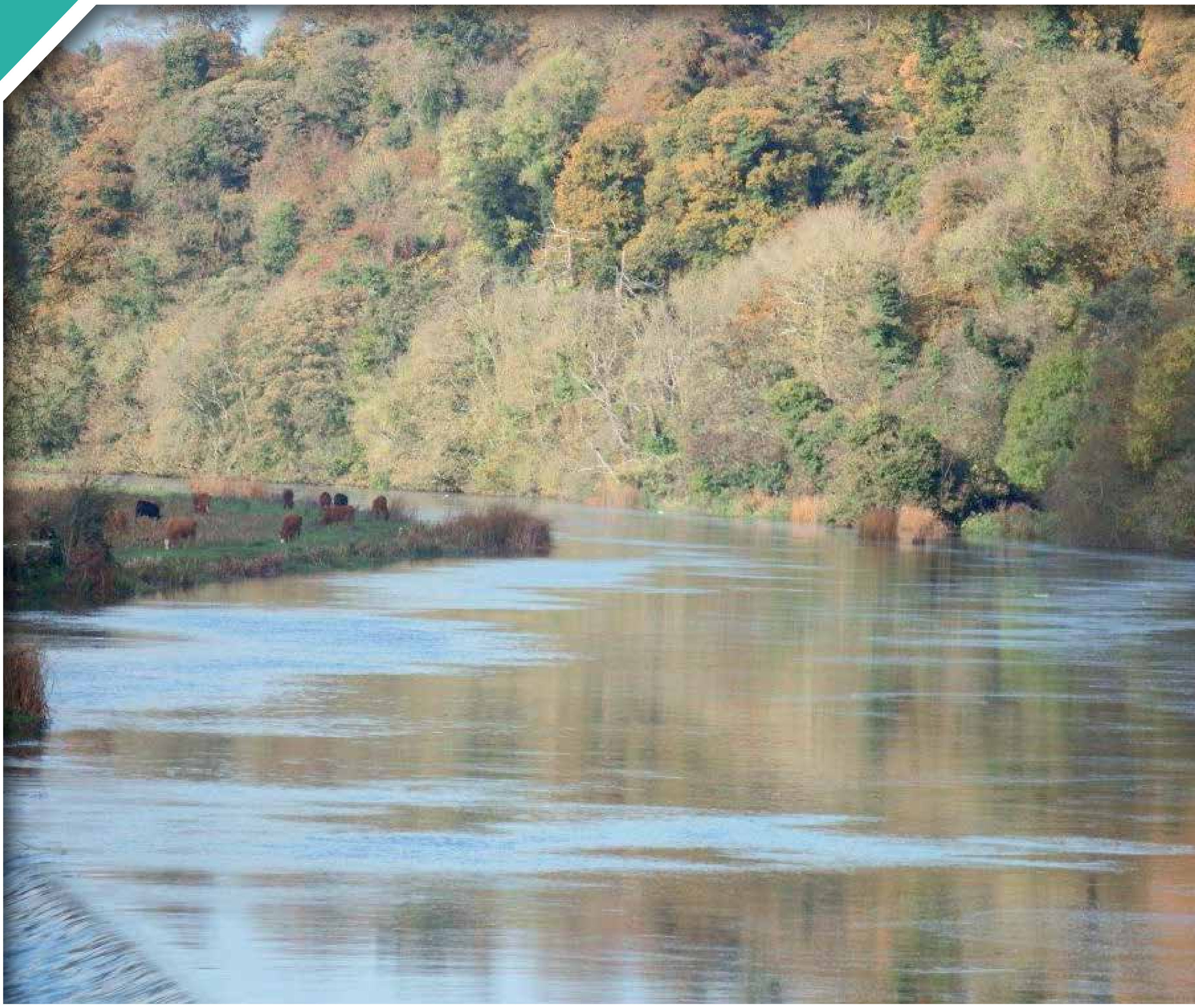
Report No. **231**

epa Research
Climate - Water - Sustainability
Identifying pressures • Informing policy • Developing solutions

Assessment of Natural Organic Matter (NOM) and Ptaquiloside in Irish Waters

Authors: Connie O'Driscoll, Liwen Xiao, Xinmin Zhan,
Bruce Misstear and Francesco Pilla



Roinn Cumarsáide, Gníomhaithe
ar son na hAeráide & Comhshaoil
Department of Communications,
Climate Action & Environment

www.epa.ie

ENVIRONMENTAL PROTECTION AGENCY

The Environmental Protection Agency (EPA) is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

The work of the EPA can be divided into three main areas:

Regulation: *We implement effective regulation and environmental compliance systems to deliver good environmental outcomes and target those who don't comply.*

