

# Monitoring and Modelling of Priority Pollutants in Irish Wastewaters

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# Presentation Outline

- Introduction
- Sampling Plan and Sampling Sites
- Extraction Methods
- Analytical Method for PAHs
- Results
- Model
- Conclusion

# Project Aim

- This project aims to create an index of emission factors, a computer model, based on experimental data collected from the monitoring of Water Framework Directive priority pollutants in waste water treatment plant effluent.

# Project Outline

- Monitor priority pollutant levels in wastewater treatment plant effluents
  - SPE, GC-MS, LC-FLD/MS, ICPAES
- Relate levels detected to emission factors
  - Population equivalents, rainfall, traffic, etc.
- Create model/index of priority substance emissions from wastewater treatment plants

# Priority Substances in Wastewater

- Wastewater major point-source
- Responsible for localised EQS exceedances
- Often upstream of drinking water abstraction
- Can be controlled
- Few data on wastewater PS discharges
- Will complement storm water studies, and inform targeted PS monitoring

# Sampling Site Overview



# WWTPs

- Cork
  - Ballincollig
  - Bandon
  - Charleville
  - Clonakilty
  - Fermoy
  - Mallow
  - Ringaskiddy
- Dublin
  - Ringsend
  - Swords

# Site Overview

WWTP	Level of Treatment	Type of Treatment	Agglomeration PE	Plant PE	Receiving Waters
<b>Ballincollig</b>	Secondary	Activated sludge (Aeration Basin)	16,339	15,000	Freshwater (R)
<b>Bandon</b>	Secondary	Activated sludge (Oxidation Ditch)	8178	20,000	Freshwater (R)
<b>Charleville</b>	Secondary		2,984	6,415	Freshwater (R)
<b>Clonakilty</b>	Secondary		7,500-15,000	15,000	Estuarine
<b>Fermoy</b>	Secondary, NR	Activated sludge (Oxidation ditches; anaerobic-, anoxic- and aeration tanks) Phosphorous Removal	5,800	12,960	Freshwater (R)



# Site Overview

WWTP	Level of Treatment	Type of Treatment	Agglomeration PE	Plant PE	Receiving Waters
<b>Mallow</b>	Secondary, NR	Activated sludge (Anaerobic-, anoxic- and aeration tanks) Phosphorous Removal	7,091	12,000	Freshwater (R)
<b>Ringaskiddy</b>	None	None	14,864	0	Estuarine
<b>Ringsend</b>	Tertiary	Activated sludge (Sequencing Batch Reactors) U.V Disinfection	2,870,333	1,640,000	Estuarine
<b>Swords</b>	Secondary	Activated sludge (Anaerobic-, anoxic- and aeration tanks)	50,000	60,000	Estuarine

# SAMPLING PLAN



# Rationale

- Populate model
- Temporal and seasonal variability
- Flexible
  - DWF / WWF
- Monthly samples
- Intensive sampling

# SAMPLING PLAN

Site	Sample Type	Timeframe (months)	Volume (L)	Sample Breakdown	
Ballincollig	Grab	14	6.5	6 x 500 mL PAH analysis (3 filtered) 6 x 500 mL Pesticide analysis (3 filtered) 500 mL Metals analysis	
Bandon	Grab	13	6.5		
Charleville	Grab	12	6.5		
Clonakilty	Grab	4	6.5		
Fermoy	Grab	13	6.5		
Mallow	Grab	13	6.5		
Ringaskiddy	Grab/Comp.	12	6.5		
Ringsend	Grab	25	12.5		6 x 1 L PAH analysis (3 filtered)
Swords	Composite	20	12.5		6 x 1 L Pesticide analysis (3 filt.) 500 mL Metals analysis

# Typical Sampling Campaign

	2009						2010												2011								
Month	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J		
<b>Ballincollig</b>																										X	
<b>Bandon</b>																											
<b>Charleville</b>																											
<b>Clonakilty</b>																											
<b>Fermoy</b>																											
<b>Mallow</b>																											
<b>Ringaskiddy</b>																											
<b>Ringsend</b>					X														X	X						X	X
<b>Swords</b>						X													X	X						X	X

