Development of a Risk Based Model for use in Water Quality Monitoring

---

By

Lisa Jones B.Sc. (Hons.)

A thesis submitted to Dublin City University in partial fulfilment of the requirements for the award of

Doctor of Philosophy

Supervisor: Prof. Fiona Regan
Head of School: Prof. Conor Long
School of Chemical Sciences
Dublin City University

2012

Authors Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: ____________________(Lisa Jones)

ID No.: 58104330

Date: September 19th, 2012

ABSTRACT

Modelling has recently emerged as an effective and efficient tool in the area of water quality monitoring with new models taking in vast quantities of data and facilitating the development of more targeted water monitoring programs. With the Water Framework Directive demanding that monitoring requirements for a list of priority substances be met, achieving ‘good’ status in all water bodies by 2015, there is a strong need for improved monitoring programmes.

In order to improve future monitoring programmes by making the process more ‘targeted’ a simple risk-based model for the occurrence of priority substances in wastewater treatment plant effluent was devised.

This model was developed through the collection of an extensive list of documents relating to priority substances emission factors. These included wastewater treatment licence applications, trade effluent licences, traffic data, rainfall data and census data. It was found that by relating data from each of these sources to historic occurrence data it was possible to conceptualise and develop to a model of risk of occurrence of priority substances. Validation of this model was carried out using data from a 24 month sampling plan at 9 sites in two counties in Ireland.

This work has allowed for the compilation of a large dataset of emission factor and priority substance occurrence in Ireland where none previously existed. For the first time a risk-based model has been developed for Irish wastewater treatment plant effluents. Together the model and dataset can be used by policy makers and inform the development of future priority substance monitoring programmes.

Glossary

Acronym	*Definition*
ACN	Acetonitrile
APHA	American Public Health Association
AMPA	Aminomethylphosphonic acid
AADT	Annual average distance travelled
AA EQS	Annual average environmental quality standard
AER	Annual Environmental Report
AAS	Atomic absorption spectroscopy
AED	Atomic emission detection
BG	Ballincollig
BN	Bandon
BOD	Biological oxygen demand
CE	Capillary electrophoresis
CSO	Central Statistics Office
CE	Charleville
CAS number	Chemical abstracts service registry number
COD	Chemical oxygen demand
CY	Clonakilty
CVAAS	Cold vapour atomic absorption spectrometry
CIS	Common Implementation Strategy
CIT	Cork Institute of Technology
DEHP	Di(2-ethylhexyl)phthalate
DDT	Dichlorodiphenyltrichloroethane
DAD	Diode array detection
DWF	Dry weather flow
DCU	Dublin City University
EF	Effluent factors; These values are calculated as the inverse of removal factors which are used for direct multiplication with loading factors.
ECD	Electron capture detection
EM	Emission factors – sources of priority substances in a catchment, i.e runoff, trade effluent, etc.
EI	Electron impact
ESI	Electrospray ionisation
ETAAS	Electrothermal Atomic Absorption Spectrometry
EPA	Environmental Protection Agency
EQS	Environmental quality standard
EC	European Commission

EEC	European economic community
EU	European Union
FY	Fermoy
FAAS	Flame atomic absorption spectroscopy
FID	Flame ionization detector
FPD	Flame photometric detection
FLD	Fluorescence detection
GC	Gas chromatography
GCMS	Gas chromatography mass spectrometry
GIS	Geographic information system
GFAAS	Graphite furnace atomic absorption spectroscopy
HCV	Heavy Commercial Vehicle
HPLC	High performance liquid chromatography
HGAAS	Hydride Generation Atomic Absorption Spectrometry
ICP	Inductively coupled plasma
ICPAES	Inductively coupled plasma atomic emission spectroscopy
ICPMS	Inductively coupled plasma mass spectroscopy
ICPOES	Inductively coupled plasma optical emission spectrometry
IDA	Industrial development authority
IPPC	Integrated Pollution Prevention and Control
IPA	Isopropanol
LOD	Limit of detection
LOQ	Limit of quantitation
LC	Liquid chromatography
LCMS	Liquid chromatography mass spectrometry
LLE	Liquid-liquid extraction
MW	Mallow
MATLAB	Matrix Laboratory (computing software)
MAC EQS	Maximum allowable concentration environmental quality standard
MeOH	Methanol
MW	Molecular weight
NRA	National Roads Authority
NPD	Nitrogen-phosphorous detection
ND	Not detected
NR	Nutrient removal
PFT	Picket fence thickener
PAH	Polycyclic aromatic hydrocarbon
PS-DVB	Polystyrene divinyl-benzene
PTFE	Polytetrafluoroethylene
P.E.	Population equivalent

PDP	Preceeding dry period
PS	Priority substance
QGIS	Quantum GIS - Open Source Geographic Information System
QFAAS	Quartz Furnace Atomic Absorption Spectrometry
RAS	Return activated sludge
RF	Risk factor – value indicating the associated risk of occurrence of a priority substance under certain conditions.
RY	Ringaskiddy
RD	Ringsend
RBD	River basin district
SEPA	Scottish environmental protection agency
SIM	Selective ion monitoring
SBR	Sequencing batch reactor
SPE	Solid phase extraction
SOP	Standard operating procedure
S.I.	Statutory Instrument
SS	Suspended solids
SD	Swords
TSD	Thermionic Sensitive Detection
TIC	Total ion chromatograph
TSS	Total suspended solids
TBT	Tributyltin
UV	Ultra-violet
VKT	Vehicles kilometre travelled
VOC	Volatile organic compound
WAS	Waste activated sludge
WW	Wastewater
WWTP	Wastewater treatment plant
WFD	Water Framework Directive
WWF	Wet weather flow

ACKNOWLEDGEMENTS

I would like to firstly acknowledge the funding and support provided by the EPA as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme, financed by the Irish Government under the National Development Plan 2007–2013.
I can't thank my supervisor, Prof. Fiona Regan, enough for her guidance and encouragement. This would not have been possible if not for her.

I wish to extend my gratitude to the technicians and my fellow researchers in the School of Chemical Sciences at DCU who have provided invaluable support and assistance over the course of this project, there are too many of you to name but you know who you are. Thank you to our project partners in CIT and to Antoin and Dave for their help, work and advice.

A heartfelt thanks to the most supportive and patient lab/house-mates, and more importantly friends, Chaps, Amy, Louise, Tony, Tim, and Rachel. I couldn't have been luckier than when I met you all. We've had many teas and chats together and will hopefully have many more. Finally a very personal thank you to my family, my mom, dad, Rach and Garry who each contributed their own special brand of love and support without which I would be nowhere. Thank you.

TABLE OF CONTENTS

List of Figures

List of Tables

1. Introduction

1.1 EU Water Framework Directive

The pollution of water by chemicals and other pollutants affects all life on Earth as habitats and ecosystems are disturbed, and biodiversity is reduced. There are many sources of pollutants in water, including agriculture, industry, transportation and incineration (Lepom, Brown *et al.* 2009). Water has also been used for many years as a medium of waste discharge (Kocasoy, Mutlu *et al.* 2008). Water pollutants can be transported over long distances, may be found in remote areas, and can be found in the water many years after the substance has been banned (Lepom, Brown *et al.* 2009). As society grows and becomes more affluent an increasing number of pollutants and chemicals are released into the atmosphere and water (Kullenberg 1999).

Since the start of the new millennium more and more legislation has been put in place to try and counteract the dramatic affects our activities are having on the world around us and the pursuit for cleaner air, water and fuels is now of paramount importance. Although many efforts had been made already in the area of environmental policy a significant step towards a cleaner environment was taken in October 2000 when the European Parliament established the Water Framework Directive (WFD) (European Parliament 2000). This document acts as a single piece of legislation that 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 (Irish EPA 2006). The WFD also 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 (European Parliament 20 November 2001). In doing so the priority pollutants were legally defined as ‘substances identified in accordance with Article 16 (2) and listed in Annex X’ of the WFD and were selected on the basis of ‘their significant risk to or via the aquatic environment’ using a scientifically based methodology.

The amendment (European Parliament 20 November 2001) also states that ‘in accordance with Article 1 (c) of Directive 2000/60/EC, the future reviews of the list of priority substances under Article 16 (4) of that Directive will contribute to the cessation of emissions, discharges and losses of all hazardous substances by 2020 by progressively adding further substances to the list.’ As such, the list of priority substances was expanded to contain 41 substances in 2006 (Irish EPA 2006). This list was further expanded to contain 25 priority hazardous substances or groups of substances which are defined as ‘substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern (Irish EPA 2006).

The levels of pollutants present in water bodies are most commonly judged against set environmental quality standards (EQSs) that vary among different countries. 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. Directive 2008/105/EC (European Parliament 2008) and S.I. 272 of 2009 (European Parliament 2009) define the latest EQS values for surface waters across Europe. The EU WFD was transposed into Irish Law in 2003, (Irish EPA 2006) and as such these EQS values now form the basis of priority substance water monitoring in Ireland.

1.2 Priority and Hazardous Substances

The list of priority pollutants was defined by Decision No. 2455/2001/EC (of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC) with the selection of priority pollutants being made 'on the basis of their significant risk to or via the aquatic environment' using a scientifically based methodology introduced in Article 16 (2) of Directive 2000/60/EC (European Parliament 2000).

With regard to the control of priority pollutants, Decision No. 2455/2001/EC states that 'specific measures must be adopted at Community level against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, including such risks to waters used for the abstraction of drinking water.' These measures are aimed at the progressive reduction of priority pollutants, with the ultimate aim of 'achieving concentrations in the marine environment approaching background values for naturally occurring substances and close to zero for man-made synthetic substances.' Therefore the list of priority substances, including the priority hazardous substances, was established as Annex X to Directive 2000/60/EC (European Parliament 2000).
It must also be noted that special rules apply to certain compounds that are naturally occurring, where complete removal or cessation would be impossible; in these cases 'measures should aim at the cessation of emissions, discharges and losses into water of those priority hazardous substances which derive from human activities.'

Finally, Decision No. 2455/2001/EC also states, 'In accordance with Article 1(c) of Directive 2000/60/EC, the future reviews of the list of priority substances under Article 16 (4) of that Directive will contribute to the cessation of emissions, discharges and losses of all hazardous substances by 2020 by progressively adding further substances to the list' as shown in Table 1-1.

Table 1-1 Annex X - List of priority substances in the field of water policy (European Parliament 2000).

	CAS Number (^{1})	*Name of Priority Substance*
(1)	15972-60-8	Alachlor
(2)	120-12-7	Anthracene
(3)	1912-24-9	Atrazine
(4)	71-43-2	Benzene
(5)	N/a	Brominated diphenylethers
(6)	7440-43-9	Cadmium and its compounds
(7)	85535-84-8	$C_{10,13}$-chloralkanes
(8)	470-90-6	Chlorfenvinphos
(9)	2921-88-2	Chlorpyrifos
(10)	107-06-2	1,2-Dichloroethane
(11)	75-09-2	Dichloromethane
(12)	117-81-7	Di(2-ethylhexyl)phthalate (DEHP)
(13)	330-54-1	Diuron
(14)	115-29-7	Endosulfan
	959-98-8	(alpha-Endosulfan)
(15)	206-44-0	Fluoranthene
(16)	118-74-1	Hexachlorobenzene
(17)	87-68-3	Hexachlorobutadiene
(18)	608-73-1	Hexachlorocyclohexane
	58-89-9	(gamma-isomer, Lindane)
(19)	34123-59-6	Isoproturon
(20)	7439-92-1	Lead and its compounds
(21)	7439-97-6	Mercury and its compounds
(22)	91-20-3	Naphthalene
(23)	7440-02-0	Nickel and its compounds
(24)	25154-52-3	Nonylphenols
	104-40-5	(4-(para)-nonylphenol)
(25)	1806-26-4	Octylphenols
	140-66-9	(para-tert-octylphenol)
(26)	608-93-5	Pentachlorobenzene
(27)	87-86-5	Pentachlorophenol
(28)	N/a	Polyaromatic hydrocarbons
	50-32-8	(Benzo(a)pyrene),
	205-99-2	(Benzo(b)Fluoranthene),
	191-24-2	(Benzo(g,h,i)perylene),
	207-08-9	(Benzo(k)Fluoranthene),
	193-39-5	(Indeno(1,2,3-cd)pyrene)
(29)	122-34-9	Simazine

(30)	688-73-3	Tributyltin compounds
	36643-28-4	(Tributyltin-cation)
(31)	12002-48-1	Trichlorobenzenes
	120-82-1	(1,2,4-Trichlorobenzene)
(32)	67-66-3	Trichloromethane (Chloroform)
(33)	1582-09-8	Trifluralin

In October 2006 the Irish EPA published Version 1.0 of a Water Framework Directive Monitoring Programme(Irish EPA 2006). This document contained an Appendix 2.1, Surface Water Parameters and Groundwater Parameters for Dangerous Substances Monitoring, wherein the list of priority pollutants was expanded to contain a total of 41 priority substances, Table 1-2.

Table 1-2 Additions to original Priority Pollutant List by the Irish EPA (Irish EPA Oct. 2006)

	Name	*CAS Number*
34	DDT total	N/a
	para-para DDT	50-29-3
35	Aldrin	309-00-2
36	Endrin	60-57-1
37	Dieldrin	72-20-8
38	Isodrin	465-73-6
39	Carbon tetrachloride	56-23-5
40	Tetrachloroethylene	127-18-4
41	Trichloroethylene	79-01-6

Also included in Appendix 2.1 was a list of identified priority hazardous substances, which means substances identified in accordance with Article 16(3) and (6) for which measures have to be taken in accordance with Article 16(1) and (8), expanding the list of chemicals to 66, see Article 2.29 of the Water Framework Directive (2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy) defines hazardous substances as ‘substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern.’ The identification of hazardous substances, according to Decision No. 2455/2001/EC subsection (12), is said to require ‘consideration of the selection of substances of concern in relevant Community legislation regarding hazardous substances or relevant international agreements’ Table 1-3.

Table 1-3 Other Relevant Pollutants/Hazardous Substances chosen based on the WFD definition of a hazardous substance (Irish EPA Oct. 2006).

Number	*Substance*	*CAS Number*
42	Epichlorohydrin	106-89-8
43	Mecoprop	96-65-2
44	Pirimiphos-methyl	29232-93-7
45	Fenitrothion	122-14-5
46	Malathion	121-75-5
47	Epoxiconazole	135319-73-2
48	Glyphosate	1071-83-6
49	Nonylphenol ethoxylates	37340-60-6
50	Arsenic	7440-38-2
51	Zinc	7440-66-6
52	Copper	7440-50-8
53	Chromium	7440-47-3
54	Selenium	7782-49-2
55	Antimony	7440-36-0
56	Molybdenum	7439-98-7
57	Tin	7440-31-5
58	Barium	7440-39-3
59	Boron	7440-42-8
60	Vanadium	7440-62-2
61	Cobalt	7440-48-4
62	Fluoride	16984-48-8
63	Maneb	124727-38-2
64	Thiram	137-26-8
65	Mancozeb	8018'-01-7
66	Zineb	12122-67-7

Based on both usage and physic-chemical characteristics the priority and hazardous substances above can be classified under the headings pesticides, polycyclic aromatic hydrocarbons (PAHs), metals and trace elements and volatile organic compounds (VOCs). This study focussed on the first three groups.

1.2.1 PESTICIDES

The largest group of compounds indicated in the WFD are the pesticides which have been used increasingly as agriculture has developed e.g. in 2004 three agrochemical companies, which together control the global market for pesticides, each logged sales of over $4 billion (Weber, Smolka 2005) and in 2005 a study reports the industry sales of pesticides globally to be $31.19 billion (Galt 2008). It is as a result of this increase that widely used pesticides constitute important water pollutants. A pesticide can be defined as ‘any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest or weed’ and they can be classified based on their physico-chemical properties, mode of action, period of action, or by target. Pesticides are important in agriculture as the most cost-effective means of pest and weed control, however overuse, mishandling or poor storage of pesticides can lead to pollution of water bodies and the atmosphere (Bonnieux, Carpentier *et al.* 1998).

Pesticides enter river systems as either point sources or diffuse sources, with point sources being certain locations on the body of water (e.g. sewage plants, sewer overflows and losses due to bad management practices of farmers) and diffuse sources which are inputs along the water course (e.g. drain-flow, deposition, runoff, drift and contribution through groundwater). This makes pesticides especially relevant to water quality management and the regulation of environmental risk as they impede the achievement of a good water quality status (Holvoet, Seuntjens *et al.* 2007).

A study conducted by Pimentel *et al.* indicates that of the amount of pesticide applied to a crop less than 0.1% actually reaches the target pest (Pimentel 1995) the rest can enter water systems as either point source or diffuse pollution (Holvoet, Seuntjens *et al.* 2007). When applied to the soil pesticides spend varying amounts of time in this matrix depending on how strongly it is bound to the soil and how quickly the pesticide is degraded (Pimentel, Levitan 1986). Through the soil pesticides can leach into groundwater which then leads them to surface waters where they can remain for long periods of time e.g. a study showed that some organochlorine insecticides were detected in surface waters 20 years after they had been banned (Arias-Estévez, López-Periago *et al.* 2008, Larson, Capel *et al.* 1997).

Holvoet *et al.* outlined the processes of pesticides in surface water which are diverse as they can be transformed by complex photochemical, chemical and microbiological processes including photolysis, volatilisation, sedimentation, sorption/desorption, biotransformation, re-suspension, bio-accumulation and biodegradation (Holvoet, Seuntjens *et al.* 2007). These processes are important to understand as they dictate how pesticides will travel in the environment affecting soil, water and air pollution. Pesticide concentrations in environmental samples are usually low with tolerance limits of around 0.1 µg L^{-1} in drinking waters (Irace-Guigand, Aaron *et al.* 2004). In fact, the content of individual pesticides in drinking water is limited to 0.1 mg L^{-1} (EEC 1980) this means that detection limits (LOD) of 0.1 mg L^{-1} and lower must be achieved by the methodology used preferably lower than four times this value in order to reduce the possibility of false positive findings (Hernández, Sancho *et al.* 2001).

Table 1-4 Largest group of compounds listed as priority pollutants in the WFD, mainly pesticides.

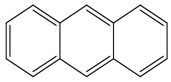
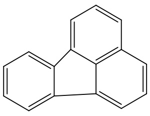
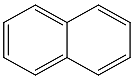
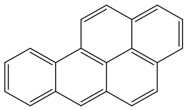
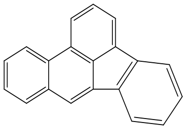
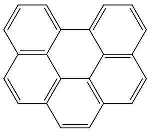
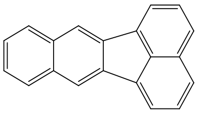
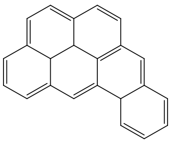
Pesticide	*MW (g)*	*GROUP*	*Function*
Alachlor	269.77	Chloroacetanilides	Herbicide
Aldrin	364.91	Organochlorine	Insecticide
Atrazine	215.68	Triazine	Herbicide
Chlorfenvinphos	359.57	Organophosphorus	Insecticide
Chlorpyrifos	350.59	Organophosphate	Insecticide
DDT	354.49	Organochlorine	Insecticide
DEHP	390.54	Phthalate	Plasticiser
Dieldrin	380.91	Organochlorine	Insecticide
Diuron	233.09	Phenyl ureas	Herbicide
Endosulfan	406.93	Organochlorine	Insecticide and Acaricide
Endrin	380.91	Organochlorine	Insecticide and Rodenticide
Epichlorohydrin	92.53	Organochlorine and Epoxide	Glycerol and epoxy resins synthesis
Fenitrothion	277.2	Organophosphate	Insecticide
Glyphosate	169.08	Organophosphate	Herbicide
Hexachlorobenzene	284.8	Chlorocarbon	Fungicide
Hexachlorobutadiene	260.76	Chlorinated aliphatic diene	Solvent
Isodrin	364.91	Organochlorine	Insecticide
Isoproturon	206.28	Phenyl ureas	Herbicide
Lindane	290.83	Organochlorine	Insecticide and Rodenticide
Malathion	330.36	Organophosphorus	Insecticide
Mancozeb	266.31	Dithiocarbamate	Fungicide
Maneb	265.3	Dithiocarbamate	Fungicide
Mecoprop	214.65	Phenoxy acids	Herbicide
Nonylphenol	220.35	Polyalkyloxy Compound	Adjuvant/surfactant
Pentachlorobenzene	250.34	Chlorinated aromatic hydrocarbon	Industrial
Pirimiphos Methyl	305.3	Organophosphorus	Insecticide
Simazine	201.66	Triazine	Herbicide
TBT	291.06	Organotin	Antifoulant, Fungicide
Thiram	240.43	Dithiocarbamate	Fungicide
Trichlorobenzene	181.45	Chlorocarbon	Solvent
Trichloroethylene	131.39	Chlorocarbon	Solvent
Trifluralin	335.28	Dinitroanilines	Herbicide
Zineb	275.74	Dithiocarbamate	Fungicide

1.2.2 POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Polycyclic aromatic hydrocarbons (PAHs) are a group of both naturally occurring and man-made chemicals which exist in over 100 different forms but are most commonly considered a group of 16 which have been chosen as priority pollutants for their carcinogenicity and mutagenicity (Graham, Allan *et al.* 2006, Countway, Dickhut *et al.* 2003, Berset, Ejem *et al.* 1999, Williamson, Petty *et al.* 2002). For the purpose of this study eight priority PAHs listed in Annex X of the EU Water Framework Directive (2000/60/EC) have been focussed upon, Table 1-5.

Also known as fused-ring aromatics they are a class of organic compounds that consist of two or more aromatic rings (Niimi, Palazzo 1986, Boehm 2005). The carcinogens and mutagens are the PAHs with four or more rings in their structures, due to their metabolic transformation capability (Luo, Mai *et al.* 2004). These are commonly found in airborne particulates, while the PAHs with two or three rings are lighter and are generally associated with the gas phase (Orecchio 2010).

Table 1-5 Properties of PAHs listed as Priority Pollutants in the WFD. Log K_{ow} is the octanol/water partition coefficient value which indicates the solubility of the chemical. Log $K_{ow =}$ (Nagpal 1993).

Priority PAH	*Molecular Weight*	*Molecular Formula*	*Structure*	Log K_{ow}
Anthracene	178.23	$C_{14}H_{10}$		4.5
Fluoranthene	202.25	$C_{16}H_{10}$		4.9
Naphthalene	128.17	$C_{10}H_8$		3.37
Benzo(a)pyrene	252.31	$C_{20}H_{12}$		6.06
Benzo(b)fluoranthene	252.31	$C_{20}H_{12}$		6.04
Benzo(g,h,i)perylene	276.33	$C_{22}H_{12}$		6.78
Benzo(k)fluoranthene	252.31	$C_{20}H_{12}$		6.21
Indeno (1,2,3-cd)pyrene	276.33	$C_{22}H_{12}$		6.58

(Ravindra, Sokhi and Van Grieken 2008) include domestic, mobile, industrial, agricultural, and natural as the five major emission sources of PAHs. The main sources of PAHs in the environment are anthropogenic as they are by-products of incomplete combustion, fossil fuel combustion, coal gasification and liquification processes, waste incineration, petroleum cracking, and in the production of coke, coal tar pitch, carbon black, and asphalt (Lebo, Zajicek *et al.* 1992), (Wilcke 2000), (Budzinski, Garrigues *et al.* 1993). PAH's may also be released into marine environments via sewage, industrial wastewater, road runoff and street dust, and through oil spills and ship traffic due to their presence in un-combusted petroleum (Countway, Dickhut *et al.* 2003), (Graham, Allan *et al.* 2006). A study carried out by Lebo, Zajicek *et al.* (1992) estimated that 230,000 metric tons/year of PAHs enter the environment globally from oil and petroleum spills, direct discharges from industry and domestic sources, transportation and biosynthesis.

PAHs are dangerous as pollutants as they are highly persistent in the environment due to their physical and chemical stability, resistance to degradation at high temperatures and their volatility (Berset, Ejem *et al.* 1999, Abad, Martínez *et al.* 2005). PAHs enter the environment mainly in the gas phase and can remain in the atmosphere in both gas and particle phases (Garban, Blanchoud *et al.* 2002), (Jaffrezo, Masclet *et al.* 1993). The particles can spend weeks in the atmosphere before being deposited on land or in water (Sanders, Jones *et al.* 1993, Orecchio 2007) while the more volatile gases take longer before deposition occurs. The particles that are deposited on the water, although not very water soluble, (Harrison, Perry *et al.* 1975) pollute the water and become embedded in sediments (Sanders, Jones *et al.* 1993). Some particles become trapped in the soil, which acts as a reservoir until they are volatilised from the soil and redistributed in the environment where they can harm both humans and the environment (Abad, Martínez *et al.* 2005).

1.2.3 METALS AND TRACE ELEMENTS

Metals and trace elements are found naturally occurring in the environment and as constituents of the earth's crust; (Naumann 1994, Terytze, Kördel *et al.* 1995) they have many uses, with metals such as iron, copper and zinc widely used in industry. Elevated levels of trace elements and metals in the environment are also as a result of human activities (municipal-, residential- and traffic- related) (Alloway 1995, Thornton 1991). These pollutants are included on the list of priority pollutants as they can accumulate in the environment and can lead to toxic effects in humans, plants and animals alike, (Kavcar, Sofuoglu *et al.* 2009) however to date there is no specific methodology to define the ecological danger of metals and the maximum allowable concentration values for some trace elements (in water) is a cause for debate and the subject of research in a number of countries (Tamasi, Cini 2004).

These pollutants can often take the form of particulates in the atmosphere that can be airborne and be dispersed over large areas (Lawlor, Tipping 2003) or can be deposited on the planet's surface (Duzgoren-Aydin 2007, Sabin, Lim *et al.* 2006) where they can accumulate in water, plants and topsoil and remain in the environment for a long time (Li, Poon *et al.* 2001). As well as polluting the environment metals interfere with the water treatment process, as metal-containing water is more difficult to recycle (Polat, Erdogan 2007).

Table 1-6 Properties of metals and trace elements listed as priority pollutants in the WFD

CAS number	*Substance*	*Molecular Weight (g)*	*Mol. formula*
7439-92-1	Lead and its compounds	207.2	Pb
7439-97-6	Mercury and its compounds	200.59	Hg
7440-02-0	Nickel and its compounds	58.69	Ni
688-73-3	Tributyltin compounds	291.06	$[CH_3(CH_2)_3]_3SnH$
7440-38-2	Arsenic	74.92	As
7440-66-6	Zinc	65.39	Zn
7440-50-8	Copper	63.54	Cu
7440-47-3	Chromium	52	Cr
7440-49-2	Selenium	78.96	Se
7440-36-0	Antimony	121.75	Sb
7439-98-7	Molybdenum	95.94	Mo
7440-31-5	Tin	118.69	Sn
7440-48-4	Cobalt	58.93	Co
7440-62-2	Vanadium	50.94	V
7440-39-3	Barium	137.34	Ba
7440-42-8	Boron	10.81	B
16984-48-8	Fluoride	18.9	F

1.3 Monitoring Requirements of the WFD

In Ireland the national regulations implementing the WFD are the European Communities (Water Policy) Regulations 2003 (S.I. No. 722 of 2003). According to Article 10 (1) of these regulations the Environmental Protection Agency (EPA) shall prepare a water status-monitoring programme in order to provide a clear and comprehensive overview of water status within each of the seven river basin districts in the State (in accordance with articles 7 (1) and 8 of the directive). River Basin Districts (RBDs) consist of river catchments or groups of catchments. The EPA specifies the authorities by which the monitoring is carried out. The programme sets out the 'nature, frequency and extent' of the monitoring to be implemented, to be in operation by 22 December 2006. For the general monitoring of water quality this programme will replace existing national programmes.

The overall objectives of the monitoring programme are to achieve the objectives of the WFD, as mentioned above. Thus, the monitoring programme:

- Covers groundwater and surface waters: rivers, lakes, coastal and transitional waters; Includes special sub-programmes for the protected areas included in the Register of Protected Areas as defined in Article 6 of the WFD:
- Includes artificial and heavily modified water bodies and these, apart from canals monitoring programs (rivers, lakes or transitional and coastal waters).

In the WFD and Common Implementation Strategy (CIS) guidance documents three types of monitoring are specified and described. These include: surveillance monitoring, operational monitoring, and investigative monitoring.

The monitoring of surface waters is more detailed than for groundwater due to the requirement to assess biological and hydro-morphological elements in surface waters to allow for the assignation of ecological status.

1.3.1 SURVEILLANCE MONITORING

The objectives of Surveillance monitoring are:

- To supplement and validate the impact assessment procedure detailed in Annex II of the Directive;
- The efficient and effective design of future monitoring programmed,
- The assessment of long-term changes in natural conditions, and
- The assessment of long-term changes resulting from widespread anthropogenic activity.

According to the WFD, Surveillance Monitoring will be carried out at each monitoring site for a one year period, a period which will be covered by a river basin management plan for: parameters indicative of all biological quality elements, hydro-morphological elements, and general physico-chemical qualities, priority list pollutants which are discharged into the river basin or sub-basin, and other pollutants discharged in significant quantities in the river basin or sub-basin.

1.3.2 INVESTIGATIVE MONITORING

Ireland's National Dangerous Substances Expert Group developed a list of priority action, candidate relevant pollutant and candidate general component substances for surface waters in Ireland in 2003 and 2004. They also designed a substances screening programme as part of the implementation of the WFD. This led to a national substances screening monitoring programme contract being procured by Carlow County Council, analysing to detect the presence of over 200 substances in water, sediment and biota. Samples were collected monthly at over 30 sites across Ireland by the South Eastern River Basin District Monitoring Team. The sampling and analysis were conducted between May 2005 and October 2006. The aim was to help inform the design of the WFD dangerous substances monitoring programme. The results were evaluated by the Dangerous Substances Expert Group in order to refine the candidate lists and to identify the WFD Monitoring Programme for the first River Basin Management Plan (2007-2009).

The purpose of the screening monitoring programme was to help inform the design of the WFD dangerous substances monitoring programme which covered priority substances and relevant pollutants. Following the evaluation of results, a number of recommendations were made, including:

(i) The identification of 41 priority action substances to be included in the monitoring programme, with monthly sampling of surface waters for one year during the plan cycle,
(ii) At each identified dangerous substances monitoring site all priority action substances should be monitored,
(iii) Standards for priority action substances are being progressed by the EU supported by a Programme of Measures and Standards Study on Environmental Standards,
(iv) All 25 substances detected in significant concentrations during the screening programme (43 relevant pollutant and general component substances) should be included in the monitoring programme with quarterly sampling for one year during the plan cycle,
(v) The sampling programme will initially be organised by the EPA and Marine Institute with much of the analysis being outsourced,
(vi) The monitoring network of dangerous substances for the second WFD cycle will be further developed,
(vii) Selected relevant pollutant and general component substances should be sampled at dangerous substances monitoring sites on the basis of the site's upstream activities, and
(viii) The first cycle WFD Dangerous Substances Monitoring Programme will include all 188 river surveillance network sites and all 25 transitional and 12 coastal surveillance network sites, this covers the range of geographical areas, types and status (Irish EPA 2006).

Section 58 of EPA Act of 1992 states that the EPA is required to collect and verify monitoring results for all water supplies in Ireland covered by the Drinking Water Regulations. In order to verify the information that has been submitted results must be collected on an annual basis (from local authorities) and audits carried out on selected local authorities. As of March 2007 new powers and responsibilities have been assigned to the EPA in the area of drinking water under the new Drinking Water Regulations published by the Department of Environment, Heritage and Local Government.

In Ireland the safety of water supplies is determined by comparing the results of over 250,000 monitoring tests carried out on 945 public water supplies, 671 public group water schemes, 497 private group water schemes and 1284 small private supplies with the drinking water standards' by the Irish EPA. In Ireland, surface waters account for 81.9% of the drinking water, followed by groundwater (10.3%) and springs (7.8%) (Hayes,N.,Page,D.,Sweeney,L.,O'Leary,G. 2011).

1.4 Modelling and the WFD

The EQS directive (2008/105/EC) requires the concentrations of specific pollutants to not exceed set thresholds. The targeted monitoring of these pollutants could confirm compliance to EQSs with a high degree of certainty, which is why modelling would allow monitoring authorities to know when threshold breaches are most likely to occur. The EU WFD was transposed into Irish Law in 2003 (Irish EPA 2006) and as such these EQS values now form the basis of priority substance water monitoring in Ireland. In order for future monitoring programmes to allow us to meet the requirements established by the WFD the gaps in current knowledge must be identified and where information is lacking for accurate emission factor data for a priority substance or group of substances this must be gathered in order to produce truly representative sampling results at the end of any monitoring campaigns.

1.5 Conclusions

The aquatic environment including lakes, rivers, ground water estuaries and coastal zones, is vulnerable to changes induced by human activities. The WFD has listed a number of priority and hazardous substances with environmental quality standards in place to limit the occurrence of these pollutants in the environment. As new and emerging compounds are discovered and incorporated into legislation and as current EQS values are lowered the need for robust and reliable analytical methods, capable of reaching the necessary limits of detection, becomes more pronounced. It is also important that strict standard operating procedures are in place and adhered to for the handling, storage and analysis of samples collected in order to ensure the integrity of the samples is preserved and that analytical results are of the highest standard.

The WFD aims to achieve and ensure “good quality status” of all European water bodies by 2015 and in setting such a goal poses a huge challenge in monitoring activities. While the monitoring methods required are not specified the widely accepted method involves grab sampling, which is the currently accepted method used for monitoring of priority pollutant chemicals in our waters. Grab sampling is expensive and labour intensive and it identifies compounds present at only a single point in time. Modelling is emerging as a useful tool for informing monitoring programs with large databases revealing gaps in current knowledge and highlighting areas for improvement.

The aim of this work is to use environmental modelling based on a wealth of data collected to inform future targeted monitoring programmes and thus enable Ireland to meet the WFD monitoring requirements. In this chapter available literature and statistical data that could be used to inform targeted PS monitoring strategies is collated. The focus is on readily available data relevant to major PS risk factors identified by conceptual modelling, and develop appropriate indicators. These indicators are applied to nine WWTP agglomerations currently being monitored in a PS study to predict the relative risk of elevated PS loading to receiving waters across agglomerations and over time.

1.6 Aims and Objectives

The aim of this thesis is to detail the creation of an index of emission factors, a computer model, based on both experimental data collected from the monitoring of priority pollutants in waste water treatment plant effluent and data compiled on sources of these pollutants in the environment. By monitoring both the emission factors and the actual levels of pollutants released a model is created which will facilitate more informed water quality monitoring programmes and will therefore help Ireland to meet European water quality deadlines and levels.

Main project objectives:

- To design and populate a risk based model for the occurrence of priority substances in wastewater;
- through the preparation of this model build a database of high quality information;
- to bring together many sources of relevant data on occurrence to one place;
- to develop simple methods for the extraction of priority substances in wastewater;
- to prepare standard operating procedures for the sampling handling, extraction and analysis of samples to meet WFD requirements;
- to improve on current methods for the analysis of priority substances and
- to produce a final simple model that can inform future monitoring programmes.

2. Site Selection and Waste Water Treatment Processes

2.1 Introduction

In Ireland, as in many other countries, wastewater is an issue as water that has not been adequately treated is being released back into the environment leading to increased pollution. There are currently around 529 wastewater treatment facilities in the country (Monaghan, Shannon *et al.* 2012). A recent report by the Irish EPA stated that for an average population equivalent of 4.97 million 1% of wastewater received primary treatment, 78% received secondary treatment (with 15% also receiving nutrient reduction), and 6% of wastewater was untreated (Monaghan, Shannon *et al.* 2012). In Ireland the main piece of legislation governing urban wastewater treatment is Council Directive 91/271/EEC which was adopted on 21 May 1991. This directive aims to counter the adverse effects of urban and industrial wastewater discharges through the principles of planning, regulation, monitoring and information and reporting on these discharges (EEC 1991).

The wastewater treatment process generally involves primary-, secondary- and sometimes tertiary treatment (Radjenovic, Petrovic *et al.* 2007, Ren 2004). The primary treatment phase incorporates the processes of screening, grit, fat, oil and grease removal, and settlement, with the overall aim being the removal of solids from the wastewater stream. After this stage it is said that 50 – 70% of suspended solids have now been removed, and that biological oxygen demand, BOD, and bacterial count have been reduced by 20 – 50% and 25 – 75%, respectively (Irish EPA 1997). Secondary treatment can follow and here the wastewater is subject to biological treatment by microorganisms allowing organic matter removal and nitrification of the wastewater thus reducing final nutrient levels in the wastewater (Radjenovic, Petrovic *et al.* 2007, Irish EPA 1997). This is followed by further settlement of the wastewater. Finally, wastewater may be exposed to a tertiary level of treatment, usually chlorination or UV treatment, (Radjenovic, Petrovic *et al.* 2007) which aims to disinfect the wastewater, removing dissolved organics and inorganics, and suspended solids before final outflow (Ren 2004). It has been shown that when a waste water treatment plant, WWTP, is functioning properly 90 – 95% of pollutants can be eliminated before reintroduction of the water to the environment (Li, Jiku *et al.* 2000).

Nutrient removal refers to the reduction of phosphorous and/or total nitrogen levels. This is required where the receiving water body is deemed sufficiently “sensitive” - e.g. waters susceptible to eutrophication. Since some algae can fix atmospheric nitrogen it is generally accepted that phosphorus is the limiting nutrient in water. Phosphates occur in sewage effluents due partly to human excretion and partly to their use in synthetic detergents. The principal means of phosphorus removal is chemical precipitation, though removal can be incorporated into primary or secondary treatment or may be added as a tertiary process. In raw wastewater the predominant forms of nitrogen are organic nitrogen and ammonia. The most common processes for removing ammonia are air stripping and biological nitrification/de-nitrification (Cork County Council 2008).

2.2 Aims and Objectives

The aim of this chapter is to describe the selection of sites and the development of a sampling plan which would cover a wide scope and encompass the characteristics of the majority of WWTP sites across Ireland. This proved a challenge as varying levels of treatment, population equivalents and source inputs need to be represented in the final model while also providing temporal variation data of high quality to populate the model.

The objectives of this work include:

- providing a rationale for the selection of the nine sites chosen in this study;
- reviewing each of the sites and the processes at work in each plant;
- outlining the sampling plan to be adopted.

2.3 Site Selections and Overview

In order to make the final model of occurrence of priority pollutants in wastewater as comprehensive as possible nine WWTPs in two different counties, Cork and Dublin, were chosen. The rationale was to examine two well-populated counties, one with a high population density and industrial input and the other with a more agricultural input.

Two large WWTPs in Dublin, Ringsend and Swords, and seven smaller scale WWTPs in Cork were finally chosen. Each site caters for different population equivalents from close to 3000 in Charleville to over 2.5 million in Ringsend. Different treatment processes are employed at the different plants and each plant serves varying levels of domestic, industrial and agricultural inputs. Table 2-1 gives an overview of the WWTPs included in this study, the population equivalents they serve, the levels and types of treatments that are provided and the receiving waters of the treated effluent most of which have been deemed ‘sensitive’ by the EPA.

As this project is a large-scale collaboration involving groups in two counties, tasks were divided with Cork IT coordinating sampling efforts with Cork County Council, and DCU coordinating with Fingal County Council for samples from Swords WWTP, and Dublin City Council and Celtic Anglian Water for samples from Ringsend WWTP, as well as managing the project and collaborating with the group in Cork.

Table 2-1 Overview of the WWTPs in this study.

WWTP and Code	*Treatment*	*Type of Treatment*	*Agglom. PE*	*Plant PE*	*Area (Ha)*	*Receiving Waters*
Ballincollig BG	Secondary	PS, SS, AS (Aeration Basin)	16,339	15,000	760	Freshwater (R)
Bandon BN	Secondary	PS, AS (OD)	8178	20,000	458	Freshwater (R)
Charleville CE	Secondary	PS, SS, AS (OD)	2,984	6,415	274	Freshwater (R)
Clonakilty CY	Secondary	PS, SS, AS (OD)	7,500 - 15,000	15,000	750	Estuarine
Fermoy FY	Secondary, NR	PS, SS, AS (OD; A-A-AT) PR	5,800	12,960	394	Freshwater (R)
Mallow MW	Secondary, NR	PS, SS, AS (A-A-AT) PR	7,091	12,000	595	Freshwater (R)
Ringaskiddy RY	None	None	14,864	0	967	Estuarine
Ringsend RD	Tertiary	PS, SS, AS (Sequencing Batch Reactors) U.V Disinfection	2,870,333	1,640,000	26,728	Estuarine
Swords SD	Secondary	PS, SS, AS (A-A-AT)	50,000	60,000	2,673	Estuarine

Table legend: Area = Area of catchment. PE = Population equivalent. (R) = River. PS = Primary settlement. SS = Secondary Settlement. AS = Activated Sludge. PR = Phosphorous removal. OD = Oxidation ditches. A-A-AT = Anaerobic-, anoxic- and aeration tanks. This information was gathered from the EPA wastewater license applications of the respective WWTPs and from the EPA Urban Wastewater Report, 2007.

Note: Ringaskiddy is listed as having a plant population equivalent of zero due to the lack of treatment at this site. This site is located in an area with several pharmaceutical companies and acts as a combined pumping system for this catchment.

2.3.1 BALLINCOLLIG

Ballincollig, as a growing town within the Cork Metropolitan area, has shown an increasing population over recent censuses, with a population of 16,339 recorded in 2006 by the Central Statistics Office, CSO. The Ballincollig catchment, as shown in Figure 5-9, covers an area of 760 km. This site represents a high population which is an expanding town near Cork city with an agricultural hinterland. Contributions to the pollution load for the Ballincollig agglomeration vary with daily, weekly and seasonal producers of effluent, with the main sources being the local population, local industries, commercial and non-domestic users.

An old sewerage collection system originally linked a cavalry barracks to the north of the town discharging to the west. As the original village extended and developed into a town a new trunk sewer was laid. As new housing estates were built they discharged from the same trunk sewer in Poulavone. After the establishment of the WWTP in Ballincollig the sewer network was extended and pumping stations were established to facilitate transportation to the WWTP.

In 2006 an approximate non-domestic population equivalent of 8,200 was calculated, giving a present total pollution load of 24,542 (Cork County Council 2009), while the hydraulic capacity is now stated as 26,000 P.E., and the capacity of the plant for carbonaceous BOD removal is ~31,500PE (60g/h/d).

2.3.1.1 Overview

At the WWTP the sewage from local industries, collected via the public sewer, and domestic waste arrive, by means of a number of pipes, at an inlet chamber upstream of the inlet works. Table 2-2 gives a detailed overview of the specific treatment at the WWTP.

Table 2-2 Overview of Treatment Processes in operation at Ballincollig Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	Screening of wastewater arriving at the plant is through two mechanically raked coarse bar screens, 25 mm^3.
Primary	If the flow arriving at the plant exceeds 509 m^3/hr the system in place to handle the excess involves diversion, after screening, to the original Primary Settling Tanks in the 'old' part of the plant, then on the to the 'old' Humus tanks until the inlet flows have reduced, allowing for the diverted stream to be pumped back to the inlet. In the event of excess storm water there is also an overflow weir which discharges to the outfall pipe. Grit is then removed from the stream by three constant velocity grit channels, followed by a further fine screening step, 5 mm.
Secondary	Secondary treatment occurs when the wastewater flows to a Carousel-type activated sludge plant with a basin volume of approximately 9000 m^3. The mixed liquor settles in three circular radial flow clarifiers, 2 old clarifiers below ground level and a third 'new' clarifier above ground level, constructed in 2008. The settled sludge (RAS) from the 2 old clarifiers is returned to the aeration basin using 2 No. Archimedes screw pumps and 1 No. pump. The settled sludge (RAS) from the third clarifier is returned to the aeration basin by gravity. The excess sludge (WAS) is pumped to the picket fence thickener (PFT) where it settles and compacts. The floating scum on the clarifiers is removed via a scum box and is pumped to the inlet works. The thickened sludge is pumped from the bottom of the PFT to the centrifuge. The centrifuge dewaters and further thickens the sludge prior to off-site disposal.
Discharge	The treated effluent is discharged from the clarifiers via a weir to a chamber. From this chamber it flows to a manhole on the north east of the treatment plant site. From this manhole it is discharged to the river Lee via the outfall pipe. There are two composite samplers in the process; one at the inlet (flow proportional) and the other at the outlet chamber from the clarifiers that is time based (Cork County Council - Southern Division 2010).

2.3.2 BANDON

The WWTP in Bandon represents a low population and is located in Bandon southwest of Cork City, the plant was upgraded in 1993, designed to treat a P.E. of 20,000, and is currently treating a P.E. of 8,178. A combined sewerage system serves this agglomeration, with four pump stations within the catchment: O'Mahony Avenue and Bridge Lane are local pump stations; Watergate Street pump station pumps waste water flows from the north of the catchment across the river to Glaslinn Road pump station.

Preliminary treatment is provided at the Glaslinn Road pump station consisting of coarse screening, fine screening and grit removal. From Glaslinn Road wastewater is pumped to the WWTP (Cork County Council 2008). The primary discharge is the treated effluent from the WWTP which is discharged to the River Bandon via an open pipe at an average discharge volume of 2370 m^3/day. Secondary discharges flow to the River Bandon from the WWTP overflow.

2.3.2.1 Overview

Table 2-3 gives a complete overview of the treatment processes employed at Bandon WWTP.

Table 2-3 Overview of Treatment Processes in operation at Bandon Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	The preliminary treatment caters for flows of up to 480 L s^{-1} which includes coarse screening and fine screening to 5mm in a 'Screezer' unit which also incorporates screening dewatering and compaction. Grit removal is provided for flows up to 200 L s^{-1}. Screenings and grit are treated on site prior to disposal to landfill. Flows of 156 L s^{-1} are pumped to the WWTP for treatment and excess flows are discharged to the River Bandon.
Primary	The WWTP was constructed in two stages and operates as two parallel systems – a biological treatment plant with primary settlement and a percolating filter system was constructed in the 1960s and an extended aeration activated sludge plant with sludge thickening, partial stabilisation and dewatering facilities was constructed in 1993. Primary treatment comprises primary settlement in two horizontal flow settlement tanks operating in parallel.
Secondary	Settled sewage gravitates to a flow splitter chamber upstream of the secondary treatment system. Flows up to 3 DWF (75 L s^{-1}) pass forward to the secondary treatment system, an oxidation ditch. A phosphate reduction system was installed in 1993 however is not operational as the system depressed the pH of the waste water which affected biological activity. Supernatant liquors from a gravity sludge thickener and filtrate from a dewatering press are pumped to the oxidation ditch, where they combine with incoming waste water and receive full biological treatment with the main process stream. There is also a facility to enable these flows to be pumped to the primary settlement tank (Cork County Council 2008).

2.3.3 CHARLEVILLE

The treatment plant at Charleville is located in north Cork on the Limerick border and is designed to cater for a P.E. of up to 15,000 although the 2006 census quotes a population for Charleville of only 2,984. The industries in this agglomeration have separate WWTPs and for the most part do not contribute to the flow in the foul sewer system. The surface water in Charleville generally drains directly to the river, therefore not overloading the wastewater treatment plant.

Charleville Wastewater Treatment Works was constructed on a green field site in the town land of Ballincolly, to the north east of Charleville. The wastewater from Charleville town and environs (274 Ha) is collected through a pipe network and flows by gravity to the wastewater treatment plant in the town land of Ballincolly north–east of the town centre. The main source of emissions is the 600mm diameter discharge pipe carrying the treated effluent from the wastewater treatment plant to Charleville Stream. Charleville Stream flows along the eastern boundary of the treatment plant (Cork County Council 2008).

2.3.3.1 Overview

Flows from Charleville town and environs flow by gravity to the treatment plant in Ballincolly. A sludge return system is in operation to ensure an adequate level of mixed liquor suspended solids. The system is flexible enough to ensure that sludge can be returned from the clarifiers to the oxidation ditches and an adequate quantity of sludge can be pumped at all times. The mixed liquor produced from the aeration system enters secondary clarifiers for the purpose of settling sludge. The main treatment processes in operation at this WWTP are highlighted in Table 2-4.

Table 2-4 Overview of Treatment Processes in operation at Charleville Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	A screen located within the inlet flume removes larger inorganic solid material.
Primary	Following screening, the inlet flume allows 510 m^3/hr (6 DWF) to pass into the splitter chamber. An overflow is located in the inlet flume to the Charleville Stream.
Secondary	The secondary treatment process is based on activated sludge system. The aeration system at the plant is in the form of oxidation ditches. Each oxidation ditch is 4500 m^3 and contains 4 No. 7.0 m long rotors used to ensure that sludge remains in suspension at all times. From the ditches, the flow passes to the two clarifiers for the purpose of settling sludge. Each clarifier is circular (160 m^2) and equipped with a rotating bridge sludge scraper, inlet, scum and sludge draw-off pipes, sludge return pipe work, v-notch weir and a system to prevent scum entering the treated effluent. The wastewater treatment system has two separate process streams with provision to isolate each stream. At present only one stream of the treatment plant is in use, as flows have not necessitated the treatment plant to be used at full capacity.
Discharge	The treated effluent flows to the outlet flume and is then discharged to Charleville Stream through a 600 mm diameter outlet pipe. The liquid discharge from a sludge-thickening tank is returned to the oxidation ditch, and treated leachate is discharged to the main oxidation ditch and treated as regular foul water.

2.3.4 CLONAKILTY

Clonakilty was an interesting choice for this study as development has generally increased in recent years and there is high seasonal variation in population of this town due to tourism; a winter population of approximately 7,500 P.E., and a summer loading of 15,000 P.E. Aside from domestic inputs, the pollution load from this agglomeration arises from Shannonvale Chickens, Clona Milk Dairies, Irish Yoghurts, Hotels, schools, a hospital, an abbatoir, a technology park, etc. (Note: Shannonvale Chickens has its own treatment plant discharging treated effluent to the public sewer.)

The wastewater in Clonakilty and its environs is collected in a partially combined foul and surface water network consisting of both gravity and pumped systems. The central part of the town gravitates in the partially combined system to the two main pump stations of the scheme - Long Quay and Clarke Street. These then along with Inchydoney main pumping station pump directly to the WWTP. There are other pumping stations on the outskirts of the town (Cork County Council 2007).

2.3.4.1 Overview

The purpose of this plant is to remove solids and pollutant matter from sewage entering the works, rendering the treated effluent suitable for discharge to a watercourse. Grit and other materials are removed at the inlet works and an extended aeration process removes the main pollutant matter prior to discharge to the harbour, Table 2-5.

Table 2-5 Overview of Treatment Processes in operation at Clonakilty Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	A grit trap is currently in operation at the plant with a design flow capacity of 0 – 180 L s^{-1}, a grit classifier was also recently installed. This receives the grit from the grit trap and separates out the grit from other materials and conveys the relatively dry grit into an adjacent wheelie bin for removal to landfill. In 2000 a mechanically brushed screen and Lisep unit (Haigh Ace Inlet System) were installed. The largest model, 991, was installed in Clonakilty and has a maximum capacity of 100 L s^{-1}. Acting as an emergency bypass, a hand-operated penstock is located between the screen and the inlet flumes at the inlet works. This penstock leads to a backdrop manhole, which connects to the treatment plant outfall at the easterly end of the site allowing bypass of plant in emergency situations.
Secondary	After the screen outlet, the inlet channel splits into two channels 300 mm wide. These channels were designed for a flow capacity of 51 L s^{-1}. The divided flows are piped from here to the oxidation ditches. Extended aeration is by means of 2 No. racetrack type oxidation ditches with 4 No. rotors located midway along the length of each ditch as a means of aeration. These ditches were designed for a much lower BOD loading than the peak 15,000 P.E. that it serves in the summer. However, the plant was designed for a higher hydraulic load of 6 DWF, whereas now most plants are designed to take a hydraulic loading of 3 DWF. Recently a further floating aerator was introduced into each ditch in order to increase the amount of oxygen available for microorganisms to cater for the increased loading. The flow from the oxidation ditches is piped to the settling tanks. There are 2 No. circular hopper-bottomed settling tanks currently in operation as a means of secondary sedimentation. Sludge settles to the bottom of these tanks and is returned to the lifting wheel chambers.
Discharge	The supernatant liquid from the settling tanks is piped to the outlet channel. The 400 mm outlet channel collects the treated effluent from the settling tanks which then flows by gravity to the sea outfall.

2.3.5 FERMOY

The WWTP in Fermoy is located in the north-east of Cork City, on the banks of the River Blackwater. The Fermoy catchment serves a total area of 394 hectares. The domestic population of Fermoy has grown over the last three censuses with the most recent census figures showing the town of Fermoy and environs having a population in excess of 5,800. The Fermoy WWTP is designed for a population equivalent of 20,000 P.E. and BOD loading of 1,200 Kg/day. The wastewater in Fermoy is collected in a partially combined foul and separated foul sewage drainage network. The wastewater drains from the town on both sides of the Blackwater River; on the north side of the river wastewater drains to a pumping station at Rathealy Road, which is then pumped across Fermoy Bridge to the main sewer. The wastewater arising on the south side of the river drains directly to the WWTW.

The maximum hydraulic capacity of the Fermoy WWTP is 673 m^3/h (2.3 DWF). In order to cope with flows above 2.3 DWF, storm storage has been provided at the WWTW. The volume of storm storage at the WWTW is approximately 1,126 m^3. In the event that the storm water holding tanks are filled and the storm continues, the storm water tanks are operated as a pre-clarification tank without sludge removal. The overflow from the storm water storage tank is connected to the final effluent outlet pipe.

The nature and quantities of foreseeable emissions from the wastewater works into the receiving aqueous environment as well as identification of significant effects of the emissions on the environment. The final effluent is discharged into the Blackwater River. At design capacity the WWTW will discharge 7,140 m^3/day to the river (Cork County Council 2007).

2.3.5.1 Overview

Table 2-6 details a breakdown of the treatment processes in operation at Fermoy WWTP.

Table 2-6 Overview of Treatment Processes in operation at Fermoy Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	At the inlet pumps force the stream through 2 No. Mechanical screens with an aerated grit and grease removal system and grit classifier.
Primary	The existing WWTW were upgraded with an additional stream, therefore the flow is split after the wastewater passes through the inlet works with 40% of the flow diverted to the existing wastewater treatment stream. The remaining 60% is directed to a new treatment system.
Secondary	The existing stream has an aeration phase (2 No. Oxidation ditches with 4 No. Surface aerators), a secondary settlement phase and return activated sludge phase. The new stream has an anaerobic (1 No. Tank with 3 No. Mixers), anoxic (1 No. Tank) and aeration phase (1 No. Tank with fine bubble disc aeration), a secondary settlement phase and return activated sludge phase. Ferric sulphate is also employed as a method of phosphorus removal. Approximately 20% of this sludge is returned to the aeration tank in order to maintain a sufficiently large microbial population in the aeration tank and the remaining 80% is sent to the sludge treatment processes. The sludge returned to the aeration process is referred as the RAS (returned activated sludge) and that which is sent directly to the sludge treatment processes is referred to as the WAS (waste activated sludge).
Discharge	Effluent is discharged into the Blackwater River.

2.3.6 MALLOW

The WWTP in Mallow is located in the north-east of Cork City, on the banks of the River Blackwater. The Mallow catchment covers a total area of 595 hectares. The domestic population of Mallow has grown with the most recent Census figures showing that Mallow Town and environs now has a population in excess of 7,091. The Mallow WWTP is designed for a P.E. of 18,000 with a BOD loading of 1,080 Kg/day.

The maximum hydraulic capacity of the Mallow WWTP is 556 m^3/h (2.5 DWF). In order to cope with flows above 2.5 DWF storm storage has been provided at the WWTW. The volume of storm storage at the WWTW is approximately 1,012 m^3. In the event that the storm water holding tanks are filled and the storm continues, the storm water tanks are operated as a pre-clarification tank without sludge removal. The overflow from the storm water storage tank is connected to the final effluent outlet pipe.

The wastewater in Mallow is collected in a partially combined foul and separated foul sewage drainage network. The wastewater drains from the town on both sides of the Blackwater River. The wastewater drains to a pumping station at Mallow Bridge, which is then pumped to the WWTP. At design capacity the WWTP will discharge 5,250 m^3/day to the river (Cork County Council 2007).

2.3.6.1 Overview

Table 2-7 details the waste treatment processes for Mallow, County Cork, with specific details collected from the EPA licensing applications of the plant.

Table 2-7 Overview of Treatment Processes in operation at Mallow Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	At the inlet pumps force the stream through 2 No. Mechanical screens with an aerated grit and grease removal system and grit classifier.
Secondary	The flow is split after the wastewater passes through the new inlet works. 50% of the flow is diverted to the existing wastewater treatment stream. The remaining 50% is directed to a new treatment system. The existing stream has an aeration phase (2 No. Oxidation ditches with 2 No. Surface aerators), a secondary settlement phase and return activated sludge phase. The new stream has an anaerobic (1 No. Tank with 3 No. Mixers), anoxic (1 No. Tank) and aeration phase (1 No. Tank with fine bubble disc aeration), a secondary settlement phase and return activated sludge phase. Ferric sulphate is also employed as a method of phosphorus removal.

2.3.7 RINGASKIDDY

The WWTP in Ringaskiddy is situated *ca.* 16 km from Cork City in the south west of the harbour and is the location of a number of pharmaceutical companies. Discharges from the industries in the area are governed by IPPC licences issued by the EPA. Treated effluent from a number of industries in the area discharge into a common industrial development authority (IDA) trunk sewer which flows by gravity through the Ringaskiddy screening plant and discharges into a long pipe into the harbour. There is no WWTP serving this agglomeration only 6 Sewage Pumping Stations with emergency overflows working for a P.E. of 97,556 as of the 2006 Census. Only 14,864 of this P.E. is the actual population of the agglomeration, while a number of industries in this catchment are licensed to discharge effluent, providing a further P.E. of licensed discharges to be estimated at 82,692. There are plans to develop this site further with a WWTP due to begin construction at this site in 2016.

