

# Wastewater using SPE, LCMS and GCMS

Lisa Jones\*, Antoin Lawlor, Fiona Regan.

<sup>1</sup>NCSR, Dublin City University, Ireland.

[lisa.a.jones@gmail.com](mailto: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.

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

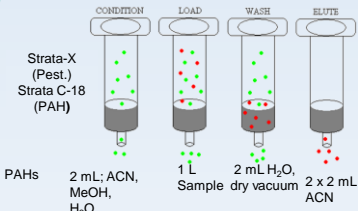


Figure 1 - SPE methods used for extraction, gives preconcentration factor of x1000

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

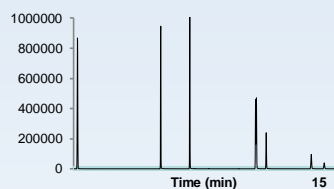


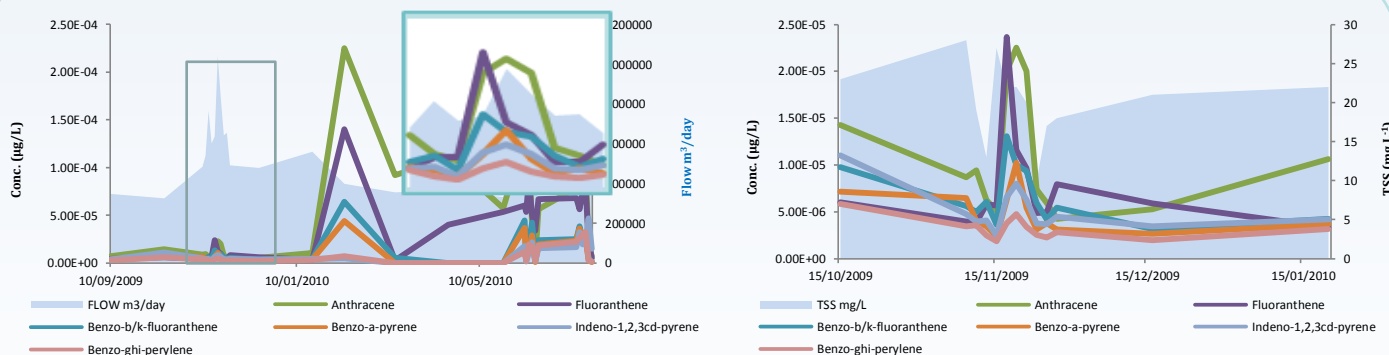
Figure 2 - Separation of PAHs; a) naphthalene, b) anthracene, c) fluoranthene, d + e) benzo-b- and benzo-k-fluoranthene, f) benzo-a-pyrene, g) benzo-ghi-perylene and h) indeno-123 cd-pyrene

## 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.