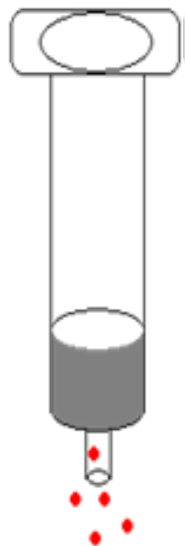
# Extraction



# Extraction of PAHs and Pesticides

## PAHs

- STRATA C<sub>18</sub> cartridges;
- 500 mg, 6 mL
- Conditioning:
  - 2 mL ACN
  - 2 mL MeOH
  - 2 mL Water
- Load 1 L sample



## Pesticides

- STRATA X cartridges;
- 500 mg, 6 mL
- Conditioning:
  - 6 mL MeOH
  - 6 mL Water
- Load 1 L sample

Wash with 2 mL water

Dry cartridge under vacuum - freeze

Elute with 2 x 2 mL ACN (PAH) or 2 mL ACN and 2 mL IPA (pesticides)

Evaporate down with nitrogen and reconstitute in 1 mL ACN

# Metals and Trace Elements

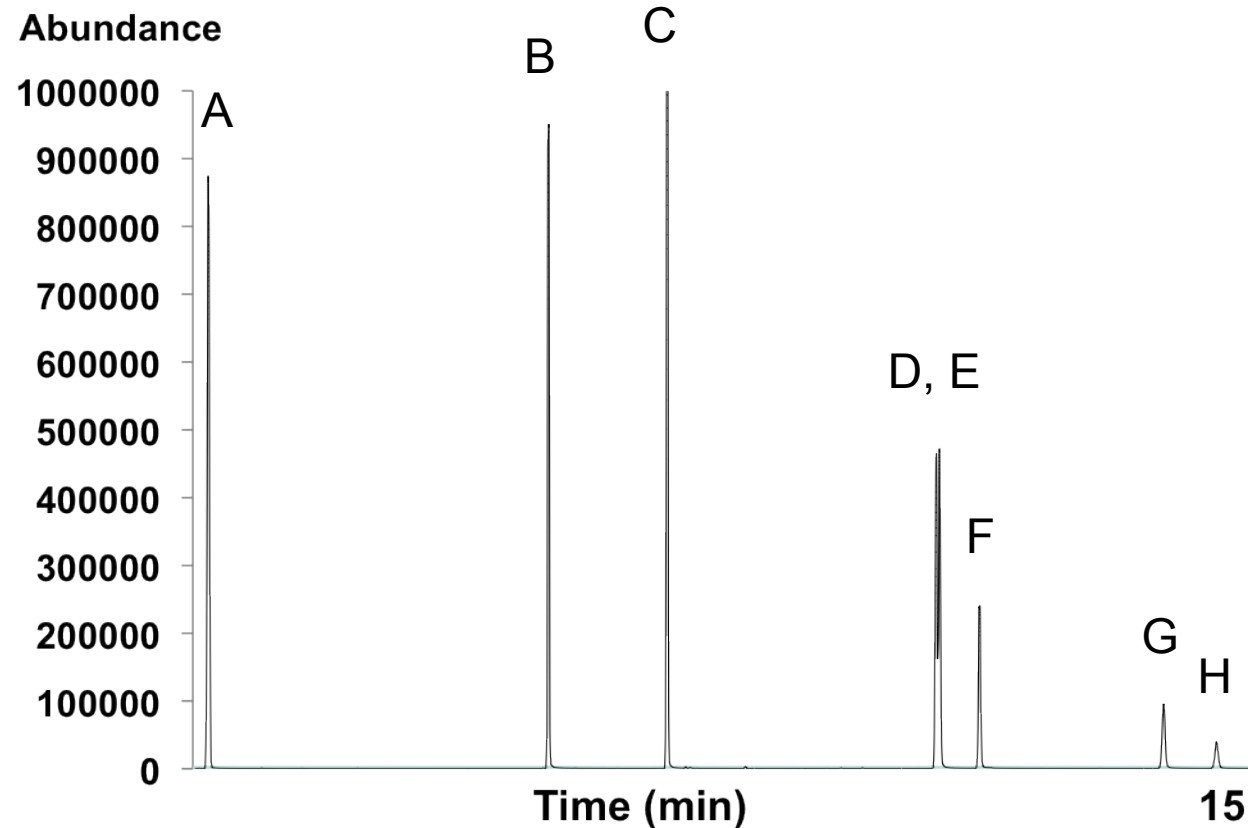
- APHA guidelines and EPA method 200.7
- Collection in PTFE bottles
- Adjust pH to 2
- Mars Express Instrument, CEM  
Microwave Sample Preparation System
- EPA Method 3015 - 665W (10 min)  
290W (10 min)