The agglomeration comprises a number of distinct areas linked by one sewer collection system. The agglomeration is made up of the village of Crosshaven, the town of Carrigaline, the village of Shanbally and also includes treated trade effluent from a number of industries in the Ringaskiddy area. Wastewater collected in Crosshaven is pumped to the sewerage system in Carrigaline. All wastewater collected in Carrigaline (including Crosshaven) is pumped through the Coolmore Pumping Station at Church road, Carrigaline to a trunk sewer at Raheens, where it is flows by gravity to the discharge point in Lower Cork Harbour. An underwater outfall pipe discharges approximately 2.6 km from the shore at a depth of approximately 30 below sea level. There is also a small collection system and pumping station in Shanbally village which conveys effluent to the trunk sewer. This WWTP represents a treatment facility in a heavily industrialised region with a high population.

2.3.8 RINGSEND

The Greater Dublin agglomeration served by the Ringsend plant includes all the areas of Dublin City and South Dublin County Councils, and parts of Fingal, Dun Laoghaire, Rathdown and Meath County Councils. The Ringsend catchment, Figure 5-11, includes a total area of 26728 hectare. The licence was issued by the EPA to all five contributory local authorities. The Greater Dublin agglomeration is the largest agglomeration in Ireland, with a measured population equivalent in 2010 of 2.45 million (maximum weekly average). Influent is composed of domestic wastewater, commercial wastewater, licensed trade effluents, surface water from combined sewers, surface water infiltration, groundwater infiltration, saline infiltration and tankered wastewaters. The older parts of the network such as Dublin city center are drained on a combined system that means both foul wastewater and storm water run-off from rainfall are carried in the same system. The treated effluent is ultimately mixed with the cooling waters from the ESB's Poolbeg Generating plant, thus providing for further dilution of the effluent. Both flow streams are then discharged together to the lower Liffey estuary. This data was collected from the EPA Annual Environmental Report (AER) 2010 for Ringsend WWTP, Table 2-8.

Table 2-8 Overview of Treatment Processes in operation at Ringsend Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	The wastewater passes through fine screens (6 mm) to remove paper, plastics and large solids. Grit, fats, oil and grease are removed in special tanks.
Primary	12 primary treatment lamellae tanks allow 40% - 50% of the pollutants in the wastewater to settle.
Secondary	The settled wastewater is pumped to 24 Sequencing Batch Reactors (SBR's) for secondary treatment. Micro-organisms developed in the process are used to take organic matter out of the wastewater, along with ammonia and nitrogen. The SBR's at Ringsend are the largest in the world and, uniquely, are contained in a two story structure, due to site limitations. The 24 SBR's are divided into 6 units, built three on top of three. Each unit consists of 4 tanks, operating in sequence. While one tank is filling with wastewater, a second is aerating wastewater with oxygen to accelerate the natural biological secondary treatment. The third tank is settling wastewater and the fourth tank is decanting treated wastewater to the next treatment stage.
Tertiary	The treated water receives tertiary treatment in the form of ultraviolet disinfection
Discharge	The water receives tertiary treatment to meet Bathing Water Standards, before being discharged into the Bay. Over 95% of the original pollutants have been removed and the treated water is comparable to good quality river water (Dublin City Council 2003).

2.3.9 SWORDS

The Swords agglomeration is centred on the town of Swords and covers nine square kilometres. The Swords catchment covers a total area of 2673 hectares. The Swords plant is a conventional aeration plant designed to cater for a P.E. of 60,000. The load for 2006 was 50,000 with main contribution to the agglomeration from domestic sources. There is some contribution from the commercial activities in the town and there are also a number of discharges from licensed trade effluent.

There are two river basins in the agglomeration area, the Ward and the Broadmeadow Rivers. A number of storm water overflows and pumping station overflows, when operational, discharge to these watercourses. The agglomeration drains by gravity to a treatment works on Spittal Hill Road. The effluent from the plant is discharged to the Broadmeadow River slightly upstream of the M1 Motorway crossing. As the Inner Broadmeadow Estuary is a designated sensitive area under the Urban Wastewater Treatment Regulations nutrient reduction is also part of the treatment process. There are two small treatment plants serving what were cottage schemes at Toberburr and at Rowlestown, both of these schemes are to the west of Swords. Planned work, expected to have been completed in 2008, would ensure that both plants would be replaced by pumping stations and the necessary rising mains and gravity sewers would be laid to transfer the sewage into the existing Swords scheme, where it would be treated in the Swords WWTP. This data was collected from the EPA licence application forms (Fingal County Council 2007).

2.3.9.1 Overview

The treatment process consists of preliminary treatment, primary settlement, activated sludge process and final settlement. The excess sludge is thickened, pasteurised, digested and dewatered. A storm water holding tank is provided to deal with storm conditions. In the event of a storm, the influent will be pumped through the inlet works and the preliminary treatment as normal. The resultant influent is stored in the storm water tank where it allowed settling i.e. the storm water tank acts as a primary tank. In the event of the storm conditions persisting the screened and settled influent will overflow the storm water holding tank and discharge at the primary discharge point.

Table 2-9 Overview of Treatment Processes in operation at Swords Wastewater Treatment Plant. Data collected from EPA licensing application.

Stage of Treatment	Processes
Preliminary	Influent to the plant is screened and grit, fats, oils and grease are removed. Screenings and grit are washed and compacted prior to disposal.
Primary	The flow to the primary settlement tanks is split into three streams, the existing treatment stream comprised of 2 circular tanks and two new streams, comprising of two rectangular tanks. All settleable material is separated in these tanks and pumped to the sludge treatment.
Secondary	The activated sludge tanks consist of an anaerobic, an anoxic and an aerobic zone for both biological phosphate removal and full nitrification and de-nitrification. The aeration is carried out using a diffused air system. Alum dosing is on standby for additional chemical phosphate removal.
Discharge	The final effluent and activated sludge are separated in the final settlement tanks. The effluent is discharged to the Broadmeadow Estuary (Fingal County Council 2004).

2.4 Sampling Plan

In order to populate the final model with valuable, comprehensive data, it was necessary to devise a sampling plan that would provide as much detail on temporal and seasonal variability as possible. This plan also needed to be flexible in order to facilitate sampling after an extreme weather event and allow for the monitoring of the weather in such a way that samples representative of both dry- and wet weather flow (DWF and WWF) could be acquired.

The rationale behind the sampling plan for the Dublin sites, Ringsend and Swords WWTPs, was to collect monthly samples with periods of intensive sampling during two winter and two summer periods. Effluent samples were collected at the same location for the same sample volumes, and strictly employed SOPs were applied to all samples.

As the Cork samples were being provided by Cork Co. Council a much more flexible sampling plan was put in place as this sampling was infrequent and it became much more difficult to adhere to the SOPs. Up until April 2011 Cork samples were irregular therefore it was not possible to conduct intensive sampling. From April to July 2011 monthly samples were received from all sites and included intensive samples from the site in Ballincollig. Table 2-10 details the specifics of the sampling plan including types of samples obtained, volumes and sample breakdowns, as well as a clear overview of the sampling dates.

Table 2-10 Overview of Sampling Plan. Timeframe in which monthly samples were collected.

Site	*Sample Type*	*Timeframe (months)*	*Volume (L)*	*Sample Breakdown*
BG	Grab	14	6.5	6 x 500 mL PAH analysis (3 filtered) 6 x 500 mL Pesticide analysis (3 filtered) 500 mL Metals analysis
BN	Grab	13	6.5	
CE	Grab	12	6.5	
CY	Grab	4	6.5	
FY	Grab	13	6.5	
MW	Grab	13	6.5	
RY	Grab/ Composite	12	6.5	
RD	Grab	25	12.5	6 x 1 L PAH analysis (3 filtered) 6 x 1 L Pesticide analysis (3 filtered) 500 mL Metals analysis
SD	Composite	20	12.5	

*Note – The Cork samples for pesticide analysis were extracted in Cork IT following the same SOPs. The composite sample from Swords was collected by an auto-sampler, which collected 100 mL per 1000 m^3 flow through the plant. In Ringaskiddy the sample is part grab and part composite in order to reach the necessary volumes required for our analyses.

Table 2-11 Overview of sampling dates at nine WWTPs under study, with shaded squares indicating samples collected. (Note: X indicates a period of intensive sampling, samples taken every second day for a period of at least one week.)

	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**
BG												▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	X	▨
BN													▨	▨	▨	▨			▨	▨		▨	▨	▨	▨
CE														▨								▨	▨	▨	▨
CY																						▨	▨	▨	▨
FY													▨	▨	▨	▨			▨	▨	▨	▨	▨	▨	▨
MW													▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
RY												▨	▨	▨	▨	▨	▨			▨	▨	▨	▨	▨	▨
RD	▨		▨	▨	X	▨	▨	▨	▨	▨	▨	X	X	▨	▨	▨		▨	X	▨	▨	▨	▨	X	X
SD					▨	X		▨	▨	▨	▨	X	X	▨	▨	▨		▨	X	▨	▨	▨	▨	X	X

2.5 Conclusion

This chapter has defined the nine sites chosen for this study, 7 sites in Cork and 2 sites in Dublin. Each of the sites represents a different demographic, type of population and type of treatment. The sampling plan devised allows for the evaluation of domestic, industrial and agricultural inputs and emission factors while also affording the opportunity to compare levels and styles of treatment and the removal efficiencies achieved by such.

Including Ringsend WWTP in the sampling plan has the added benefit of facilitating monitoring of the largest WWTP in the country, serving the most heavily populated city, and operating well over capacity, as can be seen in Table 2-1. This draws attention to an issue encountered during the data collection stage of this project; the fact that different sources of the same data were quoting different values for population equivalents and actual populations being served by each plant. EPA waste licence applications made by the respective plants, annual environmental reports (where available), and urban wastewater reports were shown to differ in the fundamental area of P.E. served by the respective WWTPs. Where plants are undergoing works, or being taken over by private companies it is important to have the correct P.E. values as removal efficiencies of plants operating above capacity are severely reduced, thus leading to increased levels of priority and hazardous substances being present in the WWTP effluent and consequently being released back into the environment.

To conclude, this chapter has described the processes of site selection and sampling plan development for this project. This was of paramount importance to the project as the final model must be filled with high-quality data on a range of different sites under varying conditions.

3. Sample Preparation and Standard Operating Procedures

3.1 Introduction to Sample Preparation and Standard Operating Procedures (SOPs)

Samples, from biological to environmental, are often not in a condition which would allow for direct analysis to be carried out therefore a sample preparation step is necessary. This step aims to ensure that the analyte(s) of interest is suitable for analysis after the step is complete. This will generally involve ensuring that the analyte is free from interferences and in solution at a concentration which will allow for its measurement or detection, it can also involve converting the analyte to another form which would allow for easier separation and detection. These aims can be achieved, depending on the original sample, through a number of techniques including extraction, derivatization, homogenisation, filtration and pre-concentration (Luthria 2006).

An environmental sample, specifically wastewater, is non-homogenous containing dissolved organic matter, particulates and will contain a wide range of substances of varying polarities. Owing to the nature of these environmental samples sample preparation steps are required, i.e. most water samples contain substances such as salts, humic acids and other humic substances which can interfere with solid-phase extraction especially the determination of polar pesticides (Ibáñez, Picó *et al.* 1998, Picó, Fernández *et al.* 2007). A good sample preparation step will separate the analyte(s) of interest from these matrix constituents which could lead to analytical interferences, leaving a clean, concentrated sample.

In the preparation of wastewater samples some of the most commonly used techniques involve solid phase extraction (SPE) and liquid-liquid extraction (LLE). SPE facilitates sample extraction and concentration while also minimising solvent consumption which is a big concern in environmental labs. The trace nature of the analytes in question require that larger sample volumes are collected and a sample preparation method which is capable of handling these large volumes, resulting in a concentrated sample of the target analyte, must be chosen. Table 3-1 below compares SPE and LLE methods.

Table 3-1 Comparison of the two most commonly used sample preparation methods in environmental sample handling – SPE and LLE.

Solid Phase Extraction	*Liquid-Liquid Extraction*
Little solvent consumption	High solvent consumption
Cartridges and disks are disposable	Heavy on glassware use – time consuming to clean
Better recoveries	Lower recoveries
No emulsions	Emulsions
More versatile, more choice	Chosen solvents must be immiscible
Cleaner extracts achievable	
Can be automated	Difficult to automate
Selective removal of interferences	

3.1.1 SOLID PHASE EXTRACTION (SPE)

SPE was developed as a cheaper and more environmentally friendly alternative to liquid-liquid extraction (LLE). Similar to LLE, SPE involves the partitioning of compounds between 2 phases. The analytes (in liquid form) are placed in a small column or cartridge containing an appropriate packing material where the analytes will have a stronger affinity for the solid packing than for the sample matrix and the liquid sample is passed through this cartridge either by suction or by positive pressure. The analytes are retained on the solid phase while many interferences are washed out and are later removed by eluting with a solvent with a greater affinity for the analytes (Huck, Bonn 2000).

The main procedure of SPE involves these steps:

- Activation of the sorbent by passing through an appropriate solvent (wetting)
- Removal of the activation solvent
- Sample introduction, and analytes retained on sorbent (retention step)
- Removal of interferences (washing)
- Analyte elution with stronger solvent

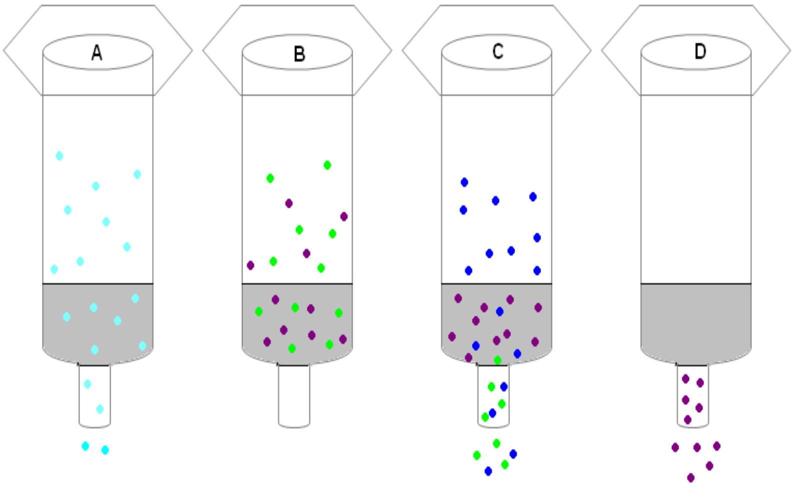


Figure 3-1 Schematic showing stages involved in SPE Method; A- Condition, B- Load, C-Wash, D- Elute

Different mechanisms of retention/elution are used and these are due to intermolecular forces between the analytes and the active sites on the surface of the adsorbent and the matrix. In SPE, another important parameter that must be controlled is known as the breakthrough volume; this is the sample volume where the analyte starts to be eluted from the exit of the cartridge and this value is a function of the chromatographic retention of analyte on the particular sorbent, it can only be changed by altering the sorbent and increasing the sorbent mass (Huck, Bonn 2000).

3.1.2 SORBENT FORMATS

With SPE the primary concern for analysts is sorbent choice, a choice that will solve their trace-analysis problems, and so a key problem with SPE is method development. The solid-phase is very important; for many years n-alkyl silica has been the universal SPE sorbent (Hennion 1999). It is also very important to obtain extracts free from matrix interferences in as few steps as possible so selectivity is given a lot of consideration, the more selective the SPE step is, the more sensitivity is obtained (Pichon 2000).

The two most common forms of SPE sorbents are as disks or cartridges. As described above the extraction can be carried out in a sorbent-packed cartridge, or, it can be carried out on a sorbent that is enmeshed in the inert matrix of a membrane-based extraction disk (Pichon 2000).

3.1.2.1 Cartridges

Cartridges contain different types and amounts of sorbent and they are also available in different sizes (Masqué, Marcé *et al.* 1998). The main limitations associated with using cartridges are restricted flow-rates and plugging of the top frit when analysing samples containing suspended solids. Therefore if samples have not been previously filtered the use of cartridges may be extremely slow and tedious (Hennion 1999). Other limitations are encountered specifically when analysing water samples: tolerance to blockages is low and channelling reduces the capacity to retain analytes. A solution to some of these problems would involve the use of disks, yet cartridges are still the most popular as they use less solvent volume than disks and also due to the fact that there is a limited commercial availability of sorbents for disks compared to cartridges (Masqué, Marcé *et al.* 1998).

3.1.2.2 Disks

Disks are 0.5 mm thick membranes where the adsorbent is immobilized in a web of micro fibrils; this allows higher flow-rates than SPE cartridges (Huck, Bonn 2000). Channelling effects are also eliminated; however many of the same limitations still exist especially with samples containing suspended matter (Hennion 1999). Disks are generally used when dealing with large sample volumes and when the concentration of the analytes is low, e.g. trace analysis of organic pollutants in water (Huck, Bonn 2000). The two main types of disks available are Empore disks containing C_{18} or PS-DVB (Masqué, Marcé *et al.* 1998). The disks can be used for extraction using one of three main processes: (i) pass the sample through the disk using a vacuum source, the analytes are retained and then removed with a small volume of eluent, (ii) suspend the membrane in the sample (liquid) for a specified period of time, allow to dry briefly in air then directly detect the analytes using a solid state spectroscopic technique and (iii) similar to (ii) except the analytes are desorbed by suspending the disk in a solvent and then detected in the extract(Huck, Bonn 2000).

The main disadvantage of using disks rather than cartridges is the decrease in the breakthrough volume, mainly for the more polar compounds, it is also for this reason that disks are used when there is a strong interaction between the analyte and the sorbent(Masqué, Marcé *et al.* 1998).

3.1.3 TYPES OF SORBENTS

3.1.3.1 Chemically Bonded Reverse Phase Silica

The most common materials used as sorbents in SPE are the chemically bonded silica's, usually with C_8 and C_{18} organic groups bonded to the surface of the porous silica. It is believed that the more organic carbon bonded to the silica surface the better the sorbent. Manufacturers use di- and tri-functional modifiers for the production of SPE sorbents due to the stability of the bonded phase and the cost of production; this leads to polymeric bonded phases usually containing 15-19% bonded carbon (Nawrocki, Da□browska 2000).

Several types of modified silica's are available commercially with different properties based on percentage of carbon loading and the type of functional alkyl-silanes used for the bonding (Hennion 1999). Among the modified silica's while the C_{18} silica's provide the greatest retention they also trap the most interferences. Other options include cyclohexyl and phenyl phases, with phenyl phases being shown to increase the retention of aromatic analytes. Cyanopropylsilica and aminopropylsilica are polar phases that exhibit both polar and non-polar interactions. Aminopropylsilica, when compared with a C_{18} sorbent, has achieved better detection and quantification limits (Hennion 1999), however during the method development for the analysis of PAHs it was found that C_{18} to be the most suitable for this sample group. Finally, selective electron-donor- and electron-acceptor-bonded silica packing's have been prepared specifically for use with hydrophobic contaminants (Hennion 1999).

The main limitation of both reversed-phase silica sorbents and many of the polymeric sorbents available is that they all require conditioning with a wetting solvent and cannot be allowed to dry before the loading of an aqueous solvent (Hennion 1999).

3.1.3.2 Functionalised Polymers

This new generation of polymers (e.g. Strata-X from Phenomenez and Abselut from Varian) has been designed to extract an extensive selection of analytes i.e. lipophilic, hydrophobic, acidic, basic and neutral with a single cartridge with a simplified procedure since no conditioning is required. These polymers have also been shown to provide a better wettability, and also increase the extraction recoveries of polar compounds (Hennion 1999).

A main group of functionalized polymers used as sorbents are apolar poly(styrene–divinylbenzene) copolymer sorbents. These resins are available in disposable cartridges, and the highly cross-linked PS-DVB sorbents have the ability to trap very polar, non-polar and ionized organic analytes (Hennion 1999). This ability of PS-DVB resins, such as Amberlite XAD-type, of trapping more polar compounds than a typical C_{18} cartridge is one advantage, with stability over pH range 1-14 being the other (Pichon 2000). Overall, it is believed that these highly cross-linked PS-DVB sorbents are the sorbents to be selected for the extraction of very polar analytes when large sample volumes are required (Hennion 1999). These cartridges are the most widely used in the area of pesticide extraction. Through this study it was found that polymeric sorbents proved sufficiently selective for our analytes, and removed many of the interferences and matrix components, leaving clean samples for analysis.

3.1.4 SPE METHOD DEVELOPMENT

There are several steps involved in the development of a method for SPE. The first step is the selection of an appropriate sorbent which will allow for the greatest sample recovery and the best removal of interferences. Figure 3-2 below provides a schematic of factors that need to be considered when selecting a SPE sorbent. Reverse phase sorbents are most suitable for environmental applications in relation to water samples.

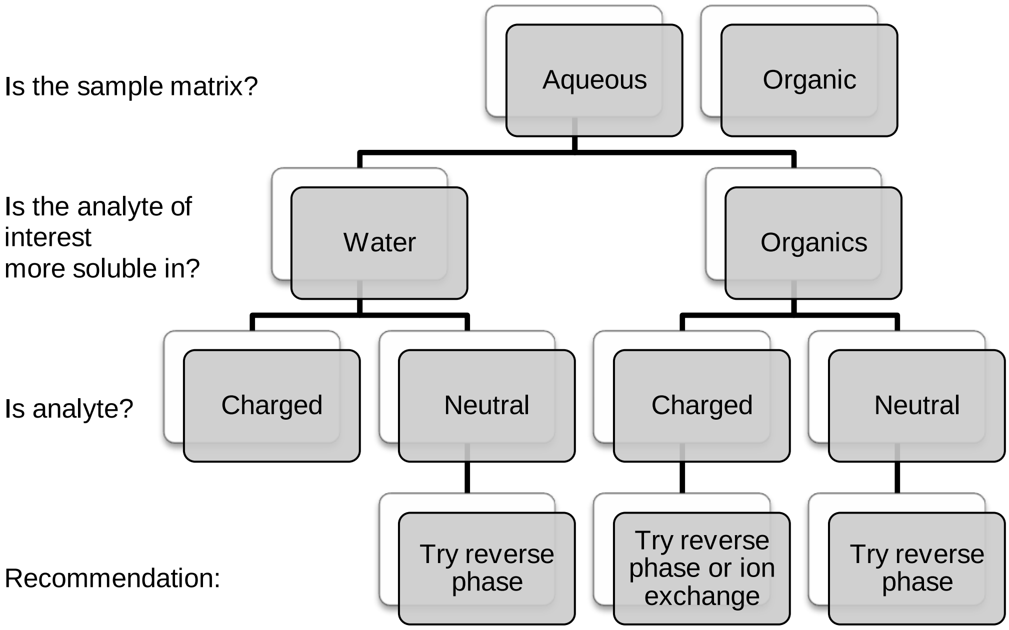


Figure 3-2 Overview of SPE sorbent selection procedure.

Sorbent mass and volume also have an important role as greater sorbent mass increases the sorbent surface area in contact with the sample and increases the analyte capacity of the sorbent which in turn affects the breakthrough volume. It must also be noted that silica-based sorbents have lower sorbent surface area than polymeric sorbents and therefore have lower analyte capacity per gram. A SPE method using a larger sorbent mass also uses higher volumes of solvent.

Elution solvent strength in SPE is based on the polarity of the solvent and the nature of the bonding between the analyte and the sorbent. Combinations of polar and non-polar solvents are used in the conditioning, washing and elution stages of a SPE procedure. Table 3-2 below lists the most commonly used solvents in SPE in order of their respective polarities. While some solvents may prove stronger and therefore better for the elution of analytes it is important to consider that some of these solvents are considered, themselves, as priority pollutants according to the WFD, i.e. carbon tetrachloride and dichloromethane.

Table 3-2 Polarity and miscibility of commonly used solvents in SPE.

POLARITY	*SOLVENT*	*Miscible in water?*
Non-polar	Hexane	No
↓	Isooctane	No
	Carbon tetrachloride	No
	Chloroform	No
	Dichloromethane	No
	Tetrahydrofuran	Yes
	Diethyl ether	No
	Ethyl acetate	Poorly
	Acetone	Yes
	Acetonitrile	Yes
	Isopropanol	Yes
	Methanol	Yes
Polar	Water	Yes
	Acetic acid	Yes

3.1.5 OVERVIEW OF SPE METHOD DEVELOPMENT STEPS

There are a number of steps involved in the development and validation of an SPE method, Figure 3-3. It is important that all steps are well optimised and validated before applying the final method to actual samples.

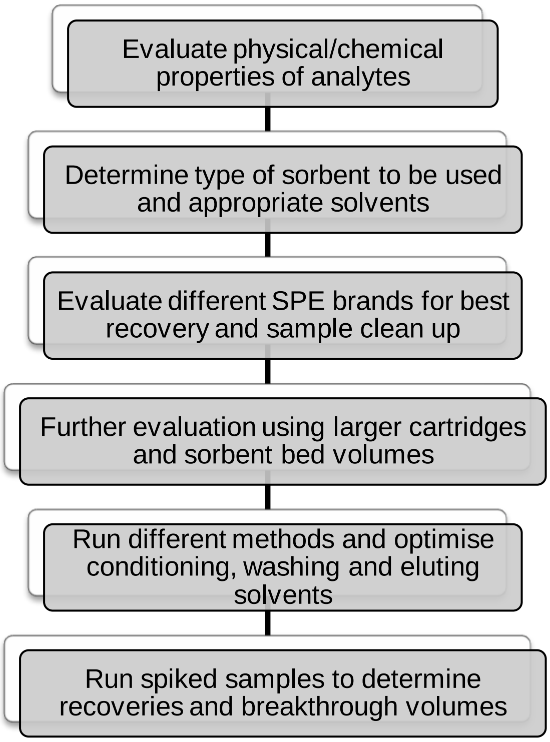


Figure 3-3 Overview of the steps involved in development and validation of the SPE methods used in this project.

Through the application of the method outlined above the result is an optimized and validated method of extraction for an analyte or group of analytes of interest.

3.1.6 STANDARD OPERATING PROCEDURES

In analysis the main source of imprecision and inaccuracy is the sample preparation step which is often tedious and time-consuming. Steps must be taken to minimise the potential for error in the analytical results and as such it is very important that standard operating procedures (SOPs) are carefully established and strictly followed during all stages of sample handling from collection through to analysis. As this work involved collaboration between two main project partners it was important that SOPs were easily understood and followed by both parties to ensure the integrity of the results.

3.2 Aims and Objectives

The aim of this chapter is to review sample preparation techniques and choose the most suitable for the purposes of this study that would best allow the requirements of the WFD to be met. As sample exchange between two research groups was also a factor it was necessary to establish early on a strict set of SOPs and sample exchange procedures which would limit inconsistencies in techniques and results between these groups.

The objectives are to:

- Introduce the concept of sample preparation,
- Highlight the importance of standard operating procedures (SOPs),
- Outline the theory of SPE and its applications within the scope of this study,
- Develop simple and fast methods for the multi-residue extraction of priority PAHs, pesticides and metals,
- Describe the method development involved in the extraction of PAHs, pesticides and metals and trace elements from a wastewater matrix and
- Summarise the SOPs adapted for use in this study.

3.3 Sample Preparation for PAHs

PAHs are hydrophobic compounds and are therefore easily extracted on typical reversed-phase sorbents and C_{18} bonded silica is, by far, the most common (Portet-Koltalo, Oukebdane *et al.* 2007, Marcé, Borrull 2000, Sun, Littlejohn *et al.* 1998). Sargenti, McNair (1998) compared C_{18}, cyano and phenyl bonded silica sorbents and found that results for C_{18} were the most acceptable, however, according to Kootstra, Straub *et al.* (1995) C_8 material is better than C_{18} for extracting PAHs in both recoveries and reproducibilities. One main issue with these sorbents is the presence of free silanol groups which result in non-reversed phase, or secondary, interactions; the PAHs are strongly retained leading to low sample recoveries (Hagestuen, Campiglia 1999). Through cartridge evaluation in this study it was found that Strata C_{18} cartridges resulted in the best recoveries and general performance for the WFD priority PAHs.

Other sorbents used include immuno-sorbents which have been applied to the selective isolation of PAHs from complex environmental samples (Marcé, Borrull 2000) and Styrosorbs MN-100 and MT-65. These styrosorbs are a type of hyper cross-linked polystyrene polymer which have been successful sorbents for the pre-concentration of phenanthrene and naphthalene (Nazarkina, Bulanova *et al.* 2001). Finally, SPE discs with a glass fibre matrix can be used to reduce extraction times of PAHs compared to other extraction systems (Urbe, Ruana 1997). As mentioned there are limitations associated with both the use of cartridges and discs for SPE, by pre-filtering the samples it was possible to avoid many of the clogging issues associated with cartridge use and the samples were not limited by the lower breakthrough volumes associated with the disc.

Owing to the non-polar nature of the PAHs and based on the literature a reversed phase approach to SPE was selected. Reversed phase SPE involves the retention of non-polar organic compounds from polar solutions such as water. Non-polar non-polar interactions occur between the functional groups on the surface of the silica sorbent in the cartridge and the non-polar analyte. To elute the PAHs a strong non-polar solvent is used to disrupt these bonds. There were 2 main stages in the SPE method development for the PAHs - cartridge selection, and solvent selection. First gas and liquid chromatographic methods were developed and these were used to evaluate the cartridges and solvents chosen for SPE, this work is detailed in Chapter 4.

3.3.1 CARTRIDGE SELECTION

Cartridge selection was an important process in the development of the PAH sample extraction method. Table 3-3 shows the results of the preliminary PAH recovery study using 11 commercially available SPE cartridges. The aim of this study was to discover which SPE cartridge would provide the best sample enrichment and highest recoveries for the priority PAHs.

Spiked water samples (100 mL) were passed through the SPE cartridges listed, in triplicate, under a vacuum, after conditioning using a basic method; 2 mL methanol (MeOH), 2 mL of deionised (di) water. The cartridges were then washed with 2 further aliquots of deionised water, dried with the vacuum, and PAHs were eluted using 2 mL acetonitrile (ACN) which was evaporated down under nitrogen and reconstituted to 1 mL with ACN. Subsequent analysis was carried out by HPLC-FLD detection and recoveries are listed in the table below, Table 3-3.

Table 3-3 Recovery study of PAHs on SPE cartridges. Recoveries represent total SUM PAH recovery using each cartridge.

Cartridge	*Sorbent*	*Average Recoveries of Cartridges N=3*			*Average Total Recovery*
		1	2	3	
Isolute TPH	NH_2 layer above C_{18}	20.65%	74.80%	86.93%	60.79%
Bond Elut ENV	Styrene divinyl benzene polymer	6.30%	5.21%	7.44%	6.32%
Strata C_{18}	**C_{18}**	**105.7%**	**107.38%**	**97.58%**	**103.52%**
Bond Elut C_{18}	**C_{18}**	**93.51%**	**132.33%**	**141.1%**	**122.30%**
Isolute PAH HC	NH_2 layer above C_{18}	20.73%	18.06%	21.89%	20.23%
Isolute C_8	C_8	12.90%	14.34%	6.87%	11.37%
Isolute C_{18}	**C_{18}**	**58.32%**	**57.75%**	**53.09%**	**56.39%**
Isolute C_2	C2	22.85%	11.70%	17.16%	17.24%
Isolute ENV+	Hydroxylated polystyrene-divinylbenzene copolymer	53.38%	54.51%	53.36%	53.75%
Strata C_8	C_8	9.96%	10.79%	12.66%	11.14%

From Table 3-3 several cartridges clearly demonstrate good sample enrichment with two also providing sample enrichment. After investigation it was discovered that this enrichment was due to breakthrough on the cartridges as the cartridges affected had sorbent beds of only 100mg. Another issue was also evident from this preliminary study, although recoveries for Isolute ENV+ seem acceptable for overall total percentage recovery there was no recovery of Benzo-a-pyrene or Benzo-ghi-perylene only high recoveries of other compounds. These cartridges were therefore ruled out as the goal was to achieve the highest possible recoveries for all eight priority PAHS. From the preliminary study the top performing cartridges for all PAHs were selected and re-evaluated at higher sorbent mass levels and a lower 'spiked' concentration.

The Isolute C_{18} and Strata C_{18} were found to be the most reliable cartridges when evaluated for recoveries of all eight PAHs. Naphthalene, due to its volatility, had the lowest recovery for both cartridges. The Strata cartridge out-performed the other cartridges for overall recoveries with the Isolute cartridge found to be second best, Figure 3-4. These two cartridges were further subjected to the solvent selection process in an attempt to further improve sample recoveries and breakthrough volumes.

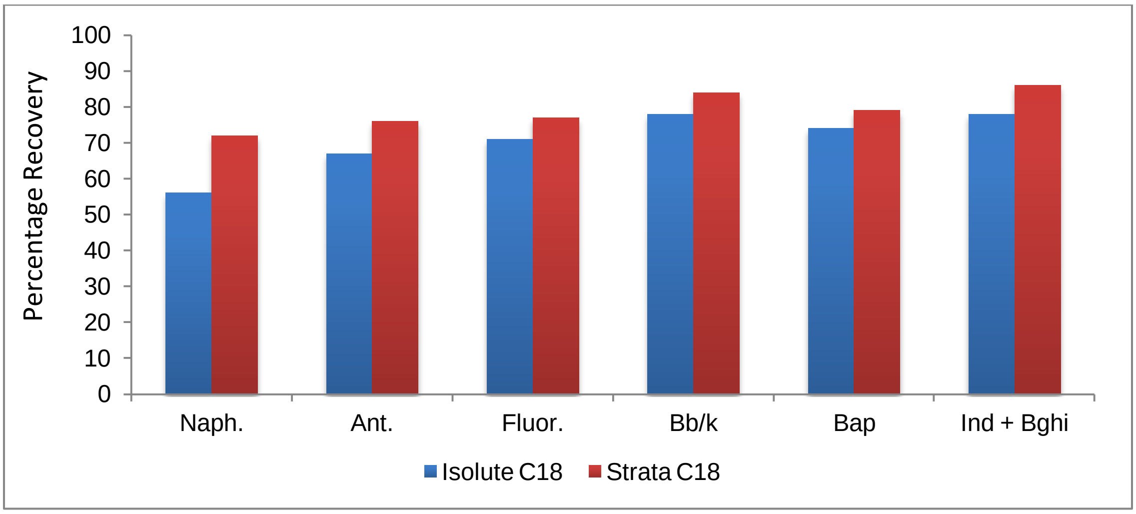


Figure 3-4 Percentage recovery of each of the PAHs using the two preferred cartridges. N=3. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

3.3.2 SOLVENT SELECTION

Selection of appropriate and efficient solvents for use in this method was important to maintain a high level of sample recovery. As mentioned in Section 3.1.1 there are several solvents involved in the typical SPE procedure: conditioning, washing and eluting solvents. Optimisation of each of these solvents leads to the most effective method. The literature was used as a starting point in the method development.

A conditioning solvent in SPE should wet the sorbent making it activated towards the analyte(s) in the sample. The cartridge must be kept in a conditioned state and not allowed to dry out between conditioning and loading of sample. This is owing to drying leading to air pockets in the sorbent bed which then reduces the interfacial contact between the sorbent and the sample. Samples are retained on the sorbent by a number of mechanisms. In reverse phase SPE these are hydrophobic interactions such as non-polar non-polar interactions and van der Waals or dispersion interactions.

The sample is loaded in a strongly non-polar solvent, water. A wash step is also performed using the same non-polar solvent, this allows for the elution of poorly retained interferences and matrix constituents leaving the analytes of interest tightly bound to the sorbent. A strong elution solvent, or mixture of solvents, is required to break the bonds and allow elution of the analyte.

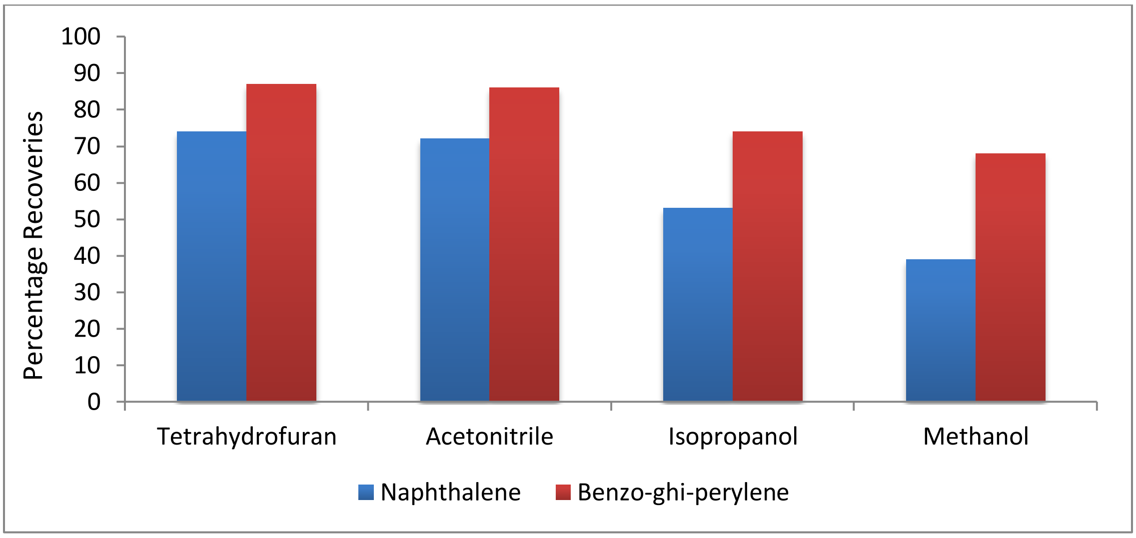


Figure 3-5 Percentage recoveries of 2 PAHs using different elution solvents after conditioning with MeOH and loading of a 1 mL spiked sample. N=3.

The PAHs are nonpolar, and have been found to be strongly binding to SPE sorbents, see Section 3.3, as such it was important to use strong eluting solvents, organic solvents. An elution solvent should be strong enough to elute the analyte in as small a volume as possible. One of the manufacturer recommended solvents from Phenomenex was a combination of dichloromethane and acetonitrile (ACN) however as dichloromethane is also listed as a priority pollutant the decision was made to evaluate ACN as well as other solvents. Figure 3-5 shows the recoveries of naphthalene and benzo-ghi-perylene when eluted with different solvents using the same method. Naphthalene and benzo-ghi-perylene were chosen as they represent the spectrum of hydrophobicity of the PAHs in this study with naphthalene having the lowest Log K_{ow} value and benzo-ghi-perylene having the highest. From the study there was only a slight difference in recoveries when using the more non-polar tetrahydrofuran (THF) compared to the ACN. Owing to the nature of these two solvents and their handling and disposable in the lab acetonitrile was chosen as the preferable elution solvent for this method. While other more non-polar solvents could be used for elution a number, as mentioned earlier, are themselves listed as priority substances and were therefore ruled out as candidates. Of the more non-polar solvents toluene was mentioned most commonly in the literature in combination with acetonitrile and other solvents and was thus investigated further.

Solvent combinations have been shown in Table 3-4. Presented are three different methods for the SPE of PAHs each using strong eluting solvents, and resulting in a pre-concentration of 1000 when applied to our 1 L sample volumes. The solvent combinations were selected after comparing methods listed in the literature and due to the non-polar nature of the PAHs. The three methods in Table 3-4 were evaluated on both the Strata C_{18} and Isolute C_{18} cartridges chosen after the cartridge evaluation study, Section 3.3.1. with final analysis by GC-MS.

Table 3-4 Overview of three method solvent combinations, (A, B, and C) evaluated for use in the extraction of PAHs in wastewater. N=3

SPE Methods		
A	**B**	**C**
Conditioning: 6 mL MeOH 6 mL Water Load 1 mL sample Wash with 2 mL water Dry cartridge under vacuum Elute with ACN: Toluene (3:1) Evaporate down with nitrogen and reconstitute in 1 mL ACN	Conditioning: 2 mL ACN 2 mL MeOH 2 mL Water Load 1 mL sample Wash with 2 mL water Dry cartridge under vacuum Elute with 2 x 2 mL ACN Evaporate down with nitrogen and reconstitute in 1 mL ACN	Conditioning: 2 mL MeOH 2 mL Toluene 2 mL Water Load 1 mL sample Wash with 2 mL water Dry cartridge under vacuum Elute with 2 mL ACN 1 mL Toluene Evaporate down with nitrogen and reconstitute in 1 mL ACN

Of the three methods in Table 3-4 method B was chosen for it's high overall recoveries, achieving recoveries of over 70% for all PAHs using the Strata cartridge, including the naphthalene which had exhibited some sample loss during the cartridge selection stage. This method was also more environmentally friendly and avoided the use of toluene when compared to the other two methods. When applied to a 1 L sample volume this method provides a 1000 times preconcentration factor allowing the method limits of detection to meet EU requirements.

3.4 Sample Preparation for Pesticides

The sorbents most commonly employed in pesticide analysis are chemically bonded silica (usually C_{18} or C_8) or styrene-divinylbenzene copolymers (PLRPs and Envichrom P). Chemically bonded silicas have been shown to achieve high retention of non-polar and moderately polar pesticides/compounds however they are not sufficient for polar samples. They also show broad interfering peaks in UV chromatograms of water samples containing pesticides due to co-extraction of interferences occurring at the low pH required for pesticide retention (Moral, Sicilia *et al.* 2008) this is due to ionic interactions (Vigna, Morais *et al.* 2006). Another problem with polar compounds is frequent poor reproducibility and recovery (Jiménez, Bernal *et al.* 2001). Extraction and recovery of polar and non-polar herbicides has been achieved through an increase in sorbent mass and/or by modification of the matrix (Wells, Yu 2000).

Styrene-divinylbenzene, as a copolymer, is a well-known hydrophobic solvent, shown to have retentions equal to, or higher, than C_{18}-bonded silica. Only apolar or moderately polar analytes can be retained on PS-DVB (Ahmed 2001). Main examples of commercial polymeric SPE sorbents are Strata-X, Oasis (poly(divinylbenzene-co-N-vinylpyrrolidone) and XAD (styrene-co-divinylbenzene) (Vigna, Morais *et al.* 2006). Recoveries of polar compounds have been found to be higher with PS-DVB than bonded silica although silica is hydrophilic the surface is hydrophobic due to the presence of hydrocarbon chains so there is little surface contact with aqueous solutions, whereas PS-DVB copolymers have a hydrophilic surface but also have many aromatic sites which allow interactions with aromatic analytes (Masqué, Galia *et al.* 1998).

As outlined earlier in this chapter there are a number of steps involved in the SPE procedure and thought must be given to the cartridges and solvents employed. Where C_{18} cartridges have proven more suitable for non-polar separations with successes in the extraction of PAHs in wastewater it is the polymeric adsorption media that have shown to retain a range of pesticides. As with the PAHs a reversed phase approach is taken to the extraction of pesticides in wastewater.

3.4.1 CARTRIDGE SELECTION

For the selection of a cartridge for the extraction of pesticides the same approach was adopted as that for the extraction of PAHs. A number of commercially available cartridges, many referenced in the literature, were evaluated for use with the pesticides of interest. A simple GCMS method was developed for the validation of this SPE work and is detailed in Chapter 4. There were issues with recovery and analysis of 7 pesticides (glyphosate and the 6 dithiocarbamates) therefore these were omitted from this SPE study and were analysed by the project partners in CIT. These issues included low/no recovery of the selected compounds and lack of compatibility between these analytes and the GCMS method. Table 3-5 shows the results of the preliminary recovery study performed using a basic MeOH and water conditioning and ACN elution of pesticides. From this study Strata-X and Strata C_{18} were chosen for further analysis due to their high recoveries.

Table 3-5 Recovery study of pesticides on SPE cartridges

Cartridge	*Sorbent*	*Average Recoveries of Cartridges N=3*			*Average Total Recovery*
		1	2	3	
Bond Elut ENV	Polymeric	23.56%	34.21%	27.45%	28.40%
Strata C_{18}	**C_{18}**	**74.17%**	**76.38%**	**81.12%**	**77.22%**
Bond Elut C_{18}	C_{18}	69.32%	65.22%	66.81%	67.11%
Isolute C_{18}	C_{18}	68.44%	64.32%	57.49%	63.41%
Isolute C_2	C_2	19.37%	13.33%	17.24%	16.64%
Isolute ENV+	Polymeric	62.35%	59.67%	62.58%	61.53%
Oasis HLB	**Polymeric**	**81.02%**	**82.36%**	**82.72%**	**82.03%**
Strata C_8	C_8	13.45%	12.68%	12.98%	13.03%
Strata-X	**Polymeric**	**85.80%**	**87.26%**	**90.43%**	**87.83%**

The Oasis HLB and Strata X yielded recoveries higher than 70%, providing the best results in the pre-concentration of 1L samples. The Isolute SPE C_{18} and the Supelclean Envicarb were not able to retain a number of the pesticides.

3.4.2 SOLVENT SELECTION

The second stage of evaluation for the extraction of pesticides in wastewater involved evaluation of solvents for optimum extraction. The pesticides cover a range of non-polar to moderately polar compounds as such it was important to use carefully tested eluting solvents. As with the PAHs many of the organic solvents are also listed as priority substances and were therefore ruled out for inclusion in the study.

Figure 3-6 shows the recoveries of atrazine, dieldrin and chlorfenvinphos when eluted with different solvents using the same method. These compounds were chosen as they represent the spectrum of hydrophobicity of the pesticides as well as the molecular size with chlorfenvinphos the largest of the pesticides. From this study as well as the literature and solvent handling/disposable considerations acetonitrile and isopropanol were further investigated and found to achieve the highest recoveries for the pesticides when used together.

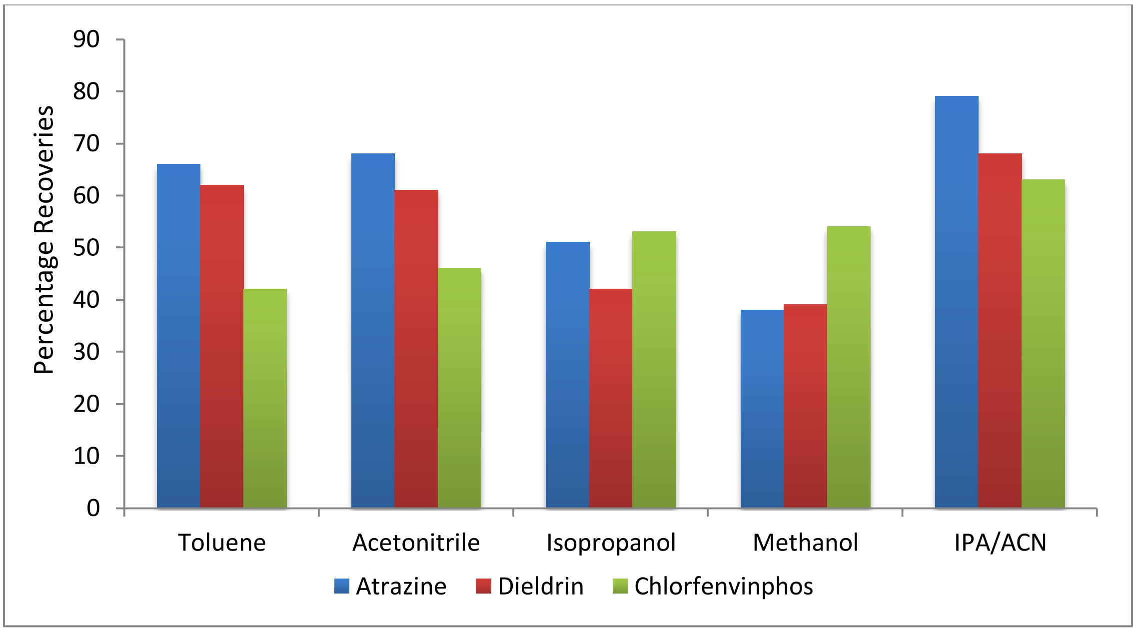


Figure 3-6 Percentage recoveries of atrazine, dieldrin and chlorfenvinphos using different elution solvents after conditioning with MeOH and loading of a spiked sample.

Table 3-6 outlines the three main solvent combinations used, A-C. Using GCMS analysis it was found that method A gave the highest recoveries when run on the Strata-X cartridges and by making the elution solvent a combination of ACN and IPA. This method has been evaluated by other researchers and has been applied to all pesticide samples included in this study.

Table 3-6 Overview of three method solvent combinations (A, B and C) evaluated for use in the extraction of pesticides in wastewater

SPE Methods		
A	**B**	**C**
Conditioning: 6 mL MeOH 6 mL Water Load 1 mL sample Wash with 2 mL water Dry cartridge under vacuum Elute with 2 mL Isopropanol, 2 mL ACN Evaporate down with nitrogen and reconstitute in 1 mL ACN	Conditioning: 2 mL ACN 2 mL MeOH 2 mL Water Load 1 mL sample Wash with 2 mL water Dry cartridge under vacuum Elute with 2 x 2 mL ACN Evaporate down with nitrogen and reconstitute in 1 mL ACN	Conditioning: 2 mL MeOH 2 mL Toluene 2 mL Water Load 1 mL sample Wash with 2 mL water Dry cartridge under vacuum Elute with 2 mL ACN 1 mL Toluene Evaporate down with nitrogen and reconstitute in 1 mL ACN

3.5 Sample Preparation for Metals and Trace Elements

For the metals and trace elements it was important to include as many of the priority and hazardous substances as possible, without making the sampling, transportation and storage procedures more difficult therefore one method of sample preparation could be applied to all metals and trace element samples. Unlike the sample preparation procedures required for the PAHs and pesticides a step is usually required to adapt the metals in the sample to the proper form for the analytical methodology.

Through review of existing preparation methods, specifically the American Public Health Association (APHA) guidelines (Eaton, Franson 2005) and EPA method 200.7 for the determination of metals and trace elements in water and wastes by inductively coupled plasma (ICP) it was clear that it would not be possible to use one method for all our analytes as different metals required different pre-treatments, e.g. Mercury. It was then necessary to introduce a method that would be as inclusive as possible and EPA method 200.7 outlined a sample preparation for total dissolved metals which was deemed appropriate. This method would allow for the preservation, preparation and analysis of 15 priority substances using one sample pre-treatment method.

3.5.1 SOP

Samples were collected in PTFE bottles; this was to remove possible interferences with the analysis of Boron, which could be encountered when collecting samples in borosilicate bottles. After collection of the wastewater sample at the sampling site the pH of the water is adjusted to below pH 2 using concentrated nitric acid (conc. HNO_3). The APHA guidelines suggested the use of nitric acid as it will adequately digest most samples and provides a suitable matrix for ICP techniques.

When trying to determine total recoverable analytes a sample digestion step is required before analysis. This is required for wastewater samples due to the particulates and suspended solids in the water. While manual acid digestion of these samples is possible it is tedious and time consuming and so microwave digestion was chosen as the final preparation step for the samples. A Mars Express Instrument CEM Microwave Sample Preparation System was used. The instrument was set to digest samples according to EPA Method 3015. This involved measuring 45 mL of the acidified wastewater into the instrument sample tube and adding 5 mL of conc. HNO_3 bringing the total sample volume to 50 mL. The instrument autosampler has the capacity for 16 samples at any one time, 15 samples and a blank. There are two stages to the microwave digestion, ten minutes at 665W followed by 10 minutes at 290W, with a final 5 minute cool down setting. Samples were then filtered into plastic sample tubes to remove any residual particulates which could become clogged in the ICP sample introduction system.

3.6 Standard Operating Procedures

In order to maintain strict quality control over the samples to ensure the integrity of the results it was necessary to establish and employ a series of standard operating procedures (SOPs) to cover all sample handling, from collection at the original site through to analysis in the lab. These SOPs were prepared according to the American Public Health Association (APHA) guidelines (Eaton, Franson 2005). As the samples were being collected for PAH, pesticide and metals analysis, it was necessary to prepare three separate SOPs to cater for the different requirements for both the stability and final analysis of the samples. The standard procedures for sample preparation in the lab have been described in Sections 3.6.1, 3.6.2 and 3.6.3 below and 3.5.1 above. The sampling materials required in order to follow the SOPs are listed in Table 3-7.

Table 3-7 Equipment and reagents required for the groups of priority pollutants specified in the SOPs

<table>
<tr><th><i>PAHs and Pesticides</i></th><th><i>Metals and Trace Elements</i></th></tr>
<tr><td colspan="2">Bucket</td></tr>
<tr><td>Shatterproof bottles (5 L) x 2, with TFE lined screw cap lids</td><td>Polypropylene containers</td></tr>
<tr><td colspan="2">Acetone</td></tr>
<tr><td colspan="2">Deionised water</td></tr>
<tr><td>10% (v/v) dichloro-dimethylsilane in toluene solution</td><td>Conc. HNO_3 and an acid solution</td></tr>
<tr><td colspan="2">Biohazard labels</td></tr>
<tr><td colspan="2">Freezer box</td></tr>
<tr><td colspan="2">Ice blocks</td></tr>
<tr><td colspan="2">Gloves</td></tr>
<tr><td colspan="2">Hard hat</td></tr>
</table>

The following sections outline the basic procedures that were followed covering all stages from sample collection to storage.

3.6.1 BRIEF OVERVIEW OF SOPS

Presented in Figure 3-7 is an overview of the procedures followed in the sampling and extraction of priority substances from wastewater as part of this study. Samples were collected in triplicate and separated for pesticide, PAH and metals and trace elements analysis.

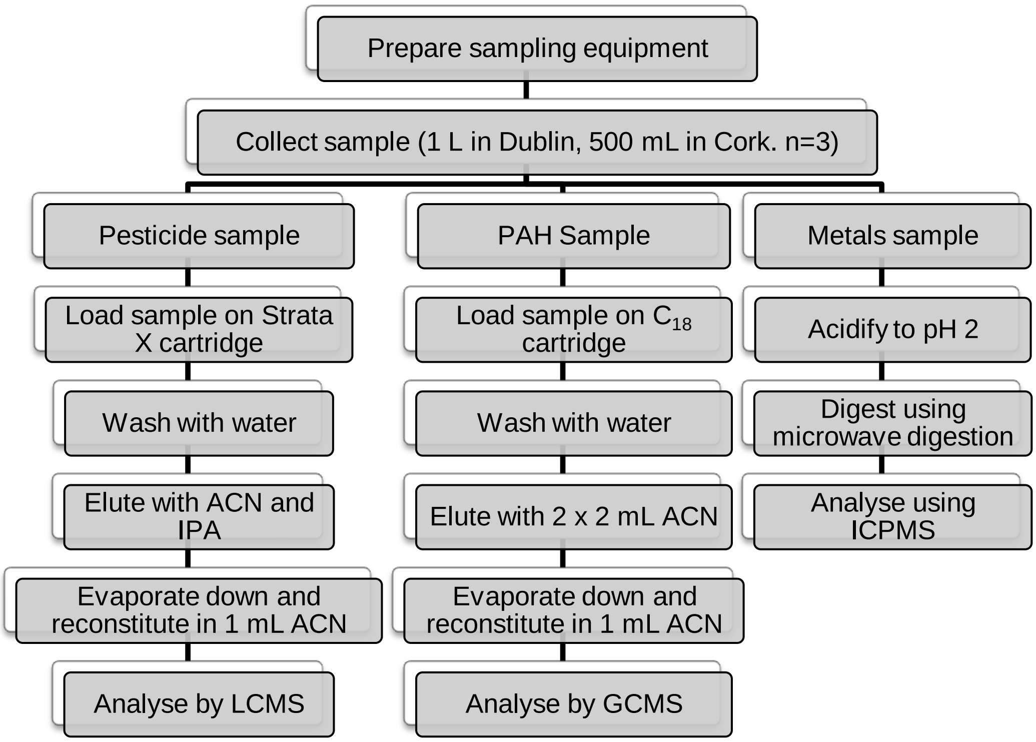


Figure 3-7 Overview of SOPs followed in sampling and extraction.

The SOPs are outlined in more details in the sections below.

3.6.2 OUTLINE OF SOP FOR PAHS

After developing a SPE method for the selective extraction of priority PAHs in wastewater the following basic SOP was applied between project partners to ensure consistent sample extraction procedures were carried out.

The collected samples of effluent were divided into 1 L/ 500 mL aliquots that were carefully poured into 1 L silanised amber glass bottles. The SPE cartridges, 6 mL, 500 mg Strata-C_{18} cartridges from Phenomenex (California, USA), were labelled appropriately and were placed in a SPE vacuum apparatus. SPE cartridges were conditioned with 2 mL acetonitrile followed by 2 mL methanol, and finally 2 mL of deionised water. Care was taken not to allow the cartridges to dry. After conditioning the samples were loaded to the cartridges after which the cartridges were rinsed with 2 x 2 mL deionised water and were allowed to vacuum dry. The SPE cartridges were stored at -18 ˚C until needed. They were then defrosted and eluted with 2 x 2 mL acetonitrile. This was evaporated down with nitrogen and reconstituted with 1 mL acetonitrile.

3.6.3 OUTLINE OF SOP FOR PESTICIDES

The collected samples of effluent were divided into 1 L aliquots, which were carefully poured into 1 L amber glass bottles. The solid phase extraction (SPE) cartridges, 6 mL, 500 mg Strata-X cartridges from Phenomenex (California, USA), were labelled appropriately and were placed in a SPE vacuum apparatus. SPE cartridges were conditioned with 6 mL methanol followed by 6 mL acetonitrile. Care was taken not to allow the cartridges to dry. After conditioning the samples were loaded to the cartridges after which the cartridges were rinsed with 2 x 2 mL deionised water and were allowed to vacuum dry. The SPE cartridges were frozen at -18 ˚C until needed. They were then defrosted and eluted with 2 mL acetonitrile and 2 mL isopropanol. This was evaporated down with nitrogen and reconstituted with 1 mL acetonitrile.

