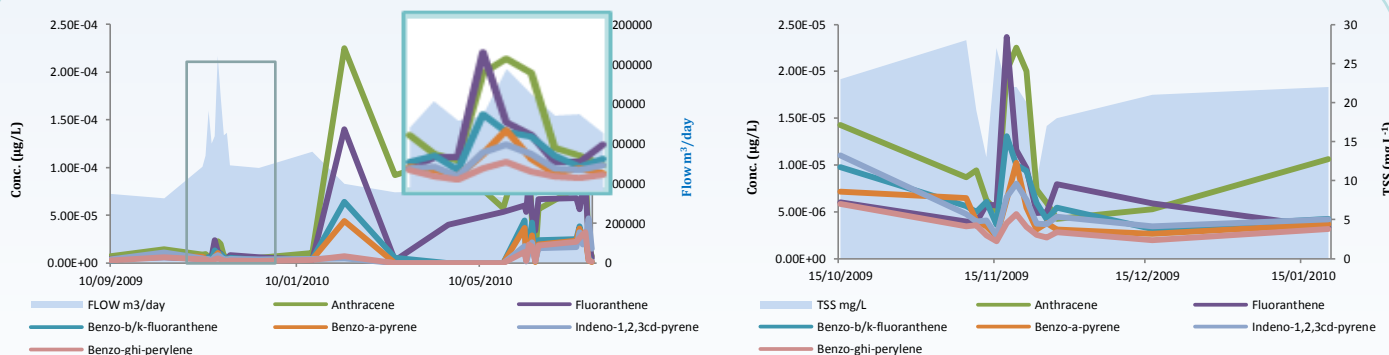
Figure 1 shows the SPE procedure for PAH extraction. This method adds a preconcentration factor of 1000.

## Results

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 ( $\mu\text{g L}^{-1}$ )	Freq. (N=71)	Range	
				Min	Max
Naphthalene	1.2	0.0001	48	$1.07 \times 10^{-4}$	0.035
Anthracene	0.1	0.0005	27	$6.30 \times 10^{-4}$	0.013
Fluoranthene	0.1	0.0001	28	$1.40 \times 10^{-4}$	0.0086
Benzo-b/k-fluoranthene	$\Sigma=0.003$	0.0001	29	$1.20 \times 10^{-4}$	0.0044
Benzo-a-pyrene	0.05	0.0005	19	$5.50 \times 10^{-4}$	0.0036
Indeno-1,2,3cd-pyrene	$\Sigma=0.002$	0.0005	35	$1.55 \times 10^{-4}$	0.0025
Benzo-ghi-perylene		0.0005	20	$5.90 \times 10^{-4}$	0.0032

## Conclusions



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.

Increased rainfall brings forward stale sewage in a flushing effect, increasing priority pollutant loads. PAHs are 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 total suspended solids content increase the PAH levels; it was found 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.



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