# ANALYSIS



# GC-MS Method for PAHs



Initial Temp: 55°C  
Initial Time: 1.00 min  
Rate: 25.00°C/min  
Final Temp: 310°C  
Final Time: 4.20 min  
Post time: 1.00 min  
Run time: 15.40 min  
Injection Volume: 5 µL  
SIM Mode

LOD: 0.00005-0.0005ppm  
LOQ: 0.00001-0.001ppm

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

# EXTERNAL DATA



# Rainfall Stations



# Rainfall Data

	<i>Dublin (Ringsend)</i>	<i>Dublin (Simmonscourt)</i>	<i>Dublin (Merrion Square)</i>
Dublin (Ringsend)	1		
Dublin (Simmonscourt)	0.66615	1	
Dublin (Merrion Square)	0.89307	0.68413	1

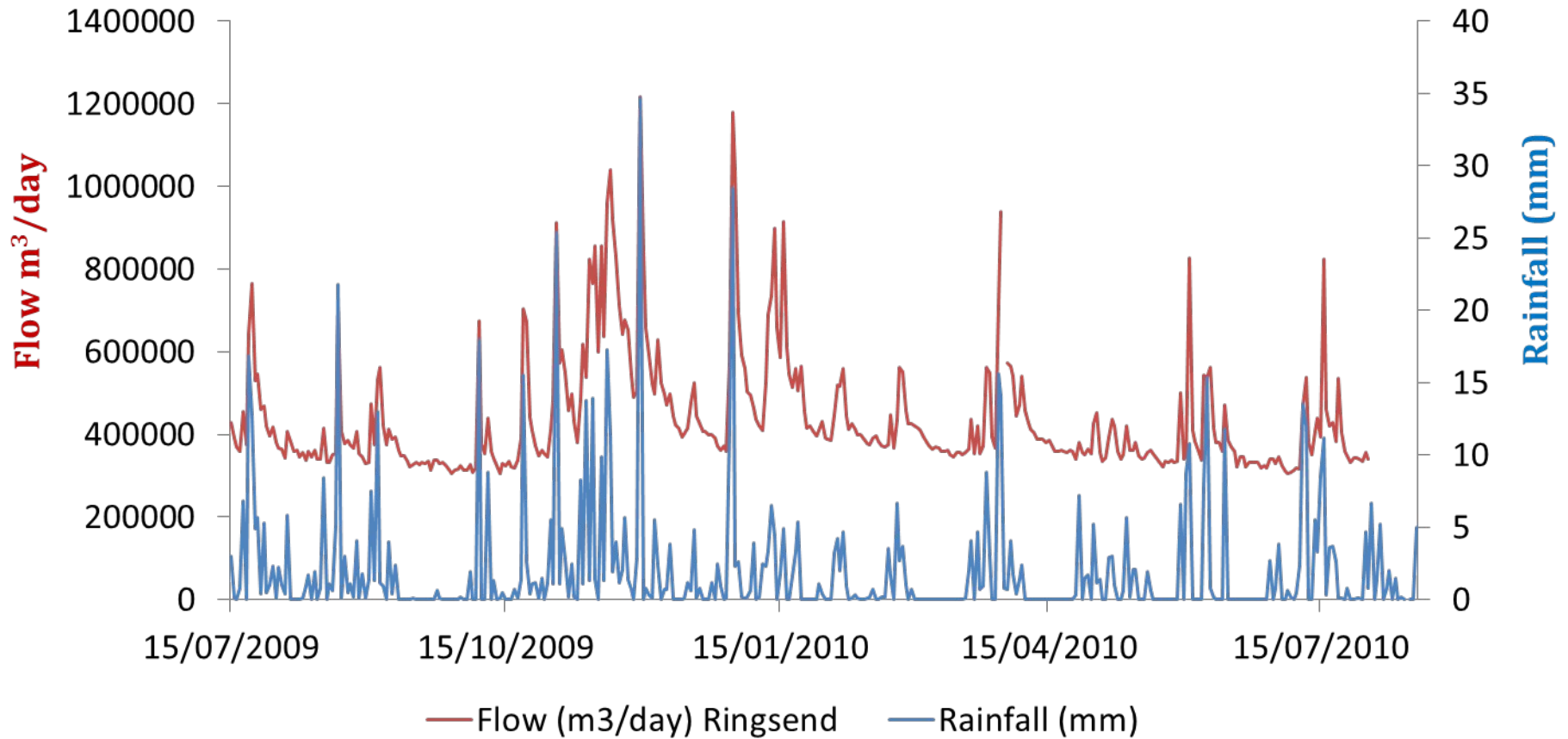
	<b>Mallow (Sewage Works)</b>	<b>Treatment Mallow (Spa House)</b>
Mallow (Sewage Works) Treatment		1
Mallow (Spa House)	0.37697	1