3.6.4 SAMPLE COLLECTION

For the priority PAHs and Pesticides prior to sampling all glass bottles used were silanised to prevent adsorption of analytes to inner bottle walls which leads to loss of sample and lower recoveries. Owing to the trace nature of these analytes this step was required as studies have shown that this ‘deactivation’ of the glassware masks the polar Si-OH groups on the glass thus decreasing its hydrophilicity. 5 L shatterproof glass bottle were taken and cleaned with detergent followed by acetone and then rinsed with deionised water. A solution of 10 % (v/v) dichloro-dimethylsilane in toluene is used to rinse the bottle. Finally, the bottle was rinsed with toluene followed by methanol.

Note: All bottles were appropriately labelled as Biohazards and included details of sampling location, time and date of collection, and initials of the sample collector. For metals and trace elements the glass bottles were first acid rinsed - no silanisation was required.

3.6.4.1 Grab Samples

The majority of samples involved in this project were grab samples with only Swords and Ringaskiddy providing composite samples. When collecting a grab sample the sampling bucket was rinsed three times with the effluent at sampling point. The bucket was filled with wastewater and used to fill the 5 L shatterproof bottles to the top, tapping the sides to remove air bubbles. Bottle lids were tightened securely and bottles were transported back to the lab, keeping the bottles in the dark to avoid exposure to light.

3.6.4.2 Composite Samples

When collecting the composite samples the bottles were given to the technicians at the wastewater treatment plant. The technicians would then fill the bottles to capacity from the plant auto-sampler. Finally after ensuring the bottle lids were tightened securely the bottles were transported back to the lab, keeping the bottles in the dark to avoid exposure to light.

3.6.5 SAMPLE PRESERVATION

In order to preserve samples, after sample collection all metals samples were acidified to pH <2 with concentrated nitric acid (HNO_3), this step is unique to the metals and trace elements. The PAH and pesticide samples were preserved as described below.

3.6.5.1 Water Samples

Water samples, of minimum sample volume 600 mL, for shipping to the project partners were stored in silanised amber bottles (or acid rinsed bottles for metals) or in dark conditions at 4˚C for a maximum period of 7 days. After this time samples required extraction or analysis. No further preservation was necessary. Samples arriving from Cork were to be extracted/digested upon arrival.

3.6.5.2 Extracted and Digested Samples

Samples collected in Dublin were extracted immediately using the sample preparation methods described earlier in this chapter. After extraction/digestion samples were stored in the dark at a temperature of -18˚C. No further preservation was necessary.

3.6.6 TRANSPORTATION

If transporting samples a short distance samples were transported by car and were extracted/digested within an hour of collection.

For long distance transportation i.e. between the Cork sites and Dublin, samples of water were to be chilled and preserved at a temperature of 4ºC and maintained at that temperature from the time of collection until analysis, in the dark or in amber bottles as PAHs and some pesticides are known to be light sensitive, and must be appropriately labelled and sealed to maintain chain of custody. Chain of custody forms were filled out and transported along with all samples exchanged throughout the course of the project. Sample bottles were placed in an ice chest for transport, this was filled with chopped or grated ice. Upon arrival samples were extracted immediately. The ice chests were sealed first with biohazard tape and then cling film.

3.7 Conclusion

This chapter highlights the need for SOPs and quality control measures especially in the area of environmental monitoring as chemicals are present in trace amounts and make for difficult analysis. In large collaborative projects it is important to establish these standard procedures between the different groups to maintain the same standard of sample handling and storage, as such SOPs are not only prepared according to APHA guidelines, but also chain of custody forms are in place which facilitate the tracking of all samples and any issues encountered, i.e. leaking of sample during transport.

The nature of the sample to be collected immediately defines the need for sample preparation procedures. In the case of WWTP effluent the presence of suspended solids, for example, is a major factor to be considered when choosing a compatible preparation procedure. This chapter summarises the process which should be followed when selecting and developing an appropriate sample preparation method.

The trace nature of the priority pollutants in this type of sample must also be taken into account, thus necessitating the procurement of larger sample volumes and large sorbent beds in the SPE procedures to allow for the concentration of analytes to a workable range. Through the procedures described in Chapter 4 it is possible to choose and develop three sample preparation methods for the priority pesticides, PAHs and metals and trace elements listed in the WFD.

To conclude this chapter has outlined the development of standard methods for the multiresidue extraction of WFD priority substances from wastewater effluent. The methods described use readily available equipment, are simple to use and allow for the requirements set out by the WFD and EQS directive to be met.

4. Method Development

4.1 Introduction

4.1.1 CHROMATOGRAPHIC SEPARATIONS

High performance liquid chromatography (HPLC) and gas chromatography (GC) are very popular analytical separation techniques. The basic principle involves the transportation of a sample in a mobile phase (liquid in HPLC, gas in GC), through a solid stationary phase, which is fixed in a thin column, and as the analyte elutes it is detected by a suitable detector. The sample becomes partitioned based on affinity for either the solid or the mobile phase. Components that are strongly retained on the stationary phase elute from the column more slowly than those weakly retained by the stationary phase. These differences in mobility through a column are the basis of separation. This method can be both quantitative and qualitative (Skoog, Holler *et al.* 1998).

The stationary phase in HPLC is generally silica based and can be either reversed-phase or normal-phase. In reversed-phase chromatography the stationary phase is nonpolar, and the mobile phase is polar, the opposite is true for normal-phase chromatography. The type of chromatography chosen is determined by the properties of the analyte. In reverse-phase chromatography non-polar samples are more strongly retained, while polar samples are more strongly retained in normal-phase chromatography. (Skoog, Holler and Nieman 1998) GC employs mainly polymeric stationary phases and capillary columns 30-60m in length. In chromatography the column diameter and length must be taken into account as they affect separation efficiency and analysis times. The most commonly used columns in LC separations are 100-250 mm long, with an internal diameter of 3-5 mm. Longer columns have longer analysis times but better resolution, while shorter columns have shorter analysis times and lose some resolution, the same theory applies to GC. Capillary columns are also popular in LC with diameters of 0.05-0.3 mm they offer high separation and sensitivity, although they do require long analysis times (Kostiainen, Kauppila 2009).

Coupled to a chromatographic instrument is a detection system that allows for the identification of compounds as they elute from the column. Detection can use optical properties or physical transformation of the analytes in order to visualize sample components. In chromatographic analysis of PAHs and pesticides ultraviolet (UV), fluorescence and mass spectrometric detection were found to commonly occur in the literature. A mass spectrometer, MS, is an instrument, which separates moving ions on the basis of their mass-to-charge-ratios (*m/z*). This involves a number of steps: atomization, ionisation, separating the ions formed on the basis of their mass-to-charge-ratio, and counting the number of ions of each type. The m/z value is generally equal to the mass of the ion as most ions formed are singly charged. (Skoog, Holler and Nieman 1998) The final product of MS, is a mass spectrum, this is characteristic of a certain compound and can be used for identification (Manahan 2000).

4.1.2 POLYCYCLIC AROMATIC HYDROCARBONS

Reverse phase columns can readily separate a number of PAHs isomers. Common solvents used with these columns are acetonitrile-water or methanol-water combinations with gradient elution. Generally fluorescent detectors are used in order to take advantage of the strong fluorescence exhibited by many PAHs, and this method is still considered the most powerful technique (comparable only to MS-SIM detection) in terms of sensitivity and selectivity. HPLC techniques are preferred over GC methods in some instances as they allow the detection of high-molecular mass PAHs which could undergo thermal decomposition at the high temperatures required for GC analysis (Moret, Conte 2000, Peltonen, Kuljukka 1995). It was found that the high-molecular weight priority PAHs were suitable for GCMS analysis, reaching low limits of detection and improved separation over the HPLC-FLD method.

While liquid chromatography is commonly used in PAH analysis when coupled with fluorescence or diode array detection, GC with flame ionization detector (FID) electron capture detection (ECD) (Singh, Spassova *et al.* 1998) or MS based detection also have many applications (Barco-Bonilla, Vidal *et al.* 2009, Gimeno, Altelaar *et al.* 2002, Peltonen, Kuljukka 1995, Brum, Netto 2009). Other forms of GC such as high resolution GC (HRGC) and capillary GC(Barro, Regueiro *et al.* 2009, Poster, Schantz *et al.* 2006, Brum, Netto 2009) are also common. The priority PAHs meet the main requirement for GC analysis, namely the ability to volatilize within a given temperature range with most PAHs containing up to 24 carbon atoms being eligible (Barton, Johnson *et al.* 1979). GC, as an analytical method, offers shorter analysis times, low limits of detection and high resolution (Peltonen, Kuljukka 1995, Bjørseth, Dennis 1980). GC methods can also easily be adapted to meet the analyst's needs with only slight modifications – such as column, detector, temperature, and, in the case of MS, change in the ionization mode.

The choice of column in GC analysis is important and stationary phases are being developed with increasing levels of thermal stability, these being polymer based and producing more reproducible chromatographic data (Peltonen, Kuljukka 1995). Separations are generally carried out on cross-linked fused silica capillaries with slightly polar to non-polar sorbents; e.g. 5% phenyl methyl silicone (Ratola, Lacorte *et al.* 2006) and methyl silicone, respectively, with the former being most frequently used. These columns are robust and commonly commercially available (De Boer, Law 2003). This is in contrast to special application columns with selective stationary phases which are being developed by several analysts, e.g. the use of nematic liquid crystal phases (De Boer, Law 2003). Capillary columns are the most widely used, favoured for greater selectivity, sensitivity and resolution when compared to LC (Barro, Regueiro *et al.* 2009, Poster, Schantz *et al.* 2006) and for their ability to highly resolve complex PAHs which form as a result of inconsistent combustion processes (Peltonen, Kuljukka 1995, De Boer, Law 2003). As with all GC analyses the column length is also an important parameter with 30 m being the most common. Studies have been carried out to compare 30 m and 60 m column lengths

(Filipkowska, Lubecki *et al.* 2005) and the improved resolution of the 60 m length must be weighed against the shorter run-times of the 30 m.

In the detection of PAHs fluorescence has been found to be a very sensitive and selective method of detection when coupled to LC (Barco-Bonilla, Vidal *et al.* 2009) while MS has found most applications in GC analysis. FID has also been applied to PAH analysis with finding that the lack of sensitivity of this detector is incomparable to the MS which provides better selectivity, more reliable results, analyte confirmation, and lower limits of detection (Barco-Bonilla, Vidal *et al.* 2009). Another group, (Singh, Spassova *et al.* 1998) however, compared GC-MS to GC-ECD finding ECD to be the more sensitive method, but though the use of selected ion monitoring (SIM) the analyst can monitor only selected ions, increasing method selectivity with specific compounds easily added to or removed from the SIM program and thus lower detection limits.

MS is generally used in the electron impact (EI) mode with selective ion monitoring (SIM) (Valero-Navarro, Fernández-Sánchez *et al.* 2007, Crozier, Plomley *et al.* 2001, Ratola, Lacorte *et al.* 2006, Bercaru, Ulberth *et al.* 2006). This method provides enhanced sensitivity (Barro, Regueiro *et al.* 2009) and PAHs, mostly, yield strong molecular ions with little fragmentation in this mode (De Boer, Law 2003).

Table 4-1 Method parameters of a selection of PAH studies with 'PAHs' column indicating the number of PAHs included in the method for analysis.

PAHs	***Analysis***	***Column***	***Run Time (min)***	***Mode***	
16	GC-IT-MS	DB-5ms	35	EI, SIM mode	(Valero-Navarro, Fernández-Sánchez *et al.* 2007)
17	GC-IT-MS	DB-5ms	35	EI, SIM mode	(Crozier, Plomley *et al.* 2001)
16	GCMS	DB5–MS	34.2	EI, SIM mode	(Bercaru, Ulberth *et al.* 2006)
16	GCMS		n/a	EI, TIM mode	(Shimmo, Adler *et al.* 2002)
17	GCMS	DB5MS	40	EI, SIM mode	(Gmeiner, Stehlik *et al.* 1997)
16	GCMS	HP 5MS	40	EI, SIM mode	(Gaga, Tuncel 2004)
16	GCMS	HP-DB 5MS	45	EI, SIM mode	(Meudec, Dussauze *et al.* 2006)
17	GCMS	DB-5	35	EI, SIM mode	(Sprovieri, Feo *et al.* 2007)
16	GCMS	DB-5MS	35	SIM mode	(Cao, Wang *et al.* 2005)
15	GCMS	HP-5	50	EI, SIM mode	(Pérez, Farré *et al.* 2001)
12	GCFID	CP-Sil	110	EI, SIM mode	(Fernandes, Sicre 1999)
22	GCFID	SE54	102	EI, SIM mode	(Readman, Fillmann *et al.* 2002)
16	GCMS	HP-5		SIM mode	(Pérez, Guillamón *et al.* 2001)
15	GCMS	HP-5MS SV	32	SIM mode	(Simon, Palme *et al.* 2006)
16	GCMS	SPB-5	50	SIM mode	(Wolska, Galer *et al.* 1999)
16	GCMS	ZB 5	28	EI	(Werres, Balsaa *et al.* 2009)

4.1.3 PESTICIDES

As the project was a collaboration between two research groups the task of method development was shared with the other research group focussing on LCMS-based methodologies, thus although LCMS is the preferred method for the analysis of pesticides in wastewater the focus of this chapter is the development of a GC method for this multi-residue analysis.

Some GC methods which are commonly implemented in the analysis of pesticides include electron capture detection (ECD) (Concha-Graña, Fernández-Martínez *et al.* 2009) flame photometric detection (FPD) (Yao, Jiang *et al.* 2001), nitrogen-phosphorous detection (NPD) (Dugay, Miege *et al.* 1998) and atomic emission detection (AED) all of which are element-selective detectors (Vinas, Campillo *et al.* 2002, Ahmed 2001), used because of the heteroatoms contained in most pesticides, with AED being more sensitive due to its multichannel ability which allows it to detect all elements, except helium, separately (Van Stee, Leonards *et al.* 1999).

From Table 4-2 below it is clear that GC-ECD is a popularly used method and studies report low limits of detection. Absolute detection limits of this model of detector are reported to be ca. 100 femtogram (fg) (De Boer, Law 2003) with a number of studies (Concha-Graña, Fernández-Martínez *et al.* 2009, Boussahel, Bouland *et al.* 2002, Junior, Re-Poppi 2007) reporting low limits of detection. These low levels allow for trace analysis which is important from an environmental point of view as many potentially harmful contaminants present in water are only at low concentrations and may go completely undetected without a method with trace analysis capabilities. These same studies also reported good linearity's using the ECD, whereas De Boer and Law (2003) reported that poor linearity is a major drawback of the ECD making it necessary to perform a method of multi-level calibration to solve this problem (De Boer, Law 2003). As an alternative to ECD, Guardia Rubio *et al.* (2007) found thermionic sensitive detection (TSD) to be the more selective detection method although it is less commonly used as a method of pesticide analysis (Guardia Rubio, Ruiz Medina *et al.* 2007).

FPD and NPD have also found many applications in the analysis of pesticides and as in Table 4-2 below both methods have been shown to achieve good linearities, limits of detection and limits of quantification. Vassilakis *et al.* (1998) found GCNPD to produce poor resolution and resorted to using LC-DAD to confirm the analysis (Vassilakis, Tsipi *et al.* 1998). In both gas- and liquid chromatographic methods detection based on MS is a powerful method, providing selective and sensitive analysis of pesticides (Planas, Puig *et al.* 2006) with the added benefit of acquirement of structural information for the analyte (Vinas, Campillo *et al.* 2002). GC-tandem MS (GC-MSMS) minimizes the level of clean-up required for complex environmental samples due to its highly specific analyses, is easy to use, and is relatively low cost, however its applications are limited to residue confirmation (Tahboub, Zaater *et al.* 2005, Bennett, Chung *et* *al.* 1997) with single MS remaining the most commonly used method (Hada, Takino *et al.* 2000, Natangelo, Tavazzi *et al.* 1999, McGowin, Adom *et al.* 2001).

In the GC analysis of pesticides fused-silica capillary columns are the most commonly employed, facilitating the separation of many pesticides with similar characteristics. As pesticides cover a large range of polarities this affects the choice of stationary phase with polar pesticides such as the organophosphorous pesticides requiring polar sorbents e.g. DB 170 (Pang, Cao *et al.* 2006) and non-polar pesticides such as organochlorine pesticides requiring non-polar sorbents e.g. DB-1 or DB-5 (Planas, Puig *et al.* 2006, Tahboub, Zaater *et al.* 2005). It must also be noted that the non-polar stationary phases are generally considered more robust (Ahmed 2001). Although many types of columns were evaluated in the methods below, (Table 4-2), the majority were fused silica capillary columns of 0.25 mm internal diameter (I.D.) and 0.25 µm film thickness with similar sorbents, and of 30 – 60 m in length, with the exception of Hada *et al.* (2000) and Korenkova *et al.* (2003) who successfully used columns of 10 and 15 m lengths, respectively. The results were both limits of detection and quantification in the ng L^{-1} region, and analysis times of 8-9 minutes. This is a major advantage in large-scale environmental analysis when large sample numbers must be analysed at regular intervals, however this method may result in reduced resolution, and selectivity (Hada, Takino *et al.* 2000, Korenkova, Matisova *et al.* 2003).

Injection volume is also comparable in the studies included in Table 4-2 the majority of which carried out sample injections of less than 4 µL with reasonable results with the exception of (Concha-Graña, Fernández-Martínez *et al.* 2009) who used large sample injection volumes of 100 µL. They found this method to be comparable to both GCECD and GCMS and achieved low limits of detection, between 0.3-25 ng L^{-1}, high recoveries, 69-107%, and finally very high precision, 0.2-1.3%. When evaluating injection volumes as part of this priority substances work it was found that injection volumes over 20 µL resulted in overloading of the column leading to split peaks with shoulders and overall poor resolution.

Table 4-2 Literature review of GC-based pesticide separation methods.

Pests. In study.	***Method***	***Column***	***Run Time (min)***	***Mode***	***Reference***
6	GC-MS	HP-5MS	14	TIC	(McGowin, Adom *et al.* 2001)
Mix	GC–MS	HP-5MS	35	Full scan	(Pérez-Carrera, León *et al.* 2007)
32	GCMS	DB-5	57	SIM	(Planas, Puig *et al.* 2006)
21	GCECD	DB-XLB		n/a	(Concha-Graña, Fernández-Martínez *et al.* 2009)
	GCECD	DB-35	23.5	n/a	
	GCMS	DB-XLB	60.3	SIM	
Mix	GCECD	n/a	54.5	n/a	(Vassilakis, Tsipi *et al.* 1998)
	GCNPD	n/a	52	n/a	
	GCMS	HP-5	52	SIM	
	GCECD	n/a	54.5	n/a	
Mix	GCECD	PTE5	41	n/a	(Boussahel, Bouland *et al.* 2002)
14	GCMSMS	DB-5.625MS	36	Full Scan	(Tahboub, Zaater *et al.* 2005)
18	GC-ECD	VF-5MS	50	n/a	(Junior, Re-Poppi 2007)
8	GCMS/MS	DB-5-MS	36	n/a	(Sauret-Szczepanski, Mirabel *et al.* 2006)
12	GCNPD	DB-5.625	37	n/a	(Dugay, Miege *et al.* 1998)
17	GCMS	HP-1	8.5	SIM	(Hada, Takino *et al.* 2000)
15	GCMS	HP-1MS	8	SIM	(Korenkova, Matisova *et al.* 2003)
16	GC-ECD	ZB-35	30	n/a	(Mmualefe, Torto *et al.* 2009)
	GC-TOFMS		30	n/a	
22	GCMS	DB-5 MS	39	SIM	(Quintana, Martí *et al.* 2001)
75	GCMS	HP-5MS	60.5	SIM	(de Almeida Azevedo, Lacorte *et al.* 2000)
10	GC-IT-MS	CP-Sil 8 CB	30	TIC, SIM	(Maloschik, Ernst *et al.* 2007)
28	GC TSD and ECD	CP-SIL 5CB CP-SIL 8CB	34 23	n/a	(Guardia Rubio, Ruiz Medina *et al.* 2007)
12	GCMS	DB-5MS	50	SIM	(Wang, Zhao *et al.* 2007)
29	GCMS	NB-5	35	SIM	(Sasano, Hamada *et al.* 2000)
46	GC-IT-MS	VF-5 MS	34.5	Full scan	(Beceiro-González, Concha-Graña *et al.* 2007)
21	GCMS	DB-1701.	38	SIM	(Chen, Yu *et al.* 2009)
8	GCMS	DB-5MS	28	SIM	(Silva, Aquino *et al.* 2008)

4.1.4 METALS AND TRACE ELEMENTS

In the analysis of trace metals and metal coordination compounds GC and HPLC are the most commonly used chromatographic techniques. Ion-pair chromatography is also rapidly gaining popularity as are other reverse phase HPLC methods such as ion exchange HPLC and size-exclusion HPLC. For example a size-exclusion ICP-MS system was set-up specifically to analyse heavy metal complexes in natural aquatic samples, Wang, Lee (1997), and Jones-Lepp, Momplaisir (2005) found LC-ESI-MS to be suitable for the analysis of organometallics such as organotin, organoboron, and organoselenium. As with Jones-Lepp, Momplaisir (2005), Reemtsma (2001) evaluated the use of LC-ESI-MS in the analysis of organometallic complexes and found it efficient. It allows the identification of the organic compounds masked by signals obtained for one element in LC-ICP-MS. In surface water a number of obstacles for the detection of organometallics exist; sample enrichment is required due to their low concentrations in natural environments, and there is limited stability of many organometallic complexes.

Most chromatographic analyses of metals require use of a complexing agent during sample preparation and these agents can produce high background interference, another method involves sample pre-treatment using hydrolysis or derivatisation, which can suffer from incomplete reactions. As mentioned above newer methods are used and these help to overcome the issues associated with sample preparation: capillary electrophoresis (CE) with indirect UV and direct absorbance detection, ICP-MS with micellar LC, and ion exchange LC-ICP-MS (Jones-Lepp, Momplaisir 2005).

While there are chromatographic methods available for the analysis of metals and trace elements it is inductively coupled plasma (ICP) based methods that are most common, i.e. ICP-MS, and ICPAES (atomic emission spectroscopy) and these also allow for the low limits of detection required by the WFD and EQS Directive to be met. This is highlighted in Table 4-3 which summarises a number of studies carried out in the area of metal and trace element analysis in environmental matrices and the methods used by the various research groups.

Table 4-3 Summary of studies carried out for trace element and metal analysis in various matrices.

Metals	*Medium*	*Analysis Method*	*Reference*
11	Water	HGAAS, ICPOES	(Kavcar, Sofuoglu *et al.* 2009)
11	Sediments and suspended solids	ICPAES, GFAAS	(Woitke, Wellmitz *et al.* 2003)
8	Drinking water	FAAS	(Bulut, Gundogdu *et al.* 2007)
7	Seawater, well water and tap water	FAAS	(Prabhakaran, Subramanian 2003)
30	Urine	ICPMS	(Heitland, Köster 2006)
23	blood	ICPMS	(Heitland, Köster 2006)
5	Water	ICPOES	(Chen, Hu *et al.* 2009)
7	Drinking water and sediment	FAAS	(Saraçoglu, Elçi 2002)
22	Water and urine	HGAAS, ICPMS, CVAAS	(Asante, Agusa *et al.* 2007)
5	Water and sediment	AAS	(Divrikli, Elçi 2002)
23	Ambient particulate matter	ICPMS	(Pekney, Davidson 2005)
2	Sea water	GFAAS	(Ceccarini, Cecchini *et al.* 2005)
11	Sea water	ICPMS	(Hirata, Ishida *et al.* 2001)
10	Sea water	ICPMS	(Hirata, Kajiya *et al.* 2003)
20	Sea water	ICPMS	(Willie, Sturgeon 2001)
10	Water	ETAAS, QFAAS	(Tueros, Rodríguez *et al.* 2008)
11	Sea water	ICPOES	(Otero-Romaní, Moreda-Piñeiro *et al.* 2005)
6	Human hair	FAAS, ETAAS	(Bermejo-Barrera, Muñiz-Naveiro *et al.* 2000)
4	Urban soils and street dusts	ICPAES	(Li, Poon *et al.* 2001)
12	Drinking water	GFAAS	(Tamasi, Cini 2004)
11	Rain water	ICPMS	(Karthikeyan, Balasubramanian 2006)

4.1.5 METHOD DEVELOPMENT

Method development is undertaken after the project has been specified and the medium selected. Figure 4-1 below illustrates the steps involved in the method development process. The first 3 steps involve the method development with the following steps outlining the stages of method validation. It is important that methods used are robust, precise, reaching low limits of detection and quantitation and have a good linear range.

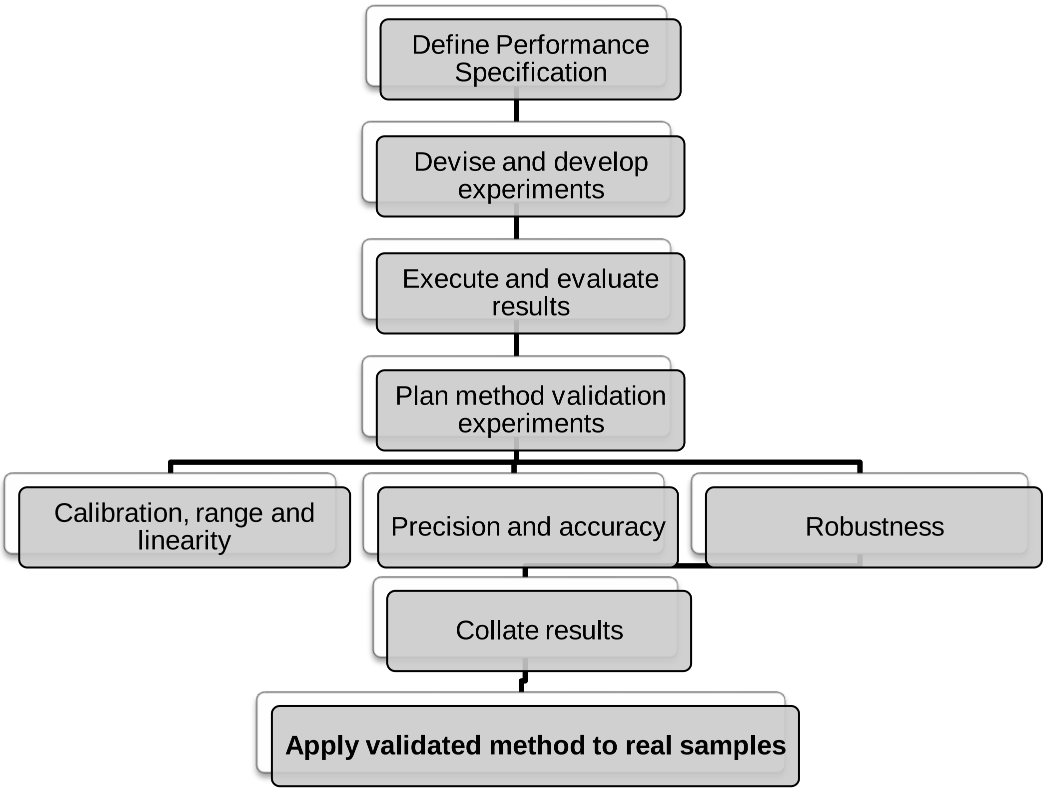


Figure 4-1 Schematic of the steps involved in method development.

The method development steps outlined above where applied to the development of methods for the analysis of all priority pesticides, PAHS and metals and trace elements listed in the WFD. The VOCs were omitted from the process due to their volatile nature and inefficient sample storage procedures. A fully developed method for the analysis of PAHs from wastewater was taken further through the stages of method validation and all PAH sample analysis was carried out in Dublin. The metals samples were sent away for analysis after sample preparation procedures were carried out, as were the pesticide samples.

4.2 Aims and Objectives

The aim of this section is to develop methods for the analysis of WFD priority substances in water. These are multiresidue methods that allow for the low levels of detection required by the EQS directive.

The objectives are to:

- Review some the literature in relation to the analysis of priority PAHs, pesticides and metals and trace elements.
- Describe the steps taken in the development of analytical methods.
- Improve on current methods of PAH analysis by reducing run-times.
- Detail method validation procedures followed.

4.3 PAH Method Development

4.3.1 HPLC METHOD

HPLC with ultraviolet (UV) and fluorescence detection (FLD) are the most common LC methods for the analysis of the 8 WFD priority PAHs listed in Table 1-5. From the literature it was found that most studies had found success with either methanol (MeOH) or acetonitrile (ACN) based mobile phases as the PAHs are nonpolar and hydrophobic the columns found to be most suitable were chemically bonded silica's, C_{18}. This echoes the results of the SPE method development as the same basic principle is applied. All analysis was carried out on an Agilent 1100 HPLC with UV and FLD detection, and the column was a Supelco Supelcosil LC-$_{18}$ HPLC column (25 cm x 4.6 mm, 5 µm) (Sigma-Aldrich, Ireland). This method was designed as a simple means of validating the SPE method during its development stages.

The first step involved the analysis of PAH standards by both UV and fluorescence in order to determine optimum wavelengths for detector settings. The UV detector chosen could be set to 4 wavelengths simultaneously, therefore 200 nm, 220 nm, 253 nm, and 300 nm were selected, as they would provide the best detection of the analytes. Table 4-4 lists the optimum detector settings for the detection of the 8 priority PAHs.

Table 4-4 Optimum wavelengths for both UV and fluorescence detection of PAHs

	Optimum Wavelengths	
	UV wavelength (nm)	Fluorescence Wavelengths (nm)
Naphthalene	220	Em. 330 Ex. 220
Anthracene	253	Em. 370 Ex. 253
Fluoranthene	220	Em. 420 Ex. 235
Benzo-b-fluoranthene	253	Em. 420 Ex. 235
Benzo-k-fluoranthene	253	Em. 420 Ex. 235
Benzo-a-pyrene	253	Em. 420 Ex. 235
Benzo-ghi-perylene	253	Em. 420 Ex. 235
Indeno-1,2,3cd-pyrene	253	Em. 420 Ex. 235

In order to validate these wavelengths a simple analysis of 10 ppm standards of each of the PAHs run using a mobile phase composed of 95 % MeOH and 5 % dionised water was carried out. Figure 4-2 shows a 10 ppm naphthalene standard run using the method outlined at 220 nm. A clear peak can be seen with no tailing effects.

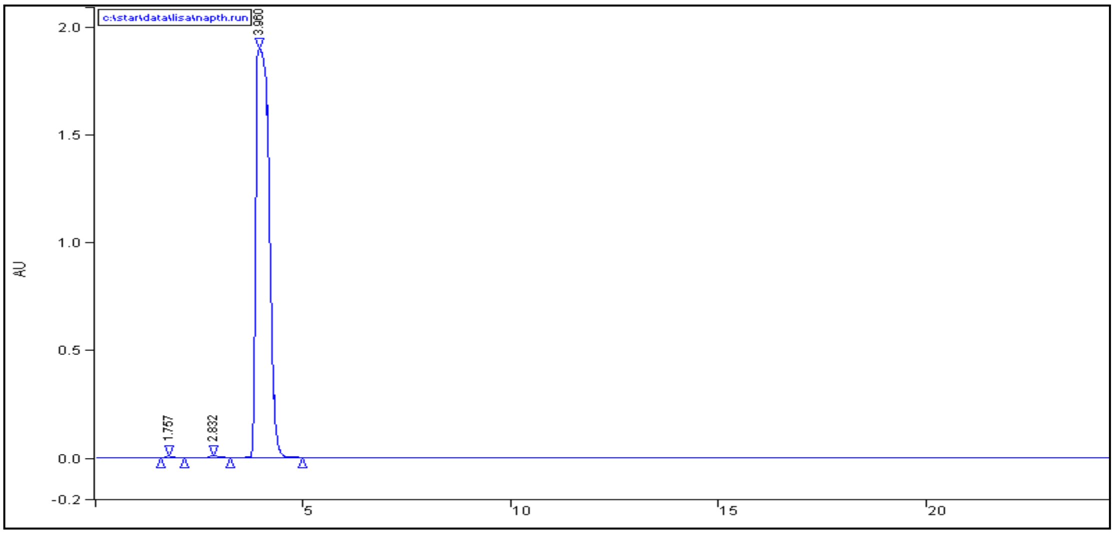


Figure 4-2 Naphthalene, 10 ppm, run on Agilent 1100 HPLC with UV detection at 220 nm.

The results of the UV detection study were further validated by the results shown in Table 4-5. While the PAHs were detected at each of the selected wavelengths 220 nm and 253 nm provided the greatest recoveries in terms of peak area.

Table 4-5 Peak areas and retention times for the PAHs at 95:5 MeOH:Water. N=3

	Time	***200nm***	***220nm***	***253nm***	***300nm***
Naphthtalene	3.883	3585591	**22812448**	861645	69035
Anthracene	4.917	2181756	5110696	**24263826**	337122
Fluoranthene	5.523	3650848	**5397719**	2199909	511676
Benzo-b/k-fluoranthene	9.053	3120331	5398191	**14900387**	8412211
Benzo-a-pyrene	10.013	2205080	3071215	**5356415**	1552418
Indeno-1,2,3cd-pyrene	12.221	2205080	3071215	**5356415**	1552418
Benzo-ghi-perylene	13.64	2099909	3203659	**4028285**	1712531

Figure 4-3 and Figure 4-4 show two chromatograms in which the analysis of the 10 ppm standards at 253 nm allowed for improved peak areas for benzo-a-pyrene and benzo-ghi-perylene.

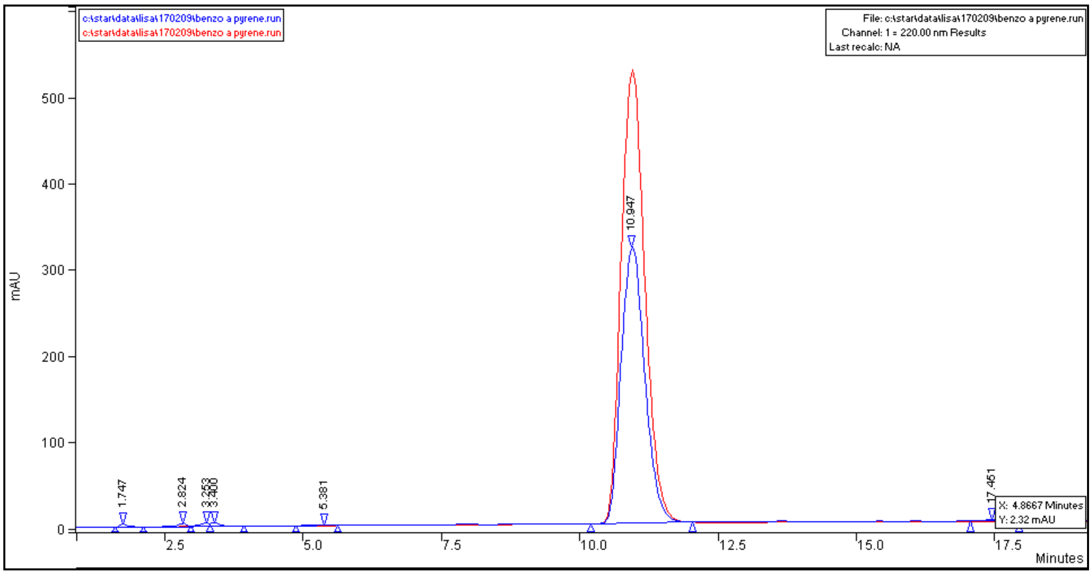


Figure 4-3 Benzo-a-pyrene, 10 ppm, run on Agilent 1100 HPLC with UV detection at 220 nm (blue) and 253 nm (red)

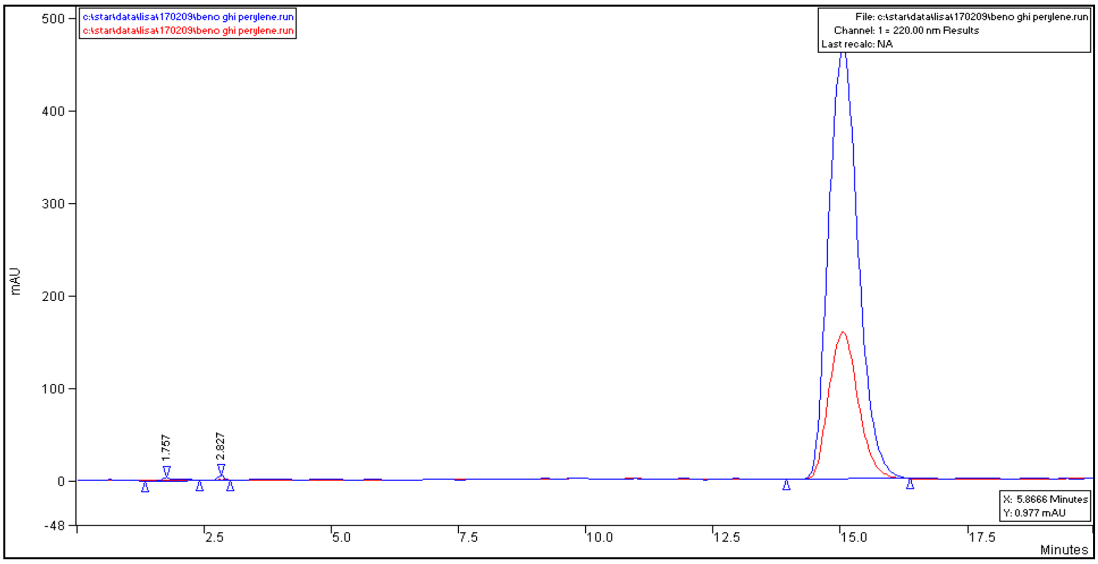


Figure 4-4 Benzo-ghi-perylene, 10 ppm, run on Agilent 1100 HPLC with UV detection at 220 nm (blue) and 253 nm (red).

After wavelength optimization the mobile phase composition was evaluated. From the literature combinations of ACN:water and MeOH:water were most common and were found to achieve good resolution and recoveries of PAHs. Therefore combinations and ratios of 95:5, 80:20, 75:25, and 50:50 each of ACN:Water and MeOH:Water were investigated. The 95:5 MeOH:Water proved to have the best resolution of samples. A simple method with 5 µL injection volume, a 1 mL min^{-1} flow rate and overall 15 minute runtime was therefore used for the validation of the PAH SPE method using the detection and mobile phase parameters described above.

4.3.2 GCMS METHOD

For the method development by GCMS for PAHs in wastewater the first step was to run all PAHs on the instrument using a basic single-step heating regime to determine relative retention times and to allow the collection of mass spectra of each of the compounds. The main ions of these mass spectra are listed in Table 4-6. 100 ppm solutions of each of the 8 priority PAHs (Sigma-Aldrich) were prepared in methanol and 1 µL aliquots were injected onto a Hewlett Packard (HP 6890 Series GC) equipped with a DB5-MS (5% Poly (dimethylsiloxy) poly (1,4-bis (dimethylsiloxy) phenylen) siloxane, 0.25 mm x 25 m x 0.25 µm) ultra-inert column (Agilent, Ireland). An ultra-inert column was chosen due to issues with column bleed at the high temperatures required to elute the higher molecular weight PAHs.

Table 4-6 List of priority PAHs with their molecular weights and mass spectrum ions. Main ions are marked in bold.

PAH	*Molecular weight (g)*	*Main Ions*
Naphthalene	128.17	**128**, 102, 98, 87, 64, 51
Anthracene	178.23	**178**, 152, 139,126,89,76,63
Fluoranthene	202.25	**202**, 174, 150, 101, 88, 75
Benzo-b-fluoranthene	252.31	281, **252**, 224, 207, 126, 113, 100, 73
Benzo-k-fluoranthene	252.31	281, **252**, 224, 207, 126, 113, 100
Benzo-a-pyrene	252.31	281, **252**, 224, 207, 126, 113, 100, 73
Benzo-ghi-perylene	276.33	355, **276**, 253, 207, 138, 124, 111, 96
Indeno-1,2,3cd-pyrene	276.33	**276**, 248, 207, 138, 112, 73

Figure 4-5 and Figure 4-6 are two examples of mass spectra obtained using the method described above.

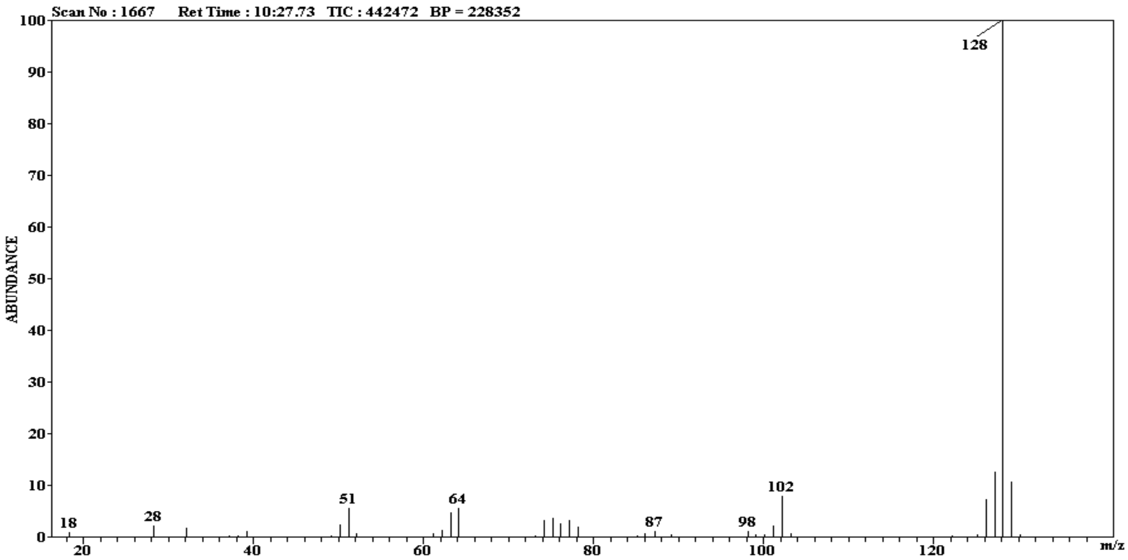


Figure 4-5 Mass Spectrum of Naphthalene obtained using method described in Section 4.2.3

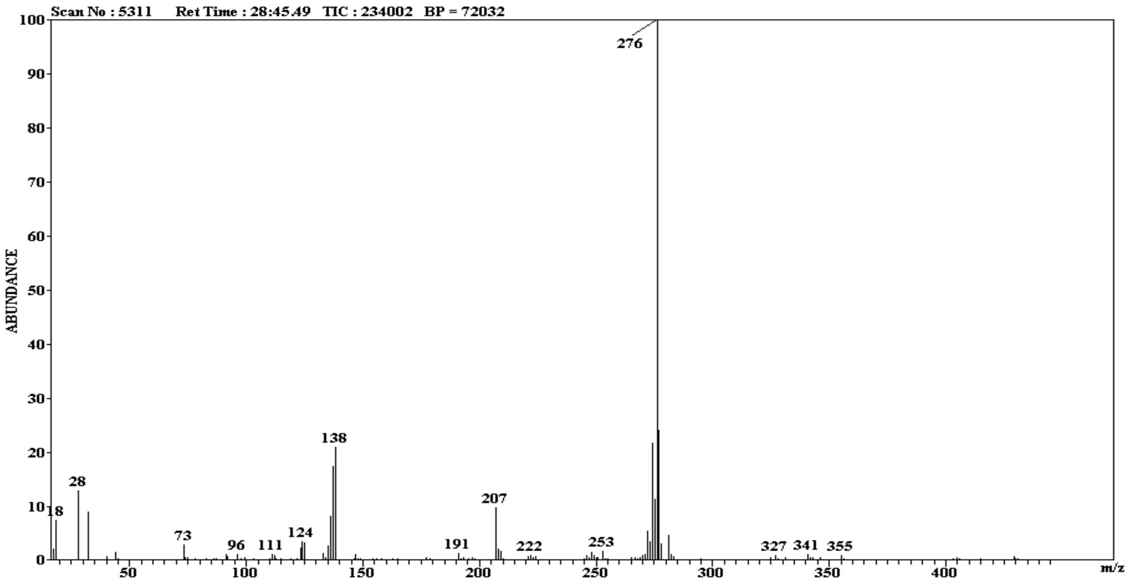


Figure 4-6 Mass Spectrum of Benzo-g,h,i-perylene obtained using method described in Section 4.2.3

After the mass spectra and relative retention times were obtained for each of the 8 priority PAHs various methods were evaluated, a selection of which are presented in

Table 4-7.

Table 4-7 Selection of some of the methods evaluated for the determination of PAHs in wastewater and method parameters. Not all methods are included as there were only small differences between some methods. TIC = total ion chromatogram.

GC Methods

Method No.	Inlet temp. (°C)	Injection Mode	He Flow (mL min^{-1})	Initial Temp (°C)	Temp gradient (°C)				MS mode	Run time (min)
					#	Rate	Final temp.	Final time		
1	180	Splitless	1	80	1	40.00	143	0.00	TIC	38.98
					2	10.00	150	2.00		
					3	10.00	170	0.00		
					4	30.00	230	2.00		
					5	1.00	250	2.00		
					6	50.00	310	5.00		
4	180	Splitless	1	60	1	60.00	220	15.00	TIC	33.67
					2	20.00	300	10.00		
6	180	Splitless	1	60	1	60.00	280	5.00	TIC	18
					2	60.00	300	7.00		
9	260	Splitless	1.3	55	1	25.00	310	10.0	TIC	21.2
11	260	Splitless	1.3	55	1	25.00	290	0.50	TIC	18.83
					2	20.00	260	2.00		
					3	35.00	310	3.00		
14	260	Splitless	1.3	55	1	25.00	290	0.50	TIC	20.74
					2	50.00	230	2.50		

					3 70.00	310	5.00		
16	260	Splitless	1.3	55	1 40.00	290	0.50	TIC	16.02
					2 60.00	230	2.50		
					3 70.00	310	1.00		
					4 10.00	320	2.00		
22	300	splitless	1.3	55	1 25.00	320	5.00	TIC	16.6
25	300	splitless	1.3	55	1 35.00	280	1.00	TIC	19.05
					2 25.00	220	1.00		
					3 45.00	320	5.00		
26	300	splitless	1.3	55	1 35.00	300	1.00	TIC	20.76
					2 35.00	200	1.50		
					3 50.00	320	4.00		
27	300	splitless	1.3	55	1 35.00	280	1.00	TIC	17.5
					2 25.00	220	0.00		
					3 60.00	320	5.00		
29	300	splitless	1.3	55	1 35.00	260	0.00	TIC	13.69
					2 60.00	220	0.50		
					3 60.00	320	4.00		
34	300	splitless	1.3	55	1 25.00	260	1.00	TIC	18.12
					2 60.00	190	0.50		
					3 60.00	325	4.00		

For each of the methods listed in

Table 4-7 the resolutions of the separate PAHs were evaluated. Table 4-8 shows the results of resolution studies for all PAHs for the selection of methods outlined in

Table 4-7. A value of 1.5 indicates perfect peak resolution, a value below this signifies poor resolution while a value above indicates increasing resolution between peaks. Much difficulty was encountered in peak separation, specifically poor resolution between benzo-b-fluoranthene and benzo-k-fluoranthene which often co-eluted. Through contact with the Irish EPA it was made clear that complete resolution of these peaks is not necessary as the EQS value that applies is a SUM value of both peaks and not the individual peaks.

Table 4-8 Table of resolutions achieved using the methods outlined in Table 4-7 for each PAH. Nap - naphthalene, Ant - anthracene, Flr -fluoranthene, BbF and BkF - benzo-b- and benzo-k-fluoranthene, Bap – benzo-a-pyrene, Indeno – indeno-1,2,3cd-pyrene, Bghi – Benzo-ghi-perylene. N=3

Method	***1***	***4***	***6***	***9***	***11***	***14***	***16***	***22***	***25***	***26***	***27***	***29***	***34***
Nap.	81.3	33.2	30.4	53.5	34.1	45.1	42.2	63.5	0.0	41.2	44.3	40.0	55.4
Ant.	28.6	22.0	15.6	14.1	18.8	18.8	19.2	21.3	17.9	16.7	16.5	23.9	18.4
Flr.	94.8	70.7	55.1	36.9	44.0	93.8	94.3	47.8	122.5	23.0	94.5	39.7	89.3
Bbf.	1.3	0.9	0.7	0.6	0.6	0.7	0.8	0.6	0.9	1.0	0.8	0.8	0.8
Bkf.	12.4	7.6	7.5	5.8	6.3	5.0	6.6	6.2	6.0	5.7	20.0	6.3	5.3
Bap.	12.4	25.9	19.8	15.4	20.9	18.6	21.9	22.2	23.4	18.5	21.3	17.7	14.9
Bghi.	0.0	4.9	5.5	3.7	5.3	4.3	4.7	5.4	5.5	5.3	4.6	4.3	4.5
Indeno	0.0	4.9	5.5	3.7	5.3	4.3	4.7	5.4	5.5	5.3	4.6	4.3	4.5

The same methods were evaluated for peak area and the results are shown in Table 4-9. This table shows the enhanced peak areas of the PAHs in some methods over others, a factor which is very important due to the trace nature of the samples.

Table 4-9 Table of peak areas achieved using the methods outlined in Table 4-7 for each of the 8 PAHs. Nap - naphthalene, Ant - anthracene, Flr -fluoranthene, BbF and BkF - benzo-b- and benzo-k-fluoranthene, Bap – benzo-a-pyrene, Indeno – indeno-1,2,3cd-pyrene, Bghi – Benzo-ghi-perylene. N=3

	PEAK AREA							
Method	**Nap.**	**Ant.**	**Flr**	**Bbf**	**Bkf**	**Bap**	**Bghi**	**Indeno**
1	1.9E+06	2.1E+06	2.1E+06	6.8E+05	6.3E+05	3.8E+05	0.0E+00	0.0E+00
4	1.5E+06	1.5E+06	1.5E+06	6.2E+05	6.2E+05	4.3E+05	3.4E+05	2.3E+05
6	1.3E+06	1.5E+06	1.6E+06	6.3E+05	6.7E+05	4.2E+05	4.9E+05	1.5E+05
9	3.8E+07	7.4E+07	8.3E+07	3.1E+07	2.9E+07	2.1E+07	1.2E+07	6.0E+06
11	3.6E+07	3.6E+07	4.0E+07	5.1E+06	4.4E+06	2.4E+06	1.1E+06	6.6E+05
14	3.0E+07	4.1E+07	4.8E+07	8.9E+06	9.0E+06	5.1E+06	2.3E+06	1.1E+06
16	3.1E+07	4.0E+07	4.7E+07	9.8E+06	1.0E+07	5.7E+06	2.4E+06	1.2E+06
22	3.1E+07	2.9E+07	3.2E+07	1.4E+07	1.2E+07	7.7E+06	5.5E+06	2.5E+06
25	0.0E+00	4.3E+07	4.9E+07	1.6E+07	1.6E+07	1.0E+07	5.5E+06	3.2E+06
26	3.5E+07	3.9E+07	4.4E+07	1.4E+07	1.3E+07	1.0E+07	7.4E+06	3.7E+06
27	4.2E+07	4.5E+06	5.4E+07	2.2E+07	2.1E+07	1.5E+07	1.1E+07	5.0E+06
29	2.8E+07	2.3E+07	2.5E+07	1.7E+07	1.4E+07	1.0E+07	7.2E+06	3.4E+06
34	3.3E+07	3.2E+07	3.7E+07	1.8E+07	1.6E+07	1.4E+07	1.0E+07	4.6E+06

Through the studies outlined above and the compilation of data it was possible to examine the results and determine a method which provided the optimum runtime, peak resolution and peak area while also improving on current available methods. After evaluating many methods for the separation of PAHs in wastewater a method with an initial temperature of 55°C, a ramp rate of 25°C min^{-1} to 310°C with an overall runtime of 15.40 minutes was chosen, Figure 4-7.

Calibration and robustness testing of this method was the next step after method development and marked the beginning of method validation. 12-point calibration curves for each PAH has been tabulated in Table 4-10 where good linearity and robustness was observed for each of the PAH compounds tested in the project.

Table 4-10 Calibration data and equation of the line for final PAH method for GCMS used in this study.

PAH	*R^2*	*Equation of the line*
Naphthalene	0.99	Y=2,510,867.35 x
Anthracene	0.99	Y=2,581,790.81 x
Fluoranthene	0.99	y = 4,284,396.60 x
Benzo-b/k-fluoranthene	0.99	y = 6,799,501.45 x
Benzo-a-pyrene	0.99	y = 2,431,801.40 x
Indeno-1,2,3cd-pyrene	0.99	Y = 1,609,433.81 x
Benzo-ghi-perylene	0.99	Y = 2,075,531.72 x

The final overview of the limits of detection (LODs) achieved for each of the PAHs is listed in Table 4-11.This table represents the limits of detection achieved using the GCMS method alone, the pre-concentration factor offered by the SPE method allows for monitoring requirements of the priority PAHs to be met. The LOQ was taken to be twice the LOD for each compound.

Table 4-11 Overview of limits of detection achieved for each PAH using the final method.

PAH	*Method*	
	LOD (ppm)	**LOD (µg L^{-1})**
Naphthalene	0.0001	0.1
Anthracene	0.0005	0.5
Fluoranthene	0.0001	0.1
Benzo-b/k-fluoranthene	0.0001	0.1
Benzo-a-pyrene	0.0005	0.5
Indeno-1,2,3cd-pyrene	0.0005	0.5
Benzo-ghi-perylene	0.0005	0.5

In order to validate the repeatability of the method an injection volume study was carried out to determine the optimum injection volume of sample which would allow lower LODs without diminishing overall method performance.

Table 4-12 Results of injection volume study showing peak areas of each PAH against injection volume. Optimum values are marked in bold. Naph - naphthalene, Ant - anthracene, Flr -fluoranthene, BbF and BkF - benzo-b- and benzo-k-fluoranthene, Bap – benzo-a-pyrene, Ind – indeno-1,2,3cd-pyrene, Bghi – Benzo-ghi-perylene. N=3

Injection	**PEAK AREA**						
Volume (µL)	**Naph.**	**Ant.**	**Flr.**	**Bbf and BkF**	**Bap.**	**Bghi.**	**Ind.**
1	18460	7586	17022	18988	7970	7355	7292
2	25226	11084	31725	23289	9996	9554	10643
4	45067	18452	73574	49449	19329	13816	18705
5	**77424**	**72729**	**218271**	**284882**	**108526**	**102868**	**80613**

From Table 4-12 it can see that peak areas increased as injection volume increased yet there is a point where tailing and peak splitting can begin interfering with resolution and general method performance. In this study this point was reached at an injection volume of 8 µL. Therefore, after completing this study 5 µL was chosen as the optimum injection volume for this method.

A repeatability study was carried out on this method whereby a series of injections of the same concentration mixture, in this case 0.01 ppm, were carried out concurrently and peak areas were recorded. All percentage relative standard deviation shown in Table 4-13 are below 5% which is an acceptable precision margin for a method.

Table 4-13 Repeatability study showing the results of repeated injections of a 0.01 ppm PAH mixture. Naph - naphthalene, Ant - anthracene, Flr -fluoranthene, BbF and BkF - benzo-b- and benzo-k-fluoranthene, Bap – benzo-a-pyrene, Indeno – indeno-1,2,3cd-pyrene, Bghi – Benzo-ghi-perylene. Ave. – average. StdDev – standard deviation. RSD – relative standard deviation. N=3

	Peak Area						
	Naph.	**Ant.**	**Flr.**	**Bap**	**Bbf and BkF**	**Indeno**	**Bghi**
0.01ppm a	49694	26543	119716	79963	29615	23468	38426
0.01ppm b	52052	29036	118748	80761	33056	26057	42458
0.01ppm c	47383	27485	126777	78641	29944	25774	39728
0.01ppm d	50128	30327	124088	89060	32343	26150	42918
0.01ppm e	50677	28096	111634	84653	31701	25895	42530
Ave.	**49986.8**	**28297.4**	**120192.6**	**82615.6**	**31331.8**	**25468.8**	**41212**
StdDev	**1704.9**	**1452.9**	**5789.9**	**4241.3**	**1500.4**	**1127.8**	**2010.2**
RSD(%)	**3.4**	**5.1**	**4.8**	**5.1**	**4.8**	**4.4**	**4.9**

4.3.3 FINAL PAH GCMS METHOD

The final validated PAH method by GCMS is described below and is represented by the chromatogram in Figure 4-7. This method allows for PAH levels below the set EQS values to be quantified in one simple and fast method. Through the use of SIM mode it was possible to detect PAH concentrations in complex wastewater samples after sample preparation.