# RESULTS

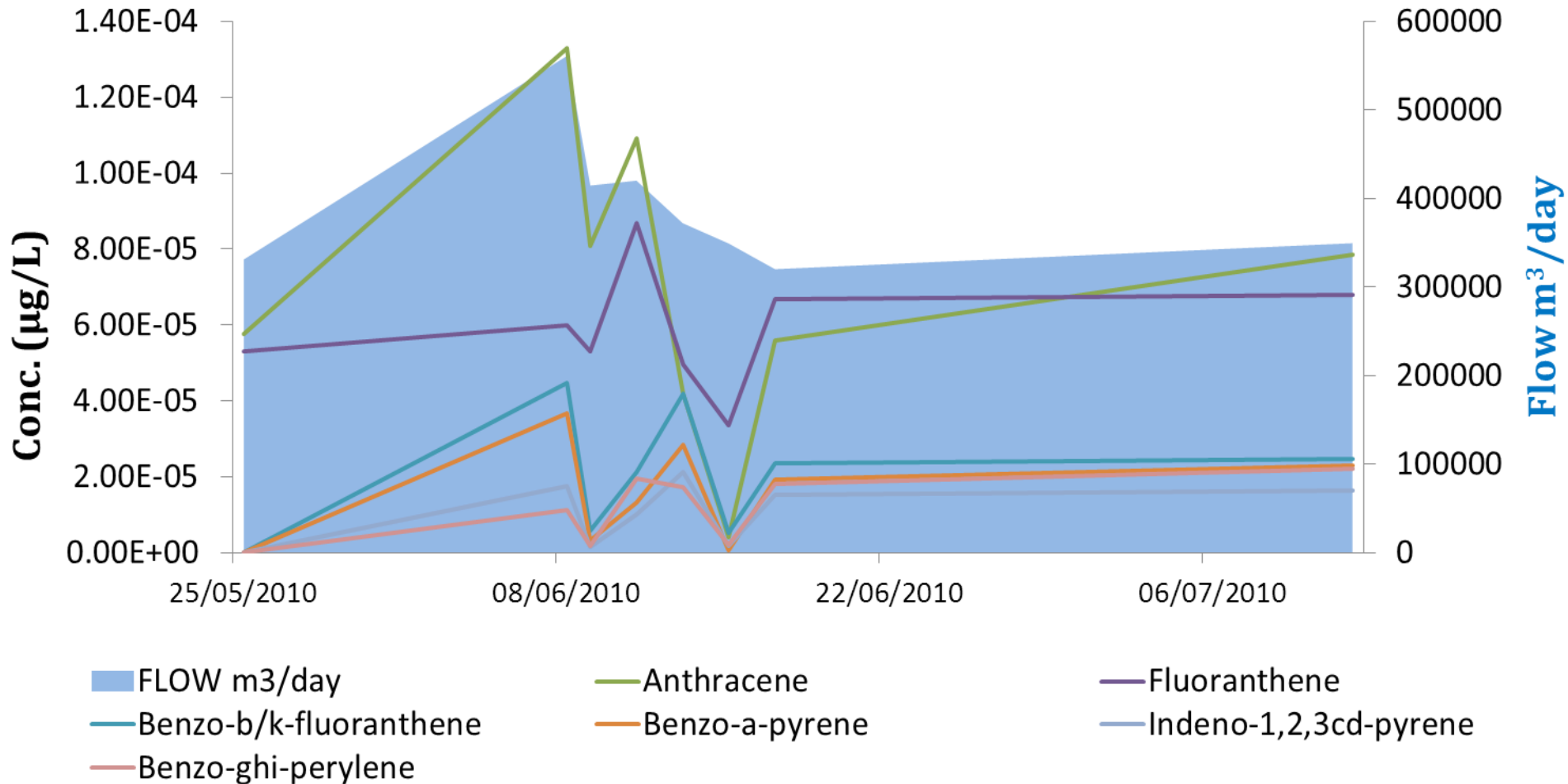




# Flow and Rainfall

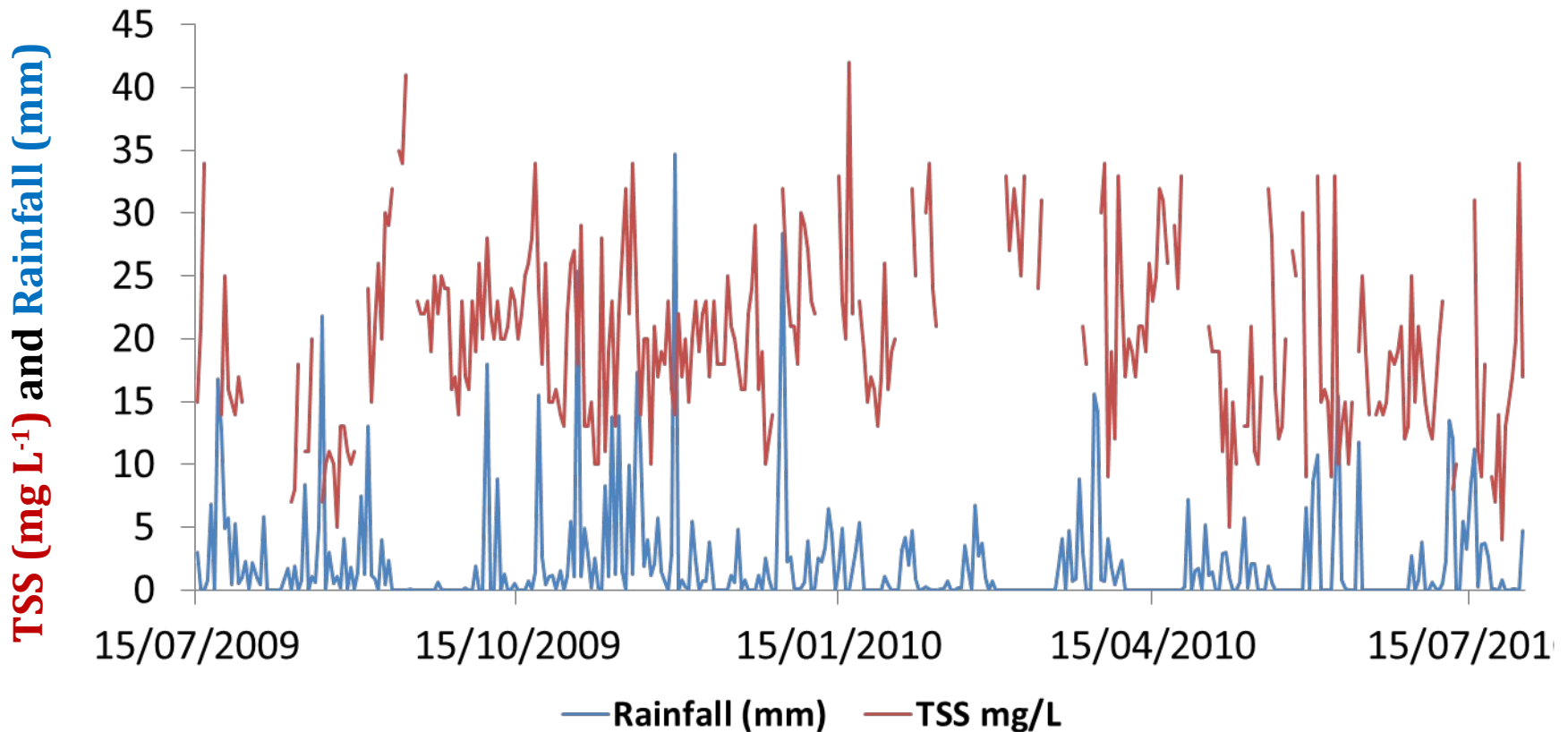


# Flow and PAH Concentration

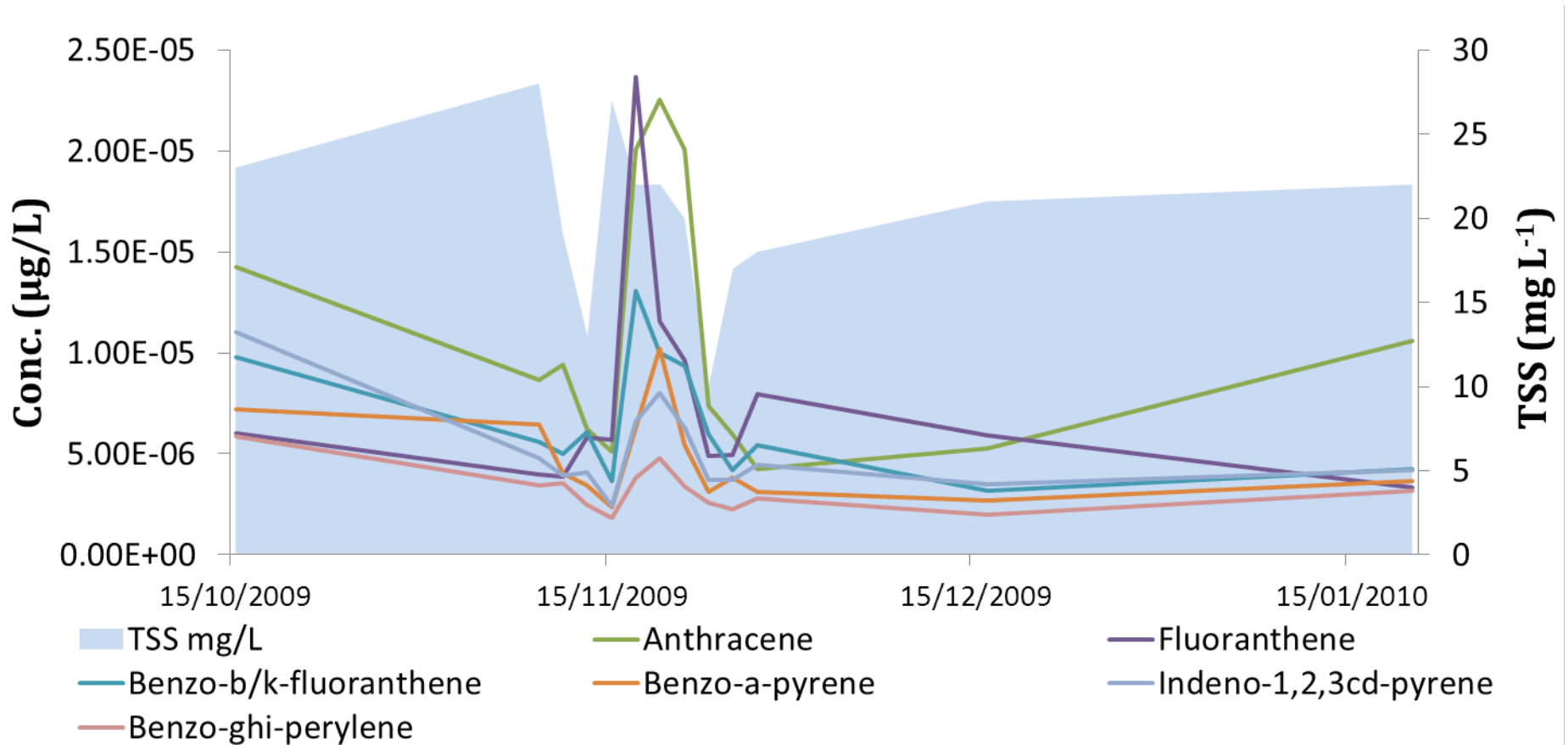




# Rainfall and Total Suspended Solids



# Total Suspended Solids and PAHs



# Summary of Results

- All 9 sites over the sampling period showed levels of PAHs.
- Few EQS exceedances.
- These are being investigated.
  
- For pesticide samples very high levels of Diuron and DEHP were noted.

# MODEL



# Work Overview

- Identified the major factors leading to Priority Pollutant (PP) loading from WWTPs
- Integrated these factors & conceptualised them in a basic conceptual model.
- Available data sources were identified for the major PP loading risk factors.