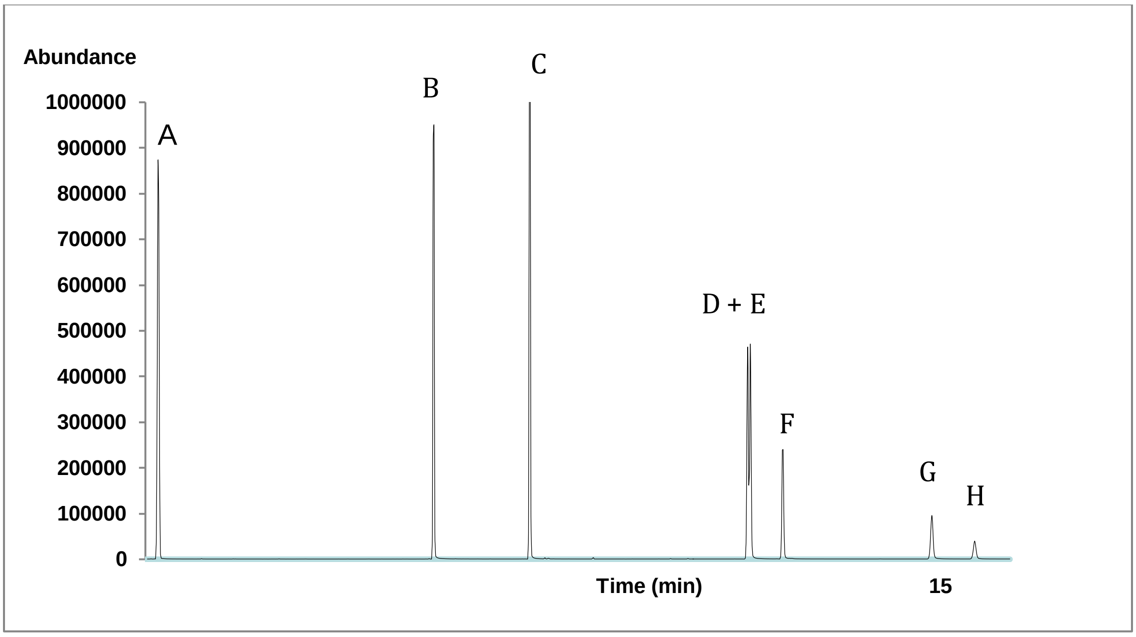


Figure 4-7 Chromatogram showing separation of 8 priority PAHs by final PAH method chosen for PAH analysis. A – Naphthalene, B – Anthracene, C – Fluoranthene, D + E – Benzo-b/k-fluoranthene, F – Benzo-a-pyrene, G – Indeno-1,2,3cd-pyrene, H – Benzo-ghi-perylene. Initial Temp: 55˚C. Initial Time: 1.00 min. 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.

A Hewlett Packard (HP 6890 Series GC) equipped with a DB5-MS (5% Poly (dimethylsiloxy) poly (1,4-bis (dimethylsiloxy) phenylen) siloxane, 0.25 mm x 25 m x 0.25 µm) Ultra-Inert capillary column (Agilent, Ireland) was used for analysis. The GC was connected to a mass selective detector (MSD) (HP 5973 Series) operated in selected ion mode. Injection of 5 µL sample was performed using the instrument autosampler. The carrier gas was helium. The oven temperature program for the GC required injection at 55˚C (held for 1 min), increased at a rate of 25˚C min^{-1} until the final temperature of 310˚C was reached (held for 4.20 min) giving an overall runtime of 15.40 min. All samples were analysed in triplicate with procedural blanks routinely analysed. The limits of quantification were determined as 10 times the noise level of the chromatogram of a blank sample. A calibration range of 0.00001 – 1 ppm was achieved with the mean correlation coefficients of the calibration curves greater than 0.99 for all compounds indicating high linearity for this concentration range. Sample components were identified by comparison of retention times and mass spectra with those of the standard mixture.

4.4 Pesticide Method Development

A simple method for the determination of priority pesticides was developed with the aim of validating SPE studies for the extraction of these pesticides from a wastewater matrix. The 33 priority pesticides listed in the WFD, Section 1.2.1 and Table 4-15, were included in the method development although the literature suggested that several would not be amenable to GC analysis owing to their physical and chemical characteristics. These pesticides included glyphosate and the six priority dithiocarbamate pesticides listed in Table 4-14.

Table 4-14 Pesticides that are not suitable for direct GCMS analysis and citations from the literature.

Pesticide	*Outcome of study*	*Reference*
Glyphosate	Lists glyphosate as one of 134 pesticides found to have no GC–MS peaks or for which sensitivity was extremely low and did not meet requirements.	(Pang, Cao *et al.* 2006)
	State that derivitisation is required prior to GCMS analysis of glyphosate.	(Börjesson, Torstensson 2000)
		(Torres, Picó *et al.* 1996)
Isoproturon	Isoproturon not thermally stable for direct GCMS analysis.	(Camino-Sánchez, Zafra-Gómez *et al.* 2011)
	Describes the best method for isoproturon analysis to be LC-MS/MS	(Pang, Cao *et al.* 2006)
Mancozeb	This paper lists mancozeb as one of the pesticides not compatible with GCMS	(Pang, Cao *et al.* 2006)
	Suggest special pre-treatment required prior to GCMS analysis.	(Armenta, Garrigues *et al.* 2005)
Maneb	This paper lists maneb as one of the pesticides not compatible with GCMS	(Pang, Cao *et al.* 2006)
Mecoprop	This paper details a preferred LCMS method for the analysis of mecoprop.	(Klein, Alder 2003)
Thiram	This paper lists thiram as one of the pesticides with poor stability	(Pang, Cao *et al.* 2006)
Zineb	This paper lists zineb as one of the pesticides not compatible with GCMS	

Note: The dithiocarbamates have limited solubility in most organic solvents making them difficult to analyse directly.

The first step was to run standards of each of the priority pesticides on a basic method, 5 minutes at 50°C then 10°C per minute to 320°C with a final hold for 10 minutes. The aim was to ensure all analytes had passed through the column to the detector this would allow for the determination of relative retention times of the various compounds, as well as providing the mass spectra for each of the analytes, and thus a point of reference.
100 ppm standards of all 33 pesticides (Sigma-Alrich) were prepared in methanol and a Hewlett Packard (HP 6890 Series GC) equipped with a HP5-MS (5% Poly (dimethylsiloxy) poly (1,4-bis (dimethylsiloxy) phenylen) siloxane, 0.25 mm x 25 m x 0.25 µm) capillary column (Agilent, Ireland) was used for analysis. The GC was connected to a mass selective detector (MSD) (HP 5973 Series) operated in total ion scan mode.

Figure 4-8, Figure 4-9 and Figure 4-10 show the mass spectrums of some of the successfully detected analytes, it is important to have these mass spectra to allow for the identification of the priority pesticide peaks in the presence of interferences which could be present in wastewater samples, having the most abundant ions and confirmation ions allows for the comparison of the mass spectra of suspect peaks.

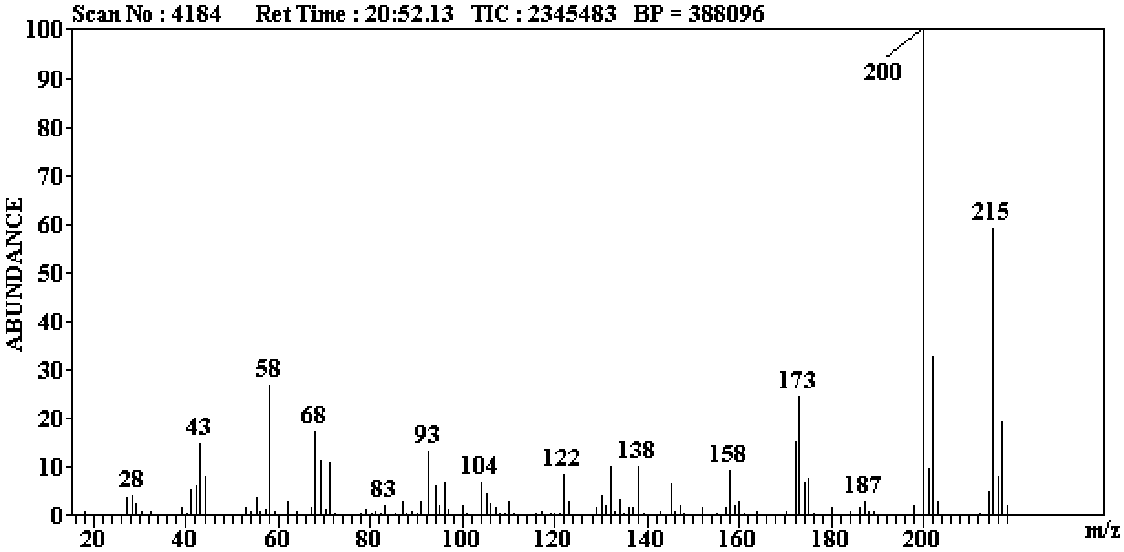


Figure 4-8 Mass Spectrum of Atrazine determined on a Hewlett Packard 6890 Series GC, with a HP-5MS column from Agilent with mass selective detection.

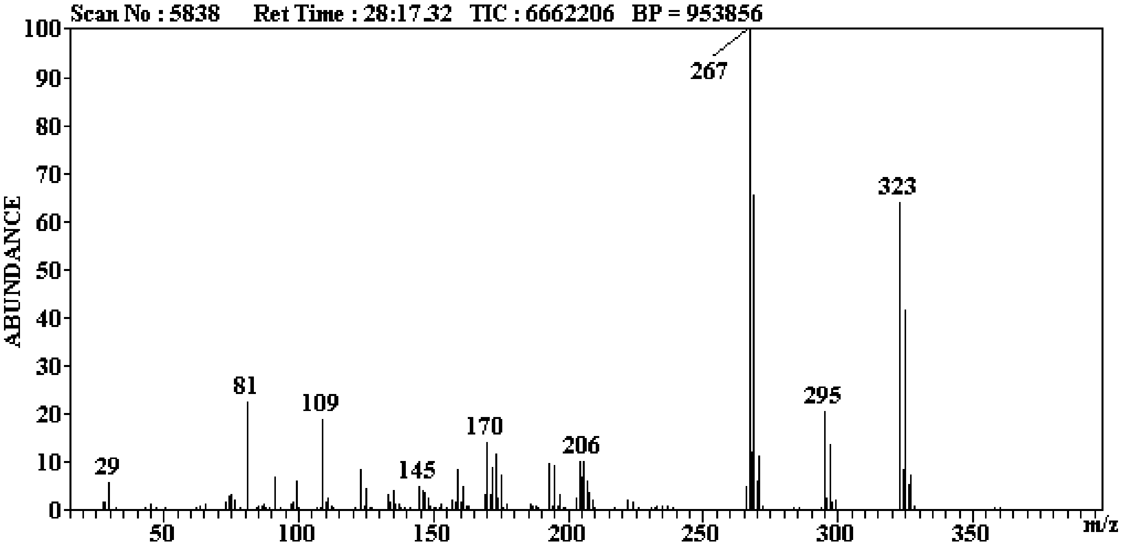


Figure 4-9 Mass Spectrum of Chlorfenvinphos determined on a Hewlett Packard 6890 Series GC, with a HP-5MS column from Agilent with mass selective detection.

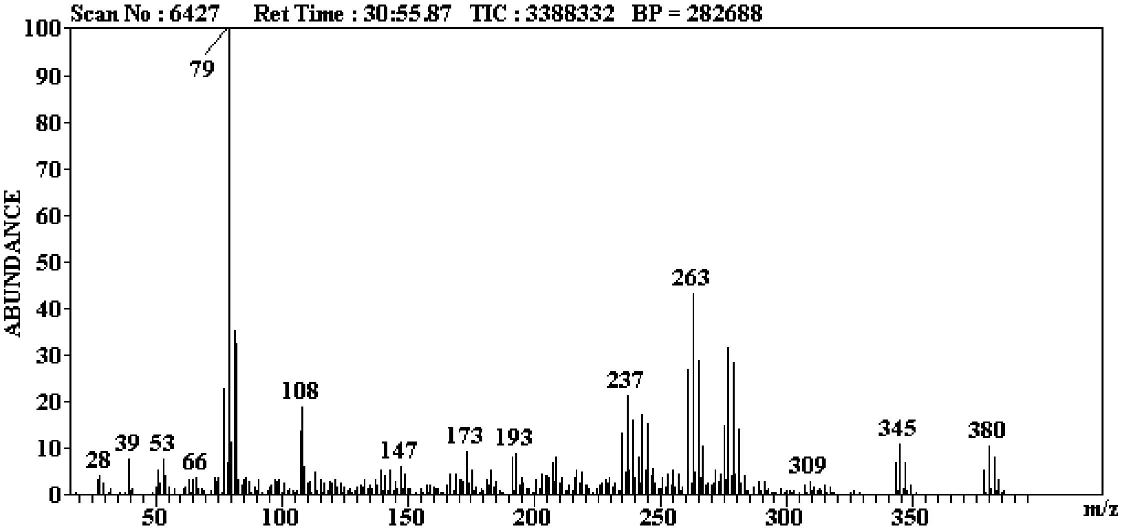


Figure 4-10 Mass Spectrum of Dieldrin determined on a Hewlett Packard 6890 Series GC, with a HP-5MS column from Agilent with mass selective detection.

A summary of the successfully detected pesticides with their respective retention times and main ions is presented in Table 4-15 below this does not include the pesticides highlighted in Table 4-14 as they were not detected using the GCMS. The chromatogram that represents the retention times and ions in Table 4-15 is shown in Figure 4-11.

Table 4-15 Summary of results of pesticide standards run using method Trial 5 150111.M showing each of the successfully separated pesticides, their retention times and main ions present in the mass spectrums.*Pesticides not included on this list: Glyphosate, Isoproturon, Mancozeb, Maneb, Mecoprop, Nonylphenol, Thiram and Zineb. *Most abundant ions are highlighted in bold.

Pesticide	*MW (g)*	*Rt (min)*	*Main Ions*
Alachlor	269.77	24.24	269,237,224,**188**,**160**,146,132,117,91,77,**45**
Aldrin	364.91	25.62	364,329,293,**263**,250,220,186,101,91,79,**66**
Atrazine	215.68	20.869	**215**,**200**,173,158,138,92,68,58
Chlorfenvinphos	359.57	28.23	360,**323**,295,**267**,206,195,173,109,81,28
		27.66	**323**,295,**267**,204,195,170,123,109,81,28
Chlorpyrifos	350.59	26.166	349,**314**,286,258,208,**197**,125,109,**97**
DDT	354.49	33.77	354,246,**235**,212,199,176,**165**,136,75
DEHP	390.54	35.319	390,279,**167**,**149**,113,71,57
Dieldrin	380.91	30.913	380,345,277,**263**,237,209,193,173,108,**79**
Diuron	233.09	28.08	232,**187,**159,124,72,44,**28**
Endosulfan	406.93	29.406	371,358,339,325,307,**277**,265,**241**,229,195,170,159, 85,**69**,31
Endrin	380.91	31.979	380,345,**317**,281,**263**,245,219,209,173,147,81,**67**
Epichlorohydrin	92.53	3.478	89,62,**57**,51,49,42,32,31,28,26
Fenitrothion	277.2	25.15	**277**,**260**,214,**125**,**109**,93,79,63,47
Hexachlorobenzene	284.8	20.191	**284**,249,214,177,**142**,107,71
Hexachlorobutadiene	260.76	12.425	**260,225,190**,153,141,118,83
Isodrin	364.91	26.996	364,329,293,**263,193**,147,111,91,66
Lindane	290.83	21.136	290,254,**219,181**,145,**109**,85,75,51
Malathion	330.36	25.728	285,256,211,**173**,158,143,**125**,101,**93**,79,63
Pentachlorobenzene	250.34	17.02	**250,215**,178,143,125,108,73
Pirimiphos Methyl	305.3	25.338	**305,290,276**,262,233,180,163,125,109,93
Simazine	201.66	20.66	**201,186,173**,158,145,138,132,123,96,85,68,55,44
TBT	291.06	18.819	291,**269**,213,177,155,121,57,41
Trichlorobenzene	181.45	11.76	**180,**145,109,74
Trichloroethylene	131.39	3.11	134,**130**,99,**95**,60,47,28
Trifluralin	335.28	19.504	335,**306**,290,**264**,248,43

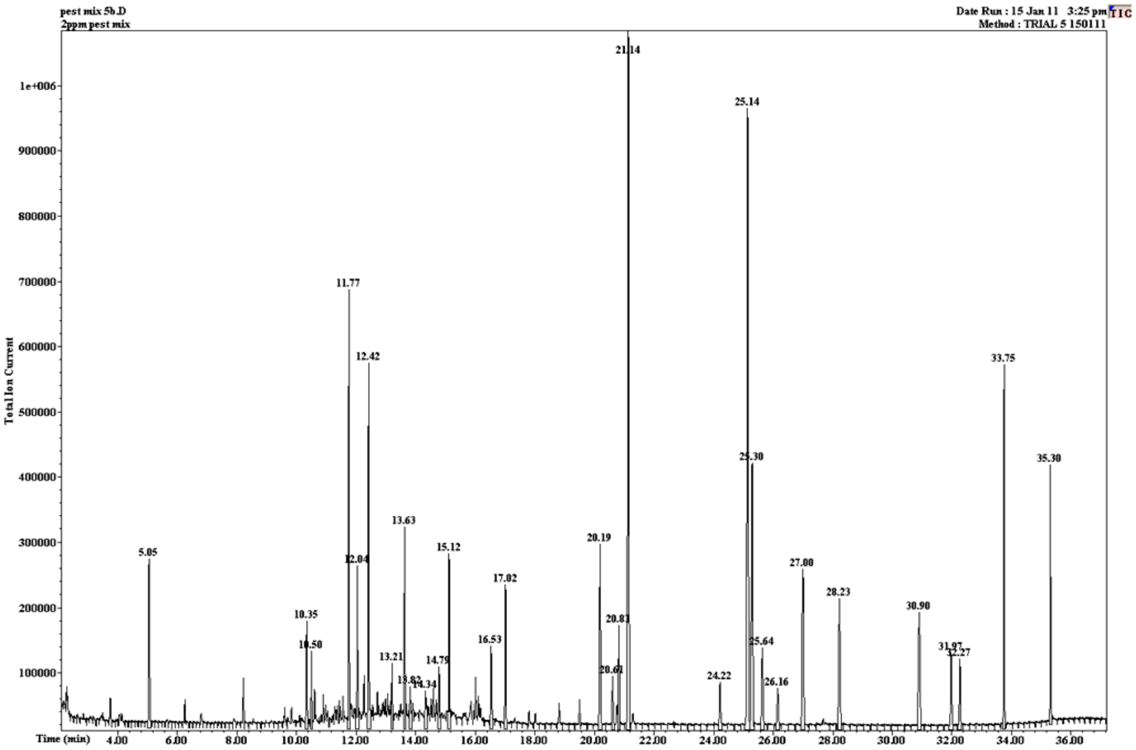


Figure 4-11 Chromatogram of 2 ppm pesticide mixture achieved using method Trial5 150111, detailed in text. Table 4-15 identifies each of these peaks and summarises the most abundant ions in the mass spectra for each of these peaks.

Simple separation of the pesticides was achieved and allowed for the development of an extraction method for the pesticides. The final method developed for the separation pesticides is as follows:

A Hewlett Packard (HP 6890 Series GC) equipped with a HP5-MS (5% Poly (dimethylsiloxy) poly (1,4-bis (dimethylsiloxy) phenylen) siloxane, 0.25 mm x 25 m x 0.25 µm) capillary column (Agilent, Ireland) was used for analysis. The GC was connected to a mass selective detector (MSD) (HP 5973 Series) operated in total ion scan mode. Injection of 10 µL sample was performed using the instrument autosampler in splitless mode. The carrier gas was helium. The oven temperature program for the GC required injection at 40˚C (hold for 2 min), increase at a rate of 9˚C/min to 170˚C, then 3˚C/min to 205˚C, 1˚C/min to 208˚C, and finally 20˚C/min until the final temperature of 290˚C was reached (hold for 2 min) giving an overall runtime of 37.21 min. Sample components were identified by comparison of retention times and mass spectra with those of the standard mixture.

As highlighted above there were several pesticides which were not suitable for GCMS determination. LC methods are becoming increasingly available for the analysis of pesticides due to their applicability to thermally labile and polar compounds, these compounds would generally require derivatisation before GC analysis. LC methods have been applied to triazines, carbamates, phenylureas, phosphorous pesticides, quaternary ammonium compounds and chlorinated phenoxy acids. The most common method of detection is UV, although MS has been gaining popularity (Careri, Mangia *et al.* 1996, Kuster, López de Alda *et al.* 2006).

LC-MS has facilitated the analysis of ‘difficult’ pesticides in an efficient and selective manner; these pesticides include quaternary ammonium compounds diquat and paraquat and the phosphonic acid glyphosate and its major metabolite aminomethylphosphonic acid (AMPA) (Hogendoorn, van Zoonen 2000). As such the project collaborators developed an LC-MS/MS method for the analysis of the priority pesticides.

4.5 Metals and Trace Elements Method Development

4.5.1 ICP-AES

For the analysis of the priority metals and trace elements, Table 1-6, it was necessary to order a custom reference standard. Elementec supplied an AccuTrace Custom Reference Standard containing 1 μg ml-1 of each of the 15 elements listed in Table 4-16. From this stock solution a calibration curve was prepared. Analysis was carried out on a Liberty 220 ICP Emission Spectrometer from Varian.

Prior to sample introduction there were a number of calibration steps that were be carried out with this instrument. The optimum plasma viewing height, wavelength of analysis, and general wavelength calibration of the instrument were set each day of analysis. As a starting point all wavelengths were chosen according to those recommended by EPA Method 200.7. Multiple wavelengths were available for each element with optimum wavelengths giving the higher intensity readings and therefore making it possible to achieve lower limits of detection for these elements.

Table 4-16 Priority metals and trace elements and their optimised conditions for analysis by ICPAES. * Denotes extra wavelength added by user, all solutions were 1 ppm stock.

Metal/Trace Element	*Symbol*	*Optimised Wavelength (nm)*	*Intensity at optimum wavelength*	*Optimised Viewing height (mm)*
Lead	Pb	220.353	2305	4
Nickel	Ni	231.604	1094	5
Arsenic	As	193.696	465	4
Antimony	Sb	206.833	593	4
Molybdenum*	Mo	281.615	1702	4
Molybdenum	Mo	203.844	1285	4
Chromium	Cr	205.552	1411	4
Zinc	Zn	213.856	4796	5
Copper	Cu	324.754	2134	4
Tin	Sn	189.926	948	5
Barium	Ba	493.409	13406	4
Boron	B	249.678	2779	4
Vanadium*	V	309.311	1411	4
Vanadium	V	292.402	538	4
Cadmium	Cd	226.502	1146	5
Selenium	Se	196.026	2591	5
Cobalt	Co	228.616	1194	4

To begin all possible wavelengths were evaluated and generally the EPA recommended wavelengths yielded superior results. However in the cases of molybdenum and vanadium a secondary wavelength provided increased intensity and, as such, was chosen for addition to the method. Some elements, i.e. arsenic, antimony, and tin, had low intensities at their optimum wavelengths, making detection of low levels impossible for some concentrations. Table 4-16 lists the priority metals and trace elements with their respective optimum viewing heights and wavelengths.

Calibration of the method was performed. The formula used to calculate volumes for the calibration curve was: concentration required (ppm)/ concentration given (ppm in stock), by the volume required, which was 50 mL. Stock solution was diluted to the mark with deionised water as per EPA method 200.7 which outlines analysis of wastewater for metals and trace elements using ICPAES. The lowest point on the calibration curve was selected after taking into account the established EQS values for the metals and trace elements in question, these EQS values can be found in S.I. 272 of 2009. As mentioned above, a number of elements were unsuitable for this low level detection due to their poor wavelength intensity on this instrument.
This initial calibration was failed by the instrument as many of the lower concentrations were not detected for some of the elements; this instrument is programmed to reject calibration where standards do not increase, or the difference between standards is over 15%. The next step was then to prepare some higher calibration standards, and so standards of 1, 0.5, and 0.1ppm were added to the calibration.

The analysis of the metals and trace elements proved challenging due to the limitations of current methods with only one available technique was suitable to meet the analytical requirements for metals and trace elements outlined in the WFD, ICP-MS. ICPAES had been evaluated for the analysis and was found not to achieve the limits of quantitation required, therefore it was necessary to send samples to the accredited Centre for Microscopy and Analysis lab for analysis by ICPMS. All samples were analysed for 15 priority metals and trace elements at the ppb level, results are presented in Chapter 6.

4.6 Conclusion

This chapter gives an overview of methods commonly applied to the analysis of priority substances in environmental matrices, citing many of the studies which were reviewed when beginning the method development work. It was important to review these methods to understand issues and problems encountered by other research groups so that the same issues might be avoided.

The need for robust, quantitative methods is highlighted in the WFD. The process of selecting a suitable analytical method has become much more difficult as there are currently a vast variety of methods applicable to the analysis of priority substances. It is therefore necessary to define analytical requirements very early in the stages of project development. Analytical and data requirements must be defined to certain criteria including run times, ease of use of the method, sample preparation requirements, precision and accuracy, and limits of detection and quantitation. Where legislation is the driver for the research it is vital that those standards are taken into account above all. In the case of the PAHs a number of approved methods were available and were evaluated with GCMS proving to meet the project remit. By reducing the runtime and improving resolution of the priority PAHs it was possible to achieve specifications outlined in the WFD. This PAH method improved on runtime and limits of detection for reported methods when used following the sample extraction method outlined in chapter 3.

With regard to the pesticide analysis most recent studies detail methods involving LCMS rather than GCMS, and through this work it was found to be difficult to reach limits of detection near the levels required and also difficulties were encountered with particular pre-treatment required by some pesticides. In order to combat issues of incompatibility between pesticides and GCMS analysis the project partners in Cork developed an LCMS method for the analysis of the pesticides in wastewater.

5. Development of a Risk-based Model

5.1 Introduction

5.1.1 INTRODUCTION

PSs originate from many sources, and are transferred to surface waters via a number of pathways. Large installations may emit PSs originating from production processes directly into surface waters, under licence from the EPA or Local Authorities. Gaseous emissions of PSs from combustion and industrial sources may be deposited on surrounding land, and washed into surface waters directly following precipitation (Sanders, Jones *et al.* 1993). Accidental or deliberate dumping of waste materials onto land may also lead to runoff of PSs into surface waters, or indirect contamination of surface waters via leaching into groundwater (Teijon, Candela *et al.* 2010).

WWTPs are major potential point sources of priority pollutants that combine direct inputs from domestic, industrial and commercial effluent with diffuse inputs from surface runoff of land-deposited PSs. Sampling of PS concentrations in WWTP effluent under different conditions (e.g. wet and dry weather) may offer insight into the sources of PSs (Gasperi, Garnaud *et al.* 2008). Furthermore, as major point sources of PS and following implementation of the Urban Waste Water Treatment Directive, WWTPs offer strong opportunities for the effective control of PS concentrations in surface waters through the implementation of management and abatement options. Establishing the concentrations of priority pollutants in WWTP effluent is important for the protection of public health.

There are a number of challenges that are encountered in the monitoring of these pollutants including the establishment of standard methods for analysis and sample handling, setting appropriate EQS values and developing methods which can reach the required LODs and adapting to include new and emerging compounds as they are added to legislative monitoring lists. When surveying work already completed and on going in this area two large studies were identified as good examples of where modelling has facilitated the monitoring of these PSs in the European arena. The SCOREPP project (Source Control Options for Reducing Emissions of Priority Pollutants) had already surveyed a number of large European cities for the occurrence of priority substance and also included a section on removal efficiencies of specific pollutants from WWTPs that was particularly relevant to this study (Seriki, Gasperi *et al.* 2008). Also the Scottish Environmental Protection Agency (SEPA) have developed an efficient monitoring tool and have reported the detailed the process involved in establishing a model relating emission factors to the occurrence of priority substances in surface waters (Clarke, Roberts *et al.* 2009).

5.1.1 REVIEW OF MODELLING APPROACHES FOR THESE PRIORITY SUBSTANCES

In order to determine the most suitable approach to adopt when preparing a model for the monitoring of emission factors for priority and hazardous substances it was first necessary to evaluate some of the potential routes available. In a study by (Ahlman, Svensson 2005) a simple GIS-based model is presented, SEWSYS, which uses basic process parameters (deposition rates, accumulation time, flushing rates during rainfall) to predict storm water PS concentrations. It focuses on land use including roof area and material type, road area, and traffic volume. This model attributes most heavy metal and PAH loading to traffic (brake dust, tyre wear, exhaust and road surface wear).

While this model provided valuable information on the type of data required and steps involved in establishing a basic working model there were, however, many limitations which would have to be overcome. The SEWSYS model is based on the MATLAB program, computing software, while the aim of the current study is to base the model in a simpler program such as Excel. The purpose of this is to make the model as user-friendly as possible while also not requiring specialist knowledge in computer programming for use. Compared to the large number of pollutants required for monitoring by the WFD the study by Ahlman *et al.* contains only 20 different substances (some organic pollutants, heavy metals and nutrients). As a much larger pollutant set with more varying physical/chemical characteristics and emission sources is being looked at in this study the SEWSYS model, while being a good stepping stone, would ultimately need more work before being suitable for the purposes of this project. Also, while the hydrological aspects of the SEWSYS model were well validated there were less reliable results in the quality parts.

(De Keyser, Gevaert *et al.* 2010) generate a dynamic model capable of simulating the dynamic release pattern of specific PSs. This model accounts for daily, weekly, and yearly patterns of release, but is extremely data intensive (geographic and average load data required for every source within a catchment), and the model was not tested on an actual catchment. Where sufficient data are available, high-resolution parameter-based models provide an invaluable tool to predict and understand temporal emission patterns, and to interpret (grab sampling) monitoring data in the full context of dynamic relationships amongst various PS sources. However, in Ireland at least, the current state of knowledge and data availability (e.g. emission data from individual installations) is insufficient to support such models. In the first step towards greater understanding of PS sources contributing to WWTP emissions, a simple risk-based model that can be applied across catchments was proposed.

5.1.2 CASE STUDY: A SCOTTISH PERSPECTIVE

Case Study:

The most influential resource in the establishment of the model for this project was the SEPA model which is further detailed in this case study.

A Scottish Perspective

SEPA evaluated over 400 priority and emerging substances in the initial stages of their research. The steps taken in the formation of their chemical prioritisation tool are detailed in Figure 5-1 below.

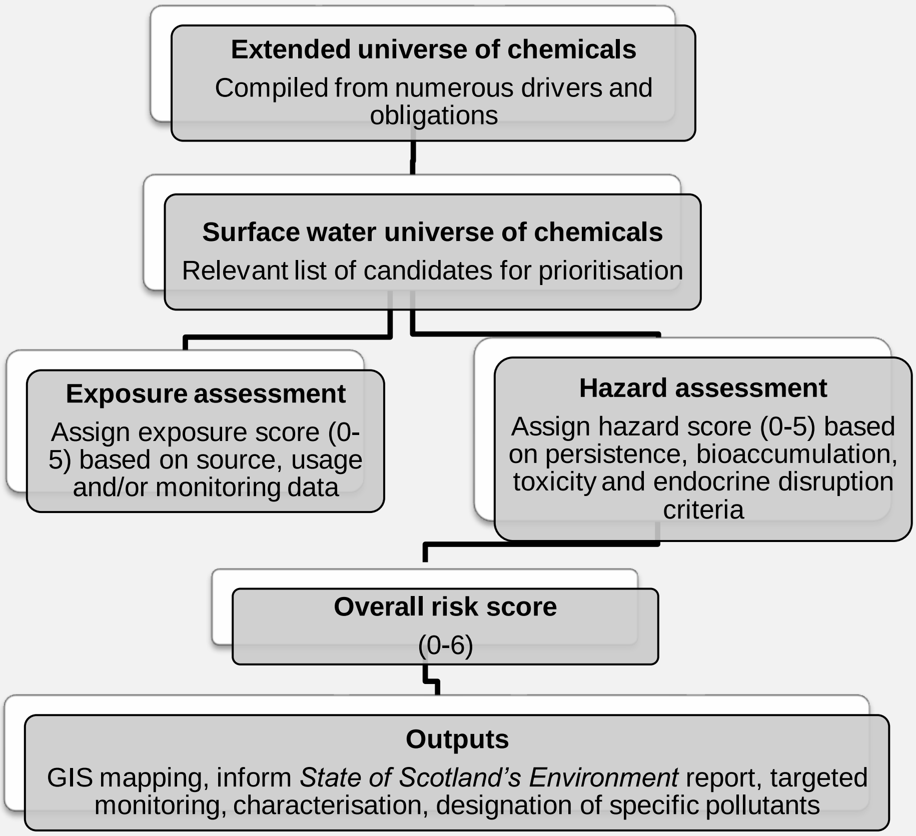


Figure 5-1 Shows the prioritisation process developed to risk assess chemicals of potential concern in Scotland. It summarises the risk assessment process in terms of chemical hazard and environmental exposure.

The prioritisation tool was developed in Microsoft Excel using a series of linked spreadsheets which are both dynamic and interdependent – when one is changed the others are automatically updated. This method allows for simpler data entry whilst maintaining a transparent and consistent approach.

> Risk scores (0–6) were calculated for each prioritised chemical as a function of their hazard and occurrence in Scotland’s environment. Hazard scores were based on an individual chemical’s environmental persistence and potential to bioaccumulate and toxicity including endocrine disruption potential. Exposure was assessed for each chemical in terms of monitoring data, point source emission data and usage information. There is currently no definitive diffuse pollution element to the source assessment, though the usage and monitoring assessments are relevant to both diffuse and point source emissions.
>
> A minimum of one robust source of exposure assessment data and one source of hazard assessment data was required to complete the assessment. Any substance that did not meet the minimum data requirements for either the exposure or hazard assessments was assigned a risk score of zero, indicating insufficient information.
>
> (Clarke, Roberts et al. 2009)

Throughout the course of this work many documents and reports were reviewed and data extracted and used to populate the model. This included 155 IPPC licenses, 62 waste discharge licenses, 9 wastewater discharge applications including environmental impact statements and historic sampling data for each of the sites, 11 annual environmental reports for the sites with approved licenses, 872 trade effluent licences and data from 102 rainfall monitoring stations. The data was compiled and the rainfall stations and WWTPs mapped. As well as these sources of data, information was extracted from traffic counters, the CSO and the NRA. This data, while not all presented within this chapter, is stored in a series of excel documents for submission to the EPA. Chapter 6 continues with the population of the model and overall observations from the model development and application process.

The data listed above was collected and analysed in full by the candidate. This data served to populate the model and allow for the relation of emission factors to the occurrence of PSs and, with the exception of the mathematical modelling, the candidate used this dataset as well as collected experimental data to complete and validate the final model.

5.2 Aims and objectives

This chapter aims to detail the steps taken in the development and population of a risk-based model for priority substances in wastewater, this includes:

- Reviewing modelling approaches for the WFD priority substances,
- Design of the model and identifying sources of data for the population of the model,
- Selecting and characterising the agglomerations in the study,
- Collating available data on occurrence and emission of priority substances in each area,
- Evaluating licensed sources and other factors (traffic and rainfall) of priority substances in each catchment,
- Determining appropriate removal efficiency factors for the groups of pollutants at the respective treatment plants and
- Conceptually modelling the information.

5.3 Schematic of Model

In order to design a model that would allow for the determination of risk factors for priority substance emission in various catchment types it was necessary to first identify all sources of background information for the population of the model. Chapter 5 provides an in-depth account of the data available and collected while also highlighting gaps in current knowledge. Figure 5-2, below, is a schematic diagram of the final model, showing the relationship between the data collected and its place in the overall model.

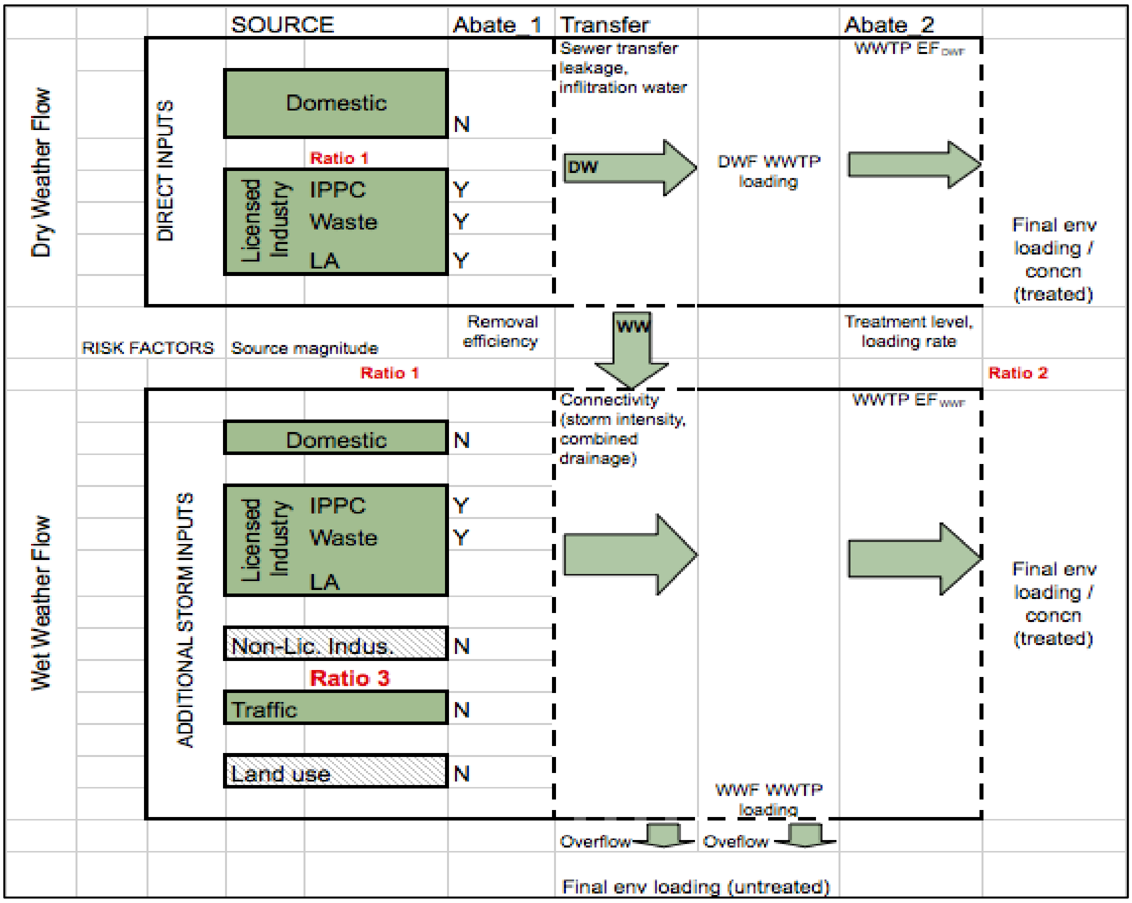


Figure 5-2 Overview of the information required to populate the model and how this information is related. LA = local authority, N = no, Y= yes, WW = DW = dry weather, WW = wet weather, env = environmental, EF$_{wwf}$ = effluent factor for wet weather flow, EF$_{dwf}$ = effluent factor for dry weather flow, Non-Lic Indus. = non-licensed industry.

Only after the framework of the model had been established and the model populated with collected data could the final step take place. Population of the model with experimental data could only be carried out after the sampling regime had been completed and the data analysed. Presented in this chapter are the sampling results for pesticides, PAHs and metals and trace elements for each of the sampling sites. The results have then been used to validate the final model, presented at the end of the chapter.

5.4 Overview of Data Input to Model

There were many sources of data drawn upon for the population of the model. Figure 5-3 depicts these sources of data and the number of each type of document evaluated.

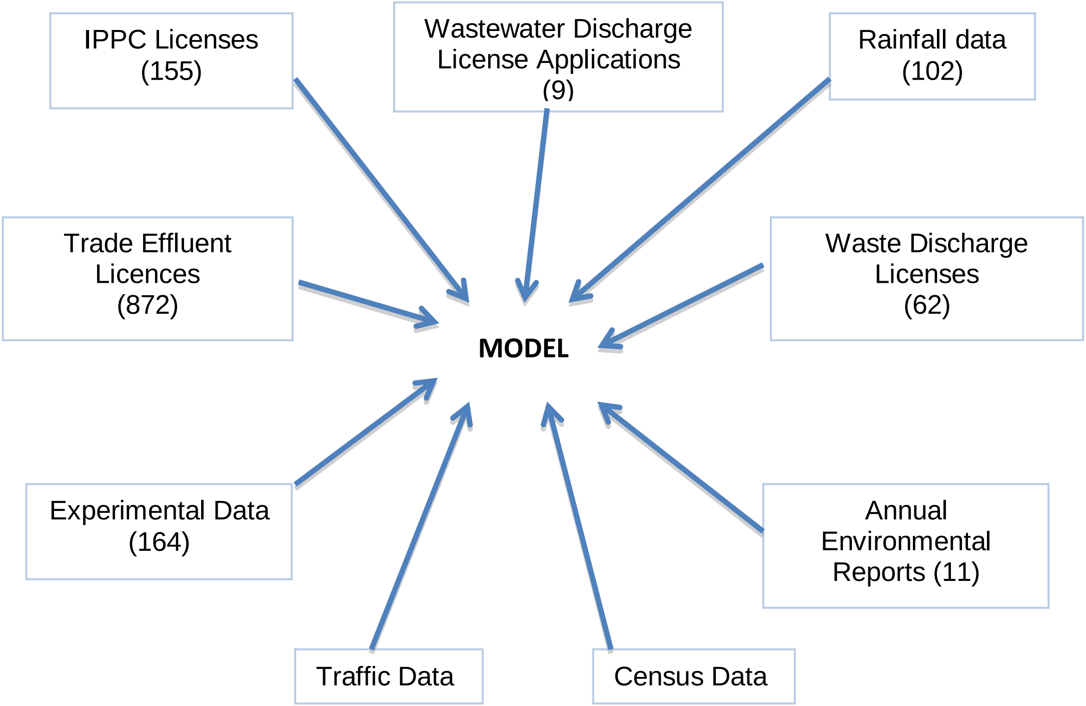


Figure 5-3 Summary of data inputs to model.

As this model formed a web of information the relationship between data sources is more clearly represented in Figure 5-4 using the Ringsend catchment as an example.

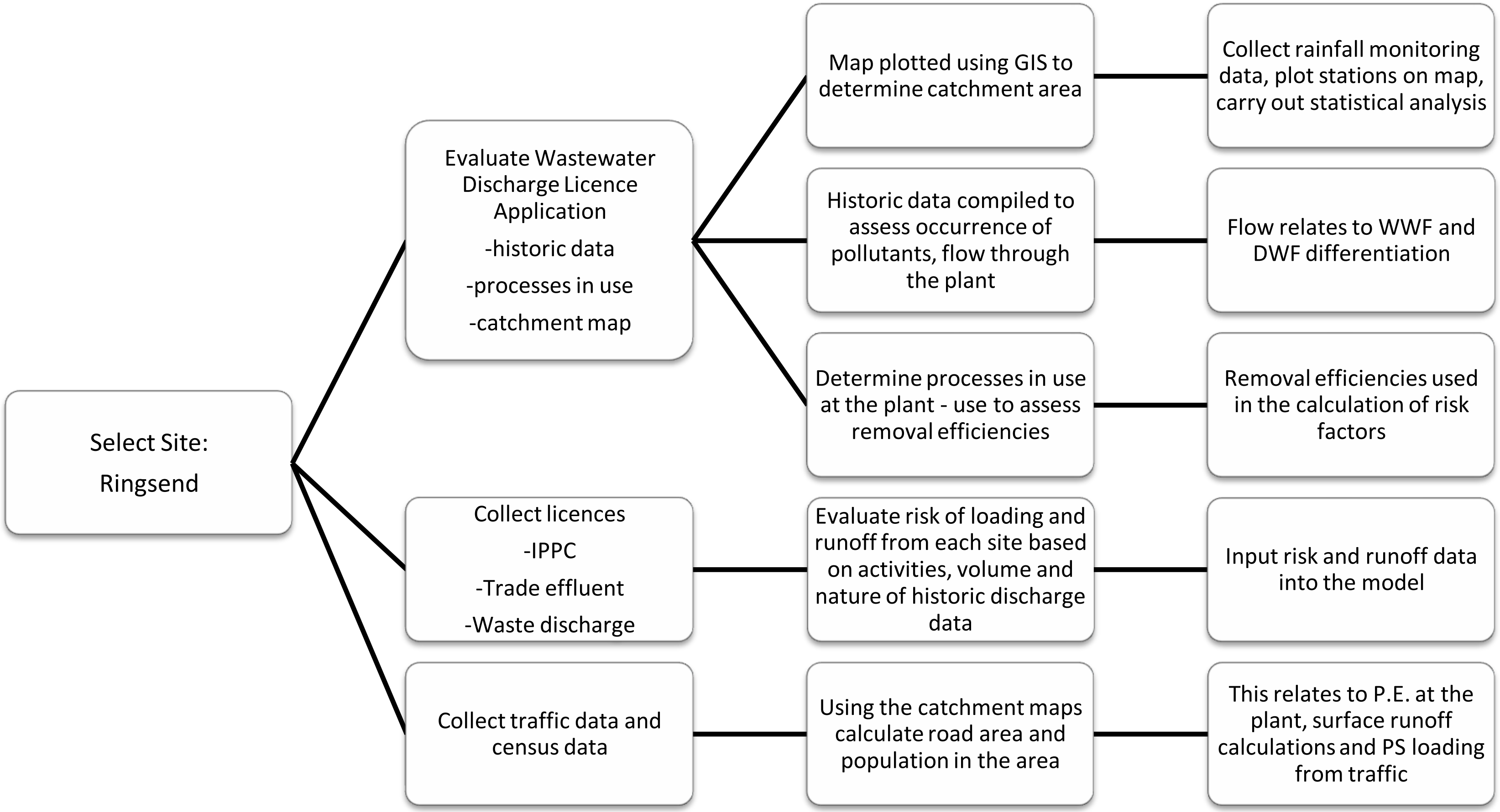


Figure 5-4 Relationship of datasets to the Ringsend catchment.

5.5 Design and Population of Model

In order to properly design a model for this project it was necessary to review current tools and models used internationally. This involved reviewing existing modelling methods and approaches taken by other research groups then deciding which format would best meet the requirements of this project as well as the WFD. This choice was restricted by limitations in the data available in Ireland. Data availability is a critical deciding factor in the design approach of the model, which later impacts on the population of the model with available data. It was important to both recognise and minimise the limitations of the model from the beginning.

In the design of the model the first draft involved a simple risk-based model. This was selected as the most effective approach to demonstrating the need for targeted monitoring programs for priority substances. The risk rankings enable both clear categorisation and ranking of various emission factors of priority substances according to the associated risk of loading attributed to each of those factors. The risk rankings are assigned based on collected data from a number of sources in conjunction with the experimental results of our sampling campaign at each of the sites included in the study. By relating the emission data to the actual determined levels in the wastewater effluent it is possible to validate the risk rankings assigned within the model, or indeed re-evaluate an assigned rank.

Table 5-1 Risk ranking scale applied to the data for the model.

Risk Ranking	*Description (high possibility of…)*
0	No loading
1	Light loading
2	Significant loading
3	Substantial loading
4	Heavy loading

For the purpose of this project Microsoft Office Excel was chosen as the platform for this model due to its simple user interface, widespread availability and as a low cost program that would be receptive to large volumes of data.

5.5.1 SELECTING AND CHARACTERISING THE AGGLOMERATION

Sites in two counties in Ireland were selected for this study. The 9 sites were chosen on the basis that a spread of varying population equivalents, levels and types of treatment, and input to the treatment plants would best support a broad framework of knowledge from which to construct a model, therefore the counties Dublin and Cork were chosen to best represent these requirements. Figure 5-5 is a flow chart detailing the first steps taken towards creating and populating the model.

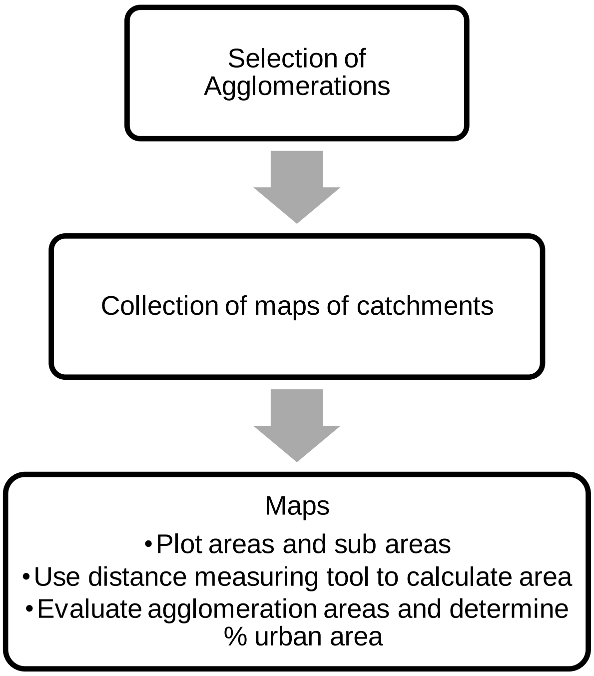


Figure 5-5 Preliminary data obtained from agglomeration mapping.

To facilitate the preparation of a valuable tool to assist priority substance monitoring for this study it was necessary to collect any available information related to each site in order to build complete datasets. Included in the wastewater discharge license applications for each of the treatment plants was an agglomeration map, i.e. Figure 5-6, a map for the Ballincollig WWTP catchment, which shows the catchment area and any sub areas as well as grid references for the treatment plants. Using this information it was possible to geo-reference each catchment map to a Google hybrid layer, as shown in Figure 5-7 the catchment borders are plotted and conversions are carried out in order to relate map distances to actual areas. This was carried out using QGIS software, Figure 5-8.

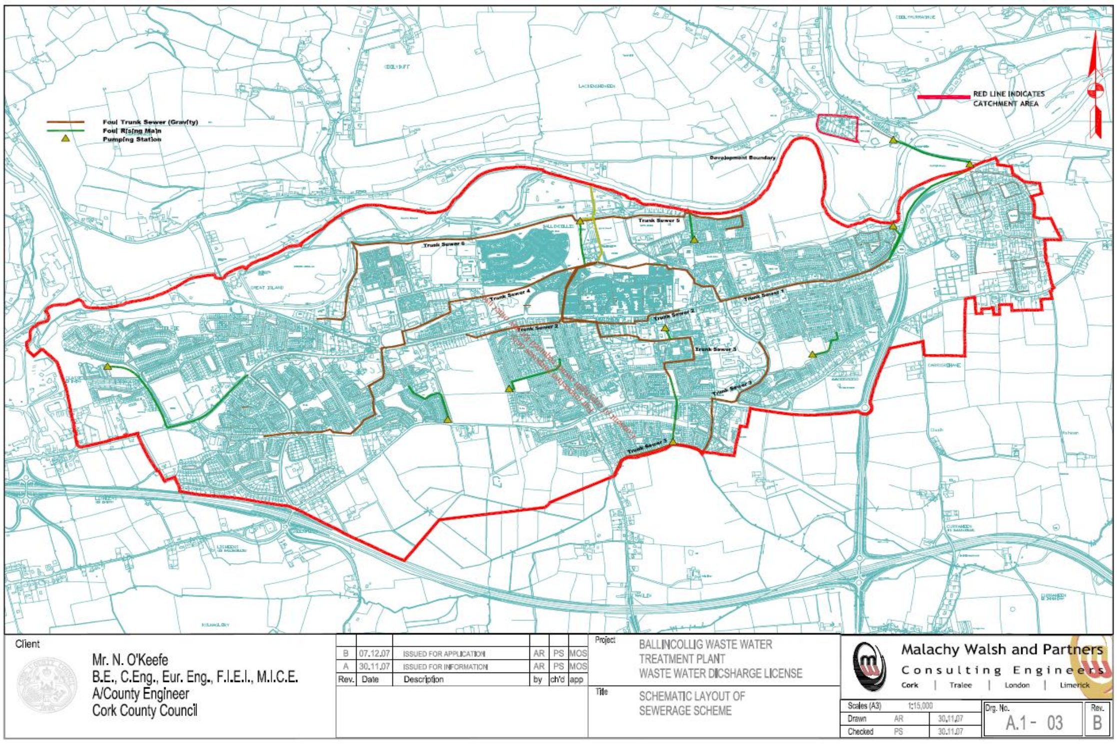


Figure 5-6 Example of a catchment map attached to a wastewater effluent discharge application for Ballincollig WWTP. This provides an outline of the catchment that can be referenced to satellite imagery (Cork County Council 2007).

In Figure 5-6 above the Ballincollig catchment is outlined on the map which was submitted to the EPA as an attachment to the wastewater effluent discharge license application. In order to convert this map to a usable map from which the catchment area can be calculated it was necessary to perform a geo-referencing step. The latter refers to the selection of several points along the catchment border and direct referencing to the same point on a hybrid map canvas. As well as an overall catchment map the license applications can often also include maps of sub-areas to the catchment, as in the case of Ringaskiddy, Figure 5-7 below, and maps showing sampling points and maps showing sampling points referred to within the application. Section 5.5.2 describes the typical information included in wastewater discharge license applications.

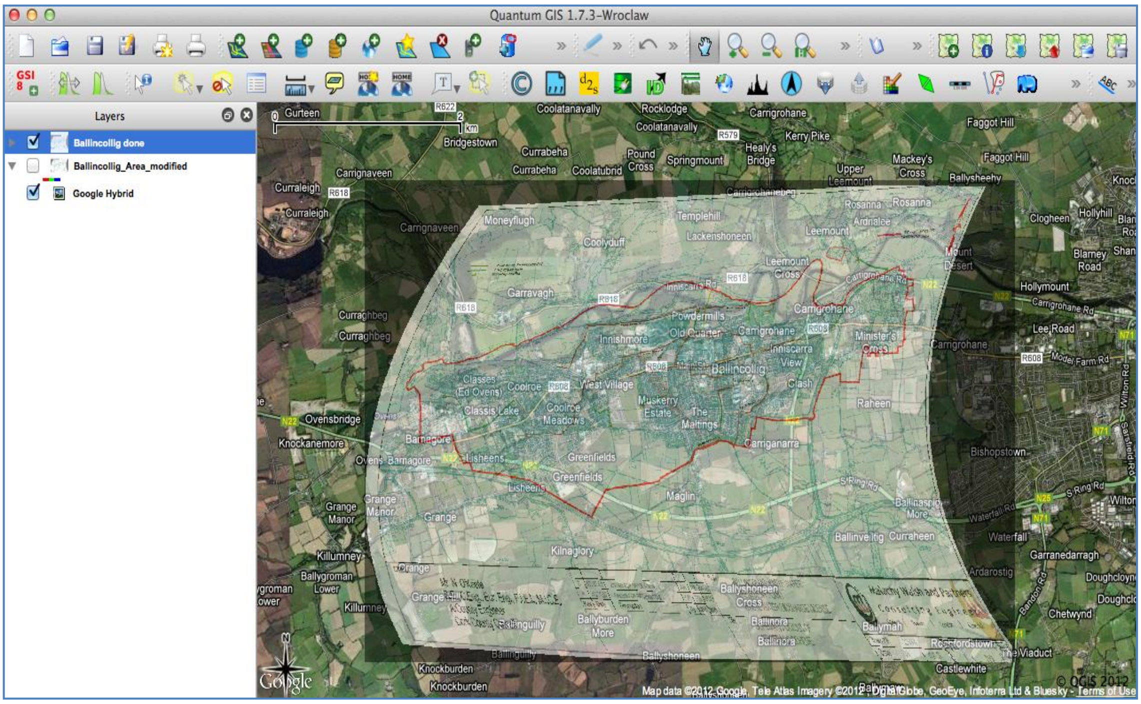


Figure 5-7 After georeferencing a .pdf version of an agglomeration map the catchment borders are clearly visible over the Google hybrid map.

In Figure 5-7 above the original map of the Ballincollig catchment has been geo-referenced and transposed onto a Google hybrid map layer. From this map the catchment border can be outlined and extracted from the original pdf map and re-projected onto the Google map, 5-8 and Figure 5-9 below.

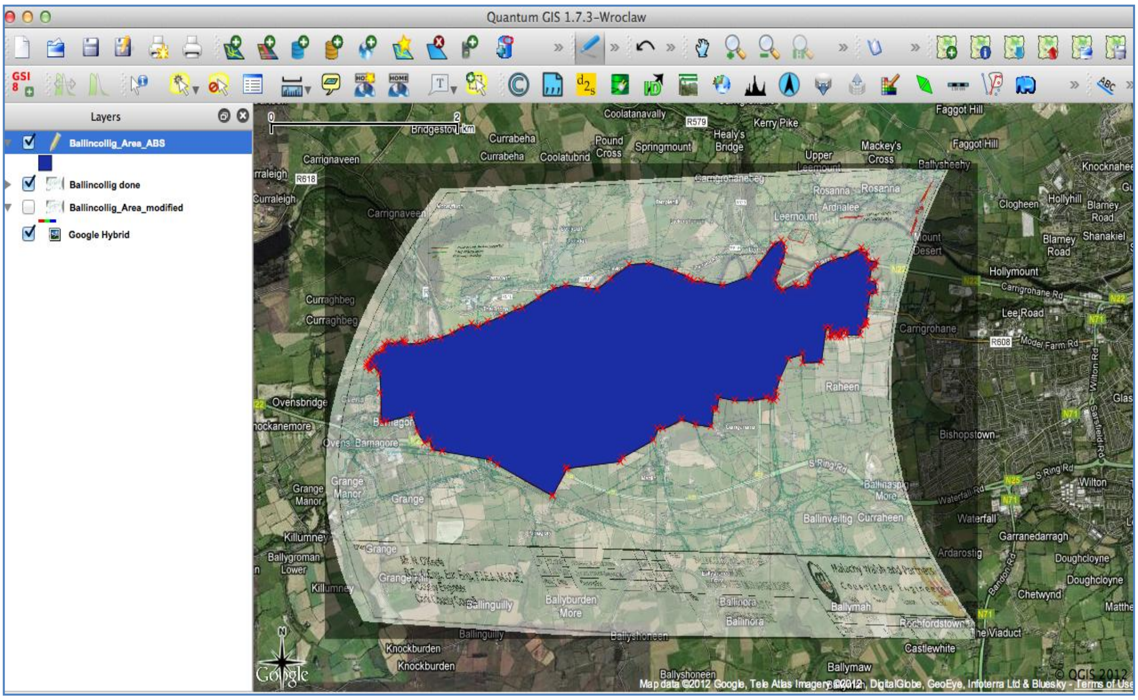


Figure 5-8 By tracing out the agglomeration border using mapping tools it was possible to calculate the internal area of each catchment.

Table 5-2 shows the steps taken in the calculation of the total areas of each catchment. From the Google hybrid map an appropriate scale was available which allowed for transformation of the original map into an exact catchment area calculation.

Table 5-2 Calculating the total areas of each catchment.

	Sub-catchment	*Length*			*Sub-area (Ha)*			
		Km	**cm**	**Km per cm**	**1**	**2**	**3**	**Total area**
BG	Ballincollig	4.902	23.7	0.207	760			760
BN	Bandon	3.541	17.3	0.205	458			458
CE	Charleville	2.96	21.5	0.138	172	58	44	274
CY	Town	3.662	20.5	0.179	499			499
	N. of town	1.347	9.5	0.142	72			72
	Inchydoney	1.79	14.2	0.126	178			178
FY	Fermoy	3.434	25.1	0.137	394			394
MW	Mallow	4.211	19.1	0.220	595			595
RY	Carrigaline	8.908	13.1	0.680	444	194		638
	Crosshaven				83			83
	Ringaskiddy				246			246
RD	Ringsend	32.82	32.4	1.013	1228	565	24934	26728
SD	Swords	9.706	25.3	0.384	2236	437		2673

Finally each agglomeration was evaluated using the catchment maps along with census data to provide us with the percentage urban area for each catchment. This data is presented in Table 5-3.

Table 5-3 Total area and urban area for each catchment.

Site	*Area (Ha)*	*Urban Area (Ha)*	*% Urban*
BG	760	532	70%
BN	458	298	65%
CE	274	137	50%
CY	750	150	20%
FY	394	177	45%
MW	595	446	75%
RY	967	290	30%
RD	26,728	20046	75%
SD	2,673	1337	50%

This map work was carried out for each WWTP included in this project. Below are the geo-referenced maps for a selection of catchments evaluated in this study.

Figure 5-9 Map of the Ballincollig catchment (Cork County Council 2007).

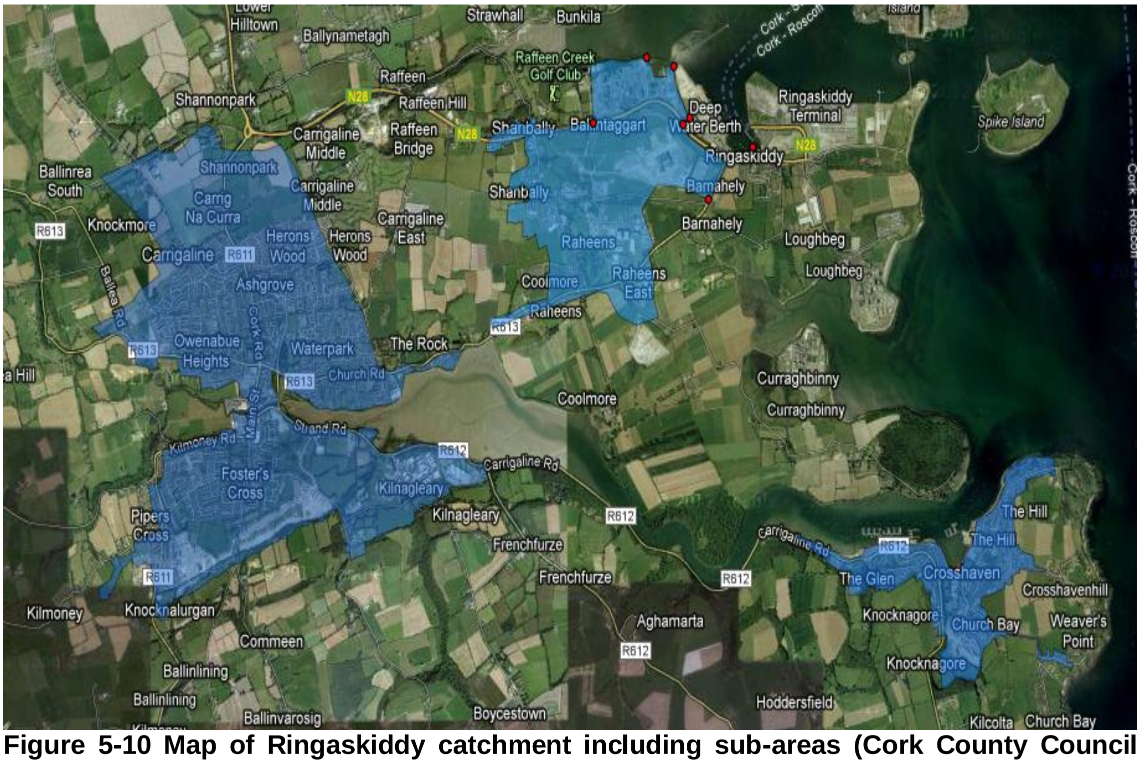


Figure 5-10 Map of Ringaskiddy catchment including sub-areas (Cork County Council 2007)

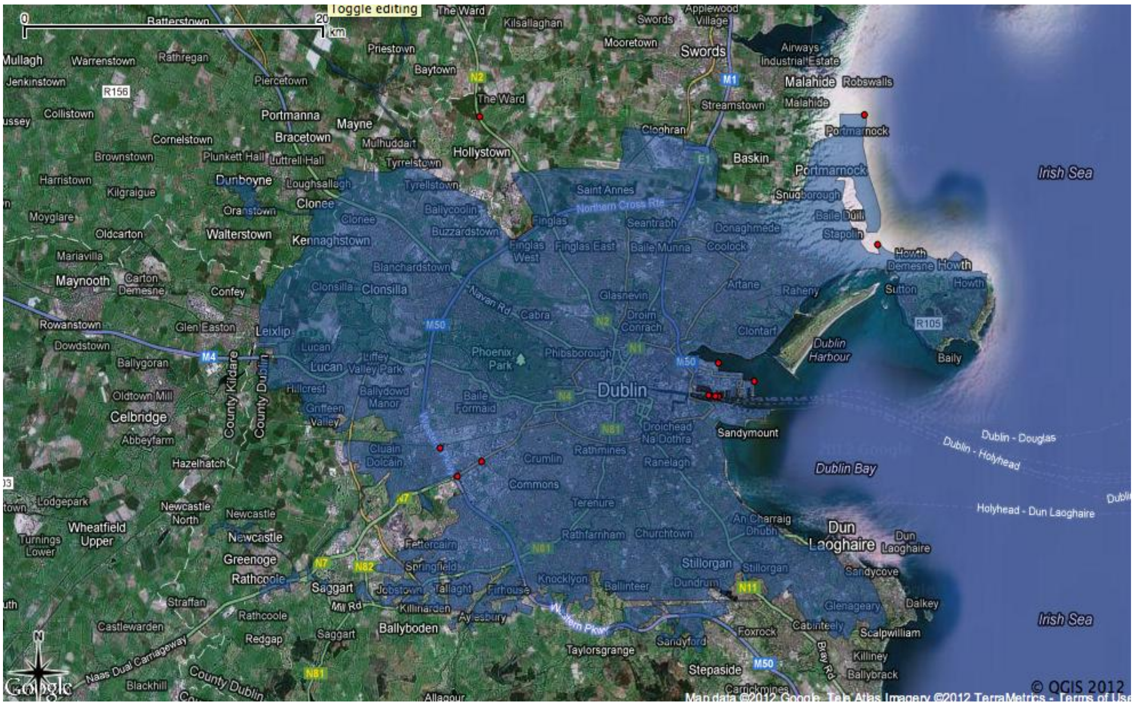


Figure 5-11 Map of Ringsend catchment (Dublin City Council 2007).

Each of the catchments is described in more detail in Chapter 2.

5.5.2 LICENSED DISCHARGES

In order to populate the model with relevant, high quality data it was necessary to evaluate the best possible sources of data. Having previously characterised the respective agglomerations, Section 5.5.1, an evaluation of the significant sources of priority substances in each, beginning with licensed emissions, was conducted. These emissions are broken down in Figure 5-12.

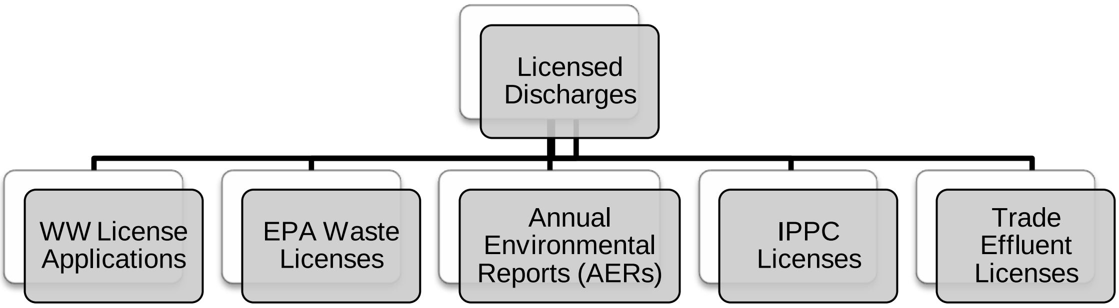


Figure 5-12 Overview of Licensed Discharges used as sources as data for populating the model.

Industrial installations performing listed activities above specified thresholds are licensed under the EU Integrated Pollution Prevention and Control (IPPC) Directive. The Irish EPA makes licence conditions and Annual Environmental Reports (AER) on emissions from these installations publicly available. (However, the level of information provided on PS emissions was found to vary across installations.) For the initial purposes of this risk-based model risk factors were defined for each installation according to activity class and refined based on some installation-specific information provided in the licences (whether or not discharge to sewers, and surface water management). Sewer loading of PSs from licensed installations was separated into direct sewer inputs and potential surface runoff inputs via combined drainage. The same simple risk index scheme was applied to each installation in relation to each PS group.

Waste management sites are also regulated by the EPA under Waste Licences. Local authorities issue Trade Effluent licences to commercial premises discharging to sewers. These licences typically contain little information, however the nature and number of each type of discharge was used in the loading calculations for each catchment. Lists of commercial installations were obtained from the relevant local authorities (excludes restaurants which are licensed under separate fats, oils and greases licences, and were excluded from this study owing to low PS emission risk relative to domestic loading). Sites were categorised based on their primary activity (from internet searches where necessary), and loading risk factors were estimated for each PS group for each activity category.

In all cases, site addresses (from EPA licences, and local authority license lists or the internet for Trade Effluent licensees) were cross-referenced with agglomeration maps in order to determine which, if any, WWTP agglomeration each sites feeds in to. To convert risk factors into estimated loading factors for the risk model, loading is considered to be exponentially related to the 4 risk factors, Table 5-1. This reflects the wide range of loading expected from different licensed sources, with large IPPC sites for example discharging up to 100 times the volume of commercial sites (albeit with more stringently monitored controls). Some degree of emission abatement is in place for most licensed sites, and emission loading will often depend on the effectiveness of the abatement methods (for runoff, this may depend on precipitation intensity).

From our research it was found that not all businesses in the agglomeration have applied for trade effluent licenses. They probably exclude a larger proportion of businesses in the small agglomerations, where sites may not be linked to the sewer network. Some such sites (e.g. garages) may still contribute to sewer PS loading via surface runoff (N.B. Some of these are represented by surface runoff rankings attributed to waste licenses in the database). Sewer loading of PSs from licensed installations was separated into direct sewer inputs and potential surface runoff inputs via combined drainage.

This can also be a problem with other unlicensed sources such as car washes, Bed and Breakfasts, shops, pubs, sporting facilities, etc., which are not taken into account. In 2008 it was reported that pollution loads arising from commercial sources were underestimated in the design at Ringsend WWTP, the same report estimated the actual contributed population equivalent from these commercial sources to be 190,000 on top of the pollution load arriving at Ringsend WWTP (Fehily 2008).

5.5.2.1 Waste Water Effluent Discharge License Applications and Annual Environmental Reports (AERs)

While the maps were an important source of background information for the model one of the greatest sources of information required for populating the model were the wastewater effluent discharge license applications and the AERs for each of the plants. AERs are reports issued annually for licenced WWTPs, they provide the most recent data on effluent quality and standards as well as any changes made to the operation of the plant. Where available these documents provided a wealth of information, as depicted in Figure 5-13.

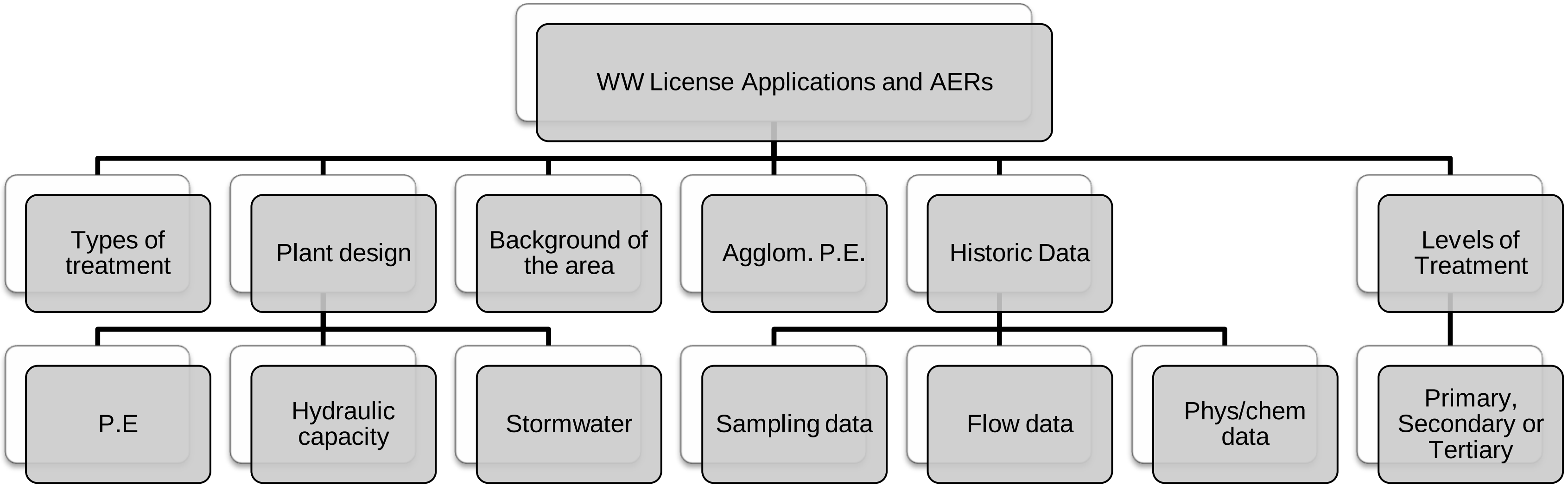


Figure 5-13 Information included in the WWTP effluent discharge license applications and AERs.

Basic information on WWTPs and the agglomerations they serve in Ireland is provided in documentation submitted to the EPA in applications for Waste Water Discharge Licences (http://www.epa.ie), summarised in Table 5-4.

Table 5-4 WWTP and agglomeration characteristics, from WW effluent discharge license applications. *From our calculations. NR – nutrient removal. R – river.

WWTP	*Treatment*	*Capacity PE*	*Agglom. Pop.*	*Area (Ha)**	*Receiving waters*
BG	Secondary	26,000	16,339	760	Freshwater-R
BN	Secondary	20,000	6,200	458	Freshwater-R
CE	Secondary	15,000	2,984	274	Freshwater-R
CY	Secondary	6,067	7,500-15,000	750	Estuarine
FY	Secondary, NR	20,000	5,800	394	Freshwater-R
MW	Secondary, NR	18,000	7,091	595	Freshwater-R
RY	None	0	14,864	967	Estuarine
RD	Tertiary	1,640,000	1,200,000	26,728	Estuarine
SD	Secondary, NR	60,000	50,000	2,673	Estuarine

Three critical factors were derived from available WWTP operational data to estimate the equivalent level of treatment achieved by each WWTP under dry-weather flow (DWF) and wet-weather flow (WWF) conditions:

- Level of treatment under normal operating conditions;
- DWF load factor;
- WWF load factor.

Table 5-5 A selection of information available for two of the nine sites from both the WW License application (App.) and annual environmental report (AER).

Report	*Conglomerate*	*Testing Date*	*TOTAL*					
			Flow m^3/day	**BOD mg L^{-1}**	**SS mg L^{-1}**	**COD mg L^{-1}**	**pH**	**Ammonia**
App.	Ringaskiddy		8121	2406 kg/day	2810 kg/day			
AER	Ballincollig	9/1/08	7888		247	111		
		10/1/08	13148		819	789		
		7/2/08	5955	2.6	6	21	7.2	<1.0
		6/3/08	4694	5.49	4	41	7.5	<1.0
		3/4/08	3453	2.1	3	21		
		6/5/08	3406	<1.0	4	22	7.6	<1.0

Table 5-5 shows some of the information gathered from the WW license application and AER for Ringaskiddy and Ballincollig WWTP. (The information available for Ringaskiddy is limited.) As well as grid reference values and sampling dates the documents provide information on the population equivalent of the agglomeration which is broken down into domestic and licensed contributions, as mentioned in Figure 5-13. This allows characterisation of the loading factors to the plant to be carried out. Biological and hydraulic capacity of each plant is also included, however the flow values are of the most value as these facilitate later calculations of base flow through each plant, allowing for the distinction of WWF and DWF conditions in relation to specific sampling results. The flow data also aids in the calculation of loading factors and can be used to evaluate the performance of a particular plant specifically when it is operating above capacity.

From the license applications and AERs a large dataset of historic sampling data was compiled. Figure 5-9 shows a small selection of the historic sampling data gathered for the Ballincollig catchment, wherein the sampling dates and plant flow volumes are compared to a number of physical and chemical parameters of the plant.

In order to model PS loading, key risk indicators for both DWF and WWF conditions were devised. Table 5-6 below shows the break down of each plant to show agglomeration population (taken from census records), population equivalent (P.E.) (equivalent population of the area including both domestic and licensed inputs)[*], DWF levels, and peak flow (PF) levels at pre-treatment (PF_PreT), at primary treatment (PF_1T) and at secondary treatment (PF_2T) stages, where the information was available. From the license applications and AERs the combined drainage area for each plant was also determined in broad ‘mostly’ or ‘partly’ terms, therefore the assigned combined drainage factor values for each are shown below to be 0.75 for ‘mostly’ and 0.50 for ‘partly’. These factors are included in conceptual model calculations discussed later in this chapter.

---

[*] Note: this value is generally taken from the license application except in the cases of Ringsend WWTP and Charleville WWTP which were derived from estimated industrial flow BOD loading and adjustment using standard 16% estimate of industrial input, respectively.

This standard 16% estimate is derived from the National Urban Wastewater study published by the Department of the Environment, Community and Local Government in 2004 which states that industrial loadings are usually 16% of all domestic/residential loadings.

Table 5-6 Excel document wherein the population, P.E., Plant P.E., area of the catchment, and flow data for each site were examined in order to determine peak flows.

Site	*Level*	*Agglom pop.*	*Agglom PE*	*Plant PE*	*DWF*	*PF_2T*	*PF_1T*	*Comb Drain*
					m^3 day^{-1}			
BG	2	16,339	24,524	26,000	2,700	12,216		0.75
BN	2	6,200	8,178	20,000	2,160	6,480	13,478	0.75
CE	2	2,984	3,461	15,000	2,050	12,240	12,240	0.50
CY	2	11,250	13,050	6,067	1,469	8,813	8,813	0.50
FY	2,NR	5,800	12,000	20,000	3,200	16,152		0.50
MW	2,NR	7,091	8,226	18,000	5,338	13,344		0.50
RY	0	14,864	97,556	97,556	9,000	N/A	N/A	0.50
RD	3	1,200,000	1,708,000	1,640,000	377,568	959,040	911,088	0.50
SD	2,NR	50,000	58,000	60,000	12,063		100%	0.75

For the Dublin sites larger datasets were available and were provided by the plant operators. They supplied files detailing flow, storm water discharge and storage levels, standard wastewater quality test results as well as some specific pollutant analysis results, specifically those for heavy metals where the data was available. This data was relevant as the sampling dates overlapped with those included in this project and allowed for comparative analysis results as well as allowing the comparison of flow data from the plant to experimental results from this project. This data was lacking for the Cork sites as there was no record of plant flow levels other than those included in the license applications, therefore those values were used as base levels, and average levels in later calculations.

5.5.2.2 EPA Waste Licenses

The EPA collects waste license information and this is made freely available on the Irish EPA website (www.epa.ie). As part of this project all waste licenses available for each agglomeration under study were collected. This enables risk factors and loading factors for both direct input and runoff risk, Table 5-7 below, to be determined.

Taking a closer look at the EPA waste license applied for by Cork County Council Western Division for a landfill facility called Derryconnell Landfill (marked with LF code in Table 5-7) which feeds into Bandon WWTP it can be seen that risk factors for all PS from direct input were assigned a value of 4, while runoff risk was assigned 0. These values were determined from the evaluation of the waste license application and accompanying documents as found on the EPA website (Irish EPA 2012).

Table 5-7 EPA waste license holders, their addresses, and risk factors and loading factors for both direct input and runoff risks to the WWTP. LF – landfill, WTF – waste transfer station, HW – hazardous waste facility, IWM – integrated waste management facility.

Code	*Plant*	*Risk Factor*							
		Direct Input				**Runoff Risk**			
		PAH	**VOC**	**HM**	**Pest.**	**PAH**	**VOC**	**HM**	**Pest.**
LF	BN	4	4	4	4	0	0	0	0
WTF	CY	2	2	2	1	2	2	2	2
HW	FY	3	3	3	3	0	0	0	0
IWM	RD	2	2	2	1	2	2	2	2
		Loading Factor							
		Direct Input				**Direct Input**			
		PAH	**VOC**	**HM**	**Pest.**	**PAH**	**VOC**	**HM**	**Pest.**
LF	BN	54.6	54.6	54.6	54.6	0	0	0	0
WTF	CY	7.4	7.4	7.4	2.7	7.4	7.4	7.4	7.4
HW	FY	20.1	20.1	20.1	20.1	0	0	0	0
IWM	RD	7.4	7.4	7.4	2.7	7.4	7.4	7.4	7.4

The website allows users to view the latest AERs for this site (2008, 2009, 2010), the original application and the EPA review documents. The information in each of these documents was evaluated and loading and risk factors were assigned. Included in the application document is information on the nature of the facility, the quantity and nature of the waste, plant methods and operating procedures, nature and impact of emissions, results of monitoring and sampling, the recovery and treatment of waste and unauthorised of unexpected emissions. This data can be verified through comparison to the latest AER which provides further information on current waste quantities and composition, site capacity, any works at the site, continuous monitoring systems and sampling results, and any environmental incidents or non-compliances.

This data was gathered and evaluated for each of the licensed waste facilities within each of the catchments in this study, however there is always the issue of illegal dumping which is difficult to take into account, therefore for the purposes of this study only licensed sources could be included.

5.5.2.3 IPPC Licenses

As with the EPA waste licenses the IPPC licenses for each catchment were gathered and evaluated as shown in Table 5-8 below. Each license application, along with any accompanying documents, was reviewed and risk and loading factors for direct input and runoff risk were attributed to each of the industries.

Take the Brewery, Chemical and Dairy Engineering Limited industry (marked as M in Table 5-8) located in Charleville as an example. This industry has been IPPC licensed since 2005 and as defined on the EPA website (http://www.epa.ie/terminalfour/ippc/ippc-view.jsp?regno=P0283-02) as carrying out activities in boiler-making and the manufacture of reservoirs, tanks and other sheet metal containers where the production area exceeds 500 square metres.

Table 5-8 IPPC license holders, their addresses, and risk factors and loading factors for both direct input and runoff risks. CL – chemical industry, FD – food and drink facility, M – metals facility, OR – other activities.

Code	*Plant*	*Risk Factor*							
		Direct Input				**Runoff Risk**			
		PAH	**VOC**	**HM**	**Pest.**	**PAH**	**VOC**	**HM**	**Pest.**
CL	RD	2	4	2	2	1	1	1	0
FD	BN	0	0	0	0	1	1	1	0
M	CE	2	2	4	0	1	1	1	0
OR	MW	1	3	3	0	1	1	1	0
		Loading Factor							
		Direct Input				**Direct Input**			
		PAH	**VOC**	**HM**	**Pest.**	**PAH**	**VOC**	**HM**	**Pest.**
CL	RD	7.4	54.6	7.4	7.4	2.7	2.7	2.7	0
FD	BN	0	0	0	0	2.7	2.7	2.7	0
M	CE	7.4	7.4	54.6	0	2.7	2.7	2.7	0
OR	MW	2.7	20.1	20.1	0	7.4	7.4	7.4	7.4

Available documentation for this site includes AERs (2008, 2009, 2010) and licence application documents. In the most recent AER for this site the only listed emissions to water/sewers are rainwater to the field drain, clean water to the field drain (emptying clean tanks filled with water for pressure testing), and office and canteen toilets connected to the mains sewerage system (volumes not available).

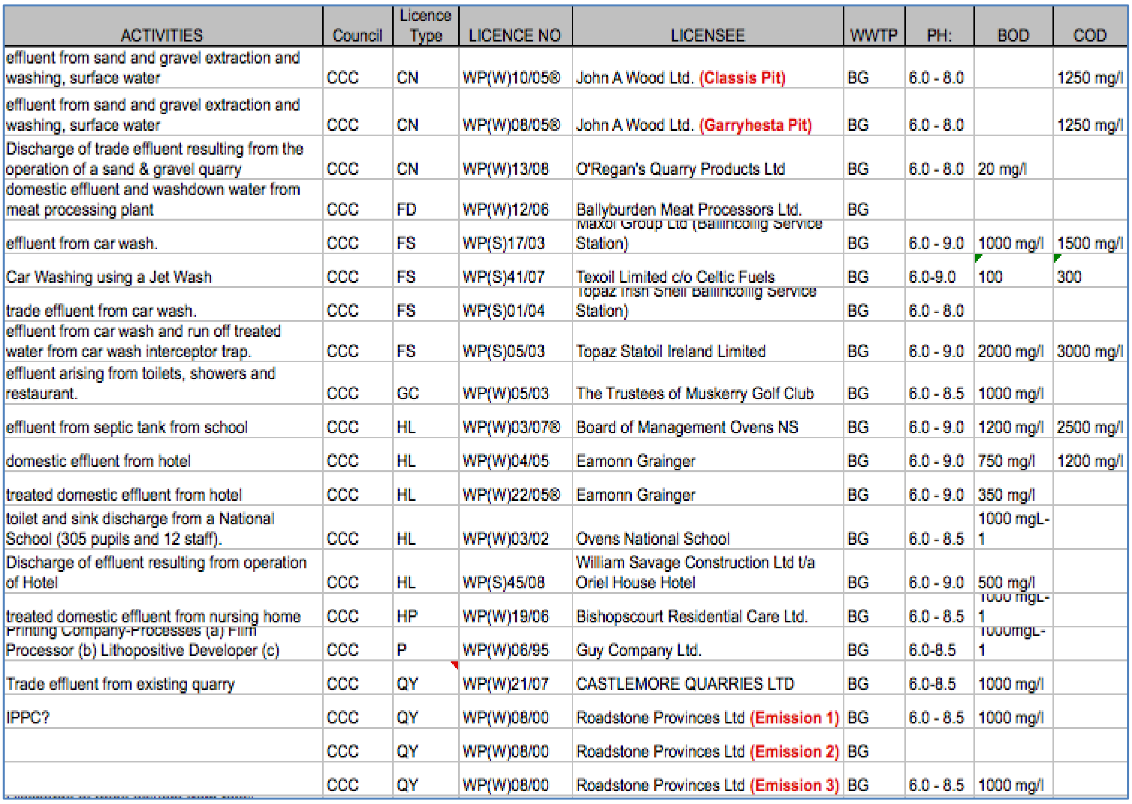
Descriptions and quantities of disposed waste are also detailed in this report and as such this industry is risk ranked for direct input of PAHs, VOCs and metals.

5.5.2.4 ***Trade Effluent Licenses***

Trade effluent licenses and loading data were acquired for each of the agglomerations under review. The licence information would provide a broad outline of industrial and commercial inputs of specific PSs to the surface waters in the agglomeration based on the licensed activities.

Lists of commercial installations were obtained from the relevant local authorities (this excluded restaurants which are licensed under separate fats, oils and greases licenses, and were excluded from this study owing to low PS emission risk relative to domestic loading). Sites were categorised based on their primary activity (from internet searches where necessary), and loading risk factors were estimated for each PS group for each activity category.

Table 5-9 Trade effluent license holders, their addresses and background data gathered from the documents available on the EPA website.



ACTIVITIES	Council	Licence Type	LICENCE NO	LICENSEE	WWTP	PH:	BOD	COD
effluent from sand and gravel extraction and washing, surface water	CCC	CN	WP(W)10/05®	John A Wood Ltd. **(Classis Pit)**	BG	6.0 - 8.0		1250 mg/l
effluent from sand and gravel extraction and washing, surface water	CCC	CN	WP(W)08/05®	John A Wood Ltd. **(Garryhesta Pit)**	BG	6.0 - 8.0		1250 mg/l
Discharge of trade effluent resulting from the operation of a sand & gravel quarry	CCC	CN	WP(W)13/08	O'Regan's Quarry Products Ltd	BG	6.0 - 8.0	20 mg/l	
domestic effluent and washdown water from meat processing plant	CCC	FD	WP(W)12/06	Ballyburden Meat Processors Ltd.	BG			
effluent from car wash.	CCC	FS	WP(S)17/03	Maxol Group Ltd (Ballincollig Service Station)	BG	6.0 - 9.0	1000 mg/l	1500 mg/l
Car Washing using a Jet Wash	CCC	FS	WP(S)41/07	Texoil Limited c/o Celtic Fuels	BG	6.0-9.0	100	300
trade effluent from car wash.	CCC	FS	WP(S)01/04	Topaz Irish Shell Ballincollig Service Station)	BG	6.0 - 8.0		
effluent from car wash and run off treated water from car wash interceptor trap.	CCC	FS	WP(S)05/03	Topaz Statoil Ireland Limited	BG	6.0 - 9.0	2000 mg/l	3000 mg/l
effluent arising from toilets, showers and restaurant.	CCC	GC	WP(W)05/03	The Trustees of Muskerry Golf Club	BG	6.0 - 8.5	1000 mg/l	
effluent from septic tank from school	CCC	HL	WP(W)03/07®	Board of Management Ovens NS	BG	6.0 - 9.0	1200 mg/l	2500 mg/l
domestic effluent from hotel	CCC	HL	WP(W)04/05	Eamonn Grainger	BG	6.0 - 9.0	750 mg/l	1200 mg/l
treated domestic effluent from hotel	CCC	HL	WP(W)22/05®	Eamonn Grainger	BG	6.0 - 9.0	350 mg/l	
toilet and sink discharge from a National School (305 pupils and 12 staff).	CCC	HL	WP(W)03/02	Ovens National School	BG	6.0 - 8.5	1000 mgL-1	
Discharge of effluent resulting from operation of Hotel	CCC	HL	WP(S)45/08	William Savage Construction Ltd t/a Oriel House Hotel	BG	6.0 - 9.0	500 mg/l	
treated domestic effluent from nursing home	CCC	HP	WP(W)19/06	Bishopscourt Residential Care Ltd.	BG	6.0 - 8.5	1000 mgL-1	
Printing Company-Processes (a) Film Processor (b) Lithopositive Developer (c)	CCC	P	WP(W)06/95	Guy Company Ltd.	BG	6.0-8.5	1000mgL-1	
Trade effluent from existing quarry	CCC	QY	WP(W)21/07	CASTLEMORE QUARRIES LTD	BG	6.0-8.5	1000 mg/l	
IPPC?	CCC	QY	WP(W)08/00	Roadstone Provinces Ltd **(Emission 1)**	BG	6.0 - 8.5	1000 mg/l	
	CCC	QY	WP(W)08/00	Roadstone Provinces Ltd **(Emission 2)**	BG			
	CCC	QY	WP(W)08/00	Roadstone Provinces Ltd **(Emission 3)**	BG	6.0 - 8.5	1000 mg/l	

Limited information was available from the trade effluent licenses due to commercial sensitivity issues therefore these sites were ranked based on their licensed activities within the catchment. Table 5-9 above shows a condensed table of one of the Excel sheets detailing activities associated with a number of licensed trade effluent discharges in the Ballincollig area. Any available sampling data was also combined. The cumulative result of this data is seen in Table 5-10 below where risk and loading factors have been assigned.

Table 5-10 Trade effluent license holders, their addresses, and risk factors and loading factors for both direct input and runoff risks. FS – fuel station, HL – hotel, RL – retail, FD – food.

Code	*Plant*	*Risk Factor*							
		Direct Input				**Runoff Risk**			
		PAH	**VOC**	**HM**	**Pest.**	**PAH**	**VOC**	**HM**	**Pest.**
FS	CE	2	2	2	0	2	2	2	0
HL	BG	1	1	1	1	0	0	0	0
RL	BN	1	1	1	1	1	1	1	0
FD	BN	1	2	1	2	1	1	1	0
		Loading Factor							
		Direct Input				**Direct Input**			
		PAH	**VOC**	**HM**	**Pest.**	**PAH**	**VOC**	**HM**	**Pest.**
FS	CE	7.4	7.4	7.4	0	7.4	7.4	7.4	0
HL	BG	2.7	2.7	2.7	2.7	0	0	0	0
RL	BN	2.7	2.7	2.7	2.7	2.7	2.7	2.7	0
FD	BN	2.7	7.4	2.7	7.4	2.7	2.7	2.7	0

5.5.2.5 Summary of Licensed Sources

Hundreds of licence applications and supporting documents were gathered during the course of this project, and any relevant data from each was identified, sorted and compiled into excel databases, all of which are linked in an intricate web which contribute directly to the final model. As numbers change as new AERs are submitted and as new information is available, the documents are amenable to change and are programmed to adjust to the new data, Table 5-11.

Table 5-11 Part of an overall summary table of total direct inputs and possible surface runoff values for each of the main groups of priority substances according to the source of information (IPPC, EPA waste, and Local Authority Trade effluent (LA-TE) licenses). These values are adjusted according to combined drainage in the catchment.

Site	***Licence***	***DIRECT INPUT***				***POSSIBLE SURFACE RUNOFF INPUT***				***Comb. Drain. Area***
		PAH	**VOC**	**Metal**	**Pest**	**PAH**	**VOC**	**Metal**	**Pest**	
BG	IPPC	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.75
	EPA Waste	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.75
	LA-TE	38	38	38	8	26	26	26	0	0.75
	TOTAL	38	38	38	8	26	26	26	0	0.75
BN	IPPC	0	0	0	0	4	4	4	0	0.75
	EPA Waste	55	55	55	55	0	0	0	0	0.75
	LA-TE	63	82	63	32	38	38	38	0	0.75
	TOTAL	118	137	118	87	42	42	42	0	0.75

5.5.3 RAINFALL DATA

Rainfall in an area leads to increased flow through a WWTP, as water runs off buildings and roads and enters the sewerage system before eventually making its way to the plant. This creates a flushing effect at the plant, as this rainwater brings with it many pollutants that had been present as street dust, pesticides on grass and fields, and airborne particulates. During these periods of rainfall an increased flow reaches the plant, often pushing a plant above capacity, and the stream is diverted to storm water overflow where the water can be released, untreated, back into the effluent stream. Met Éireann were able to provide an extensive list of rainfall monitoring stations nationwide, including grid references (Table 5-12) which allowed for their mapping (Figure 5-14 and Figure 5-15).

Table 5-12 A selection of rainfall monitoring stations in the Dublin and Cork areas.

Station number	*Station Name*	*River Catchment*	*Grid Reference*
9523	Dublin (Blackrock College)	Coastal	O204297
1823	Dublin (Glasnevin)	Tolka	O150370
3923	Dublin (Merrion Square)	Liffey	O164335
1723	Dublin (Phoenix Park)	Liffey	O100361
2523	Dublin (Ringsend)	On coast	O189339
5102	Bandon (Hillview)	Bandon	W493547
3604	Carrigadrohid (Gen.Stn.)	Lee	W405720
6004	Carrigaline (Kilnagleary)	Owenboy	W740616
8606	Castlelyones (Ballymacsimon)	Douglas-Bride	W894899
5202	Clonakilty (Castleview)	Argideen	W429441

Figure 5-14 Google map showing rainfall monitoring stations in the Dublin area. The WWTPs are indicated in red.

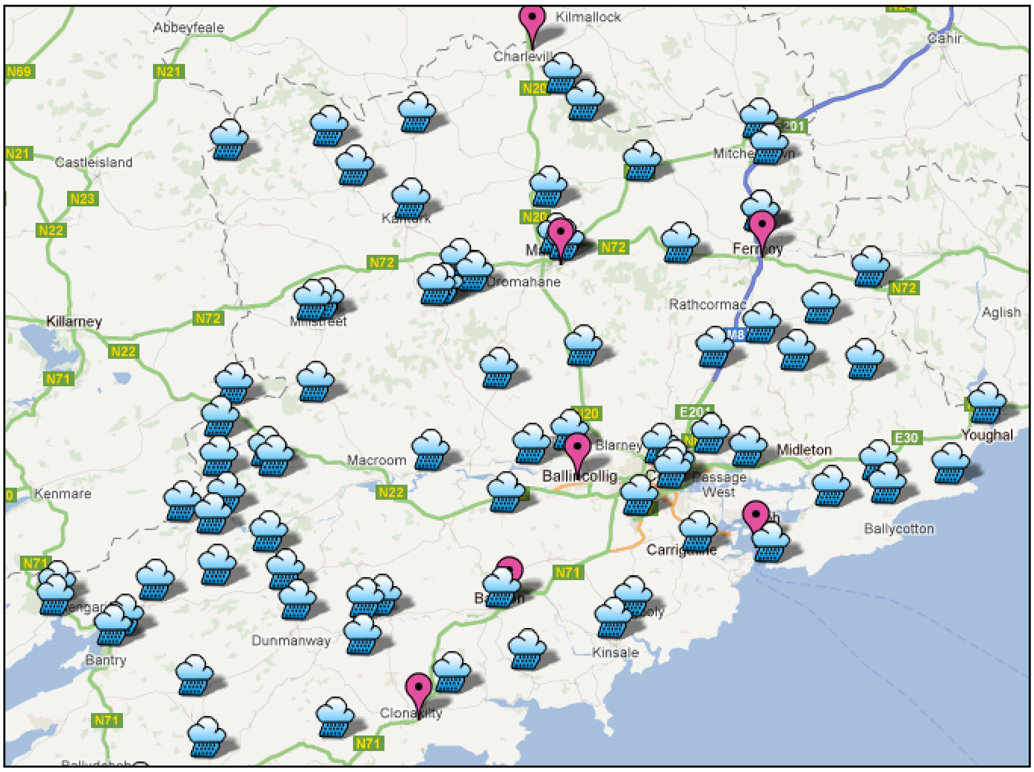


Figure 5-15 Google map showing rainfall monitoring stations in the Cork area. The WWTPs are indicated in pink.

The rainfall data was used to assess the dry periods, rain intensity and rain duration and the effect of meteorological conditions at the time of sampling. It is important to emphasise that the model will just rank risk relative to average agglomerations - for dry weather flow and wet weather flow. Further work is required to define meteorological relationships for more detailed risk rankings, in particular to account for the preceding dry period.

After plotting the rainfall stations the next step was to determine which of the sites would give the most accurate representation of the level of rainfall reaching the WWTPs. As there are a number of rainfall monitoring stations in close proximity to each of the WWTPs it was required that a study be carried out to discover which of the stations had the most representative values in relation to the site. Sites within a 5 km radius of each of the sites were selected and statistical analysis was carried out to determine the levels of correlation between the rainfalls measured at each of the sites. This was determined using the Pearson correlation coefficient. If high correlation was observed it would be possible to take the mean rainfall of the monitoring stations when comparing to the flow through the plant, and, in turn, the detected pollutant levels.

Table 5-13 Rainfall stations within 5 km of the respective WWTPs.

WWTP	*Rainfall Stations within 5 km*
Bandon	Bandon (Hillview) 5102
Ballincollig	Inishcarra (Gen.Stn.) 3704
	Muskerry (Golf Club) 6104
Charleville	Rathluirc (For.Stn.) 3706
Clonakilty	Clonakilty (Castleview) 5202
Fermoy	Moorepark 575
Mallow	Mallow (Sewage Treatment Works) 6606
	Mallow (Spa House) 7406
Ringaskiddy	Carrigaline (Kilnagleary) 6004
	Roches Point 1075 and 1004
Ringsend	Dublin (Ringsend) 2523
	Dublin (Simmonscourt) 7523
	Dublin (Merrion Square) 3923
	Dublin (Blackrock College) 9523
Swords	Dublin Airport 532
	Malahide Castle 1332

Table 5-13 gives an overview of the WWTPs and rainfall stations within 5 km of their locations. In the cases of Bandon, Charleville, Clonakilty and Fermoy only one station was located within this radius and so this would be representative alone of the rainfall at the plants. It must also be noted that there was not enough information from the Carrigaline (Kilnagleary) station to perform a correlation study.

Table 5-14 shows some of the results of these correlation studies. A value of 1 indicates full correlation between datasets while a value above 0.8 indicates a strong correlation between the two variables; therefore the aim was to achieve the highest possible correlations between rainfall stations. For the Ringsend WWTP there are three rainfall stations in the area. After analysis of the data it was shown that the greatest correlation was achieved between the Ringsend and Merrion Square stations, correlation coefficient of 0.89307, with much lower correlation between both sites and the Simmonscourt station, with correlation coefficients of 0.66615 and 0.68413 respectively.

Table 5-14 Results of correlation study on rainfall stations located within a 5 km radius of Ringsend WWTP, Swords WWTP and Ballincollig WWTP 2008-2010.

WWTP	*Rainfall Station*	*Dublin (Ringsend) 2523*	*Dublin Airport 532*	*Muskerry (Golf Club) 6104*
RD	Dublin (Merrion Square)	0.89307		
SD	Malahide Castle 1332		0.89357	
BG	Inishcarra (Gen.Stn.) 3704			0.83284

Swords WWTP is represented by both Dublin Airport and Malahide Castle rainfall stations. After comparing the two datasets an overall correlation coefficient of 0.89357 was achieved, indicating that the mean rainfall of these two sites would be representative of rainfall in the area, and thus rainfall reaching the WWTP. Ballincollig WWTP can also be represented by the mean rainfall of its neighbouring rainfall stations as they have a correlation coefficient of 0.83284.

The final WWTP with more than one rainfall station nearby was Mallow WWTP, located near both Mallow Spa House and Mallow Sewage Treatment Works rainfall stations. This correlation study offered a very low correlation coefficient of only 0.37697, therefore data from both sites could not be used when analysing the effluent data. In this situation it was fortunate as one of the rainfall stations is located at the actual plant, allowing for the use of the Mallow Sewage Treatment Works rainfall data for comparison to experimental results.

Following this statistical analysis it was clear which stations were representative of rainfall at each of the WWTPs. For the Dublin and Swords sites, where detailed flow data was available, it was possible to establish base flow levels and assign benchmarks above and below which dry and wet weather flow conditions could be defined. For the Cork sites this definition relied on flow data provided in the license applications. The flow data was evaluated in order to determine a base level flow through the plant in relation to rainfall conditions at the time. This allowed for the definition of WWF and DWF parameters for the Cork sites. For the final model the separation of WWF and DWF results was necessary, therefore this was an important step.

5.5.4 TRAFFIC DATA

Traffic data obtained from National Roads Authority (NRA) as well as the Central Statistics Office (CSO) was used in conjunction with mapping techniques which allowed for the determination of average road usage in each catchment.

Table 5-15 Compilation of some of the NRA traffic counter data collected for one area. This dataset provides information on daily traffic volume on a certain road for each month of the year, with information also broken down into holiday traffic, direction of traffic, and percentage heavy commercial vehicle (%HCV) traffic.

Traffic Counter Data for "Poulavone N20-1" in year 2008, based on 365 days recorded data								
Bank Holiday Directional Volumes in 2008 by number of vehicles								
Month	**Jan**		**Feb**		**Mar**		**Apr**	
Daily Volume	13330		14343		13613		15036	
Holiday	**Easter (March)**				**May**			
Date	21st	22nd	23rd	24th	2nd	3rd	4th	5th
Southbound	6322	5333	3849	4175	9174	6301	4651	4618
Northbound	5586	4989	3658	4138	8251	5493	4432	4656
Average Hourly Directional Volumes on Weekdays (Monday - Friday) in 2008								
Hour Ending	1	2	3	4	5	6	7	8
Southbound	44	24	21	14	13	33	110	350
Southbound %HCV	1	2	2	6	8	6	6	5
Northbound	40	18	11	9	7	18	107	582
Northbound %HCV	2	5	4	15	14	9	7	3
Average Hourly Directional Volumes on Saturdays in 2008								
Hour Ending	1	2	3	4	5	6	7	8
Southbound	80	61	53	34	20	22	49	129
Southbound %HCV	1	1	1	3	3	5	7	7
Northbound	67	48	39	25	13	14	44	127
Northbound %HCV	1	2	2	4	5	9	11	5
Average Hourly Directional Volumes on Sundays in 2008								
Hour Ending	1	2	3	4	5	6	7	8
Southbound	87	74	63	43	22	20	27	59
Southbound %HCV	1	0	1	1	2	1	4	3
Northbound	65	58	46	31	13	12	27	60
Northbound %HCV	1	1	1	2	2	3	1	1

Traffic-induced loading to WWTP (PAH, VOCs, HMs) should be largely proportional to traffic volume within agglomeration combined drainage areas, as measured by Vehicle km Travelled (VKT). Relevant available statistics are traffic flow on national roads in the vicinity of study agglomerations, total VKT for different vehicle types 22 (National Roads Authority 2010) and national VKT for six major road types (National Primary, National Secondary, Regional, Local Primary, Local Secondary, Local Tertiary) (CSO 2009).

Table 5-16 2004 Road Data from the NRA. In this table the catchment and road are named and described in terms of road usage statistics. AADT - annual average distance travelled in km. HCV - heavy commercial vehicle. Area established is measured in hectare.

Catchment		*Location*	*Year*	*Aadt*	*HCV%*	*2008 car aadt*	*2008 HCV aadt*	*Length km*
RD	N4		2003	46168	11.3	49029	7715	8.01
RD	N7		2004	57734	15.1	56775	10856	4.6
RD	N11	Fosters Ave	2004	48420	3.9	53897	2662	5.2
RD	N81	After Tallaght bypass	2004	30929	5.8	33747	2479	8.12
SD	M1	N airport interchange	2008	80232	7.2	74455	5361	3.13
BG	N22	By-pass	2008	19982	5.6	18863	1056	3.4

Traffic was divided into two components: local traffic and through traffic. Local traffic was considered to be a function of agglomeration population, and was calculated based on the national average VKT per car on Regional and Local roads estimated to occur within urbanized (i.e. WWTP agglomeration) areas – it was assumed that national average car ownership data (CSO, 2009) translated into a ratio of 0.4 cars per capita in Dublin city, and 0.5 cars per capita elsewhere in Ireland.

Local VKT within agglomerations was taken to equal the standard VKT per car (2359 km a^{-1}; 2949 km a^{-1} in Dublin), or twice the agglomeration length if this was smaller (to bound traffic volume by catchment size for smaller catchments). Local Heavy Commercial Vehicle (HCV) traffic (lorries and buses) was calculated as a fixed ratio to car traffic based on CSO (2009) data. A weighting factor of 3 was applied to HCV traffic to generate car-equivalent VKMs that reflect higher PS deposition from HCVs (e.g. greater road wear and generation of brake dust, higher fuel use. The estimated proportional area under combined drainage was multiplied by agglomeration VKT to estimate the traffic-loading index for the catchment.

Table 5-17 Summary table showing traffic data gathered for each of the catchments in the study. Each catchment is broken down into population, local traffic, traffic distributions, types of vehicle, equivalent vehicles per kilometre travelled (eq VKT), and an overall ranking of traffic loads for each WWTP in order from most (1) to least (10).

Site	*Cars*			*Heavy Commercial Vehicles*		
	Local traffic corrected	**N-Rd traffic-C**	**N-Rd traffic-P**	**Local traffic**	**N-Rd traffic-C**	**N-Rd traffic-P**
BG	19,275,015		16,811,941	7,100,215		605,230
BN	5,095,151	18,294,390		1,876,868	1,324,682	
CE	2,399,192	27,557,100		883,775	3,058,838	
CY	5,134,615		11,325,335	1,891,406		1,018,271
FY	4,199,673	4,832,484	3,487,179	1,547,007	401,247	484,718
MW	6,847,523	2,089,568	23,298,954	2,522,378	156,718	2,073,607
RY	17,534,967		9,990,981	6,459,245		1,768,952
RD	1,415,632,449		956,110,597	521,467,533		96,861,695
SD	58,984,685		85,061,453	21,727,814		6,124,425
	Pop.	**Comb. Sewer**	**RELEVANT CAR eq VKT** Central AND combined sewer	**ADD CAR eq VKT** Peripheral AND central non-combined	**CAR eq vkm C/C.A**	**Rank**
BG	16,339	0.75	30,431,745	28,771,546	**53,404**	**5**
BN	6,200	0.75	24,745,644	8,248,548	**72,087**	**3**
CE	2,964	0.50	20,892,065	20,892,065	**152,506**	**1**
CY	11,250	0.50	5,404,416	19,784,564	**14,415**	**10**
FY	5,800	0.50	7,438,458	12,379,790	**37,803**	**7**
MW	7,091	0.50	8,487,189	38,006,963	**28,530**	**8**
RY	14,854	0.50	27,684,526	24,526,012	**57,238**	**4**
RD	1,200,000	0.50	1,490,017,524	2,736,713,206	**111,496**	**2**
SD	50,000	0.75	93,126,095	134,476,758	**46,447**	**6**

Through traffic was assumed to occur on N-roads within agglomeration boundaries. National road traffic count data for points on N roads in the vicinity of agglomerations (NRA, 2009) were multiplied by the length of the N-road within agglomeration boundaries to generate N-road VKT for each agglomeration. N-roads were classified as peripheral to the agglomeration (e.g. bypass roads) and central to the agglomeration. Peripheral roads were assumed to have independent drainage systems, whilst central roads were assumed to have combined drainage according to individual agglomeration proportional combined drainage estimates. For Dublin, where N-roads radiate out of the centre and carry most commuter traffic to and from the city, through traffic was assumed equal to traffic on radial M50 motorway. NRA data is reported as Annual Average Daily Traffic (AADT) and % HCV, enabling car-eq. VKT to be calculated for each N road.

5.6 WWTP Removal Efficiencies and Conceptual Modelling

Wastewater treatment plants (WWTPs) can be major point source inputs of priority substances to surface waters, and while many studies show that wastewater treatment removes 90-95% of pollutants, this removal efficiency depends on a number of factors. In order to calculate the loading of PSs attributed to the WWTPs it was first necessary to determine approximate removal efficiencies for each of the pollutants within the respective plants.

This level is directly related to the operations at the plant, the input to the plant, the treatment levels/types received by the water at each site, the handling of storm water and extreme weather events and the ScorePP project, Seriki *et al.* (2008). Moore (2009) reported on measured PS removal efficiencies at WWTPs, mainly based on secondary treatment with activated sludge. For seven of the WWTPs considered in this study, removal efficiencies for each group of PSs were approximated to average removal efficiencies for relevant PSs reported by Seriki *et al.* (2008). Removal efficiencies used in the model calculations are detailed in Table 5-18 below.

Table 5-18 A selection of removal efficiencies for PSs according to literature review. Level indicates the level of treatment with 1 being primary and 2 being secondary treatment.

				Removal efficiency (%)	
Group	**Compound**	**Data sources**	**Level**	**Primary treatment**	**Secondary treatment**
VOC	Benzene	(Escalas, Guadayol *et al.* 2003)	2		83%
VOC	Benzene	(Barbosa, Tandlich *et al.* 2007)	2		99%
VOC	Benzene	(Parkerton 2001)	2		94%
VOC	Chloroform	(RDSE 2006)			72%
VOC AVERAGE					**84%**
PAH	Naphthalene	(RDSE 2006)	2		93%
PAH	Anthracene	RDSE (2006)	2		55%
PAH	Fluoranthene	(Busetti, Heitz *et al.* 2006)	2		73%
PAH	Benzo(a)pyrene	RDSE (2006)	2		50%
PAH	Benzo(ghi)perylene	RDSE (2006)	2		59%
PAH AVERAGE					**77%**
Pesticide	Diuron	(Lapertot, Pulgarín *et al.* 2006)	2		10%
Pesticide	Alachor	(Zhu, Yan *et al.* 2006)	2		10%
Pesticide	Isoproturon	(Nitschke, Wilk *et al.* 1999)	2		10%
Pesticide	Simazine	(Meakins, Bubb *et al.* 1994)	1	10%	
Pesticide	Chlorfenvinphos	(Gómez, Martínez Bueno *et al.* 2007)	2		83%
PESTICIDE AVERAGE					**57%**
HM	Lead compds	(Buzier, Tusseau-Vuillemin *et al.* 2006)	2		70%
HM	Nickel compds	Buzier *et al.* (2006)	2		50%
Phthalate ester	DEHP	(Fauser, Vikelsøe *et al.* 2003)	2		96%
Alkyl phenolic compound	Nonylphenols	(Clara, Scharf *et al.* 2007)	2		57%
HM AVERAGE					**67%**

Table 5-19 Removal efficiencies for certain chemical and biological elements of wastewater effluent in some WWTPs in Cork based on historic sampling data. AER – Annual Environmental Report. APP – EPA Wastewater Discharge license application.

Report	*Area*	*Test date*	*Flow (m^3/day)*	*% REMOVAL EFFICIENCY*				
				BOD mg L^{-1}	**SS mg L^{-1}**	**COD mg L^{-1}**	**Ammonia mg L^{-1}**	**Total Phosphorous mg L^{-1}**
AER	**BG**	07/02/08	5955					49%
		06/03/08	4694		99%	96%		60%
		03/04/08	3453					45%
APP	**CY**	19/09/07	2257		96%	100%	51%	
		24/10/07	2500		96%	95%	62%	59%
		25/10/07	2064	100%	48%	96%		-43%
APP	**CE**	16/01/08		90%	53%	86%	37%	65%
		14/02/08	10488			85%		69%
		08/04/08		94%	58%	98%	83%	17%

After determining removal efficiencies for the three main groups of priority substances it was possible to compile all data collected (licensed information, rainfall and traffic data and removal data) into a functional model. The data was organised and tabulated as has been shown in this chapter in such a way that excel functions could be applied between documents, forming a link and allowing for easy updating or alteration of data.

Note: The VOCs were also evaluated in that a theoretical model based solely on collected data was also developed.

5.6.1.1 Conceptual Modelling

Following the compilation of all relevant available data the conceptual model was developed. This is the basis of the framework of the model and affords certain flexibility to the model with regards to additions to the background data. Many calculations were derived as part of the development of this model and are discussed and rationalised below.

WWTP load factors were calculated as a ratio of agglomeration PE loading to WWTP PE capacity. For Clonakilty WWTP, with a calculated load factor of 2.2, DWF removal factors were based on the assumption that half the flow received secondary treatment, and half received primary treatment only. For WWTPs working in excess of or close to capacity, WW removal factors were based on the assumption that overall removal efficiencies under high loading conditions were equivalent to primary treatment removal efficiencies. Removal factors were inversed into Effluent Factors (EF) for direct multiplication with loading factors.

The conceptual modelling of PS loading is to devise key risk indicators applicable under Dry Weather Flow (DWF) and Wet Weather Flow (WWF) conditions. To convert risk factors into estimated loading factors for the risk model, loading was considered to be exponentially related to the 4 risk factors. This reflects the wide range of loading expected from different licensed sources, with large IPPC sites for example discharging up to 100 times the volume of commercial sites.

Loading to the environment from each WWTP under DWF can be expressed as DWF domestic loading (population size) plus DWF industrial loading (total agglomeration PE), multiplied by EF_{DWF}.

[Eq.1] Risk of elevated DWF PS conc. = $(Industry_{DWF} / popn) \times EF_{DWF}$

Equation 1 can be further expanded as below:

[Eq.2] Risk of elevated DWF PS conc. = $((Agg\_Ind_{DWF} / Nat\_Ind_{DWF}) / (Agg\_Pop / Nat\_Pop)) \times EF_{DWF}$

Agg_Ind_{DWF}	= Total industrial contributions from the agglomeration under dry weather flow conditions. Taken from number of industrial licensed inputs in each agglomeration.
Nat_Ind_{DWF}	= Total national industrial contributions under dry weather flow conditions. Taken from total number of industrial licensed inputs nationwide.
Agg_Pop	= Total population loading for the agglomeration, this represents domestic inputs.
Nat_Pop	= Total national population loading.
EF_{DWF}	= Effluent factor under dry weather flow conditions.

Under WWF, WWTP loading is a function of DWF loading, plus WWF Domestic loading, plus WWF Industrial loading, plus WWF traffic loading, plus WWF Land use loading, all multiplied by EF_{WWF}. Assuming that Industry and Transport sources are major contributors to WWTP PS loading, then the risk of elevated PS concentrations can be simplified thus:

[Eq.3] Risk elevated WWF PS conc. = ($Industry_{DWF}$ / Pop) + ($Industry_{CD}$ / $area_{CD}$) + ($Traffic_{CD}$/$area_{CD}$) x PDP x EF_{WWF}

PDP = Preceding Dry Period, should be linearly related to loading.
$Industry_{DWF}$ = Total industrial loading under dry weather flow conditions.
Pop = Domestic population of the agglomeration.
$Industry_{CD}$ = Total industrial loading in the combined drainage area.
$area_{CD}$ = Total combined drainage area.
$Traffic_{CD}$ = Traffic loading in the combined drainage area.
EF_{WWF} = Effluent factor under wet weather flow conditions.

Where specific data on lag time at the treatment plant and the effects of preceeding dry period and storm water contributions have not been fully investigated a simpler equation is:

[Eq.4] Risk WWF conc. = (WWF Loading / WWF volume) x (1-RE_{WWF})

WWF conc. = Risk of concentration of priority substances in WW effluent under wet weather flow conditions.
RE_{WWF} = Removal efficiency under wet weather flow conditions.