- Through a combination of quantitative data collation and qualitative risk assessment, risk databases were compiled for major sources.

# Study Approach

- Nine catchments, ranging in size, physical characteristics, industrial contributions, treatment levels
  - Data collated on potential sources (e.g. industry) and risk factors (e.g. combined drainage) for each catchment
  - Literature compiled on source magnitudes and WWTP removal efficiencies
  - Investigated associations between meteorological or physico-chemical parameters and PS conc. / loads
  - Devised risk index for high PS in effluent (across catchments, over time)

# Risk factor for PP loading from licensed installations...

Three major licence types were identified to be of relevance to PP loading of sewers:

1. Local Authority (LA) discharge licences;
2. EPA IPPC discharge licences;
3. EPA Waste licences

# ...Risk factor for PP loading from licensed installations

A basic risk ranking scheme was derived based on the type and scale of licensed activity discharging into the sewer network.





# Risk Scale

Risk ranking	Description
	(High possibility of...)
0	No loading
1	Light loading
2	Significant loading
3	Substantial loading
4	Heavy loading



For the model, loading risk is assumed to be exponentially related to this basic risk ranking (largest sources orders of magnitude larger than smallest sources).

# Licensed Risk...

"Typical" risk factors applied to licensed sites. For IPPC and waste sites, risk factors were site dependent (based on licence info). No direct input if no licence conditions for sewer release (some sites release direct to waters)										
ACTIVITY		DIRECT INPUT				RUNOFF RISK				
		PAH	VOC	Metals	Pest.	PAH	VOC	Metals	Pest.	
IPPC	Chemicals	2	4	2	2	1	1	1	0	
	Food & Drink	2	1	2	0	1	1	1	0	
	Metals	2	2	4	0	1	1	1	0	
	Minerals Fibre Glass	2	2	4	0	1	1	1	0	
	Power Generation	NA	NA	NA	NA	4	3	3	0	
	Surface Coatings	2	4	2	0	1	1	1	0	
	Wood Paper Textiles	NA	NA	NA	NA	3	3	2	0	
Waste	Hazardous Waste	3	3	3	3	2	2	2	2	
	Integrated Waste Management	2	2	2	1	2	2	2	2	
	Landfill	4	4	4	4	NA	NA	NA	NA	
	Materials Recovery Facility	2	2	2	1	2	2	2	2	
	Waste Transfer Facility	3	3	3	3	2	2	2	2	

# Overall Summary

- Data continuously updated.
- Gaps in knowledge.
- Further work to be carried out.

# Further Work

- Total suspended solids
- Final sample analysis
- Gather external data
- Data analysis
- Populate model

# Acknowledgements

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