Using the equations above with both collected data and the results of a 3-year sampling campaign it was possible to produce a final model for the four main groups of priority substances (pesticides, polycyclic aromatic hydrocarbons (PAHs), metals and trace elements and volatile organic hydrocarbons (VOCs)).

5.6.1.2 Assigning Risk

Assigning risk values for different PSs under different conditions follows the procedure outlined in Figure 5-16 and is used along with the conceptual modelling described in Section 5.6.1.1.

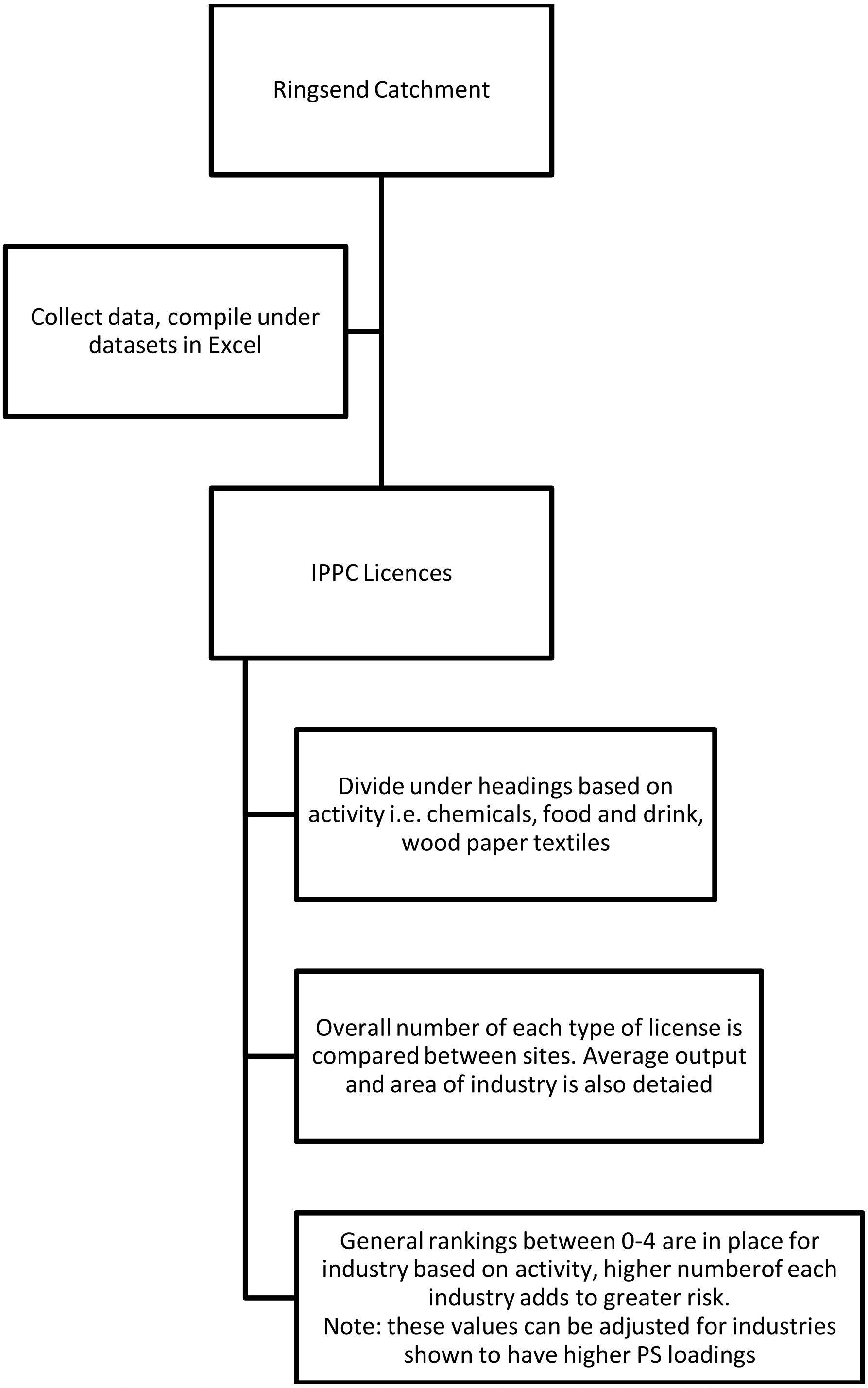


Figure 5-16 Overview of procedures involved in assigning risk factors using IPPC licences as a sample source from the Ringsend catchment.

Using another example to illustrate assigning of risk values to the different catchments the site of Ballincollig is expanded upon below, Figure 5-17.

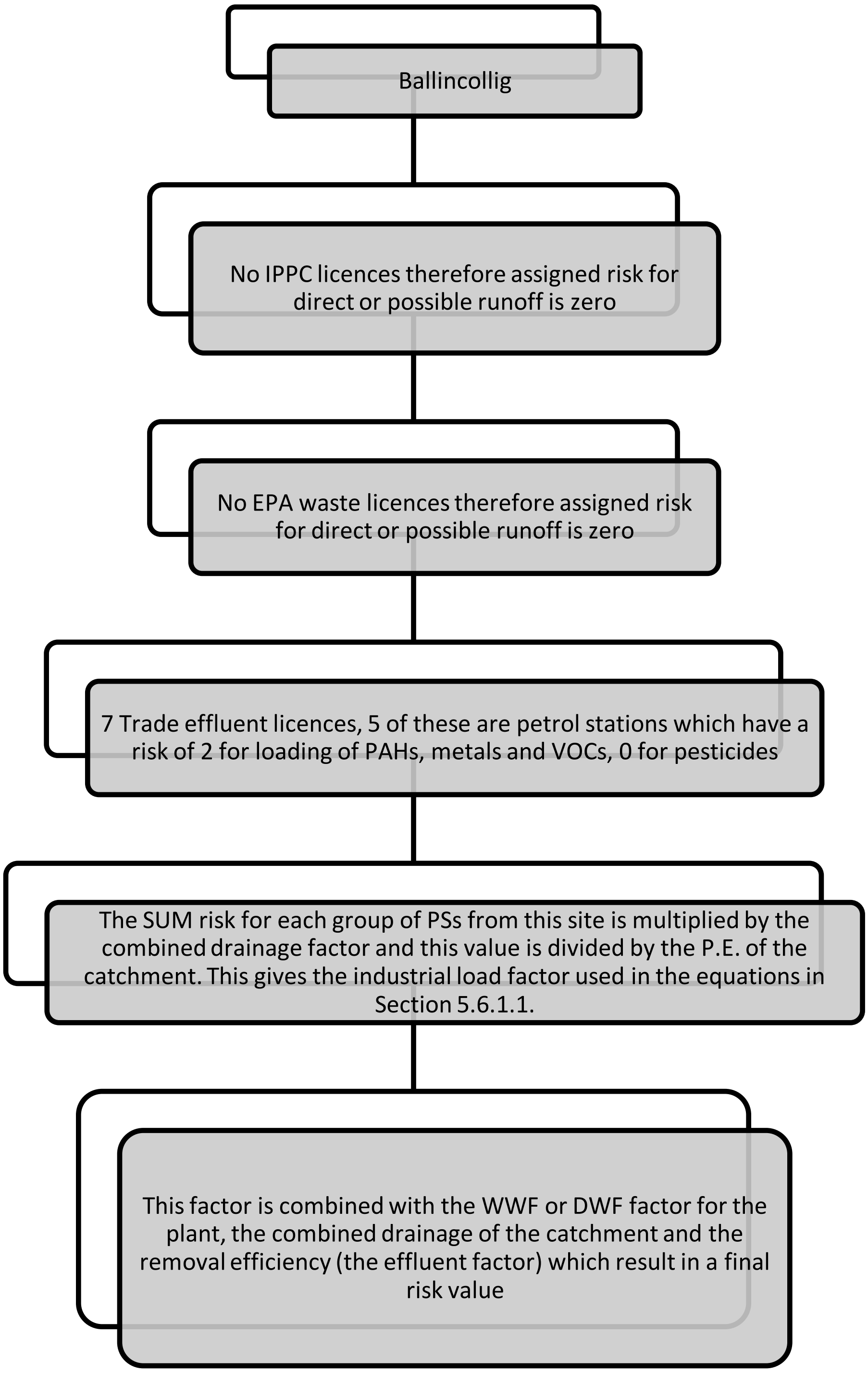
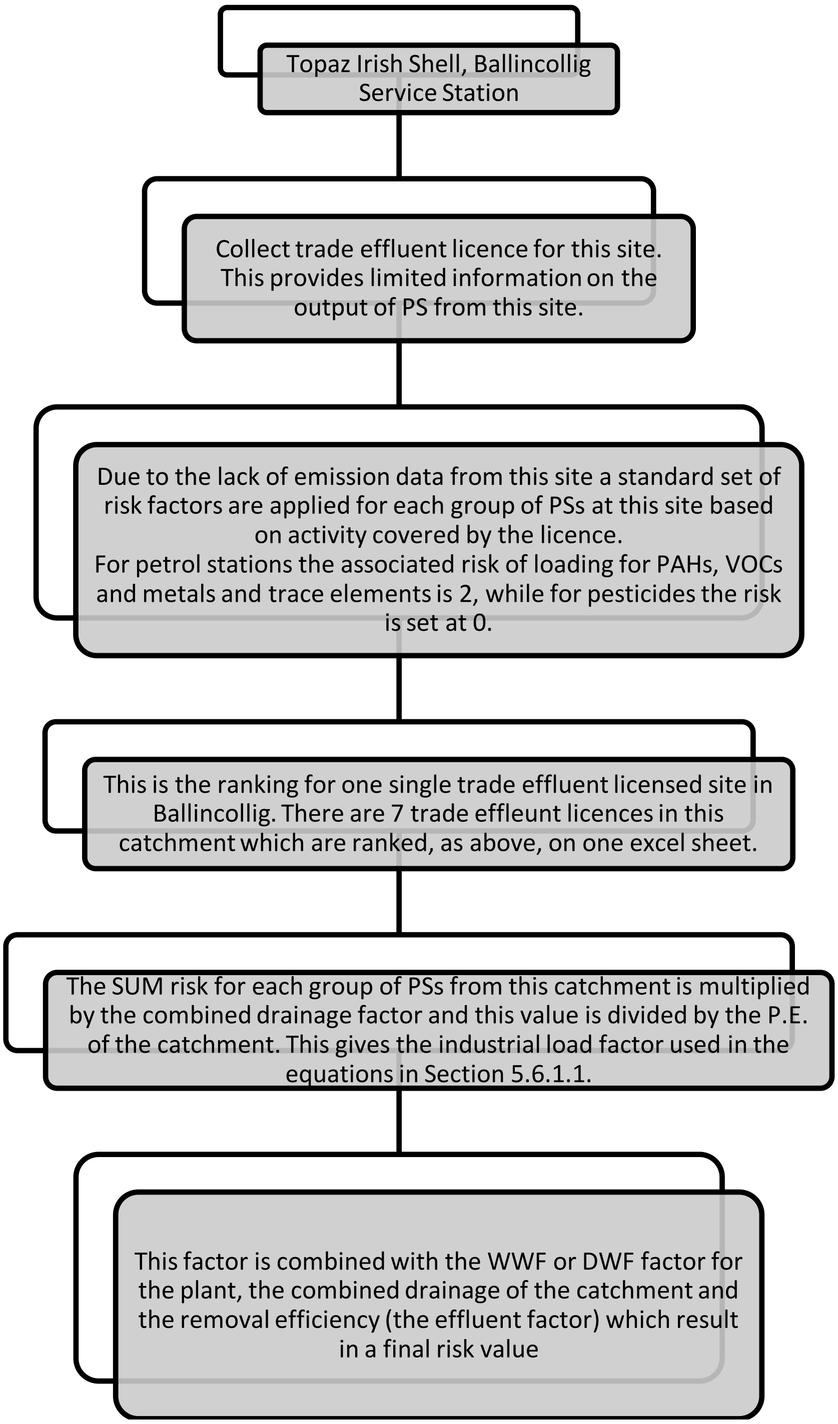


Figure 5-17 Outline on assigning risk based on IPPC licences in Ballincollig.

To give a more specific example Figure 5-18 tracks a single trade effluent licence, for a petrol station, from collection of the licence to the assignment of a risk factor.



Topaz Irish Shell, Ballincollig Service Station

Collect trade effluent licence for this site. This provides limited information on the output of PS from this site.

Due to the lack of emission data from this site a standard set of risk factors are applied for each group of PSs at this site based on activity covered by the licence.
For petrol stations the associated risk of loading for PAHs, VOCs and metals and trace elements is 2, while for pesticides the risk is set at 0.

This is the ranking for one single trade effluent licensed site in Ballincollig. There are 7 trade effleunt licences in this catchment which are ranked, as above, on one excel sheet.

The SUM risk for each group of PSs from this catchment is multiplied by the combined drainage factor and this value is divided by the P.E. of the catchment. This gives the industrial load factor used in the equations in Section 5.6.1.1.

This factor is combined with the WWF or DWF factor for the plant, the combined drainage of the catchment and the removal efficiency (the effluent factor) which result in a final risk value

Figure 5-18 From licence to risk factor for a petrol station in Ballincollig, Cork.

The risk factor determined for the site described in Figure 5-18 is a single risk for a single site. For a single petrol station the risk of PAH, VOC and metals and trace elements occurrence is 2 (per group) while pesticides are risked 0. When all trade effluent licences for Ballincollig have been evaluated in this same manner the same procedure is carried out for waste discharge licences and IPPC licences. As Ballincollig had no licences other than trade effluent this was the simplest site to model. The SUM risk for each group of pollutants assigned from the 7 trade effluent licences was used to calculate final risk. For example, the SUM PAH risk for Ballincollig was 38, Table 5-20 shows how this number relates to the final DWF risk for PAHs in Ballincollig.

Table 5-20 Final calculation of DWF risk factor for PAHs in Ballincollig

	P.E.	*Industrial risk factor*	*Effluent factor*	***DWF Risk***
Ballincollig	17,989	38	0.2	**0.09**
National	4,240,000	20000		

Taking Ballincollig as an example, and focussing on PAHs during DWF, Table 5-20 sets out how the final risk factor is achieved.

- The P.E. has been gathered from WWTP licence application and census records for this catchment.
- The calculation of the industrial risk factor has been outlined above in Figure 5-18.
- The effluent factor is assigned as 0.2. This was derived from the standard removal efficiency of PAHs from secondary treatment. The effluent factor can be any value from 1 to 0 with 1 indicating no removal of the pollutant and 0 indicating 100% removal of the pollutant. The value of 0.2 here indicates 80% removal of PAHs at this site under normal operating conditions.
- The national population is under National P.E.
- The national industrial risk factor is the total number of trade effluent licences.

Finally the DWF risk is calculated.

DWF Risk for PAHs = (Industrial risk divided by national industrial risk) divided by (P.E. divided by national P.E.) multiplied by the effluent factor = **0.09**

5.7 Conclusion

This chapter highlighted the process followed in the establishment, development and population of a risk-based model for the relation of emission factors to occurrence of priority and hazardous substances in wastewater. This involved a review of modelling approaches that could be adapted for the WFD priority substances. The model was then designed using identified sources of data for the population of the model. Each site was characterised and sources of information identified.

The information gathering was a continuous process with data tabulated as it became available. Emission factors for the priority substances were evaluated by agglomeration and this data was collated and used to populate the model. As no such model previously existed in Ireland no single database of relevant information relating emission factors to PS occurrence was available. Through the course of this project this dataset has been compiled and has been made available to the Irish EPA for use in future monitoring programmes.

6. Validation and Testing of Model

6.1 Aims and objectives

The aim of this chapter is to outline the population of the model with experimental data, using this data to validate the theoretical risk assigned based on the literature.

The objectives are to:

- present the results of analysis for priority PAHs, pesticides and metals and trace elements for the nine sites selected for study,
- provide an overview of these results in relation to WWF and DWF conditions,
- use the analytical results to validate the model with a focus on two sites for comparison,
- outline the basic use of the model and the application of this model to other sites.

6.2 Ballincollig

6.2.1 INTRODUCTION

At the Ballincollig site 16 samples were collected monthly over a sampling period that spanned June 2010 through July 2011. Table 6-1 shows dates of sample collection at Ballincollig WWTP. Of the sampling locations located in County Cork Ballincollig was the only site where it was possible to carry out intensive sampling, with sampling carried out in June 2011. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream.

Table 6-1 Dates of sample collections at Ballincollig WWTP.

	2010	*2011*
Sampling Dates	24/06/2010	18/01/2011
	08/07/2010	03/02/2011
	25/08/2010	03/03/2011
	09/09/2010	26/04/2011
	28/10/2010	17/05/2011
	16/12/2010	07/06/2011
		27/06/2011
		29/06/2011
		01/07/2011
		12/07/2011

6.2.2 PAHS

Presented in this section are the PAH results for Ballincollig WWTP, Table 6-2. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-2 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-2 Results of PAH analysis for Ballincollig WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=16***	***Range***		***Percentile***		
			Min.	***Max.***	50	75	90
Naph.	1.2	16	5.44^{E-04}	1.69^{E-03}	8.72^{E-04}	1.21^{E-03}	1.42^{E-03}
Ant.	0.1	16	<LOD	2.33^{E-02}	6.89^{E-04}	8.51^{E-04}	1.32^{E-03}
Fluor.	0.1	16	<LOD	1.89^{E-02}	2.57^{E-04}	3.35^{E-04}	3.57^{E-04}
Bb/k	Σ=0.003	9	<LOD	**4.02^{E-02}**	<LOD	2.85^{E-05}	1.99^{E-02}
Bap	0.05	8	<LOD	3.03^{E-02}	2.41^{E-05}	6.56^{E-03}	1.83^{E-02}
Ind + Bghi	Σ=0.002	11	<LOD	**4.21^{E-02}**	7.23^{E-05}	1.91^{E-02}	2.32^{E-02}

Table 6-2 shows that naphthalene, anthracene and fluoranthene, the more water soluble PAHs were detected in all samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were less frequently detected. Of these PAHs there were exceedences of the EQS limits for the benzo-b/k-fluoranthene and the indeno-1,2,3cd-pyrene and benzo-ghi-perylene (marked in bold in Table 6-2).

6.2.3 PESTICIDES

Presented in this section are the pesticide results for Ballincollig WWTP. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-3 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-3 Results of pesticide analysis for Ballincollig WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=13***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Alachlor	0.7	5	5.1^{E-02}	1.3^{E-01}	8.61^{E-02}	9.78^{E-02}	1.05^{E-01}
Atrazine	2.00^{E+00}	10	ND	2.1^{E-01}	4.35^{E-02}	1.48^{E-01}	1.61^{E-01}
Chlorfenvinphos	3.00^{E-01}	9	3.0^{E-01}	**2.2^{E+00}**	7.89^{E-01}	1.20^{E+00}	1.73^{E+00}
Diuron	1.8	13	<LOD	6.2^{E-01}	2.06^{E-01}	2.46^{E-01}	3.45^{E-01}
Malathion		7	ND	9.9^{E-01}	1.36^{E-01}	5.38^{E-01}	8.52^{E-01}
Simazine	4	9	1.5^{E-02}	1.7^{E-01}	5.67^{E-02}	1.17^{E-01}	1.26^{E-01}
Fenitrothion		9	ND	7.8^{E-01}	1.83^{E-01}	3.30^{E-01}	5.20^{E-01}
Pirimiphos methyl		9	ND	6.9^{E-01}	2.63^{E-01}	4.50^{E-01}	4.86^{E-01}
Chlorpyrifos	0.1	3	ND	6.0^{E-02}	2.16^{E-02}	3.92^{E-02}	4.98^{E-02}
DEHP	1.3*	11	ND	**1.4^{E+01}**	1.60^{E+00}	2.01^{E+00}	2.20^{E+00}
Mecoprop		2	2.0^{E-02}	3.4^{E-01}	1.74^{E-01}	2.46^{E-01}	2.89^{E-01}

Table 6-3 shows that eleven of the priority pesticides were detected in samples from Ballincollig WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos and DEHP (marked in bold in Table 6-3). Of the thirteen samples collected at this site only diuron was found to occur in all samples.

6.2.4 METALS AND TRACE ELEMENTS

Ten samples collected at Ballincollig WWTP were microwave digested, stored and sent to the Centre for Microscopic Analysis (CMA) in Trinity College Dublin for analysis by ICP-MS. The analysis determined trace levels of 15 WFD priority metals and trace elements in the samples. Presented in Table 6-4 below are the results of this analysis.

Table 6-4 ICPMS results for samples collected at Ballincollig WWTP from June 2010 to July 2011. Samples were analysed for 15 elements in a total of 10 samples. Results are shown in µg L^{-1}. Exceedances are marked in bold.

Parameter	***Target EQS***	***Freq. n=10***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		10	3.37^{E+01}	6.13^{E+01}	4.47^{E+01}	5.52^{E+01}	6.07^{E+01}
Vanadium		0					
Chromium	0.6-4.7	4	1.37^{E+00}	3.63^{E+00}	1.86^{E+00}	2.42^{E+00}	3.14^{E+00}
Cobalt		0					
Nickel	20	4	1.41^{E+00}	7.74^{E+00}	4.61^{E+00}	5.85^{E+00}	6.98^{E+00}
Copper	5.0-30	10	3.82^{E+00}	1.16^{E+01}	5.70^{E+00}	6.97^{E+00}	9.07^{E+00}
Zinc	8-100	10	4.03^{E+01}	7.08^{E+01}	5.67^{E+01}	6.08^{E+01}	6.48^{E+01}
Arsenic	20-25	0					
Selenium		0					
Molybdenum		0					
Cadmium	0.08-0.25	0					
Tin	0.0002	2	1.16^{E+00}	**1.18^{E+00}**	1.17^{E+00}	1.18^{E+00}	1.18^{E+00}
Antimony		1	1.15^{E+00}	1.15^{E+00}	1.15^{E+00}	1.15^{E+00}	1.15^{E+00}
Barium		9	2.23^{E+00}	1.09^{E+01}	3.10^{E+00}	7.39^{E+00}	1.05^{E+01}
Lead	7.2	2	1.05^{E+00}	**2.21^{E+01}**	1.16^{E+01}	1.68^{E+01}	2.00^{E+01}

According to Table 6-4 all samples collected were found to contain levels of trace elements with Zinc present in the highest concentrations. Tin exceeded the EQS value in 2 of the 10 samples with lead exceeding the EQS value in one sample.

6.3 Bandon

6.3.1 INTRODUCTION

At the Bandon site 10 samples were collected monthly over a sampling period that spanned July 2010 through July 2011. Table 6-5 shows dates of sample collection at Bandon WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream.

Table 6-5 Dates of sample collections at Bandon WWTP.

	2010	*2011*
Sampling Dates	08/07/2010	18/01/2011
	12/08/2010	10/02/2011
	09/09/2010	26/04/2011
	28/10/2010	17/05/2011
		07/06/2011
		12/07/2011

6.3.2 PAHS

Presented in this section are the PAH results for Bandon WWTP, Table 6-6. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-6 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-6 Results of PAH analysis for Bandon WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=10***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Naph.	1.2	10	<LOD	2.92^{E-03}	9.24^{E-04}	1.02^{E-03}	1.57^{E-03}
Ant.	0.1	10	<LOD	1.10^{E-03}	4.64^{E-04}	7.11^{E-04}	9.03^{E-04}
Fluor.	0.1	9	<LOD	6.14^{E-04}	3.10^{E-04}	3.55^{E-04}	4.57^{E-04}
Bb/k	Σ=0.003	7	<LOD	1.84^{E-04}	0.00^{E+00}	2.24^{E-05}	6.28^{E-05}
Bap	0.05	3	<LOD	<LOD	<LOD	<LOD	<LOD
Ind + Bghi	Σ=0.002	4	<LOD	<LOD	<LOD	<LOD	<LOD

Table 6-6 shows that naphthalene and anthracene, the more water soluble PAHs, were detected in all samples collected while the less water soluble, higher octanol/water partition coefficient PAHs, were less frequently detected. None of the maximum detected levels were above EQS limits for the PAHs.

6.3.3 PESTICIDES

Presented in this section are the pesticide results for Bandon WWTP, Table 6-7. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-7 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-7 Results of pesticide analysis for Bandon WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=10***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Alachlor	0.7	3	7.2^{E-02}	1.3^{E-01}	8.87^{E-02}	9.89^{E-02}	1.05^{E-01}
Atrazine	2.00^{E+00}	7	8.4^{E-03}	4.2^{E-01}	9.26^{E-02}	1.67^{E-01}	2.65^{E-01}
Chlorfenvinphos	3.00^{E-01}	6	5.5^{E-01}	**1.9^{E+00}**	9.96^{E-01}	1.57^{E+00}	1.79^{E+00}
Diuron	1.8	10	5.0^{E-02}	1.0^{E+00}	2.46^{E-01}	3.69^{E-01}	4.79^{E-01}
Malathion		5	ND	7.0^{E-01}	2.86^{E-01}	5.54^{E-01}	6.00^{E-01}
Simazine	4	7	2.3^{E-02}	1.8^{E-01}	6.90^{E-02}	1.15^{E-01}	1.60^{E-01}
Fenitrothion		6	1.3^{E-02}	6.4^{E-01}	3.11^{E-01}	3.71^{E-01}	4.41^{E-01}
Pirimiphos methyl		6	ND	4.1^{E-01}	2.26^{E-01}	2.72^{E-01}	3.32^{E-01}
Chlorpyrifos	0.1	2	ND	6.3^{E-02}	2.79^{E-02}	3.74^{E-02}	4.31^{E-02}
DEHP	1.3*	9	2.0^{E-01}	**3.8^{E+01}**	1.85^{E+00}	1.44^{E+01}	1.94^{E+01}
Mecoprop		1	4.1^{E-01}	5.0^{E-01}	4.45^{E-01}	4.45^{E-01}	4.45^{E-01}

Table 6-7 shows that eleven of the priority pesticides were detected in samples from Bandon WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos and DEHP (marked in bold in Table 6-7). Of the ten samples collected at this site only diuron was found to occur in all samples.

6.3.4 METALS AND TRACE ELEMENTS

The results of ICP-MS analysis carried out on the 8 samples collected at Bandon WWTP are presented in Table 6-8. All 8 samples showed the presence of trace elements, with highest detected concentrations determined for Boron, Zinc and Copper.

Table 6-8 ICPMS results for samples collected at Bandon WWTP from July 2010 to July 2011. Samples were analysed for 15 elements in a total of 8 samples. Results are shown in µg L^{-1}. Exceedances are marked in bold.

Parameter	*Target EQS*	*Freq. n=8*	*Range*		*Percentile*		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		8	4.50^{E+01}	1.34^{E+02}	6.86^{E+01}	8.84^{E+01}	1.09^{E+02}
Vanadium		1	1.32^{E+00}	1.32^{E+00}	1.32^{E+00}	1.32^{E+00}	1.32^{E+00}
Chromium	0.6-4.7	7	1.20^{E+00}	4.47^{E+00}	2.14^{E+00}	3.08^{E+00}	4.13^{E+00}
Cobalt		0					
Nickel	20	8	2.46^{E+00}	1.08^{E+01}	3.47^{E+00}	6.57^{E+00}	1.08^{E+01}
Copper	5.0-30	8	1.83^{E+01}	**4.68^{E+01}**	3.40^{E+01}	3.94^{E+01}	4.19^{E+01}
Zinc	8-100	8	5.75^{E+01}	**1.18^{E+02}**	8.27^{E+01}	1.04^{E+02}	1.13^{E+02}
Arsenic	20-25	4	1.11^{E+00}	1.67^{E+00}	1.35^{E+00}	1.54^{E+00}	1.62^{E+00}
Selenium		1	1.32^{E+00}	1.32^{E+00}	1.32^{E+00}	1.32^{E+00}	1.32^{E+00}
Molybdenum		4	1.26^{E+00}	1.30^{E+01}	5.29^{E+00}	9.68^{E+00}	1.17^{E+01}
Cadmium	0.08-0.25	0					
Tin	0.0002	7	1.51^{E+00}	**6.47^{E+00}**	2.02^{E+00}	3.87^{E+00}	5.91^{E+00}
Antimony		3	1.54^{E+00}	2.79^{E+00}	2.03^{E+00}	2.41^{E+00}	2.64^{E+00}
Barium		8	3.08E^{+00}	1.54^{E+01}	8.15^{E+00}	1.24^{E+01}	1.49^{E+01}
Lead	7.2	5	1.15^{E+00}	2.38^{E+00}	2.04^{E+00}	2.12^{E+00}	2.28^{E+00}

A high frequency of occurrence was noted for the boron, barium, copper, nickel and zinc. It was also found that a number of exceedances of EQS values were detected with tin, copper and zinc detected in high concentrations.

6.4 Charleville

6.4.1 INTRODUCTION

At the Charleville site 5 samples were collected monthly over a sampling period that spanned August 2010 through July 2011. Table 6-9 shows dates of sample collection at Charleville WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream.

Table 6-9 Dates of sample collections at Charleville WWTP.

	2010	*2011*
Sampling Dates	25/08/2010	26/04/2011 17/05/2011 07/06/2011 12/07/2011

6.4.2 PAHS

Presented in this section are the PAH results for Charleville WWTP, Table 6-10. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-10 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-10 Results of PAH analysis for Charleville WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	*Target EQS µg L^{-1}*	*Freq. n=5*	*Range*		*Percentile*		
			Min.	*Max.*	**50**	**75**	**90**
Naph.	1.2	5	<LOD	2.98^{E-03}	3.54^{E-04}	1.08^{E-03}	1.51^{E-03}
Ant.	0.1	5	<LOD	2.87^{E-03}	5.52^{E-04}	1.11^{E-03}	1.45^{E-03}
Fluor.	0.1	5	<LOD	1.44^{E-03}	1.88^{E-04}	5.15^{E-04}	7.12^{E-04}
Bb/k	Σ=0.003	2	<LOD	1.79^{E-03}	1.08^{E-03}	1.08^{E-03}	1.08^{E-03}
Bap	0.05	2	<LOD	1.57^{E-03}	9.44^{E-04}	9.44^{E-04}	9.44^{E-04}
Ind + Bghi	Σ=0.002	5	<LOD	$\mathbf{4.67^{E-02}}$	0.00^{E+00}	1.47^{E-02}	2.35^{E-02}

Table 6-10 shows that naphthalene, anthracene and fluoranthene, the more water soluble PAHs were detected in all samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were less frequently detected. Of these PAHs there were exceedences of the EQS limits for the indeno-1,2,3cd-pyrene and benzo-ghi-perylene (marked in bold in Table 6-10).

6.4.3 PESTICIDES

Presented in this section are the pesticide results for Charleville WWTP, Table 6-11. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-11 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-11 Results of pesticide analysis for Charleville WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=5***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Atrazine	2	4	6.8^{E-03}	1.2^{E-02}	1.02^{E-02}	1.14^{E-02}	1.15^{E-02}
Chlorfenvinphos	3.00^{E-01}	1	1.8^{E+00}	**2.2^{E+00}**	1.96^{E+00}	1.96^{E+00}	1.96^{E+00}
Diuron	1.8	5	3.4^{E-02}	3.6^{E-01}	5.65^{E-02}	1.63^{E-01}	2.72^{E-01}
Malathion		1	4.8^{E-01}	6.1^{E-01}	5.41^{E-01}	5.41^{E-01}	5.41^{E-01}
Simazine	4	4	5.9^{E-03}	1.9^{E-01}	1.82^{E-02}	6.15^{E-02}	1.33^{E-01}
Fenitrothion		1	7.3^{E-02}	2.4^{E-01}	1.74^{E-01}	1.74^{E-01}	1.74^{E-01}
Pirimiphos methyl		1	2.1^{E-01}	2.5^{E-01}	2.28^{E-01}	2.28^{E-01}	2.28^{E-01}
DEHP	1.3*	5	4.8^{E-01}	**1.1^{E+01}**	2.39^{E+00}	3.87^{E+00}	7.57^{E+00}

Table 6-11 shows that 8 of the priority pesticides were detected in samples from Charleville WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos and DEHP (marked in bold in Table 6-11). Of the 5 samples collected at this site only diuron and DEHP were found to occur in all samples.

6.4.4 METALS AND TRACE ELEMENTS

Of the 4 samples collected at Charleville WWTP all were shown to contain some levels of priority trace elements. From Table 6-12 it can be seen that highest detected levels were determined for Copper, Zinc, Boron, Barium and Molybdenum.

Table 6-12 ICPMS results for samples collected at Charleville WWTP from August 2010 to June 2011. Samples were analysed for 15 elements in a total of 4 samples. Results are shown in µg L^{-1}. Exceedances of EQSs are marked in bold.

Parameter	***Target EQS***	***Freq. n=4***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		4	1.88^{E+01}	5.50^{E+01}	4.46^{E+01}	5.20^{E+01}	5.38^{E+01}
Vanadium		2	1.06$_{E+00}$	1.06^{E+00}	1.06^{E+00}	1.06^{E+00}	1.06^{E+00}
Chromium	0.6-4.7	1	1.57$_{E+00}$	1.57^{E+00}	1.57^{E+00}	1.57^{E+00}	1.57^{E+00}
Cobalt		0					
Nickel	20	3	1.12$_{E+00}$	5.18^{E+00}	2.06^{E+00}	3.62^{E+00}	4.56^{E+00}
Copper	5.0-30	4	1.00$_{E+01}$	1.93^{E+01}	1.29^{E+01}	1.45^{E+01}	1.74^{E+01}
Zinc	8-100	4	1.51$_{E+01}$	3.67^{E+01}	2.83^{E+01}	3.52^{E+01}	3.61^{E+01}
Arsenic	20-25	1	1.18$_{E+00}$	1.18^{E+00}	1.18^{E+00}	1.18^{E+00}	1.18^{E+00}
Selenium		0					
Molybdenum		3	1.51^{E+01}	2.49^{E+01}	2.16^{E+01}	2.33^{E+01}	2.43^{E+01}
Cadmium	0.08-0.25	0					
Tin	0.0002	1	1.05^{E+00}	**1.05^{E+00}**	1.05^{E+00}	1.05^{E+00}	1.05^{E+00}
Antimony		1	1.23^{E+00}	1.23^{E+00}	1.23^{E+00}	1.23^{E+00}	1.23^{E+00}
Barium		4	3.25^{E+01}	9.64^{E+01}	7.79^{E+01}	9.52^{E+01}	9.59^{E+01}
Lead	7.2	1	1.23^{E+00}	1.23^{E+00}	1.23^{E+00}	1.23^{E+00}	1.23^{E+00}

Boron, barium, copper and zinc occurred in the highest frequency at this site with only tin exceeding the EQS value.

6.5 Clonakilty

6.5.1 INTRODUCTION

At the Clonakilty site 4 samples were collected monthly over a sampling period that spanned April through July 2011. Table 6-13 shows dates of sample collection at Clonakilty WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream.

Table 6-13 Dates of sample collections at Clonakilty WWTP.

	2011
Sampling Dates	26/04/2011
	17/05/2011
	07/06/2011
	12/07/2011

6.5.2 PAHS

Presented in this section are the PAH results for Clonakilty WWTP, Table 6-14. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-14 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-14 Results of PAH analysis for Clonakilty WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=4***	***Range***		**Percentile**		
			Min.	***Max.***	**50**	**75**	**90**
Naph.	1.2	4	<LOD	1.67^{E-03}	2.58^{E-04}	3.86^{E-04}	4.64^{E-04}
Ant.	0.1	4	<LOD	7.60^{E-04}	4.00^{E-04}	4.47^{E-04}	4.75^{E-04}
Fluor.	0.1	4	<LOD	2.34^{E-04}	4.79^{E-05}	7.19^{E-05}	8.63^{E-05}
Bb/k	Σ=0.003	0	ND	ND	0.00^{E+00}	0.00^{E+00}	0.00^{E+00}
Bap	0.05	0	ND	ND	0.00^{E+00}	0.00^{E+00}	0.00^{E+00}
Ind + Bghi	Σ=0.002	0	ND	ND	0.00^{E+00}	0.00^{E+00}	0.00^{E+00}

Table 6-14 shows that naphthalene, anthracene and fluoranthene, the more water soluble PAHs were detected in all samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were not detected at all.

6.5.3 PESTICIDES

Presented in this section are the pesticide results for Clonakilty WWTP, Table 6-15. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-15 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-15 Results of pesticide analysis for Clonakilty WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound.

Parameter	*Target EQS µg L^{-1}*	*Freq. n=4*	*Range*		*Percentile*		
			Min.	***Max.***	**50**	**75**	**90**
Atrazine	2	4	4.5^{E-03}	3.2^{E-02}	8.25^{E-03}	1.47^{E-02}	2.44^{E-02}
Diuron	1.8	4	4.5^{E-03}	3.2^{E-02}	3.61^{E-02}	4.46^{E-02}	4.86^{E-02}
Simazine	4	2	4.5^{E-03}	3.2^{E-02}	4.37^{E-03}	4.56^{E-03}	4.68^{E-03}
DEHP	1.3*	4	4.5^{E-03}	3.2^{E-02}	6.31^{E+00}	1.28^{E+01}	2.39^{E+01}

Table 6-15 shows that 4 of the priority pesticides were detected in samples from Clonakilty WWTP. Of these pesticides there were no detected exceedences of the EQS limits. Of the 4 samples collected at this site only simazine was found not to occur in all samples, with atrazine, diuron and DEHP detected in all samples.

6.5.4 METALS AND TRACE ELEMENTS

Of the 4 samples collected at Clonakilty WWTP all were shown to contain some levels of priority trace elements. From Table 6-16 it can be seen that highest detected levels were determined for Copper, Zinc, Boron, Barium and Molybdenum.

Table 6-16 ICPMS results for samples collected at Clonakilty WWTP from August 2010 to June 2011. Samples were analysed for 15 elements in a total of 4 samples. Results are shown in µg L^{-1}. Exceedances of EQSs are marked in bold.

Parameter	***Target EQS***	***Freq. n=4***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		4	2.99^{E+01}	1.26^{E+02}	4.11^{E+01}	6.77^{E+01}	1.03^{E+02}
Vanadium		2	5.29^{E+00}	5.29^{E+00}	5.29^{E+00}	5.29^{E+00}	5.29^{E+00}
Chromium	0.6-4.7	1	1.29^{E+00}	**1.22^{E+01}**	6.74^{E+00}	9.46^{E+00}	1.11^{E+01}
Cobalt		0	2.10^{E+00}	2.10^{E+00}	2.10^{E+00}	2.10^{E+00}	2.10^{E+00}
Nickel	20	3	1.04^{E+00}	1.18^{E+01}	1.68^{E+00}	4.50^{E+00}	8.86^{E+00}
Copper	5.0-30	4	6.82^{E+00}	**2.46^{E+02}**	1.24^{E+01}	7.12^{E+01}	1.76^{E+02}
Zinc	8-100	4	1.69^{E+01}	**4.42^{E+02}**	5.40^{E+01}	1.65^{E+02}	3.31^{E+02}
Arsenic	20-25	1	4.99^{E+00}	4.99^{E+00}	4.99^{E+00}	4.99^{E+00}	4.99^{E+00}
Selenium		0	5.34^{E+00}	5.34^{E+00}	5.34^{E+00}	5.34^{E+00}	5.34^{E+00}
Molybdenum		3	1.89^{E+00}	2.94^{E+01}	6.48^{E+00}	1.80^{E+01}	2.48^{E+01}
Cadmium	0.08-0.25	0					
Tin	0.0002	1	1.24^{E+01}	**1.24^{E+01}**	1.24^{E+01}	1.24^{E+01}	1.24^{E+01}
Antimony		1	6.43^{E+00}	6.43^{E+00}	6.43^{E+00}	6.43^{E+00}	6.43^{E+00}
Barium		4	2.66^{E+00}	6.50^{E+01}	5.01^{E+00}	2.10^{E+01}	4.74^{E+01}
Lead	7.2	1	1.28^{E+01}	**1.28^{E+01}**	1.28^{E+01}	1.28^{E+01}	1.28^{E+01}

High frequency of occurrence was observed for several of the metals and trace elements: bron, nickel, copper, zinc and barium. There were also EQS exceedances detected for five of the analytes as marked in bold in Table 6-16.

6.6 Fermoy

6.6.1 INTRODUCTION

At the Fermoy site 11 samples were collected monthly over a sampling period that spanned July 2010 through July 2011. Table 6-17 shows dates of sample collection at Fermoy WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream.

Table 6-17 Dates of sample collections at Fermoy WWTP.

	2010	*2011*
Sampling Dates	01/07/2010	18/01/2011
	05/08/2010	03/02/2011
	23/09/2010	03/03/2011
	28/10/2010	26/04/2011
		17/05/2011
		07/06/2011
		12/07/2011

6.6.2 PAHS

Presented in this section are the PAH results for Fermoy WWTP, Table 6-18. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-18 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-18 Results of PAH analysis for Fermoy WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	***Target EQS*** ***µg L^{-1}***	***Freq.*** ***n=11***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Naph.	1.2	11	<LOD	2.76^{E-03}	7.90^{E-04}	1.48^{E-03}	1.79^{E-03}
Ant.	0.1	8	<LOD	1.52^{E-03}	3.92^{E-04}	4.31^{E-04}	4.75^{E-04}
Fluor.	0.1	9	<LOD	2.56^{E-04}	7.01^{E-05}	1.14^{E-04}	1.57^{E-04}
Bb/k	Σ=0.003	0	<LOD	ND	0.00^{E+00}	0.00^{E+00}	0.00^{E+00}
Bap	0.05	3	<LOD	2.07^{E-02}	9.91^{E-03}	1.49^{E-02}	1.78^{E-02}
Ind + Bghi	Σ=0.002	3	<LOD	$\mathbf{4.36^{E-03}}$	0.00^{E+00}	5.40^{E-04}	8.64^{E-04}

Table 6-18 shows that naphthalene, anthracene and fluoranthene, the more water soluble PAHs were detected in many of the samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were less frequently detected, with benzo-b/k-fluoranthene not detected at all. Of these PAHs there were exceedences of the EQS limits for the indeno-1,2,3cd-pyrene and benzo-ghi-perylene (marked in bold in Table 6-18).

6.6.3 PESTICIDES

Presented in this section are the pesticide results for Fermoy WWTP, Table 6-19. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-19 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-19 Results of pesticide analysis for Fermoy WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound

Parameter	***Target EQS µg L^{-1}***	***Freq. n=10***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Alachlor	0.7	6	4.9^{E-03}	2.3^{E-01}	7.03^{E-02}	1.61^{E-01}	2.05^{E-01}
Atrazine	2.0	10	ND	5.3^{E-01}	5.16^{E-02}	1.16^{E-01}	3.98^{E-01}
Chlorfenvinphos	0.3	6	1.5^{E-01}	**2.2^{E+00}**	4.66^{E-01}	1.44^{E+00}	1.90^{E+00}
Diuron	1.8	10	ND	8.3^{E-01}	1.22^{E-01}	1.95^{E-01}	7.73^{E-01}
Epoxiconazole		2	1.8^{E-03}	2.0^{E-02}	7.18^{E-03}	9.81^{E-03}	1.14^{E-02}
Isoproturon	1.0	1	4.6^{E-03}	1.3^{E-02}	8.06^{E-03}	8.06^{E-03}	8.06^{E-03}
Malathion		5	2.2^{E-03}	4.3^{E-01}	8.53^{E-02}	1.22^{E-01}	2.87^{E-01}
Simazine	4.0	10	ND	4.5^{E-01}	4.50^{E-02}	8.33^{E-02}	2.94^{E-01}
Fenitrothion		6	2.1^{E-02}	6.6^{E-01}	9.16^{E-02}	2.12^{E-01}	4.37^{E-01}
Pirimiphos methyl		6	4.0^{E-03}	8.0^{E-01}	1.23^{E-01}	2.08^{E-01}	4.98^{E-01}
Chlorpyrifos	0.1	4	2.6^{E-02}	**1.2^{E-01}**	6.11^{E-02}	9.25^{E-02}	9.87^{E-02}
DEHP	1.3*	10	4.5^{E-01}	**1.7^{E+01}**	1.53^{E+00}	1.98^{E+00}	4.91^{E+00}

Table 6-19 shows that 12 of the priority pesticides were detected in samples from Fermoy WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos, chlorpyrifos and DEHP (marked in bold in Table 6-19). Of the ten samples collected at this site only atrazine, diuron, simazine and DEHP were found to occur in all samples.

6.6.4 METALS AND TRACE ELEMENTS

Of the 8 samples collected at Fermoy WWTP all were shown to contain some levels of priority trace elements. From Table 6-20 it can be seen that highest detected levels were determined for Copper, Zinc, Boron, Barium and Molybdenum.

Table 6-20 ICPMS results for samples collected at Fermoy WWTP from July 2010 to July 2011. Samples were analysed for 15 elements in a total of 8 samples. Results are shown in µg L^{-1}. Exceedances of EQS levels are marked in bold.

Parameter	***Target EQS***	***Freq. n=4***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		4	5.04^{E+01}	2.89^{E+02}	1.54^{E+02}	2.51^{E+02}	2.72^{E+02}
Vanadium		1					
Chromium	0.6-4.7	2	1.28^{E+00}	**4.74^{E+00}**	2.91^{E+00}	3.83^{E+00}	4.37^{E+00}
Cobalt		1					
Nickel	20	4	1.58^{E+00}	3.83^{E+00}	2.17^{E+00}	2.70^{E+00}	3.38_{E+00}
Copper	5.0-30	4	5.50^{E+00}	2.69^{E+01}	1.79^{E+01}	2.24^{E+01}	2.42^{E+01}
Zinc	8-100	4	1.49^{E+01}	8.11^{E+01}	4.04^{E+01}	5.21^{E+01}	6.50^{E+01}
Arsenic	20-25	1					
Selenium		1					
Molybdenum		3	4.28^{E+00}	1.54^{E+01}	6.00^{E+00}	8.11^{E+00}	1.20^{E+01}
Cadmium	0.08-0.25	0					
Tin	0.0002	1	6.63^{E+00}	**6.63^{E+00}**	6.63^{E+00}	6.63^{E+00}	6.63^{E+00}
Antimony		1	1.50^{E+00}	1.50^{E+00}	1.50^{E+00}	1.50^{E+00}	1.50^{E+00}
Barium		4	3.48^{E+00}	1.60^{E+01}	9.85^{E+00}	1.18^{E+01}	1.32^{E+01}
Lead	7.2	1	1.13_{E+00}	1.80^{E+00}	1.47^{E+00}	1.63^{E+00}	1.73^{E+00}

Barium, copper, zinc and boron had the highest frequency of detection with tin and chromium exceeding their respective EQS levels.

6.7 Mallow

6.7.1 INTRODUCTION

At the Mallow site 12 samples were collected monthly over a sampling period that spanned July 2010 through July 2011. Table 6-21 shows dates of sample collection at Mallow WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream.

Table 6-21 Dates of sample collections at Mallow WWTP.

	2010	*2011*
Sampling Dates	08/07/2010	18/01/2011
	05/08/2010	17/02/2011
	23/09/2010	03/03/2011
	28/10/2010	26/04/2011
	24/11/2010	17/05/2011
		07/06/2011
		12/07/2011

6.7.2 PAHS

Presented in this section are the PAH results for Mallow WWTP, Table 6-22. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-22 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-22 Results of PAH analysis for Mallow WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	*Target EQS* *µg L^{-1}*	*Freq.* *n=12*	*Range*		*Percentile*		
			Min.	*Max.*	**50**	**75**	**90**
Naph.	1.2	12	<LOD	3.00^{E-03}	5.93^{E-04}	1.13^{E-03}	1.87^{E-03}
Ant.	0.1	9	<LOD	6.53^{E-04}	3.05^{E-04}	4.28^{E-04}	5.53^{E-04}
Fluor.	0.1	8	<LOD	7.36^{E-04}	4.56^{E-05}	1.58^{E-04}	4.21^{E-04}
Bb/k	Σ=0.003	7	<LOD	3.12^{E-04}	0.00^{E+00}	6.54^{E-05}	1.83^{E-04}
Bap	0.05	4	<LOD	1.24^{E-03}	0.00^{E+00}	4.87^{E-04}	7.78^{E-04}
Ind + Bghi	Σ=0.002	7	<LOD	$\mathbf{7.13^{E-03}}$	0.00^{E+00}	2.40^{E-04}	4.01^{E-03}

Table 6-22 shows that the most water soluble PAH, naphthalene, was detected in all samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were less frequently detected. Of these PAHs there were exceedences of the EQS limits for the benzo-b/k-fluoranthene and the indeno-1,2,3cd-pyrene and benzo-ghi-perylene (marked in bold in Table 6-22).

6.7.3 PESTICIDES

Presented in this section are the pesticide results for Mallow WWTP, Table 6-23. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-23 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-23 Results of pesticide analysis for Mallow WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound

Parameter	***Target EQS µg L^{-1}***	***Freq. n=12***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Alachlor	0.7	6	ND	9.93^{E-02}	5.16^{E-02}	7.04^{E-02}	8.18^{E-02}
Atrazine	2.0	10	5.0^{E-03}	1.9^{E-01}	6.08^{E-02}	1.12^{E-01}	1.42^{E-01}
Chlorfenvinphos	0.3	8	ND	$\mathbf{1.9^{E+00}}$	6.18^{E-01}	8.90^{E-01}	1.57^{E+00}
Diuron	1.8	12	ND	4.8^{E-01}	1.17^{E-01}	2.08^{E-01}	2.56^{E-01}
Epoxiconazole		2	1.0^{E-03}	1.9^{E-03}	1.59^{E-03}	1.71^{E-03}	1.79^{E-03}
Isoproturon	1.0	1	ND	2.2^{E-02}	1.26^{E-02}	1.26^{E-02}	1.26^{E-02}
Malathion		5	3.6^{E-02}	4.0^{E-01}	1.07^{E-01}	1.78^{E-01}	2.63^{E-01}
Simazine	4.0	10	9.9^{E-03}	2.2^{E-01}	4.76^{E-02}	1.01^{E-01}	1.13^{E-01}
Fenitrothion		8	3.7^{E-02}	5.0^{E-01}	9.44^{E-02}	1.71^{E-01}	2.08^{E-01}
Pirimiphos methyl		8	ND	5.3^{E-01}	1.24^{E-01}	2.24^{E-01}	2.51^{E-01}
Chlorpyrifos	0.1	3	ND	4.2^{E-02}	2.33^{E-02}	2.87^{E-02}	3.19^{E-02}
DEHP	1.3*	12	ND	$\mathbf{2.1^{E+01}}$	1.20^{E+00}	1.68^{E+00}	2.05^{E+00}

Table 6-23 shows that 12 of the priority pesticides were detected in samples from Mallow WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos and DEHP (marked in bold in Table 6-23). Of the 12 samples collected at this site only diuron and DEHP were found to occur in all samples.

6.7.4 METALS AND TRACE ELEMENTS

Of the 7 samples collected at Mallow WWTP all were shown to contain some levels of priority trace elements. From Table 6-24 it can be seen that highest detected levels were determined for Copper, Zinc, Boron, Barium, Nickel and Molybdenum.

Table 6-24 ICPMS results for samples collected at Mallow WWTP from July 2010 to July 2011. Samples were analysed for 15 elements in a total of 7 samples. Results are shown in µg L^{-1}.

Parameter	***Target EQS***	***Freq. n=7***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		7	2.61^{E+01}	9.01^{E+01}	5.19^{E+01}	7.36^{E+01}	8.40^{E+01}
Vanadium		1	1.78^{E+00}	1.78^{E+00}	1.78^{E+00}	1.78^{E+00}	1.78^{E+00}
Chromium	0.6-4.7	4	1.06^{E+00}	1.85^{E+00}	1.57^{E+00}	1.84^{E+00}	1.84_{E+00}
Cobalt		1	1.38^{E+00}	1.38^{E+00}	1.38^{E+00}	1.38^{E+00}	1.38^{E+00}
Nickel	20	7	1.39^{E+00}	4.55^{E+00}	3.44^{E+00}	4.20^{E+00}	4.35^{E+00}
Copper	5.0-30	7	5.38^{E+00}	1.32^{E+01}	1.05^{E+01}	1.17^{E+01}	1.30^{E+01}
Zinc	8-100	7	6.61^{E+00}	$\mathbf{1.22^{E+02}}$	3.83^{E+01}	5.32^{E+01}	$8.27E^{+01}$
Arsenic	20-25	2	1.09^{E+00}	1.24^{E+00}	1.17^{E+00}	1.20^{E+00}	1.23^{E+00}
Selenium		0					
Molybdenum		4	1.89^{E+00}	4.52_{E+00}	2.59^{E+00}	3.46^{E+00}	4.10^{E+00}
Cadmium	0.08-0.25	0					
Tin	0.0002	1	2.00^{E+00}	$\mathbf{2.00^{E+00}}$	2.00^{E+00}	2.00^{E+00}	2.00^{E+00}
Antimony		0					
Barium		7	3.52^{E+00}	4.40^{E+01}	9.03^{E+00}	1.05^{E+01}	2.46^{E+01}
Lead	7.2	0					

Five of the metals were found to occur in high frequency at the Mallow site with zinc and tin exceeding EQS values.

6.8 Ringaskiddy

6.8.1 INTRODUCTION

At the Ringaskiddy site 12 samples were collected monthly over a sampling period that spanned June 2010 through July 2011. Table 6-25 shows dates of sample collection at Ringaskiddy. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the effluent stream. As Ringaskiddy does not provide any level of treatment to the wastewater higher levels of pollutants would be expected in the effluent stream when compared to the other Cork sites.

Table 6-25 Dates of sample collections at Ringaskiddy WWTP.

	2010	*2011*
Sampling Dates	15/06/2010	24/02/2011
	24/06/2010	03/03/2011
	01/07/2010	26/04/2011
	05/08/2010	17/05/2011
	09/09/2010	07/06/2011
	28/11/2010	12/07/2011

6.8.2 PAHS

Presented in this section are the PAH results for Ringaskiddy WWTP, Table 6-26. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-26 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-26 Results of PAH analysis for Ringaskiddy WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	*Target EQS µg L^{-1}*	*Freq. n=12*	*Range*		*Percentile*		
			Min.	*Max.*	**50**	**75**	**90**
Naph.	1.2	12	<LOD	2.00^{E-02}	3.58^{E-03}	4.37^{E-03}	1.13^{E-02}
Ant.	0.1	12	<LOD	5.79^{E-02}	8.38^{E-04}	2.85^{E-03}	2.53^{E-02}
Fluor.	0.1	12	<LOD	5.75^{E-02}	8.32^{E-03}	2.21^{E-02}	4.09^{E-02}
Bb/k	Σ=0.003	12	<LOD	**5.48^{E-03}**	1.82^{E-04}	3.85^{E-04}	2.66^{E-03}
Bap	0.05	10	<LOD	8.98^{E-03}	3.51^{E-03}	4.32^{E-03}	4.47^{E-03}
Ind + Bghi	Σ=0.002	12	<LOD	**4.91^{E-02}**	0.00^{E+00}	1.17^{E-04}	8.02^{E-03}

Table 6-26 shows that all PAHs were found to occur in most of the samples analysed. Of these PAHs there were exceedences of the EQS limits for the benzo-b/k-fluoranthene and the indeno-1,2,3cd-pyrene and benzo-ghi-perylene (marked in bold in Table 6-26).

6.8.3 PESTICIDES

Presented in this section are the pesticide results for Ringaskiddy WWTP, Table 6-27. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-27 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-27 Results of pesticide analysis for Ringaskiddy WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound.

Parameter	***Target EQS***	***Freq. n=14***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Alachlor	0.7	4	8.30^{E-03}	6.93^{E-02}	4.41^{E-02}	5.25^{E-02}	6.18^{E-02}
Atrazine	2	1	6.4^{E-02}	1.6^{E-01}	1.32^{E-01}	1.48^{E-01}	1.52^{E-01}
Chlorfenvinphos	0.3	5	1.8^{E-01}	**2.0^{E+00}**	8.86^{E-01}	1.02^{E+00}	1.25^{E+00}
Diuron	1.8	1	ND	4.1^{E-01}	1.75^{E-01}	2.19^{E-01}	3.33^{E-01}
Malathion		4	2.7^{E-02}	5.9^{E-01}	2.98^{E-01}	3.03^{E-01}	3.06^{E-01}
Simazine	4	1	6.1^{E-03}	1.2^{E-01}	7.03^{E-02}	1.03^{E-01}	1.10^{E-01}
Fenitrothion			ND	8.9^{E-01}	1.85^{E-01}	3.44^{E-01}	4.11^{E-01}
Pirimiphos methyl		1	ND	7.4^{E-01}	3.13^{E-01}	3.81^{E-01}	4.57^{E-01}
DEHP	1.3*	5	ND	**3.1^{E+01}**	2.82^{E+00}	5.90^{E+00}	1.94^{E+01}

Table 6-27 shows that 9 of the priority pesticides were detected in samples from Ringaskiddy WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos and DEHP (marked in bold in Table 6-27). Of the 14 samples collected at this site no single pesticides was found to occur in all samples, rather each pesticide showed only low levels of frequency of occurrence in the results.

6.8.4 METALS AND TRACE ELEMENTS

Of the 9 samples collected at Ringaskiddy WWTP all were shown to contain some levels of priority trace elements. From Table 6-28 it can be seen that higher levels of all trace elements were determined in these samples when compared to those collected at the other sampling sites, with notably high levels of Boron, Copper, Zinc, Molybdenum and Barium.

Table 6-28 ICPMS results for samples collected at Ringaskiddy WWTP from June 2010 to July 2011. Samples were analysed for 15 elements in a total of 9 samples. Results are shown in µg L^{-1}.

Parameter	***Target EQS***	***Freq. n=7***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		7	8.43^{E+01}	5.56^{E+02}	2.49^{E+02}	3.35^{E+02}	4.84^{E+02}
Vanadium		1	1.04^{E+00}	5.93^{E+00}	1.57^{E+00}	3.01^{E+00}	4.00^{E+00}
Chromium	0.6-4.7	4	2.45^{E+00}	**2.26^{E+01}**	3.87^{E+00}	8.78^{E+00}	1.21^{E+01}
Cobalt		1	1.20^{E+00}	4.74^{E+00}	1.96^{E+00}	2.35^{E+00}	3.78^{E+00}
Nickel	20	7	3.05^{E+00}	**2.36^{E+01}**	8.18^{E+00}	1.79^{E+01}	2.14^{E+01}
Copper	5.0-30	7	2.11^{E+01}	**1.22^{E+02}**	4.36^{E+01}	6.27^{E+01}	9.00^{E+01}
Zinc	8-100	7	4.97^{E+01}	**4.65^{E+02}**	1.14^{E+02}	2.01^{E+02}	3.25^{E+02}
Arsenic	20-25	2	1.09^{E+00}	3.85^{E+00}	1.48^{E+00}	1.84^{E+00}	2.76^{E+00}
Selenium		0	1.30^{E+00}	3.75^{E+00}	1.67^{E+00}	2.52^{E+00}	3.26^{E+00}
Molybdenum		4	3.76^{E+00}	4.43^{E+01}	1.51^{E+01}	2.99^{E+01}	3.63^{E+01}
Cadmium	0.08-0.25	0					
Tin	0.0002	1	1.45^{E+00}	**9.38^{E+00}**	3.06^{E+00}	5.46^{E+00}	6.60^{E+00}
Antimony		0	1.69^{E+00}	6.99^{E+00}	2.69^{E+00}	3.77^{E+00}	4.81^{E+00}
Barium		7	8.32^{E+00}	6.82^{E+01}	1.37^{E+01}	1.69^{E+01}	4.17^{E+01}
Lead	7.2	0	1.57^{E+00}	**9.62^{E+01}**	2.27^{E+00}	1.57^{E+01}	3.87^{E+01}

This site had the highest percentage occurrence of metals of the Cork sites. Many of the metals were found to occur at levels high above their EQS levels.

6.9 Ringsend

6.9.1 INTRODUCTION

At the Ringsend site 50 samples were collected monthly over a sampling period that spanned July 2009 through July 2011. Table 6-29 shows dates of sample collection at Ringsend WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream. At the Ringsend site there were a number of periods of intensive sampling carried out, with samples collected every second day during the winter and summer months.

Table 6-29 Dates of sample collections at Ringsend WWTP.

	2009	*2010*	*2011*
Sampling Dates	16/07/2009	20/01/2010	10/01/2011
	10/09/2009	10/02/2010	12/01/2011
	15/10/2009	15/03/2010	14/01/2011
	09/11/2009	19/04/2010	10/02/2011
	11/11/2009	25/05/2010	28/03/2011
	13/11/2009	08/06/2010	14/04/2011
	15/11/2009	09/06/2010	30/05/2011
	17/11/2009	11/06/2010	27/06/2011
	19/11/2009	13/06/2010	28/06/2011
	21/11/2009	15/06/2010	05/07/2011
	23/11/2009	17/06/2010	06/07/2011
	25/11/2009	12/07/2010	08/07/2011
	27/11/2009	14/07/2010	12/07/2011
	16/12/2009	16/07/2010	13/07/2011
		18/07/2010	20/07/2011
		20/07/2010	
		22/07/2010	
		16/08/2010	
		28/09/2010	
		29/10/2010	
		15/12/2010	

6.9.2 PAHS

Presented in this section are the PAH results for Ringsend WWTP, Table 6-30. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-30 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-30 Results of PAH analysis for Ringsend WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	***Target EQS***	***Freq. n=50***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Naph.	1.2	50	<LOD	5.37^{E-02}	2.29^{E-04}	2.98^{E-03}	2.18^{E-02}
Ant.	0.1	50	<LOD	4.10^{E-02}	2.00^{E-05}	9.95^{E-03}	2.96^{E-02}
Fluor.	0.1	50	<LOD	2.49^{E-02}	1.06^{E-05}	1.25^{E-02}	1.83^{E-02}
Bb/k	Σ=0.003	46	<LOD	1.51^{E-04}	3.41^{E-06}	6.05^{E-06}	1.03^{E-05}
Bap	0.05	43	<LOD	9.02^{E-03}	5.42^{E-06}	1.71^{E-03}	5.68^{E-03}
Ind + Bghi	Σ=0.002	42	<LOD	$\mathbf{5.74^{E-02}}$	5.94^{E-06}	8.21^{E-06}	1.88^{E-05}

Table 6-30 shows that the most water soluble PAHs, naphthalene, anthracene and fluoranthene, were detected in all samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were slightly less frequently detected. Of these PAHs there were exceedences of the EQS limits for the indeno-1,2,3cd-pyrene and benzo-ghi-perylene (marked in bold in Table 6-30).

6.9.3 PESTICIDES

Presented in this section are the pesticide results for Ringsend WWTP, Table 6-31. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-31 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-31 Results of pesticide analysis for Ringsend WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound

Parameter	*Target EQS*	*Freq. n=36*	*Range*		*Percentile*		
	µg L^{-1}		*Min.*	*Max.*	**50**	**75**	**90**
Alachlor	0.7	15	ND	**7.11^{E-01}**	1.35^{E-01}	2.87^{E-01}	3.57^{E-01}
Atrazine	2.0	30	ND	8.1^{E-01}	1.75^{E-01}	2.74^{E-01}	4.42^{E-01}
Chlorfenvinphos	0.3	19	ND	**5.8^{E+00}**	2.12^{E+00}	2.81^{E+00}	3.43^{E+00}
Diuron	1.8	36	ND	**1.8^{E+00}**	2.11^{E-01}	7.26^{E-01}	9.72^{E-01}
Isoproturon	1.0	10	ND	7.5^{E-03}	2.65^{E-03}	2.87^{E-03}	3.65^{E-03}
Malathion		18	ND	2.7^{E+00}	6.48^{E-01}	1.03^{E+00}	1.60^{E+00}
Simazine	4.0	24	ND	1.8^{E+00}	2.46^{E-01}	5.43^{E-01}	7.37^{E-01}
Fenitrothion		24	ND	3.8^{E+00}	5.55^{E-01}	1.11^{E+00}	2.04^{E+00}
Pirimiphos methyl		26	ND	2.0^{E+00}	1.86^{E-01}	4.21^{E-01}	8.67^{E-01}
Chlorpyrifos	0.1	10	ND	**4.3^{E-01}**	4.71^{E-02}	8.44^{E-02}	1.42^{E-01}
DEHP	1.3*	25	ND	**6.2^{E+00}**	5.77^{E-01}	1.11^{E+00}	1.76^{E+00}

Table 6-31 shows that eleven of the priority pesticides were detected in samples from Ringsend WWTP. Of these pesticides there were exceedences of the EQS limits for the alachlor, chlorfenvinphos, diuron, chlorpyrifos and DEHP (marked in bold in Table 6-31). Of the 36 samples collected at this site only diuron was found to occur in all samples.

6.9.4 METALS AND TRACE ELEMENTS

Of the 34 samples collected at Ringsend WWTP all were shown to contain some levels of priority trace elements. From the tables below it can be seen that highest detected levels were determined for Copper, Zinc, Boron, Barium and Molybdenum.

Table 6-32 ICPMS results for samples collected at Ringsend WWTP. Samples were analysed for 15 elements in a total of 34 samples. Results are shown in µg L^{-1}. EQS exceedances are marked in bold.

Parameter	***Target EQS***	***Freq. n=34***	***Range***		***Percentile***		
	µg L^{-1}		***Min.***	***Max.***	**50**	**75**	**90**
Boron		34	8.00^{E+01}	2.52^{E+02}	1.32^{E+02}	1.67^{E+02}	1.95^{E+02}
Vanadium		12	1.06^{E+00}	2.88^{E+00}	1.63^{E+00}	1.88^{E+00}	1.98^{E+00}
Chromium	0.6-4.7	23	1.10^{E+00}	$\mathbf{1.24^{E+01}}$	1.82^{E+00}	2.89^{E+00}	5.38_{E+00}
Cobalt		5	1.04^{E+00}	2.36^{E+00}	2.03^{E+00}	2.04^{E+00}	2.23^{E+00}
Nickel	20	34	1.88^{E+00}	$\mathbf{4.45^{E+01}}$	3.50^{E+00}	4.66^{E+00}	8.53^{E+00}
Copper	5.0-30	34	4.25^{E+00}	$\mathbf{1.24^{E+02}}$	1.58^{E+01}	2.69^{E+01}	3.90^{E+01}
Zinc	8-100	34	2.48^{E+01}	$\mathbf{6.86^{E+02}}$	5.73^{E+01}	8.86^{E+01}	1.23^{E+02}
Arsenic	20-25	32	1.01^{E+00}	3.81^{E+00}	1.53^{E+00}	1.99^{E+00}	2.50^{E+00}
Selenium		12	1.01^{E+00}	2.86^{E+00}	1.25^{E+00}	1.50^{E+00}	2.01^{E+00}
Molybdenum		34	1.68^{E+00}	1.11^{E+01}	3.04^{E+00}	4.36^{E+00}	6.54^{E+00}
Cadmium	0.08-0.25						
Tin	0.0002	20	1.02^{E+00}	$\mathbf{5.94^{E+00}}$	1.48^{E+00}	1.83^{E+00}	3.15^{E+00}
Antimony		10	1.02^{E+00}	1.77^{E+00}	1.31^{E+00}	1.66^{E+00}	1.77^{E+00}
Barium		34	9.66^{E+00}	6.88^{E+01}	1.84^{E+01}	2.45^{E+01}	3.18^{E+01}
Lead	7.2	19	1.01^{E+00}	6.71^{E+00}	1.83^{E+00}	3.19^{E+00}	5.73^{E+00}

At this site many of the metals were found to occur at a high frequency with five of the metals detected at levels above EQS values.

6.10 Swords

6.10.1 INTRODUCTION

At the Swords site 44 samples were collected monthly over a sampling period that spanned November 2009 through July 2011. Table 6-33 shows dates of sample collection at Swords WWTP. This section will provide an overview of sampling results collected from this site providing information of levels of PAHs, pesticides and metals and trace elements determined in the WWTP effluent stream. At the Swords site there were a number of periods of intensive sampling carried out, with samples collected every second day during the winter and summer months.

Table 6-33 Dates of sample collections at Swords WWTP.

	2009	*2010*	*2011*
Sampling Dates	17/11/2009	10/02/2010	09/01/2011
	02/12/2009	15/03/2010	20/01/2011
	04/12/2009	19/04/2010	21/01/2011
	09/12/2009	31/05/2010	28/02/2011
	11/12/2009	08/06/2010	28/03/2011
	16/12/2009	09/06/2010	12/04/2011
	18/12/2009	11/06/2010	30/05/2011
		14/06/2010	27/06/2011
		16/06/2010	28/06/2011
		18/06/2010	01/07/2011
		12/07/2010	05/07/2011
		14/07/2010	06/07/2011
		16/07/2010	08/07/2011
		19/07/2010	11/07/2011
		21/07/2010	13/07/2011
		23/07/2010	15/07/2011
		16/08/2010	
		18/08/2010	
		22/09/2010	
		29/10/2010	
		15/12/2010	

6.10.2 PAHS

Presented in this section are the PAH results for Swords WWTP, Table 6-34. All samples were analysed for the eight priority PAHs listed in the WFD. Table 6-34 summarises the occurrence and detected levels of each of the PAHs in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective PAHs.

Table 6-34 Results of PAH analysis for Swords WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. Naph = naphthalene. Ant = Anthracene. Fluor = fluoranthene. Bb/k = benzo-b- and benzo-k-fluoranthene. Bap = benzo-a-pyrene. Ind = indeno-1,2,3cd-pyrene. Bghi = Benzo-ghi-perylene. <LOD = below limit of detection.

Parameter	***Target EQS µg L^{-1}***	***Freq. n=44***	***Range***		***Percentile***		
			Min.	***Max.***	**50**	**75**	**90**
Naph.	1.2	44	<LOD	6.26^{E-02}	5.54^{E-04}	4.69^{E-03}	1.43^{E-02}
Ant.	0.1	44	<LOD	5.96^{E-02}	6.24^{E-04}	3.03^{E-02}	4.48^{E-02}
Fluor.	0.1	44	<LOD	3.42^{E-02}	6.13^{E-04}	1.73^{E-02}	3.17^{E-02}
Bb/k	Σ=0.003	39	<LOD	2.55^{E-04}	0.00^{E+00}	1.46^{E-06}	3.12^{E-06}
Bap	0.05	36	<LOD	1.79^{E-02}	6.80^{E-06}	8.67^{E-03}	1.78^{E-02}
Ind + Bghi	Σ=0.002	39	<LOD	9.20^{E-04}	0.00^{E+00}	2.69^{E-07}	1.53^{E-06}

Table 6-34 shows that the more water soluble PAHs, naphthalene, anthracene and fluoranthene, were detected in all samples collected, while the less water soluble, higher octanol/water partition coefficient PAHs, were slightly less frequently detected. Of these PAHs there were no exceedences of the EQS limits detected.

6.10.3 PESTICIDES

Presented in this section are the pesticide results for Ballincollig WWTP, Table 6-35. All samples were analysed for 14 of the priority pesticides listed in the WFD. Table 6-35 summarises the occurrence and detected levels of each of the pesticides in the wastewater effluent samples collected and analysed. The results are compared to the EQS levels applicable to the respective pesticides, where available.

Table 6-35 Results of pesticide analysis for Swords WWTP. Results are compared to their respective Maximum Allowable Concentration Environmental Quality Standard (MAC EQS). All units are in µg L^{-1}. ND = Not detected. *No MAC EQS value available so taken as Annual Average EQS (AA EQS) for this compound.

Parameter	*Target EQS µg L^{-1}*	*Freq. n=40*	*Range*		*Percentile*		
			Min.	*Max.*	**50**	**75**	**90**
Alachlor	0.7	27	ND	4.9^{E-01}	1.31^{E-01}	2.47^{E-01}	2.66^{E-01}
Atrazine	2.0	27	ND	7.1^{E-01}	2.77^{E-01}	4.25^{E-01}	5.26^{E-01}
Chlorfenvinphos	0.3	28	ND	**5.6^{E+00}**	1.92^{E+00}	3.79^{E+00}	4.49^{E+00}
Diuron	1.8	40	ND	1.4^{E+00}	4.53^{E-01}	9.88^{E-01}	1.11^{E+00}
Epoxiconazole		5	1.0^{E-03}	2.9^{E-03}	1.61^{E-03}	2.24^{E-03}	2.53^{E-03}
Isoproturon	1.0	8	9.5^{E-04}	3.9^{E-02}	4.46^{E-03}	6.23^{E-03}	1.58^{E-02}
Malathion		19	ND	2.0^{E+00}	5.21^{E-01}	8.83^{E-01}	1.65^{E+00}
Simazine	4.0	24	ND	1.2^{E+00}	2.49^{E-01}	4.78^{E-01}	6.19^{E-01}
Fenitrothion		29	ND	4.0^{E+00}	8.04^{E-01}	1.40^{E+00}	2.78^{E+00}
Pirimiphos methyl		28	ND	2.3^{E+00}	5.48^{E-01}	9.69^{E-01}	1.53^{E+00}
Chlorpyrifos	0.1	19	ND	**5.2^{E-01}**	1.86^{E-02}	3.67^{E-02}	6.95^{E-02}
DEHP	1.3*	33	ND	**2.3^{E+00}**	3.22^{E-01}	5.96^{E-01}	6.81^{E-01}

Table 6-35 shows that 12 of the priority pesticides were detected in samples from Swords WWTP. Of these pesticides there were exceedences of the EQS limits for the chlorfenvinphos, chlorpyrifos and DEHP (marked in bold in Table 6-35). Of the 40 samples collected at this site only diuron was found to occur in all samples.

6.10.4 METALS AND TRACE ELEMENTS

Of the 29 samples collected at Swords WWTP all were shown to contain some levels of priority trace elements. From Table 6-36 it can be seen that highest detected levels were determined for Copper, Zinc, Boron, Barium and Molybdenum.

Table 6-36 ICPMS results for samples collected at Swords WWTP. Samples were analysed for 15 elements in a total of 29 samples. Results are shown in µg L^{-1}. EQS exceedances are marked in bold.

Parameter	***Target EQS***	***Freq. n=29***	***Range***		***Percentile***		
	µg L^{-1}		**Min**	**Max**	**50**	**75**	**90**
Boron		29	3.84^{E+01}	1.75^{E+02}	7.64^{E+01}	9.51^{E+01}	1.03^{E+02}
Vanadium		5	1.45^{E+00}	6.32^{E+00}	3.49^{E+00}	3.94^{E+00}	5.37^{E+00}
Chromium	0.6-4.7	11	1.04^{E+00}	$\mathbf{6.54^{E+00}}$	2.12^{E+00}	3.07^{E+00}	5.71^{E+00}
Cobalt		3	1.11^{E+00}	2.98^{E+00}	1.17^{E+00}	2.08^{E+00}	2.62^{E+00}
Nickel	20	29	1.22^{E+00}	1.05^{E+01}	2.52^{E+00}	4.91^{E+00}	5.98^{E+00}
Copper	5.0-30	29	7.27^{E+00}	$\mathbf{3.14^{E+02}}$	1.79^{E+01}	2.87^{E+01}	6.72^{E+01}
Zinc	8-100	29	1.74^{E+01}	$\mathbf{3.05^{E+02}}$	4.15_{E+01}	9.98^{E+01}	1.51^{E+02}
Arsenic	20-25	6	1.03^{E+00}	6.30^{E+00}	1.64^{E+00}	2.92^{E+00}	4.80^{E+00}
Selenium		7	1.04^{E+00}	3.99^{E+00}	1.26^{E+00}	2.24^{E+00}	3.16^{E+00}
Molybdenum		26	1.12^{E+00}	1.29^{E+01}	1.86^{E+00}	2.55^{E+00}	3.75^{E+00}
Cadmium	0.08-0.25	0					
Tin	0.0002	6	1.06^{E+00}	$\mathbf{5.44^{E+00}}$	2.74^{E+00}	3.62^{E+00}	4.54^{E+00}
Antimony		5	1.04^{E+00}	6.66^{E+00}	1.25^{E+00}	2.46^{E+00}	4.98^{E+00}
Barium		29	2.40^{E+00}	1.29^{E+02}	1.01^{E+01}	1.55^{E+01}	3.74^{E+01}
Lead	7.2	11	1.48^{E+00}	$\mathbf{7.78^{E+00}}$	2.48^{E+00}	5.06^{E+00}	6.81^{E+00}

Chromium, copper, zinc, tin and lead were found to occur at levels above EQS values in the Swords WWTP effluent.

6.11 Overview of Results

A total of 164 samples were collected from the 9 sites over the sampling period. In this section the summaries of the analytical results obtained are presented, allowing for the evaluation of each site based on the information. Along with results on the levels of occurrence of priority PAHs, pesticides and metals and trace elements information on conditions at each site was obtained where available.

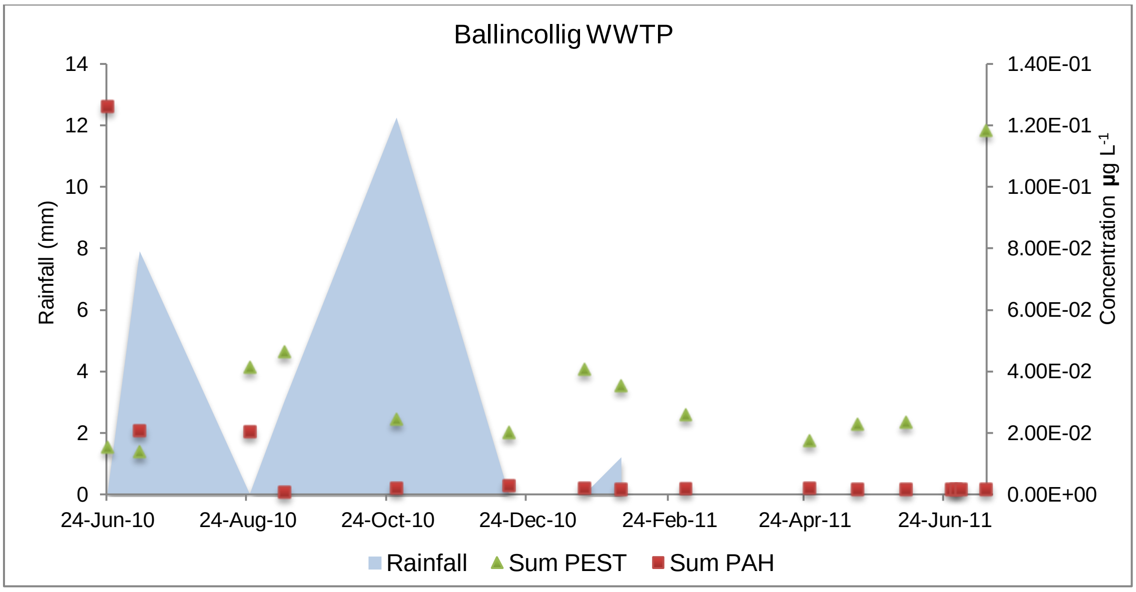


Figure 6-1 Rainfall in the Ballincollig catchment in relation to SUM PAH and Pesticide concentrations in WWTP effluent over the sampling period.

In Ballincollig information on rainfall was available for the sampling period making it possible to determine SUM levels of priority pesticides and PAHs at both dry and wet weather flow, Figure 6-1. No relationship between levels of PAHs and pesticides can discerned, with high PAH levels occurring at different times than those of the pesticides.

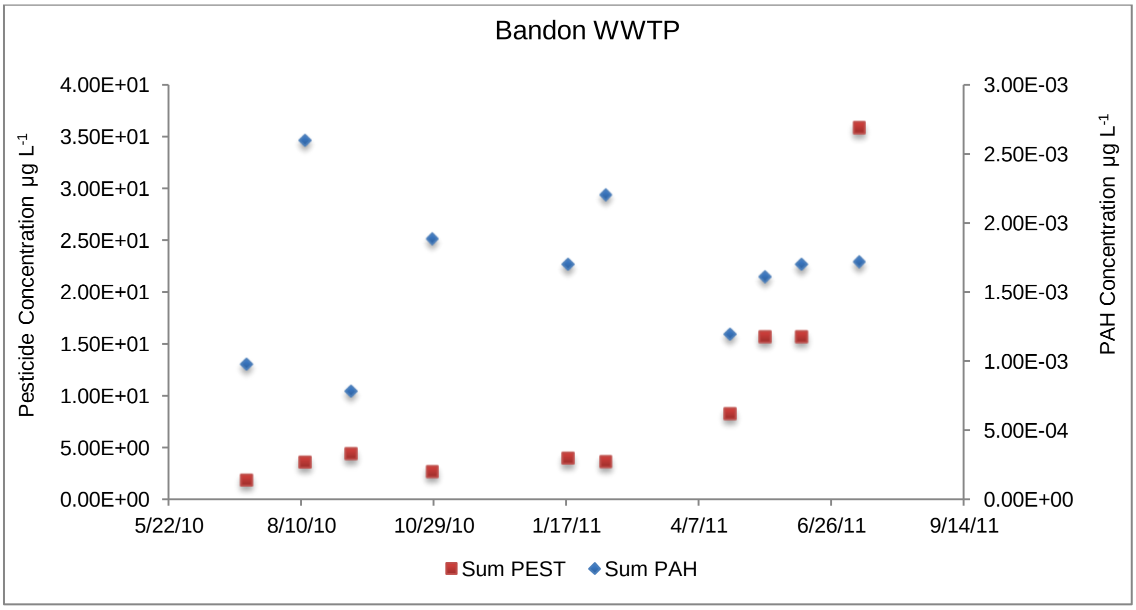


Figure 6-2 SUM PAH and Pesticide concentrations detected in the WWTP effluent in Bandon over the sampling period.

In Bandon information on rainfall or flow was not available for the sampling period, therefore PAH and pesticide levels are plotted over time in Figure 6-2. No relationship between levels of PAHs and pesticides can discerned, with high PAH levels occurring at different times than those of the pesticides.

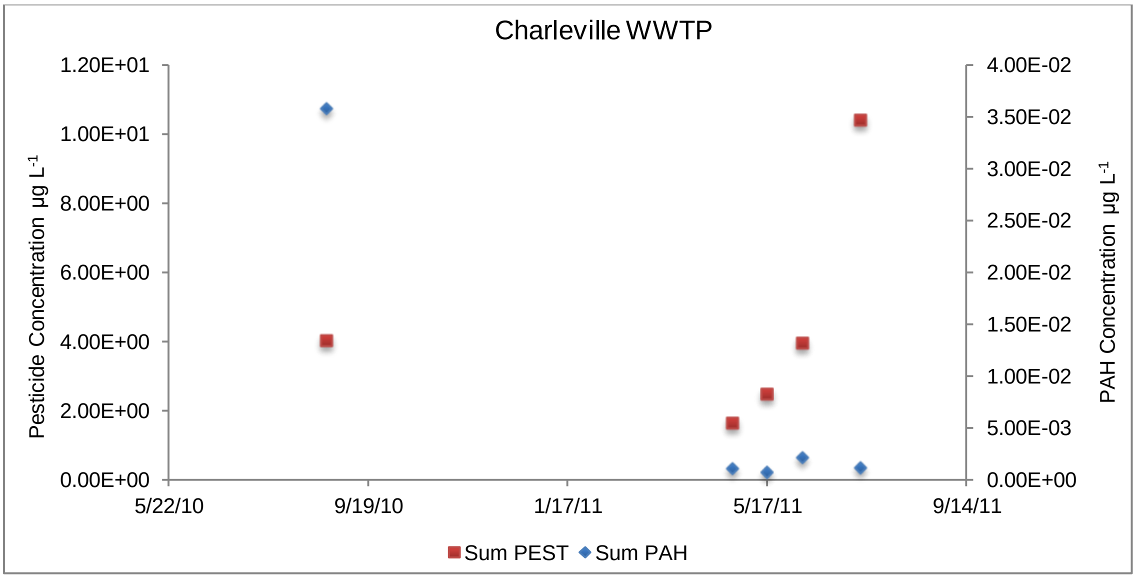


Figure 6-3 SUM PAH and Pesticide concentrations detected in the Charleville WWTP effluent over the sampling period.

In Charleville information on rainfall or flow was not available for the sampling period, therefore PAH and pesticide levels are plotted over time in Figure 6-3. There was no apparent relationship between pesticide and PAH occurrence in the samples.

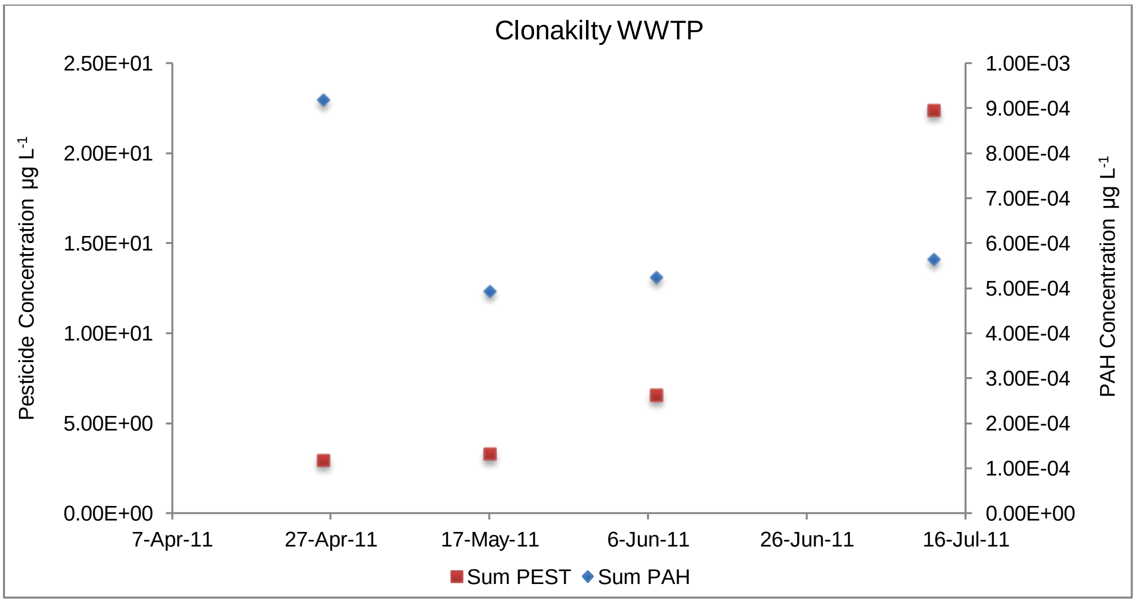


Figure 6-4 SUM PAH and Pesticide concentrations detected in the WWTP effluent in Clonakilty over the sampling period.

No information on rainfall or flow was available for the sampling period at Clonakilty WWTP, therefore PAH and pesticide levels are plotted over time, Figure 6-4. No relationship between levels of PAHs and pesticides can discerned, with high PAH levels occurring at different times than those of the pesticides.

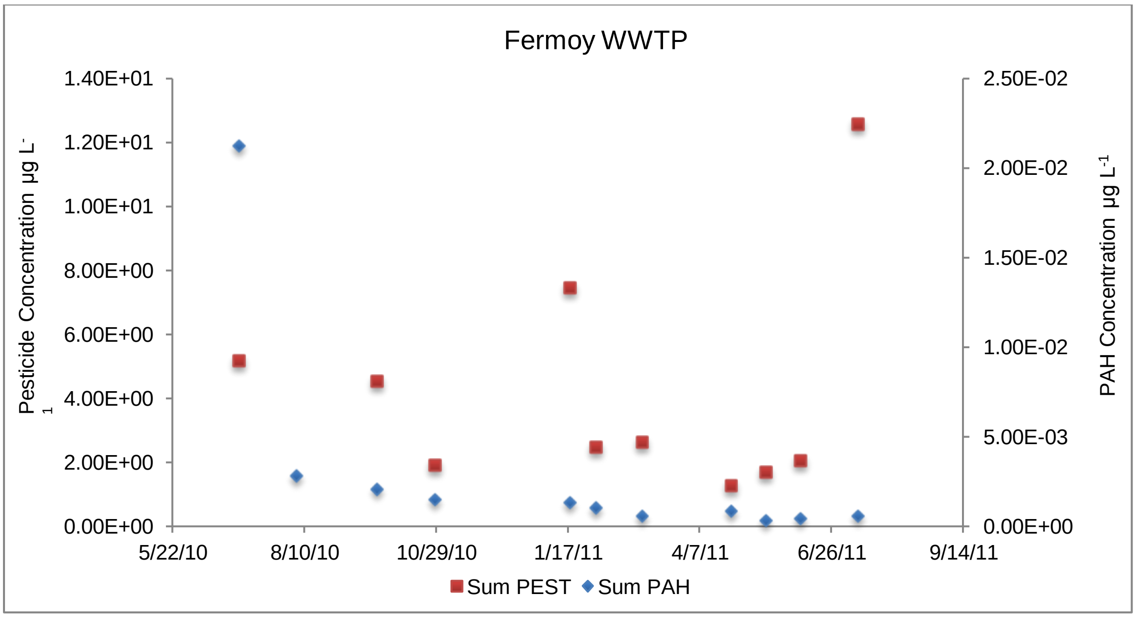


Figure 6-5 SUM PAH and Pesticide concentrations detected in effluent samples from Fermoy WWTP over the sampling period.

In Fermoy information on rainfall or flow was not available for the sampling period, therefore PAH and pesticide levels are plotted over time in Figure 6-5. No relationship between levels of PAHs and pesticides can discerned, with high PAH levels occurring at different times than those of the pesticides.

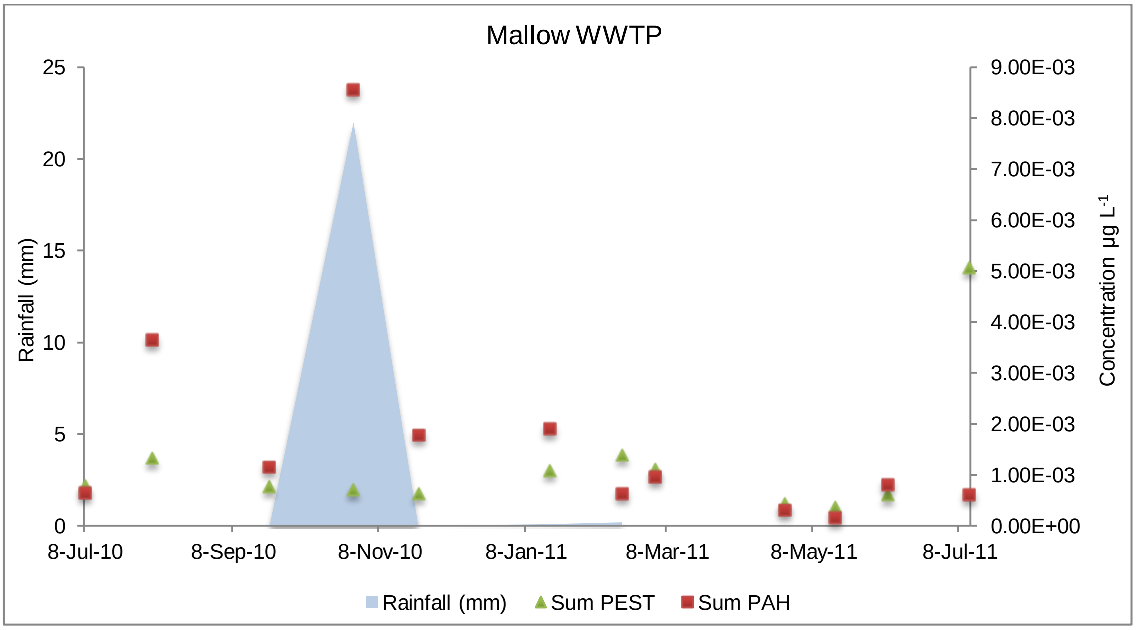


Figure 6-6 Rainfall in the Mallow catchment in relation to SUM PAH and Pesticide concentrations in WWTP effluent over the sampling period.

In Mallow information on rainfall was available for the sampling period, therefore PAH and pesticide levels are plotted over time with rainfall superimposed, Figure 6-6, this allows for the comparison between samples collected during wet and dry wither conditions. No relationship between levels of PAHs and pesticides can discerned, with high PAH levels occurring at different times than those of the pesticides.

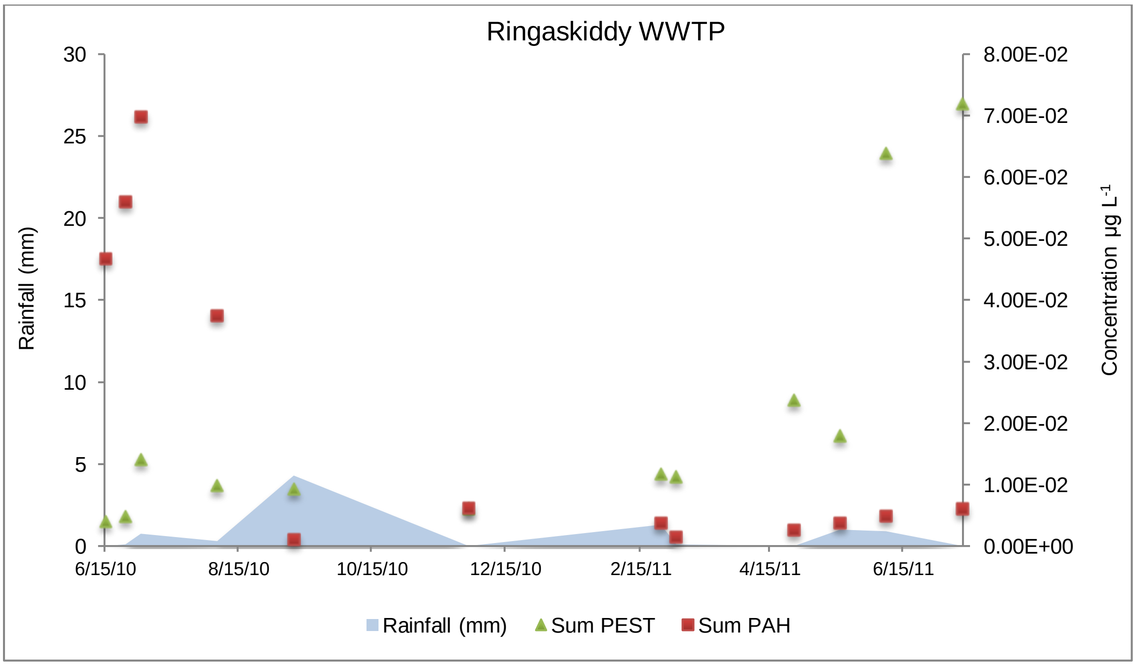


Figure 6-7 Rainfall in the Ringaskiddy catchment in relation to SUM PAH and Pesticide concentrations in WWTP effluent over the sampling period.

In Ringaskiddy information on rainfall was available for the sampling period, therefore PAH and pesticide levels are plotted over time with rainfall superimposed, Figure 6-7. This allows for the comparison between samples collected during wet and dry weather conditions. No relationship between levels of PAHs and pesticides can be discerned, with high PAH levels occurring at different times than those of the pesticides.

Information on rainfall was available for the sampling period in the Ringsend catchment therefore PAH and pesticide levels are plotted over time with rainfall superimposed, Figure 6-8 and Figure 6-9. This allows for the comparison between samples collected during wet and dry weather conditions. In order to evaluate results and characterise as occurring during 'wet' or 'dry' conditions it was necessary to plot rainfall against flow through the plant for the entire sampling period. Then the relationship between rainfall and flow was assessed. In Ringsend there was no delay between rainfall increase and flow increase. No relationship between levels of PAHs and pesticides can discerned, with high PAH levels occurring at different times than those of the pesticides.

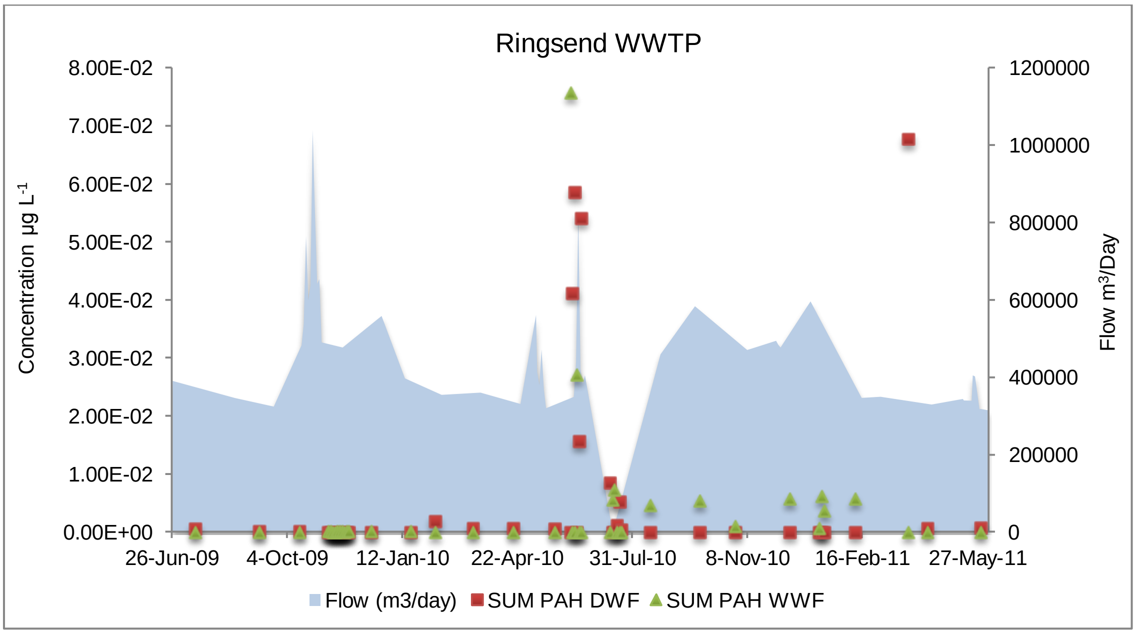


Figure 6-8 WWTP flow levels in the Ringsend catchment in relation to SUM PAH concentrations in WWTP effluent over the sampling period for both WWF and DWF conditions.

In both Figure 6-8 and Figure 6-9 a sharp increase in the levels of detected PAHs was noted in samples collected in June 2010. This increase coincided with an increase in the flow through the plant at this time however past peaks had not had such a notable effect on the levels of PAHs. From contact with technicians at the WWTP it was found that during this same time period the plant had not been operating fully with the digesters not in operation. This in turn reduces the removal efficiency of the plant for priority substances during this period of down-time. While it is possible to compensate for this type of occurrence by reducing the removal efficiency value and thus the effluent factor in modelling calculations it is important to note that these periods of down-time must be recorded and reported so that appropriate monitoring procedures can be put in place.

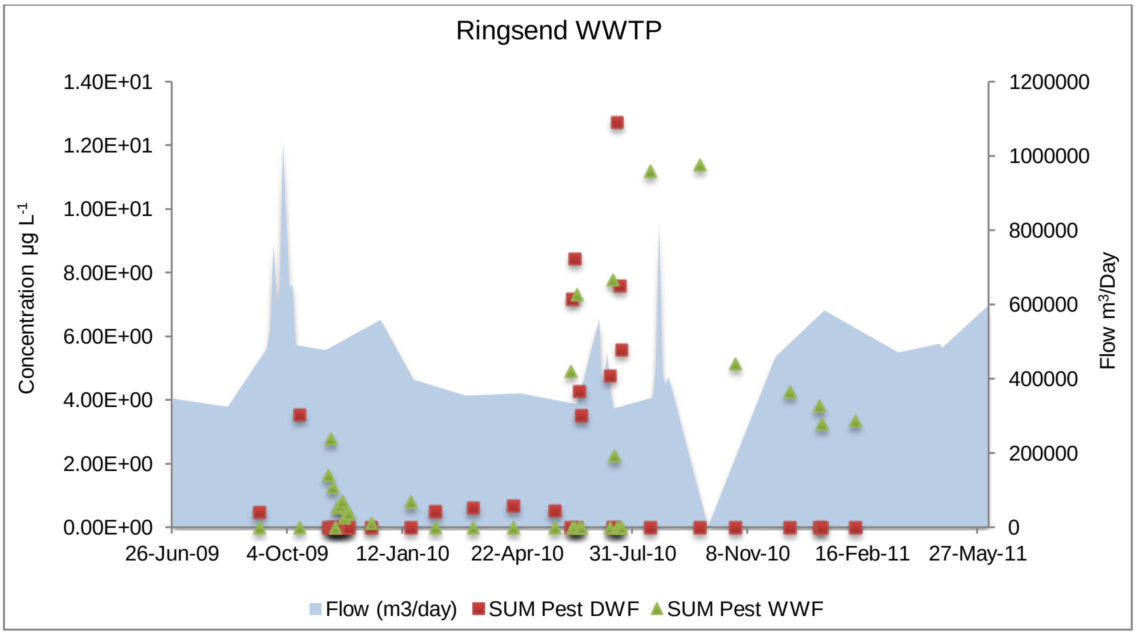


Figure 6-9 WWTP flow levels in the Ringsend catchment in relation to SUM Pesticide concentrations in WWTP effluent over the sampling period for both WWF and DWF conditions.

In Swords WWTP information on rainfall and was available for the sampling period therefore PAH and pesticide levels are plotted over time with rainfall superimposed, Figure 6-10 and Figure 6-11. This allows for the comparison between samples collected during wet and dry weather conditions. In order to evaluate results and characterise as occurring during ‘wet’ or ‘dry’ conditions it was necessary to plot rainfall against flow through the plant for the entire sampling period. Then the relationship between rainfall and flow was assessed. In Swords there was a 1-day delay between rainfall increases and flow increase, therefore this was taken into account when judging WWF and DWF samples. No relationship between levels of PAHs and pesticides can discerned with high PAH levels occurring at different times than those of the pesticides.

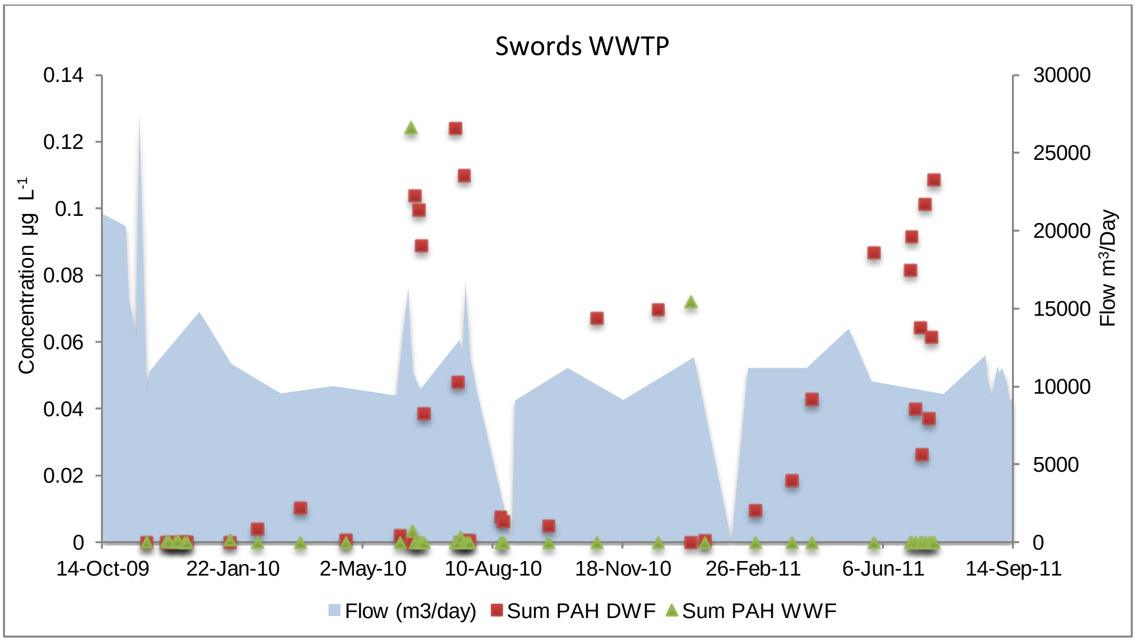


Figure 6-10 WWTP flow levels in the Swords catchment in relation to SUM PAH concentrations in WWTP effluent over the sampling period for both WWF and DWF conditions.

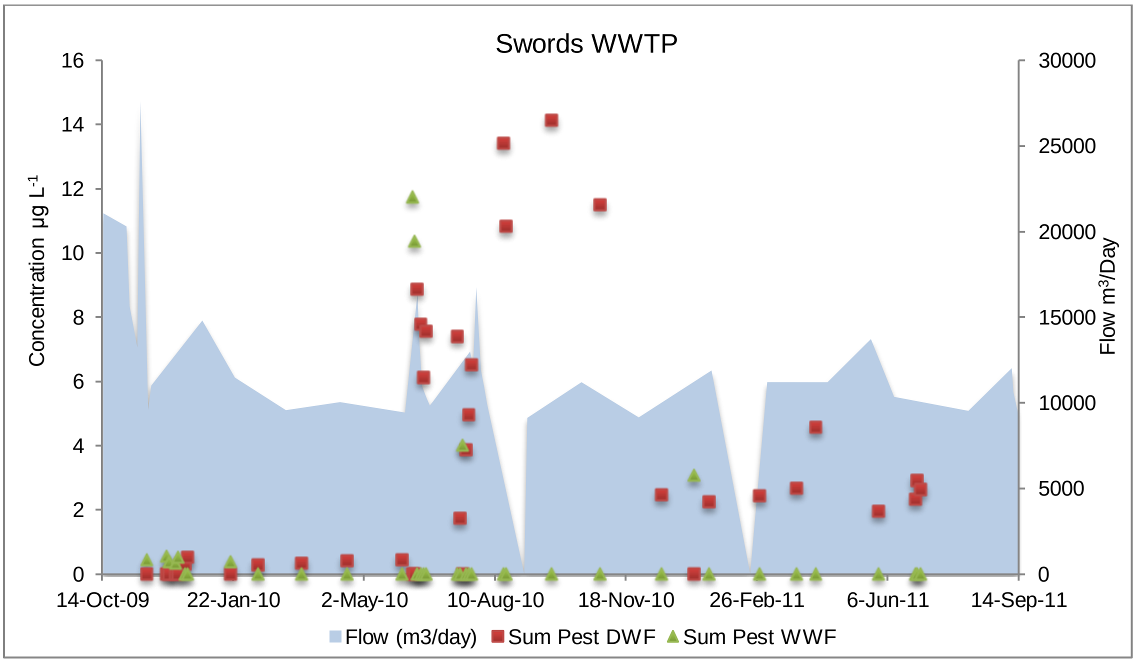


Figure 6-11 WWTP flow levels in the Swords catchment in relation to SUM Pesticide concentrations in WWTP effluent over the sampling period for both WWF and DWF conditions.

6.12 Model evaluation with comparison of 2 sites

The final step in the establishment of the risk model was the population of the model with sampling data. This includes data collected at the 9 WWTPs over the 24 month (2009-2011) period for an overall sample set of 164 samples. Samples were analysed for the presence of trace levels of 8 PAHs, 14 pesticides and 15 metals and trace elements, with the VOC model based solely on collected historic data. Historic sampling datasets allow models to be populated with high-quality, representative data, making the final model more reliable and robust. They also identify data needs in the area. Through the sampling regime carried out in this project it is important to highlight the value of intensive sampling data. The analysis of samples for VOCs was not carried out in this work however it is possible to establish risk information based on the available information and literature reports.

Table 6-37 Summary of final risk values assigned to each of the four main groups of PSs during periods of both dry weather flow (DWF) and wet weather flow (WWF) for each of the sites included in this study.

Site	*PAHs*		*PESTICIDES*		*METALS*		*VOCs*	
	DWF	**WWF**	**DWF**	**WWF**	**DWF**	**WWF**	**DWF**	**WWF**
BG	0.09	0.15	0.02	0.04	0.05	0.66	0.03	0.93
BN	0.80	0.37	0.65	1.31	0.44	1.17	0.30	0.80
CE	1.90	0.09	1.75	3.50	1.39	2.32	0.60	1.23
CY	0.26	0.19	0.31	2.64	0.11	1.06	0.17	1.60
FY	0.48	0.05	0.38	0.77	0.26	0.69	0.28	0.58
MW	0.35	0.06	0.30	0.59	0.27	0.53	0.13	0.26
RY	3.79	0.82	1.60	7.10	1.44	5.55	2.56	6.71
RD	0.06	0.21	0.03	1.30	0.04	1.72	0.03	2.34
SD	0.06	0.03	0.01	0.08	0.04	0.29	0.04	0.21

Table 6-37 presents an overview of the final risk factors for each group of priority substances at the 9 WWTPs under both wet and dry weather flow conditions. For the pesticides, VOCs and metals and trace elements there are consistently higher risks associated with wet weather flow conditions. This is representative of the higher run-off risk loadings attributed to sources of PSs in the catchments. The PAHs were found to have higher risk of direct loading from licensed sources than from run-off with traffic proving to be one of the largest contributors of PAHs. This would indicate that these sites should be monitored specifically for PAHs at periods of DWF when there is a greater likelihood of elevated priority substance occurrence to be detected.

High risk values are marked in red in Table 6-39 with Ringaskiddy being high risk in all areas this is owing to both contributions from licensed sources in the area and the lack of any removal of pollutants at the sampling site which as yet provides no treatment and acts merely as a pumping station.

By examining two of the sites more closely, Ballincollig in Cork and Ringsend in Dublin, it is possible to validate the model making it applicable to any site. As no VOC analysis was carried out that model is based entirely on historic, license and collected data.
Ballincollig and Ringsend were chosen as the sites to be included in this model validation step as they represent both counties in the study, two different levels of treatment and removal efficiency, two different types of input to the respective plants and were the sites with the most available data for collection and population of the model. They are representative of the range of conditions evaluated in the model. Specific flow data for each of these WWTPs allowed for a clear distinction between WWF and DWF conditions whereas a number of the other sites did not collect flow data sets and flow data was determined solely from weather conditions and historic data. These facts made Ringsend and Ballincollig the most rational choices for the validation study.

Table 6-38 Exceedances of priority substances at two WWTPs.

	Ballincollig	*Ringsend*
PAHs	Benzo-b/k-fluoranthene and indeno-1,2,3cd-pyrene/benzo-ghi-perylene all exceed EQS in 90 percentile	indeno-1,2,3cd-pyrene/benzo-ghi-perylene exceed EQS above 90 percentile
Pesticides	Chlorfenvinphos and DEHP exceed EQS in 50 percentile	Alachlor, DEHP, chlorfenvinphos, diuron, and chlorpyrifos exceed EQS in 90 percentile
Metals and Trace Elements	Tin and lead exceed EQS above 50 percentile	Chromium, copper, zinc and tin exceed EQS in 50 percentile Nickel exceeds EQS in 90 percentile

A true comparison of the two sites can be demonstrated in Table 6-38 above. This table shows detected exceedence of EQS values for specific pollutants from each group of pollutants by site. The percentile of exceedence is also included to show the frequency of occurrence of these high levels of PSs.

Ballincollig was found to have low risk attributed to all areas even during WWF while Ringsend is classified as at risk of high levels of both pesticides and metals under the same conditions. Breaking this down by group it is possible to rationale these results. First focussing on the PAHs the results show that Ringsend was found to have higher frequency of occurrence for the WFD priority PAHs than Ballincollig, and the WWF risk is corroborated by the maximum sum PAH concentration detected during WWF which was only 2.06 x 10^{-02} at Ballincollig compared to 7.56 x 10^{-02} at Ringsend, the same was true for mean PAH concentrations. This result is expected when taking into account the catchment characteristics, while Ringsend has over 200 licensed sources of PSs that were evaluated for risk Ballincollig has only 7 trade effluent licenses, 4 of which are petrol stations that are considered to be sources of PAHs making them the main licensed sources of PAHs in that catchment. Also, in conjunction with the much lower population in the Ballincollig catchment compared to the Ringsend catchment there is a higher level of traffic contributing PAHs to Ringsend than site Ballincollig. However, when taking into account notably high levels of occurrence, Table 6-38 shows that while there was a higher frequency of occurrence of PAHs at Ringsend, there were more exceedences of EQS levels in Ballincollig.

The pesticides were risked higher at Ringsend for both WWF and DWF than Ballincollig. While results show higher percentage occurrence of most pesticides at Ringsend results gave both higher maximum sum pesticide concentration and average sum pesticide concentration at WWF for Ballincollig. Table 6-38 shows that while Ballincollig has a higher level of EQS exceedence for two pesticides, Ringsend has a greater range of pesticides exceeding EQS values in the 90 percentile of samples. Ballincollig, although covering a much smaller area than Ringend, has both a higher combined drainage factor and a higher percentage nonurban area than Ringsend (30% compared to 25%).

The issue with pesticide loading factors can be attributed to data gaps in this area, specifically usage data and unlicensed sources. Large comprehensive datasets are needed which would cover the usage statistics, import and purchasing of priority substances, especially pesticides, as there are currently unexplained levels of banned substances occurring in Irish wastewaters. For example pesticides such as atrazine and simazine were found to be present in a number of samples collected at sites in both Dublin and Cork, substances which have been banned for several years. Other pesticides such as alachlor and aldrin were also detected even though these substances would have to be sourced from African or Mediterranean countries and would not be expected to be found here in Ireland. It is discoveries such as these which lead us to recommend that banned and obscure pollutants are not removed completely from current and future monitoring programs as their continued presence in water systems must be noted and steps to remediation taken. There are also potentially large sources of pesticides which are unlicensed, e.g. golf courses apply pesticides but are not required to report usage of-, account for disposal of- or potential run-off of pesticides from their greens leading to official loading factors of zero. Through the development of this model it is observations such as these which will facilitate the success of future monitoring programs.

The metals and trace elements risk assessments met expectations with Ringsend ranked as a higher risk than Ballincollig. Ringsend shows both higher percentage frequency of occurrence for the metals and trace elements, but also a wider variety of these substances than Ballincollig.

Table 6-38 shows results in agreement with the model with a number of metals found to exceed EQS levels at a higher percentage occurrence in Ringsend than for Ballincollig. Ringsend also covers a much larger catchment with a higher percent urban area than site 1 (75% compared to 70%). This catchment included 36 waste licenses, 66 IPPC licenses and 253 trade effluent licenses, many of which are for laboratories, construction and machinery companies, the transport industry and other sources which are highly ranked for loading of PSs.

Through the comparison of these sites the model has been found to be true to analytical results from a strict sampling regime with results fitting the model created based on a large dataset of licenses, annual environmental reports and historic data. The model can be further adapted and is receptive to unlimited amounts of data making it amenable to continuous updating.

Table 6-39 Comparison of predicted risk to actual risk determined from sampling data for two sites.

	Conditions	**Ballincollig**		**Ringsend**	
		Predicted	**Actual**	**Predicted**	**Actual**
PAHs	DWF	Low Risk (0.1)	Low Risk (0.09)	Some Risk (0.14)	Low Risk (0.06)
	WWF	Medium Risk (0.15)	Medium Risk (0.15)	Medium Risk (0.15)	Medium Risk (0.21)
Pesticides	DWF	Low Risk (0.02)	Low Risk (0.02)	Some Risk (0.08)	Low Risk (0.03)
	WWF	Low Risk (0)	Low Risk (0.04)	High/Very High Risk (1.4)	High/Very High Risk (1.3)
Metals and trace elements	DWF	Low Risk (0.05)	Low Risk (0.05)	Low/Some Risk (0.08)	Low Risk (0.04)
	WWF	Some/Medium Risk (0.7)	Some/ Medium Risk (0.66)	Medium/High Risk (1.2)	Very High Risk (1.72)

6.13 Application of Model

The main application of this model is the use in identifying the risks of priority substance occurrence at a site under both wet and dry weather conditions. This simple model can therefore be used in the development of future monitoring programmes, reducing the need for and cost of non-specific monitoring methods. Table 6-40 shows the final risk based model for the occurrence of priority substances in wastewater. The rankings applied relate to the scale of risk of occurrence of priority substances, Table 6-41. Green indicates a low risk of PS loading during certain conditions with risk progressively increasing to a high risk of loading indicated in red. The Ringaskiddy site has been ranked as very high risk owing to the lack of treatment of the wastewater at this site.

Table 6-40 Final risk rankings attributed to each site for the four main groups of WFD priority substances under both WWF and DWF conditions. Dark green = low risk. Light green = some risk. Yellow = moderate risk. Orange = high risk. Red = very high risk.

Site	*PAHs*		*PESTICIDES*		*METALS*		*VOCs*	
	DWF	**WWF**	**DWF**	**WWF**	**DWF**	**WWF**	**DWF**	**WWF**
BG	0.09	0.15	0.02	0.04	0.05	0.66	0.03	0.93
BN	0.8	0.37	0.65	1.31	0.44	1.17	0.3	0.8
CE	1.9	0.09	1.75	3.5	1.39	2.32	0.6	1.23
CY	0.26	0.19	0.31	2.64	0.11	1.06	0.17	1.6
FY	0.48	0.05	0.38	0.77	0.26	0.69	0.28	0.58
MW	0.35	0.06	0.3	0.59	0.27	0.53	0.13	0.26
RY	3.79	0.82	1.6	7.1	1.44	5.55	2.56	6.71
RD	0.06	0.21	0.03	1.3	0.04	1.72	0.03	2.34
SD	0.06	0.03	0.01	0.08	0.04	0.29	0.04	0.21

Through the collection of data as described in chapter 5 it can be concluded that the same ranking system can be applied to other catchments and can be used as a guidance document for the monitoring of PSs in an area. By generating risk factors using the methods described the scale outlined in Table 6-41 below can be used to evaluate the risks of occurrence of PSs at a site under both wet and dry weather conditions.

Table 6-41 Ranking system converting risk factors to scale of risk of PS occurrence under different conditions. LR – low risk. SR – some risk. MR – moderate risk. HR – high risk. VHR – very high risk.

Scale	***PAHs***		***PESTICIDES***		***METALS***		***VOCs***	
	DWF	**WWF**	**DWF**	**WWF**	**DWF**	**WWF**	**DWF**	**WWF**
<0.05	LR	LR	LR	LR	LR	LR	LR	LR
0.06-0.1	LR	LR-SR	SR	LR	LR-SR	LR	LR	LR
0.11-0.5	SR-MR	MR	MR	LR	SR-HR	LR-SR	SR-MR	LR-SR
0.51-1	MR-HR	HR-VHR	HR	SR-MR	HR-VHR	SR-MR	MR-HR	SR-MR
1.1-1.5	HR	VHR	HR-VHR	MR-HR	VHR	MR-HR	HR-VHR	MR-HR
>1.5	VHR	VHR	VHR	HR-VHR	VHR	HR-VHR	VHR	VHR

6.14 Conclusion

This chapter has continued on from the work detailed in chapter 5 and has presented the results of sampling and analysis for each of the groups of priority substances at each of the nine catchments included in the project. These samples were collected under different weather conditions thus the weather conditions on the day of sampling as well the preceding days and the subsequent effect on flow levels at the plant were all plotted and taken into account. This allowed for the differentiation between samples collected under dry weather conditions and those collected under wet weather conditions.

The collected data was statistically evaluated, the results of which are presented in this chapter. This allowed for the data to be used to validate the theoretical model as outlined in chapter 5. A thorough validation was carried out between the Ballincollig and Ringsend sites within this chapter. Finally the model was simplified and a risk-scale legend was provided in Table 6-41 which can be directly applied to other sites for which this risk-based approach has been applied.

7. Conclusion

The development and implementation of targeted monitoring programmes for priority substances in water is now more important than ever. Legislation has been put in place in the form of the Water Framework Directive which has set a deadline of 2015 for all water bodies to be of ‘good’ quality status. This thesis has examined the requirements of the WFD and the associated list of priority substances. The chapters within the thesis identify and draw attention to the current gaps in knowledge and provide a solution to monitoring issues in the form of a risk based model. Throughout the course of this work 164 samples were collected. Each sample was split and subjected to three different forms of sample preparation and analysis in triplicate. This lead to the compilation of a database of thousands of chromatograms and mass spectra which have each been statistically analysed and summarised. The time-consuming process of simplifying the data resulted in a concise dataset in a format acceptable for input into the risk-based model.

Chapters 1 and 2 summarise the legislation in the area of water quality in Ireland, specifically the WFD and later amendments and statutory instruments. The project aims were outlined with the main aim being the development of a risk-based model which could be used to inform targeted monitoring programmes thus allowing Ireland to meet the water quality requirements of the WFD. Wastewater input to surface waters is considered to be a major point source contributor and was therefore selected as the medium to be studied. In order to accomplish this task a database of sampling information representing sites across Ireland was required. This involved the development of a strategic sampling plan which would provide information of wastewater effluent quality over a large time-frame including periods of intensive sampling which provides data on temporal variability in terms of pollutant concentrations. Site selection was of prime importance as it was necessary to select a broad spectrum of sites covering a span of population equivalents, input sources and levels of treatment. A well thought-out sampling plan allowed for the achievement of these goals and nine different sites in both Dublin and Cork were chosen.

After selecting the sampling sites and devising a sampling plan it was necessary to develop methods for the extraction and analysis of the samples collected. Chapters 3 and 4 detail the processes involved in method development and validation for the extraction and analysis of priority PAHs, pesticides and metals and trace elements from a wastewater medium. It was important that complete sample integrity was maintained throughout the process as high quality data was required for the development of a model. Methods were selected based on extensive literature review with due consideration given to extraction and analysis times and the achievement of LODs sufficiently low to meet WFD and EQS requirements. Robust and reliable multi-residue methods were developed with the PAH method by GCMS analysis improving on current available methods in this area in terms of analysis times.

In chapter 5 the development and subsequent population of the model is presented. As with the original aims of this project a database of information on emission factors, past priority substance occurrence and other factors was built where no such database currently existed for Ireland. This collection of data allowed for the identification of gaps in datasets and areas in which the data was lacking and where this is a distinct need for improvement in the handling of, storage of and access to complete datasets. An output of this project includes a report to the EPA listing many recommendations in which improvements can be made to these identified issues.

The creation of a framework for the model and population of the model was an on-going process throughout the course of the project with the final stage being the inclusion of the results of the 24 month sampling campaign. This data was thoroughly evaluated in terms of emission factors and risk of loadings, both direct and indirect, at each of the sampling sites. The results of this work are presented in chapter 6 in which analytical results for each group of priority substances have been tabulated and statistically evaluated by sampling site. The data is then compared and the final model is introduced. The results of three years of sampling and data collection is a simple risk-based model which indicates the risk of occurrence of a group of pollutants at a site under both wet and dry weather conditions.

This model is not restricted to only the sites included in this study, rather it allows for the evaluation of any site. By implementing the same procedures as described, risk factors can be attributed to any site where sufficient data is available. These risk factors can be directly used in developing a monitoring strategy as they inform the analyst under which conditions specific groups of priority substances will be a risk of occurring. Implementation of this model has the potential to reduce the costs, both time and monetary, associated with currently employed non-specific monitoring/sampling regimes which can often miss high levels of pollutants as they do not take into account emission factors such as weather conditions.

To conclude, this work has achieved the aims to which it has set out. A validated risk-based model has been prepared and a database of high-quality information has been created. This database brings together information on emission factors and occurrence of WFD priority substances and contains data from over 1000 licenses and reports as well as three years of experimental data. Recommendations from this project will be used by policy-makers in the implementation of future monitoring programmes and this work has improved on the current state of knowledge on the relationship between emission factors and priority substance occurrence in Ireland.

References

ABAD, E., MARTÍNEZ, K., PLANAS, C., PALACIOS, O., CAIXACH, J. and RIVERA, J., 2005. Priority organic pollutant assessment of sludges for agricultural purposes. *Chemosphere,* **61**(9), pp. 1358-1369.

AHLMAN, S. and SVENSSON, G., 2005. *SEWSYS - a tool for simulation of substance flows in urban sewer systems.* ISSN 1650-3791; no 2005:11. Göteborg: Chalmers University of Technology.

AHMED, F.E., 2001. Analyses of pesticides and their metabolites in foods and drinks. *TrAC Trends in Analytical Chemistry,* **20**(11), pp. 649-661.

ALLOWAY, B.J., 1995. *Heavy Metals in Soils.* Springer.

ARIAS-ESTÉVEZ, M., LÓPEZ-PERIAGO, E., MARTÍNEZ-CARBALLO, E., SIMAL-GÁNDARA, J., MEJUTO, J.C. and GARCÍA-RÍO, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems & Environment,* **123**(4), pp. 247-260.

ARMENTA, S., GARRIGUES, S. and DE LA GUARDIA, M., 2005. Solid sampling Fourier transform infrared determination of Mancozeb in pesticide formulations. *Talanta,* **65**(4), pp. 971-979.

ASANTE, K.A., AGUSA, T., SUBRAMANIAN, A., ANSA-ASARE, O.D., BINEY, C.A. and TANABE, S., 2007. Contamination status of arsenic and other trace elements in drinking water and residents from Tarkwa, a historic mining township in Ghana. *Chemosphere,* **66**(8), pp. 1513-1522.

BARBOSA, V.L., TANDLICH, R. and BURGESS, J.E., 2007. Bioremediation of trace organic compounds found in precious metals refineries' wastewaters: A review of potential options. *Chemosphere,* **68**(7), pp. 1195-1203.

BARCO-BONILLA, N., VIDAL, J., GARRIDO FRENICH, A. and ROMERO-GONZÁLEZ, R., 2009. Comparison of ultrasonic and pressurized liquid extraction for the analysis of polycyclic aromatic compounds in soil samples by gas chromatography coupled to tandem mass spectrometry. *Talanta,* **78**(1), pp. 156-164.

BARRO, R., REGUEIRO, J., LLOMPART, M. and GARCIA-JARES, C., 2009. Analysis of industrial contaminants in indoor air: Part 1. Volatile organic compounds, carbonyl compounds, polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Journal of Chromatography A,* **1216**(3), pp. 540-566.

BARTON, S.C., JOHNSON, N.D. and DAS, B.S., 1979. *Final Report to Air Resources Branch Canadian Ministry of Environment: A feasibility study of alternatives to high-volume sampling for labile constituents of atmospheric particulates.* Ontario, Canada.: Ontario Research Foundation.

BECEIRO-GONZÁLEZ, E., CONCHA-GRAÑA, E., GUIMARAES, A., GONÇALVES, C., MUNIATEGUI-LORENZO, S. and ALPENDURADA, M., 2007. Optimisation and validation of a solid-phase microextraction method for simultaneous determination of different types of pesticides in water by gas chromatography–mass spectrometry. *Journal of Chromatography A,* **1141**(2), pp. 165-173.

BENNETT, D.A., CHUNG, A.C. and LEE, S.M., 1997. Multiresidue method for analysis of pesticides in liquid whole milk. *Journal of AOAC International,* **80**(5), pp. 1065-1077.

BERCARU, O., ULBERTH, F., EMONS, H. and VANDECASTEELE, C., 2006. Accurate quantification of PAHs in water in the presence of dissolved humic acids using isotope dilution mass spectrometry. *Analytical and bioanalytical chemistry,* **384**(5), pp. 1207-1213.

BERMEJO-BARRERA, P., MUÑIZ-NAVEIRO, O., MOREDA-PIÑEIRO, A. and BERMEJO-BARRERA, A., 2000. Experimental designs in the optimisation of ultrasonic bath–acid-leaching procedures for the determination of trace elements in human hair samples by atomic absorption spectrometry. *Forensic science international,* **107**(1), pp. 105-120.

BERSET, J., EJEM, M., HOLZER, R. and LISCHER, P., 1999. Comparison of different drying, extraction and detection techniques for the determination of priority polycyclic aromatic hydrocarbons in background contaminated soil samples. *Analytica Chimica Acta,* **383**(3), pp. 263-275.

BJØRSETH, A. and DENNIS, A.J., 1980. *Polynuclear aromatic hydrocarbons: chemistry and biological effects.[Lead abstract],* .

BOEHM, P.D., 2005. Environmental Forensics. In: R.D. MORRISON PH.D., B.L. MURPHY, ed, Burlington: Academic Press, pp. 313-337.

BONNIEUX, F., CARPENTIER, A. and WEAVER, R., 1998. Reducing soil contamination: economic incentives and potential benefits. *Agriculture, Ecosystems & Environment,* **67**(2-3), pp. 275-288.

BÖRJESSON, E. and TORSTENSSON, L., 2000. New methods for determination of glyphosate and (aminomethyl)phosphonic acid in water and soil. *Journal of Chromatography A,* **886**(1–2), pp. 207-216.

BOUSSAHEL, R., BOULAND, S., MOUSSAOUI, K., BAUDU, M. and MONTIEL, A., 2002. Determination of chlorinated pesticides in water by SPME/GC. *Water research,* **36**(7), pp. 1909-1911.

BRUM, D.M. and NETTO, A.D.P., 2009. Polycyclic aromatic hydrocarbons in Tripuí River, Ouro Preto, MG, Brazil. *Journal of hazardous materials,* **165**(1-3), pp. 447-453.

BUDZINSKI, H., GARRIGUES, P., RADKE, M., CONNAN, J. and OUDIN, J.L., 1993. Thermodynamic calculations on alkylated phenanthrenes: geochemical applications to maturity and origin of hydrocarbons. *Organic Geochemistry,* **20**(7), pp. 917-926.

BULUT, V.N., GUNDOGDU, A., DURAN, C., SENTURK, H.B., SOYLAK, M., ELCI, L. and TUFEKCI, M., 2007. A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000. *Journal of hazardous materials,* **146**(1), pp. 155-163.

BUSETTI, F., HEITZ, A., CUOMO, M., BADOER, S. and TRAVERSO, P., 2006. Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant. *Journal of Chromatography A,* **1102**(1–2), pp. 104-115.

BUZIER, R., TUSSEAU-VUILLEMIN, M., DIT MERIADEC, C.M., ROUSSELOT, O. and MOUCHEL, J., 2006. Trace metal speciation and fluxes within a major French wastewater treatment plant: Impact of the successive treatments stages. *Chemosphere,* **65**(11), pp. 2419-2426.

CAMINO-SÁNCHEZ, F.J., ZAFRA-GÓMEZ, A., PÉREZ-TRUJILLO, J.P., CONDE-GONZÁLEZ, J.E., MARQUES, J.C. and VÍLCHEZ, J.L., 2011. Validation of a GC–MS/MS method for simultaneous determination of 86 persistent organic pollutants in marine sediments by pressurized liquid extraction followed by stir bar sorptive extraction. *Chemosphere,* **84**(7), pp. 869-881.

CAO, Z., WANG, Y., MA, Y., XU, Z., SHI, G., ZHUANG, Y. and ZHU, T., 2005. Occurrence and distribution of polycyclic aromatic hydrocarbons in reclaimed water and surface water of Tianjin, China. *Journal of hazardous materials,* **122**(1), pp. 51-59.

CARERI, M., MANGIA, A. and MUSCI, M., 1996. Applications of liquid chromatography-mass spectrometry interfacing systems in food analysis: pesticide, drug and toxic substance residues. *Journal of chromatography A,* **727**(2), pp. 153-184.

CECCARINI, A., CECCHINI, I. and FUOCO, R., 2005. Determination of trace elements in seawater samples by on-line column extraction/graphite furnace atomic absorption spectrometry. *Microchemical journal,* **79**(1), pp. 21-24.

CHEN, D., HU, B. and HUANG, C., 2009. Chitosan modified ordered mesoporous silica as micro-column packing materials for on-line flow injection-inductively coupled plasma optical emission spectrometry determination of trace heavy metals in environmental water samples. *Talanta,* **78**(2), pp. 491-497.

CHEN, S., YU, X., HE, X., XIE, D., FAN, Y. and PENG, J., 2009. Simplified pesticide multiresidues analysis in fish by low-temperature cleanup and solid-phase extraction coupled with gas chromatography/mass spectrometry. *Food Chemistry,* **113**(4), pp. 1297-1300.

CLARA, M., SCHARF, S., SCHEFFKNECHT, C. and GANS, O., 2007. Occurrence of selected surfactants in untreated and treated sewage. *Water research,* **41**(19), pp. 4339-4348.

CLARKE, R., ROBERTS, A. and CONRAD, A., 2009. *Chemical prioritisation: ranking chemicals of concern to Scotland's environment, Phase 1: Surface Waters.* Scotland: Scottish EPA.

CONCHA-GRAÑA, E., FERNÁNDEZ-MARTÍNEZ, G., FERNÁNDEZ-VILLARRENAGA, V., TURNES-CAROU, M., MUNIATEGUI-LORENZO, S., LÓPEZ-MAHÍA, P. and PRADA-RODRÍGUEZ, D., 2009. A study of large-volume on-column injection GC-ECD for the ultratrace analysis of organochlorine pesticides in water. *Talanta,* **78**(3), pp. 764-771.

CORK COUNTY COUNCIL, 2009. *Ballincollig and Environs Agglomeration Annual Environmental Report.* Johnstown Castle Estate, County Wexford, Ireland: Environmental Protection Agency.

CORK COUNTY COUNCIL, 2008-last update, Bandon Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/licences/lic_eDMS/090151b28024f684.pdf2012].

CORK COUNTY COUNCIL, 2008-last update, Charleville Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0204-012012].

CORK COUNTY COUNCIL, 2008. *Fermoy Waste Licence Application.* Ireland: Irish EPA.

CORK COUNTY COUNCIL, 2007-last update, Ballincollig Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0049-012012].

CORK COUNTY COUNCIL, 2007-last update, Clonakilty Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view-filter.jsp?regno=D0051-01&filter=b&docfilter=go2012].

CORK COUNTY COUNCIL, 2007-last update, Fermoy Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0058-012012].

CORK COUNTY COUNCIL, 2007-last update, Mallow Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0052-012012].

CORK COUNTY COUNCIL, 2007-last update, Ringaskiddy Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0057-012012].

CORK COUNTY COUNCIL - SOUTHERN DIVISION, 2010. *Ballincollig and Environs Agglomeration Annual Environmental Report January 2010-December 2010.* Johnstown Castle Estate, County Wexford, Ireland: Environmental Protection Agency.

COUNTWAY, R.E., DICKHUT, R.M. and CANUEL, E.A., 2003. Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. *Organic Geochemistry,* **34**(2), pp. 209-224.

CROZIER, P.W., PLOMLEY, J.B. and MATCHUK, L., 2001. Trace level analysis of polycyclic aromatic hydrocarbons in surface waters by solid phase extraction (SPE) and gas chromatography-ion trap mass spectrometry (GC-ITMS). *Analyst,* **126**(11), pp. 1974-1979.

CSO, 2009. *Central Statistics Office Yearly Report.* Ireland: Central Statistics Office.

DE ALMEIDA AZEVEDO, D., LACORTE, S., VINHAS, T., VIANA, P. and BARCELÓ, D., 2000. Monitoring of priority pesticides and other organic pollutants in river water from Portugal by gas chromatography–mass spectrometry and liquid chromatography–atmospheric pressure chemical ionization mass spectrometry. *Journal of chromatography A,* **879**(1), pp. 13-26.

DE BOER, J. and LAW, R.J., 2003. Developments in the use of chromatographic techniques in marine laboratories for the determination of halogenated contaminants and polycyclic aromatic hydrocarbons. *Journal of Chromatography A,* **1000**(1), pp. 223-251.

DE KEYSER, W., GEVAERT, V., VERDONCK, F., DE BAETS, B. and BENEDETTI, L., 2010. An emission time series generator for pollutant release modelling in urban areas. *Environmental Modelling & Software,* **25**(4), pp. 554-561.

DIVRIKLI, Ü and ELÇI, L., 2002. Determination of some trace metals in water and sediment samples by flame atomic absorption spectrometry after coprecipitation with cerium (IV) hydroxide. *Analytica Chimica Acta,* **452**(2), pp. 231-235.

DUBLIN CITY COUNCIL, 2007-last update, Ringsend Waste Water Discharge License Application [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0034-012012].

DUBLIN CITY COUNCIL, 2003. *Ringsend (sbr) Wastewater Treatment Plant Overview.* Ireland: Dublin City Council.

DUGAY, J., MIEGE, C. and HENNION, M.C., 1998. Effect of the various parameters governing solid-phase microextraction for the trace-determination of pesticides in water. *Journal of Chromatography A,* **795**(1), pp. 27-42.

DUZGOREN-AYDIN, N.S., 2007. Sources and characteristics of lead pollution in the urban environment of Guangzhou. *Science of the Total Environment,* **385**(1-3), pp. 182-195.

EATON, A.D. and FRANSON, M.A.H., 2005. *Standard methods for the examination of water & wastewater.* Amer Public Health Assn.

EEC, 1991. *Council Directive of 21 May 1991 Concerning Urban Waste Water Treatment (91/271/EEC).* Directive edn. European Union: European Union.

EEC, 1980. *Council Directive 80/788/EEC.* L 229. European Union: Official Journal of the European Communities.

ESCALAS, A., GUADAYOL, J.M., CORTINA, M., RIVERA, J. and CAIXACH, J., 2003. Time and space patterns of volatile organic compounds in a sewage treatment plant. *Water research,* **37**(16), pp. 3913-3920.

EUROPEAN PARLIAMENT, 2009. *S.I. No. 272 of 2009 European Communities Environmental Objectives (Surface Waters) Regulations.* Statutory Instrument edn. Ireland: .

EUROPEAN PARLIAMENT, 2008. *Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008.* Directive edn. European Union: .

EUROPEAN PARLIAMENT, 2000. *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.* Articles 2(30) and 16(2). European Union: European Parliament.

EUROPEAN PARLIAMENT, 20 November 2001. *Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC.* European Union: European Parliament and of the Council of 20 November 2001.

FAUSER, P., VIKELSØE, J., SØRENSEN, P.B. and CARLSEN, L., 2003. Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant—fate modelling based on measured concentrations in wastewater and sludge. *Water research,* **37**(6), pp. 1288-1295.

FEHILY, B., 2008. *A Review of and Report on Certain Matters Relating to Dublin City Council's Ringsend Wastewater Treatment Plant.* Ireland: Department of the Environment.

FERNANDES, M. and SICRE, M.A., 1999. Polycyclic aromatic hydrocarbons in the Arctic: Ob and Yenisei estuaries and Kara Sea shelf. *Estuarine, Coastal and Shelf Science,* **48**(6), pp. 725-737.

FILIPKOWSKA, A., LUBECKI, L. and KOWALEWSKA, G., 2005. Polycyclic aromatic hydrocarbon analysis in different matrices of the marine environment. *Analytica Chimica Acta,* **547**(2), pp. 243-254.

FINGAL COUNTY COUNCIL, 2007-last update, Swords Waste Water Discharge License Application 2007, EPA website: [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/wwda/wwda-view.jsp?regno=D0024-012012].

FINGAL COUNTY COUNCIL, 2004. *Swords Wastewater Treatment Works.* Ireland: Fingal County Council.

GAGA, E.O. and TUNCEL, S.G., 2004. Extraction and Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) from rain samples, *4th Aegean Analytical Chemistry Days Congress*, 29 Sept-3 Oct.2004 2004, pp. Proceedings Book 246.

GALT, R.E., 2008. Beyond the circle of poison: Significant shifts in the global pesticide complex, 1976–2008. *Global Environmental Change,* **18**(4), pp. 786-799.

GARBAN, B., BLANCHOUD, H., MOTELAY-MASSEI, A., CHEVREUIL, M. and OLLIVON, D., 2002. Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites. *Atmospheric Environment,* **36**(34), pp. 5395-5403.

GASPERI, J., GARNAUD, S., ROCHER, V. and MOILLERON, R., 2008. Priority pollutants in wastewater and combined sewer overflow. *Science of the Total Environment,* **407**(1), pp. 263-272.

GIMENO, R., ALTELAAR, A., MARCE, R. and BORRULL, F., 2002. Determination of polycyclic aromatic hydrocarbons and polycylic aromatic sulfur heterocycles by high-performance liquid chromatography with fluorescence and atmospheric pressure chemical ionization mass spectrometry detection in seawater and sediment samples. *Journal of Chromatography A,* **958**(1), pp. 141-148.

GMEINER, G., STEHLIK, G. and TAUSCH, H., 1997. Determination of seventeen polycyclic aromatic hydrocarbons in tobacco smoke condensate. *Journal of Chromatography A,* **767**(1), pp. 163-169.

GÓMEZ, M.J., MARTÍNEZ BUENO, M.J., LACORTE, S., FERNÁNDEZ-ALBA, A.R. and AGÜERA, A., 2007. Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast. *Chemosphere,* **66**(6), pp. 993-1002.

GRAHAM, M.C., ALLAN, R., FALLICK, A.E. and FARMER, J., 2006. Investigation of extraction and clean-up procedures used in the quantification and stable isotopic characterisation of PAHs in contaminated urban soils. *Science of the total environment,* **360**(1), pp. 81-89.

GUARDIA RUBIO, M., RUIZ MEDINA, A., PASCUAL REGUERA, M. and FERNÁNDEZ DE CÓRDOVA, M., 2007. Multiresidue analysis of three groups of pesticides in washing waters from olive processing by solid-phase extraction-gas chromatography with electrón capture and thermionic specific detection. *Microchemical journal,* **85**(2), pp. 257-264.

HADA, M., TAKINO, M., YAMAGAMI, T., DAISHIMA, S. and YAMAGUCHI, K., 2000. Trace analysis of pesticide residues in water by high-speed narrow-bore capillary gas chromatography–mass spectrometry with programmable temperature vaporizer. *Journal of Chromatography A,* **874**(1), pp. 81-90.

HAGESTUEN, E.D. and CAMPIGLIA, A.D., 1999. New approach for screening polycyclic aromatic hydrocarbons in water samples. *Talanta,* **49**(3), pp. 547-560.

HARRISON, R., PERRY, R. and WELLINGS, R., 1975. Polynuclear aromatic hydrocarbons in raw, potable and waste water. *WATER RESEARCH, VOL 9, NO 4, P 331-346, APRIL 1975.2 FIG, 20 TAB, 147 REF.,* .

HAYES,N.,PAGE,D.,SWEENEY,L.,O'LEARY,G., 2011. *The Provision and Quality of Drinking Water in Ireland: A Report for the Year 2010.* Ireland: Irish Environmental Protection Agency.

HEITLAND, P. and KÖSTER, H.D., 2006. Biomonitoring of 30 trace elements in urine of children and adults by ICP-MS. *Clinica Chimica Acta,* **365**(1), pp. 310-318.

HEITLAND, P. and KÖSTER, H.D., 2006. Biomonitoring of 37 trace elements in blood samples from inhabitants of northern Germany by ICP–MS. *Journal of trace elements in medicine and biology,* **20**(4), pp. 253-262.

HENNION, M.C., 1999. Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography. *Journal of Chromatography A,* **856**(1), pp. 3-54.

HERNÁNDEZ, F., SANCHO, J., POZO, O., LARA, A. and PITARCH, E., 2001. Rapid direct determination of pesticides and metabolites in environmental water samples at sub-µg/l level by on-line solid-phase extraction-liquid chromatography–electrospray tandem mass spectrometry. *Journal of Chromatography A,* **939**(1), pp. 1-11.

HIRATA, S., ISHIDA, Y., AIHARA, M., HONDA, K. and SHIKINO, O., 2001. Determination of trace metals in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry. *Analytica Chimica Acta,* **438**(1-2), pp. 205-214.

HIRATA, S., KAJIYA, T., TAKANO, N., AIHARA, M., HONDA, K., SHIKINO, O. and NAKAYAMA, E., 2003. Determination of trace metals in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry using metal alkoxide glass immobilized 8-quinolinol. *Analytica Chimica Acta,* **499**(1-2), pp. 157-165.

HOGENDOORN, E. and VAN ZOONEN, P., 2000. Recent and future developments of liquid chromatography in pesticide trace analysis. *Journal of Chromatography A,* **892**(1), pp. 435-453.

HOLVOET, K., SEUNTJENS, P. and VANROLLEGHEM, P.A., 2007. Monitoring and modeling pesticide fate in surface waters at the catchment scale. *Ecological Modelling,* **209**(1), pp. 53-64.

HUCK, C. and BONN, G., 2000. Recent developments in polymer-based sorbents for solid-phase extraction. *Journal of Chromatography A,* **885**(1), pp. 51-72.

IBÁÑEZ, M., PICÓ, Y. and MAÑES, J., 1998. Improving the solid-phase extraction of “quat” pesticides from water samples: Removal of interferences. *Journal of Chromatography A,* **823**(1), pp. 137-146.

IRACE-GUIGAND, S., AARON, J., SCRIBE, P. and BARCELÓ, D., 2004. A comparison of the environmental impact of pesticide multiresidues and their occurrence in river waters surveyed by liquid chromatography coupled in tandem with UV diode array detection and mass spectrometry. *Chemosphere,* **55**(7), pp. 973-981.

IRISH EPA, Oct. 2006. *Appendix, 2.1 Surface Water Parameters and Groundwater Parameters for Dangerous Substances Monitoring, IRISH WFD Monitoring Programme.* Ireland: Irish Environmental Protection Agency.

IRISH EPA, 2012, 2012-last update, Database of EPA Waste Discharge License Applications [Homepage of Irish EPA], [Online]. Available: http://www.epa.ie/terminalfour/waste/waste-view.jsp?regno=W0089-022011].

IRISH EPA, 2006. *Irish Water Framework Directive Monitoring Programme V1.0.* V1.0. Ireland: EPA.

IRISH EPA, 1997. *Wastewater Treatment Manuals, Primary, Secondary & Tertiary Treatment.* Ardcavan, Wexford, Ireland: Irish Environmental Protection Agency.

JAFFREZO, J.L., MASCLET, P., CLAIN, M., WORTHAM, H., BEYNE, S. and CACHIER, H., 1993. Transfer function of polycyclic aromatic hydrocarbons from the atmosphere to the polar ice--I. Determination of atmospheric concentrations at dye 3, Greenland. *Atmospheric Environment.Part A.General Topics,* **27**(17-18), pp. 2781-2785.

JIMÉNEZ, J., BERNAL, J., DEL NOZAL, M.J., TORIBIO, L. and ARIAS, E., 2001. Analysis of pesticide residues in wine by solid-phase extraction and gas chromatography with electron capture and nitrogen–phosphorus detection. *Journal of chromatography A,* **919**(1), pp. 147-156.

JONES-LEPP, T.L. and MOMPLAISIR, G.M., 2005. New applications of LC–MS and LC–MS< sup> 2</sup> toward understanding the environmental fate of organometallics. *TrAC Trends in Analytical Chemistry,* **24**(7), pp. 590-595.

JUNIOR, J.L.R. and RE-POPPI, N., 2007. Determination of organochlorine pesticides in ground water samples using solid-phase microextraction by gas chromatography-electron capture detection. *Talanta,* **72**(5), pp. 1833-1841.

KARTHIKEYAN, S. and BALASUBRAMANIAN, R., 2006. Interlaboratory study to improve the quality of trace element determinations in rainwater. *Analytica Chimica Acta,* **576**(1), pp. 9-16.

KAVCAR, P., SOFUOGLU, A. and SOFUOGLU, S.C., 2009. A health risk assessment for exposure to trace metals via drinking water ingestion pathway. *International journal of hygiene and environmental health,* **212**(2), pp. 216-227.

KLEIN, J. and ALDER, L., 2003. Applicability of Gradient Liquid Chromatography with Tandem Mass Spectrometry to the Simultaneous Screening for About 100 Pesticides in Crops. *Journal of AOAC International,* **86**(5), pp. 1015-1037.

KOCASOY, G., MUTLU, H.İ and AYLIN ZEREN ALAGÖZ, B., 2008. Prevention of marine environment pollution at the tourism regions by the application of a simple method for the domestic wastewater. *Desalination,* **226**(1), pp. 21-37.

KOOTSTRA, P., STRAUB, M., STIL, G., VAN DER VELDE, E., HESSELINK, W. and LAND, C., 1995. Solid-phase extraction of polycyclic aromatic hydrocarbons from soil samples. *Journal of chromatography A,* **697**(1), pp. 123-129.

KORENKOVA, E., MATISOVA, E. and SLOBODNÍK, J., 2003. Study on the feasibility of coupling large- volume injection to fast gas chromatography with mass spectrometric detection for analysis of organochlorine pesticides. *Journal of separation science,* **26**(12- 13), pp. 1193-1197.

KOSTIAINEN, R. and KAUPPILA, T.J., 2009. Effect of eluent on the ionization process in liquid chromatography-mass spectrometry. *Journal of Chromatography A,* **1216**(4), pp. 685-699.

KULLENBERG, G., 1999. Approaches to addressing the problems of pollution of the marine environment: an overview. *Ocean & Coastal Management,* **42**(12), pp. 999-1018.

KUSTER, M., LÓPEZ DE ALDA, M. and BARCELÓ, D., 2006. Analysis of pesticides in water by liquid chromatography-tandem mass spectrometric techniques. *Mass Spectrometry Review,* **25**(6), pp. 900-916.

LAPERTOT, M., PULGARÍN, C., FERNÁNDEZ-IBÁÑEZ, P., MALDONADO, M., PÉREZ-ESTRADA, L., OLLER, I., GERNJAK, W. and MALATO, S., 2006. Enhancing Biodegradability of Priority Substances (Pesticides) by Solar Photo-Fenton. *Water Research,* **40**(5), pp. 1086-1094.

LARSON, S.J., CAPEL, P.D. and MAJEWSKI, M.S., eds, 1997. *Pesticides in Surface Waters - Distribution, rends, and governing factors In Gilliom, R.J. (Ed.), series of pesticides in hydrologic system.* Vol 3 edn. Chelsea, Michigan: Ann Arbor press.

LAWLOR, A. and TIPPING, E., 2003. Metals in bulk deposition and surface waters at two upland locations in northern England. *Environmental Pollution,* **121**(2), pp. 153-167.

LEBO, J., ZAJICEK, J., HUCKINS, J., PETTY, J. and PETERMAN, P., 1992. Use of semipermeable membrane devices for in situ monitoring of polycyclic aromatic hydrocarbons in aquatic environments. *Chemosphere,* **25**(5), pp. 697-718.

LEPOM, P., BROWN, B., HANKE, G., LOOS, R., QUEVAUVILLER, P. and WOLLGAST, J., 2009. Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European Water Framework Directive. *Journal of Chromatography A,* **1216**(3), pp. 302-315.

LI, H.Q., JIKU, F. and SCHRÖDER, H.F., 2000. Assessment of the pollutant elimination efficiency by gas chromatography/mass spectrometry, liquid chromatography–mass spectrometry and–tandem mass spectrometry: Comparison of conventional and membrane-assisted biological wastewater treatment processes. *Journal of chromatography A,* **889**(1), pp. 155-176.

LI, X., POON, C. and LIU, P.S., 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry,* **16**(11-12), pp. 1361-1368.

LI, X., POON, C. and LIU, P.S., 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry,* **16**(11–12), pp. 1361-1368.

LUO, X., MAI, B., YANG, Q., FU, J., SHENG, G. and WANG, Z., 2004. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China. *Marine pollution bulletin,* **48**(11), pp. 1102-1115.

LUTHRIA, D., 2006. Perspective - Significance of sample preparation in developing analytical methodologies for accurate estimation of bioactive compounds in functional foods. *Journal of the Science of Food and Agriculture,* **86**, pp. 2266-2272.

MALOSCHIK, E., ERNST, A., HEGEDŰS, G., DARVAS, B. and SZÉKÁCS, A., 2007. Monitoring water-polluting pesticides in Hungary. *Microchemical journal,* **85**(1), pp. 88-97.

MANAHAN, S.E., 2000. *Fundamentals of Environmental Chemistry.* 2 edn. USA: CRC Press.

MARCÉ, R. and BORRULL, F., 2000. Solid-phase extraction of polycyclic aromatic compounds. *Journal of Chromatography A,* **885**(1), pp. 273-290.

MASQUÉ, N., GALIA, M., MARCÉ, R. and BORRULL, F., 1998. New chemically modified polymeric resin for solid-phase extraction of pesticides and phenolic compounds from water. *Journal of Chromatography A,* **803**(1), pp. 147-155.

MASQUÉ, N., MARCÉ, R. and BORRULL, F., 1998. New polymeric and other types of sorbents for solid-phase extraction of polar organic micropollutants from environmental water. *TrAC Trends in Analytical Chemistry,* **17**(6), pp. 384-394.

MCGOWIN, A.E., ADOM, K.K. and OBUBUAFO, A.K., 2001. Screening of compost for PAHs and pesticides using static subcritical water extraction. *Chemosphere,* **45**(6-7), pp. 857-864.

MEAKINS, N.C., BUBB, J.M. and LESTER, J.N., 1994. The behaviour of the s-triazine herbicides, atrazine and simazine, during primary and secondary biological waste water treatment. *Chemosphere,* **28**(9), pp. 1611-1622.

MEUDEC, A., DUSSAUZE, J., JOURDIN, M., DESLANDES, E. and POUPART, N., 2006. Gas chromatographic–mass spectrometric method for polycyclic aromatic hydrocarbon analysis in plant biota. *Journal of Chromatography A,* **1108**(2), pp. 240-247.

MMUALEFE, L.C., TORTO, N., HUNTSMAN-MAPILA, P. and MBONGWE, B., 2009. Headspace solid phase microextraction in the determination of pesticides in water samples from the Okavango Delta with gas chromatography-electron capture detection and time-of-flight mass spectrometry. *Microchemical Journal,* **91**(2), pp. 239-244.

MONAGHAN, S., SHANNON, D., WALL, B. and O'LEARY, G., 2012. *Focus on Urban Waste Water Discharges in Ireland.* Ireland: Irish Environmental Protection Agency.

MOORE, K., 2009. *Using administrative data to estimate vehicle-kilometres for the national vehicle fleet.* Ireland: Central Statistics Office - Transport Statistics.

MORAL, A., SICILIA, M.D., RUBIO, S. and PÉREZ-BENDITO, D., 2008. Multifunctional sorbents for the extraction of pesticide multiresidues from natural waters. *Analytica Chimica Acta,* **608**(1), pp. 61-72.

MORET, S. and CONTE, L.S., 2000. Polycyclic aromatic hydrocarbons in edible fats and oils: occurrence and analytical methods. *Journal of Chromatography A,* **882**(1), pp. 245-253.

NAGPAL, N.K., 1993, 1993-last update, Ambient Water Quality Criteria For Polycyclic Aromatic Hydrocarbons (PAHs), 2.0 PAHs and Their Characteristics [Homepage of Ministry of Environment, Lands and Parks Province of British Columbia], [Online]. Available: http://www.env.gov.bc.ca/wat/wq/BCguidelines/pahs/pahs-01.htm2009].

NATANGELO, M., TAVAZZI, S., FANELLI, R. and BENFENATI, E., 1999. Analysis of some pesticides in water samples using solid-phase microextraction–gas chromatography with different mass spectrometric techniques. *Journal of Chromatography A,* **859**(2), pp. 193-201.

NATIONAL ROADS AUTHORITY, 2010. *National Roads Authority Report: National Route Lengths as of 31/12/2009.* Ireland: National Roads Authority.

NAUMANN, K., 1994. Natürlich vorkommende Organohalogene. *Nachrichten aus Chemie, Technik und Laboratorium,* **42**(4), pp. 389-392.

NAWROCKI, J. and DA□BROWSKA, A., 2000. Low-carbon silica sorbents for solid-phase extraction. *Journal of Chromatography A,* **868**(1), pp. 1-12.

NAZARKINA, S., BULANOVA, A. and LARIONOV, O., 2001. Solid-phase extraction of polycyclic aromatic hydrocarbons using polymer sorbents. *Journal of Analytical Chemistry,* **56**(4), pp. 348-350.

NIIMI, A. and PALAZZO, V., 1986. Biological half-lives of eight polycyclic aromatic hydrocarbons (PAHs) in rainbow trout (< i> Salmo gairdneri). *Water research,* **20**(4), pp. 503-507.

NITSCHKE, L., WILK, A., SCHÜSSLER, METZENER, G. and LIND, G., 1999. Biodegradation in Laboratory Activated Sludge Plants and Aquatic Toxicity of Herbicides. *Chemosphere,* **39**(13), pp. 2313.

ORECCHIO, S., 2010. Analytical method, pattern and sources of polycyclic aromatic hydrocarbons (PAHs) in the stone of the Temples of Agrigento (Italy). *Journal of hazardous materials,* **176**(1-3), pp. 339-347.

ORECCHIO, S., 2007. PAHs associated with the leaves of Quercus ilex L.: Extraction, GC-MS analysis, distribution and sources:: Assessment of air quality in the Palermo (Italy) area. *Atmospheric Environment,* **41**(38), pp. 8669-8680.

OTERO-ROMANÍ, J., MOREDA-PIÑEIRO, A., BERMEJO-BARRERA, A. and BERMEJO-BARRERA, P., 2005. Evaluation of commercial C18 cartridges for trace elements solid phase extraction from seawater followed by inductively coupled plasma-optical emission spectrometry determination. *Analytica Chimica Acta,* **536**(1–2), pp. 213-218.

PANG, G.F., CAO, Y.Z., ZHANG, J.J., FAN, C.L., LIU, Y.M., LI, X.M., JIA, G.Q., LI, Z.Y., SHI, Y.Q. and WU, Y.P., 2006. Validation study on 660 pesticide residues in animal tissues by gel permeation chromatography cleanup/gas chromatography–mass spectrometry and liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A,* **1125**(1), pp. 1-30.

PARKERTON, T., 2001. *A preliminary analysis of benzene fate in industrial wastewater treatment plants: implications for the EU existing substances risk assessment.* 17 p. CEFIC Aromatics Producers Association and CONCAWE.

PEKNEY, N.J. and DAVIDSON, C.I., 2005. Determination of trace elements in ambient aerosol samples. *Analytica Chimica Acta,* **540**(2), pp. 269-277.

PELTONEN, K. and KULJUKKA, T., 1995. Air sampling and analysis of polycyclic aromatic hydrocarbons. *Journal of Chromatography A,* **710**(1), pp. 93-108.

PÉREZ, S., FARRÉ, M., GARCÍA, M.J. and BARCELÓ, D., 2001. Occurrence of polycyclic aromatic hydrocarbons in sewage sludge and their contribution to its toxicity in the ToxAlert® 100 bioassay. *Chemosphere,* **45**(6-7), pp. 705-712.

PÉREZ, S., GUILLAMÓN, M. and BARCELÓ, D., 2001. Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants. *Journal of Chromatography A,* **938**(1), pp. 57-65.

PÉREZ-CARRERA, E., LEÓN, V.M.L., PARRA, A.G. and GONZÁLEZ-MAZO, E., 2007. Simultaneous determination of pesticides, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in seawater and interstitial marine water samples, using stir bar sorptive extraction-thermal desorption-gas chromatography-mass spectrometry. *Journal of Chromatography A,* **1170**(1-2), pp. 82-90.

PICHON, V., 2000. Solid-phase extraction for multiresidue analysis of organic contaminants in water. *Journal of Chromatography A,* **885**(1), pp. 195-215.

PICÓ, Y., FERNÁNDEZ, M., RUIZ, M.J. and FONT, G., 2007. Current trends in solid-phase-based extraction techniques for the determination of pesticides in food and environment. *Journal of Biochemical and Biophysical Methods,* **70**(2), pp. 117-131.

PIMENTEL, D. and LEVITAN, L., 1986. Pesticides: amounts applied and amounts reaching pests. *Bioscience,* **36**(2), pp. 86-91.

PIMENTEL, D., 1995. Amounts of pesticides reaching target pests: Environmental impacts and ethics. *Journal of Agricultural and Environmental Ethics,* **8**(1), pp. 17-29.

PLANAS, C., PUIG, A., RIVERA, J. and CAIXACH, J., 2006. Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction: Estimation of the uncertainty of the analytical results. *Journal of Chromatography A,* **1131**(1), pp. 242-252.

POLAT, H. and ERDOGAN, D., 2007. Heavy metal removal from waste waters by ion flotation. *Journal of hazardous materials,* **148**(1-2), pp. 267-273.

PORTET-KOLTALO, F., OUKEBDANE, K., ROBIN, L., DIONNET, F. and DESBÈNE, P., 2007. Quantification of volatile PAHs present at trace levels in air flow by aqueous trapping—SPE and HPLC analysis with fluorimetric detection. *Talanta,* **71**(5), pp. 1825-1833.

POSTER, D.L., SCHANTZ, M.M., SANDER, L.C. and WISE, S.A., 2006. Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: a critical review of gas chromatographic (GC) methods. *Analytical and bioanalytical chemistry,* **386**(4), pp. 859-881.

PRABHAKARAN, D. and SUBRAMANIAN, M., 2003. A new chelating sorbent for metal ion extraction under high saline conditions. *Talanta,* **59**(6), pp. 1227-1236.

QUINTANA, J., MARTÍ, I. and VENTURA, F., 2001. Monitoring of pesticides in drinking and related waters in NE Spain with a multiresidue SPE-GC–MS method including an estimation of the uncertainty of the analytical results. *Journal of Chromatography A,* **938**(1), pp. 3-13.

RADJENOVIC, J., PETROVIC, M. and BARCELÓ, D., 2007. Advanced mass spectrometric methods applied to the study of fate and removal of pharmaceuticals in wastewater treatment. *TrAC Trends in Analytical Chemistry,* **26**(11), pp. 1132-1144.

RATOLA, N., LACORTE, S., ALVES, A. and BARCELÓ, D., 2006. Analysis of polycyclic aromatic hydrocarbons in pine needles by gas chromatography–mass spectrometry: Comparison of different extraction and clean-up procedures. *Journal of Chromatography A,* **1114**(2), pp. 198-204.

RDSE, 2006. *Action Nationale de Recherche et de Réduction des Rejets de Substances Dangereuses dans l'Eau par les installations classées.* 53 p. Rapport d'étape.

READMAN, J., FILLMANN, G., TOLOSA, I., BARTOCCI, J., VILLENEUVE, J.P., CATINNI, C. and MEE, L., 2002. Petroleum and PAH contamination of the Black Sea. *Marine pollution bulletin,* **44**(1), pp. 48-62.

REEMTSMA, T., 2001. The use of liquid chromatography-atmospheric pressure ionization-mass spectrometry in water analysis-Part I: Achievements. *TrAC Trends in Analytical Chemistry,* **20**(9), pp. 500-517.

REN, S., 2004. Assessing wastewater toxicity to activated sludge: recent research and developments. *Environment international,* **30**(8), pp. 1151-1164.

SABIN, L.D., LIM, J.H., STOLZENBACH, K.D. and SCHIFF, K.C., 2006. Atmospheric dry deposition of trace metals in the coastal region of Los Angeles, California, USA. *Environmental toxicology and chemistry,* **25**(9), pp. 2334-2341.

SANDERS, G., JONES, K.C. and HAMILTON-TAYLOR, J., 1993. A simple method to assess the susceptibility of polynuclear aromatic hydrocarbons to photolytic decomposition. *Atmospheric Environment.Part A.General Topics,* **27**(2), pp. 139-144.

SARAÇOGLU, S. and ELÇI, L., 2002. Column solid-phase extraction with Chromosorb-102 resin and determination of trace elements in water and sediment samples by flame atomic absorption spectrometry. *Analytica Chimica Acta,* **452**(1), pp. 77-83.

SARGENTI, S.R. and MCNAIR, H.M., 1998. Comparison of solid- phase extraction and supercritical fluid extraction for extraction of polycyclic aromatic hydrocarbons from drinking water. *Journal of Microcolumn Separations,* **10**(1), pp. 125-131.

SASANO, R., HAMADA, T., KURANO, M. and FURUNO, M., 2000. On-line coupling of solid-phase extraction to gas chromatography with fast solvent vaporization and concentration in an open injector liner: Analysis of pesticides in aqueous samples. *Journal of Chromatography A,* **896**(1), pp. 41-49.

SAURET-SZCZEPANSKI, N., MIRABEL, P. and WORTHAM, H., 2006. Development of an SPME–GC–MS/MS method for the determination of pesticides in rainwater: Laboratory and field experiments. *Environmental pollution,* **139**(1), pp. 133-142.

SCOREPP, 2008-last update, European Initiatives: Source Control Options for Reducing Emissions of Priority Pollutants [Homepage of Euro-mediterranean Information System], [Online]. Available: http://www.emwis.net/initiatives/fol060732/proj9501262012].

SERIKI, K., GASPERI, J., CASTILLO, L., SCHOLES, L., ERIKSSON, E., REVITT, M., MEINHOLD, J. and ATANASOVA, N., 2008. Priority pollutants behaviour in end of pipe wastewater treatment plants. *Deliverable report,* **5**, pp. 1-91.

SHIMMO, M., ADLER, H., HYÖTYLÄINEN, T., HARTONEN, K., KULMALA, M. and RIEKKOLA, M.L., 2002. Analysis of particulate polycyclic aromatic hydrocarbons by on-line coupled supercritical fluid extraction-liquid chromatography-gas chromatography-mass spectrometry. *Atmospheric Environment,* **36**(18), pp. 2985-2995.

SILVA, M.G.D., AQUINO, A., DÓREA, H.S. and NAVICKIENE, S., 2008. Simultaneous determination of eight pesticide residues in coconut using MSPD and GC/MS. *Talanta,* **76**(3), pp. 680-684.

SIMON, R., PALME, S. and ANKLAM, E., 2006. Single-laboratory validation of a gas chromatography–mass spectrometry method for quantitation of 15 European priority polycyclic aromatic hydrocarbons in spiked smoke flavourings. *Journal of Chromatography A,* **1103**(2), pp. 307-313.

SINGH, A.K., SPASSOVA, D. and WHITE, T., 1998. Quantitative analysis of polychlorinated biphenyls, organochlorine insecticides, polycyclic aromatic hydrocarbons, polychlorinated hydrocarbons and polynitrohydrocarbons in spiked samples of soil, water and plasma by selected-ion monitoring gas chromatography-mass spectrometry. *Journal of Chromatography B: Biomedical Sciences and Applications,* **706**(2), pp. 231-244.

SKOOG, HOLLER and NIEMAN, 1998. *Principles of Instrumental Analysis.* 5th edn. USA: Brooks/Cole.

SPROVIERI, M., FEO, M.L., PREVEDELLO, L., MANTA, D.S., SAMMARTINO, S., TAMBURRINO, S. and MARSELLA, E., 2007. Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere,* **67**(5), pp. 998-1009.

SUN, F., LITTLEJOHN, D. and DAVID GIBSON, M., 1998. Ultrasonication extraction and solid phase extraction clean-up for determination of US EPA 16 priority pollutant polycyclic aromatic hydrocarbons in soils by reversed-phase liquid chromatography with ultraviolet absorption detection1. *Analytica Chimica Acta,* **364**(1-3), pp. 1-11.

TAHBOUB, Y.R., ZAATER, M.F. and AL-TALLA, Z.A., 2005. Determination of the limits of identification and quantitation of selected organochlorine and organophosphorous pesticide residues in surface water by full-scan gas chromatography/mass spectrometry. *Journal of Chromatography A,* **1098**(1), pp. 150-155.

TAMASI, G. and CINI, R., 2004. Heavy metals in drinking waters from Mount Amiata (Tuscany, Italy). Possible risks from arsenic for public health in the Province of Siena. *Science of the total environment,* **327**(1), pp. 41-51.

TEIJON, G., CANDELA, L., TAMOH, K., MOLINA-DÍAZ, A. and FERNÁNDEZ-ALBA, A., 2010. Occurrence of emerging contaminants, priority substances (2008/105/CE) and heavy metals in treated wastewater and groundwater at Depurbaix facility (Barcelona, Spain). *Science of the Total Environment,* **408**(17), pp. 3584-3595.

TERYTZE, K., KÖRDEL, W., ALDAG, R., HANEL, J., HEIN, D., KELLER, E., KLEIN, M., KUHNT, G., MÜLLER-WEGENER, U. and SCHEUNERT, I., 1995. Detection and determination limits of priority organic pollutants in soil. *Chemosphere,* **31**(4), pp. 3051-3083.

THORNTON, I., 1991. Metal contamination of soils in urban areas. *Soils in the urban environment,* , pp. 47-75.

TORRES, C.M., PICÓ, Y. and MAÑES, J., 1996. Determination of pesticide residues in fruit and vegetables. *Journal of Chromatography A,* **754**(1–2), pp. 301-331.

TUEROS, I., RODRÍGUEZ, J., BORJA, A., SOLAUN, O., VALENCIA, V. and MILLÁN, E., 2008. Dissolved metal background levels in marine waters, for the assessment of the physico-chemical status, within the European Water Framework Directive. *Science of the Total Environment,* **407**(1), pp. 40-52.

URBE, I. and RUANA, J., 1997. Application of solid-phase extraction discs with a glass fiber matrix to fast determination of polycyclic aromatic hydrocarbons in water. *Journal of Chromatography A,* **778**(1), pp. 337-345.

VALERO-NAVARRO, A., FERNÁNDEZ-SÁNCHEZ, J., MEDINA-CASTILLO, A., FERNÁNDEZ-IBÁÑEZ, F., SEGURA-CARRETERO, A., IBÁÑEZ, J. and FERNÁNDEZ-GUTIÉRREZ, A., 2007. A rapid, sensitive screening test for polycyclic aromatic hydrocarbons applied to Antarctic water. *Chemosphere,* **67**(5), pp. 903-910.

VAN STEE, L.L.P., LEONARDS, P.E.G., VREULS, R.J.J. and BRINKMAN, U.A.T., 1999. Identification of non-target compounds using gas chromatography with simultaneous atomic emission and mass spectrometric detection (GC-AED/MS): analysis of municipal wastewater. *ANALYST-LONDON-SOCIETY OF PUBLIC ANALYSTS THEN ROYAL SOCIETY OF CHEMISTRY-,* **124**, pp. 1547-1552.

VASSILAKIS, I., TSIPI, D. and SCOULLOS, M., 1998. Determination of a variety of chemical classes of pesticides in surface and ground waters by off-line solid-phase extraction, gas chromatography with electron-capture and nitrogen–phosphorus detection, and high-performance liquid chromatography with post-column derivatization and fluorescence detection. *Journal of Chromatography A,* **823**(1), pp. 49-58.

VIGNA, C.R.M., MORAIS, L.S.R., COLLINS, C.H. and JARDIM, I.C.S.F., 2006. Poly (methyloctylsiloxane) immobilized on silica as a sorbent for solid-phase extraction of some pesticides. *Journal of Chromatography A,* **1114**(2), pp. 211-215.

VINAS, P., CAMPILLO, N., LÓPEZ-GARCÍA, I., AGUINAGA, N. and HERNÁNDEZ-CÓRDOBA, M., 2002. Determination of pesticides in waters by capillary gas chromatography with atomic emission detection. *Journal of Chromatography A,* **978**(1), pp. 249-256.

WANG, P. and LEE, H., 1997. Recent applications of high-performance liquid chromatography to the analysis of metal complexes. *Journal of Chromatography A,* **789**(1), pp. 437-451.

WANG, S., ZHAO, P., MIN, G. and FANG, G., 2007. Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid-phase extraction and gas chromatography-mass spectrometry. *Journal of Chromatography A,* **1165**(1-2), pp. 166-171.

WEBER, C. and SMOLKA, S., 2005. *Towards Pesticide Use Reduction in Germany.* Germany: Pestizid Aktions-Netzwerk e.V. (PAN Germany).

WELLS, M.J.M. and YU, L.Z., 2000. Solid-phase extraction of acidic herbicides. *Journal of Chromatography A,* **885**(1), pp. 237-250.

WERRES, F., BALSAA, P. and SCHMIDT, T.C., 2009. Total concentration analysis of polycylic aromatic hydrocarbons in aqueous samples with high suspended particulate matter content. *Journal of Chromatography A,* **1216**(12), pp. 2235-2240.

WILCKE, W., 2000. Synopsis polycyclic aromatic hydrocarbons (PAHs) in soil—a review. *Journal of Plant Nutrition and Soil Science,* **163**(3), pp. 229-248.

WILLIAMSON, K.S., PETTY, J.D., HUCKINS, J.N., LEBO, J.A. and KAISER, E.M., 2002. HPLC-PFD determination of priority pollutant PAHs in water, sediment, and semipermeable membrane devices. *Chemosphere,* **49**(7), pp. 703-715.

WILLIE, S. and STURGEON, R., 2001. Determination of transition and rare earth elements in seawater by flow injection inductively coupled plasma time-of-flight mass spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy,* **56**(9), pp. 1707-1716.

WOITKE, P., WELLMITZ, J., HELM, D., KUBE, P., LEPOM, P. and LITHERATY, P., 2003. Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere,* **51**(8), pp. 633-642.

WOLSKA, L., GALER, K., GÓRECKI, T. and NAMIESNIK, J., 1999. Surface water preparation procedure for chromatographic determination of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Talanta,* **50**(5), pp. 985-991.

YAO, Z., JIANG, G., LIU, J. and CHENG, W., 2001. Application of solid-phase microextraction for the determination of organophosphorous pesticides in aqueous samples by gas chromatography with flame photometric detector. *Talanta,* **55**(4), pp. 807-814.

ZHU, J.H., YAN, X.L., LIU, Y. and ZHANG, B., 2006. Improving Alachlor Biodegradability by Ferrate Oxidation. *Journal of hazardous materials,* **B135**, pp. 94-99.