Knowledge: *We provide high quality, targeted and timely environmental data, information and assessment to inform decision making at all levels.*

Advocacy: *We work with others to advocate for a clean, productive and well protected environment and for sustainable environmental behaviour.*

Our Responsibilities

Licensing

We regulate the following activities so that they do not endanger human health or harm the environment:

- waste facilities *(e.g. landfills, incinerators, waste transfer stations)*;
- large scale industrial activities (*e.g. pharmaceutical, cement manufacturing, power plants)*;
- intensive agriculture *(e.g. pigs, poultry)*;
- the contained use and controlled release of Genetically Modified Organisms *(GMOs)*;
- sources of ionising radiation *(e.g. x-ray and radiotherapy equipment, industrial sources)*;
- large petrol storage facilities;
- waste water discharges;
- dumping at sea activities.

National Environmental Enforcement

- Conducting an annual programme of audits and inspections of EPA licensed facilities.
- Overseeing local authorities' environmental protection responsibilities.
- Supervising the supply of drinking water by public water suppliers.
- Working with local authorities and other agencies to tackle environmental crime by co-ordinating a national enforcement network, targeting offenders and overseeing remediation.
- Enforcing Regulations such as Waste Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS) and substances that deplete the ozone layer.
- Prosecuting those who flout environmental law and damage the environment.

Water Management

- Monitoring and reporting on the quality of rivers, lakes, transitional and coastal waters of Ireland and groundwaters; measuring water levels and river flows.
- National coordination and oversight of the Water Framework Directive.
- Monitoring and reporting on Bathing Water Quality.

Monitoring, Analysing and Reporting on the Environment

- Monitoring air quality and implementing the EU Clean Air for Europe (CAFÉ) Directive.
- Independent reporting to inform decision making by national and local government *(e.g. periodic reporting on the State of Ireland's Environment and Indicator Reports)*.

Regulating Ireland's Greenhouse Gas Emissions

- Preparing Ireland's greenhouse gas inventories and projections.
- Implementing the Emissions Trading Directive, for over 100 of the largest producers of carbon dioxide in Ireland.

Environmental Research and Development

- Funding environmental research to identify pressures, inform policy and provide solutions in the areas of climate, water and sustainability.

Strategic Environmental Assessment

- Assessing the impact of proposed plans and programmes on the Irish environment *(e.g. major development plans)*.

Radiological Protection

- Monitoring radiation levels, assessing exposure of people in Ireland to ionising radiation.
- Assisting in developing national plans for emergencies arising from nuclear accidents.
- Monitoring developments abroad relating to nuclear installations and radiological safety.
- Providing, or overseeing the provision of, specialist radiation protection services.

Guidance, Accessible Information and Education

- Providing advice and guidance to industry and the public on environmental and radiological protection topics.
- Providing timely and easily accessible environmental information to encourage public participation in environmental decision-making *(e.g. My Local Environment, Radon Maps)*.
- Advising Government on matters relating to radiological safety and emergency response.
- Developing a National Hazardous Waste Management Plan to prevent and manage hazardous waste.

Awareness Raising and Behavioural Change

- Generating greater environmental awareness and influencing positive behavioural change by supporting businesses, communities and householders to become more resource efficient.
- Promoting radon testing in homes and workplaces and encouraging remediation where necessary.

Management and structure of the EPA

The EPA is managed by a full time Board, consisting of a Director General and five Directors. The work is carried out across five Offices:

- Office of Environmental Sustainability
- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

The EPA is assisted by an Advisory Committee of twelve members who meet regularly to discuss issues of concern and provide advice to the Board.

EPA RESEARCH PROGRAMME 2014–2020

Assessment of Natural Organic Matter (NOM) and Ptaquiloside in Irish Waters

(2013-W-MS-14)

EPA Research Report

Prepared for the Environmental Protection Agency

by

Trinity College Dublin and National University of Ireland, Galway

Authors:

Connie O'Driscoll, Liwen Xiao, Xinmin Zhan, Bruce Misstear and Francesco Pilla

ENVIRONMENTAL PROTECTION AGENCY
An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 916 0699
Email: info@epa.ie Website: www.epa.ie

ACKNOWLEDGEMENTS

This report is published as part of the EPA Research Programme 2014–2020. The programme is financed by the Irish Government. It is administered on behalf of the Department of Communications, Climate Action and Environment by the EPA, which has the statutory function of co-ordinating and promoting environmental research.

The authors would like to acknowledge the support of the project steering committee, namely Dorothy Stewart and Niall Dunne (EPA); John Gray (consultant); and Cait Gleeson (Irish Water).

The authors acknowledge the contribution of the project partners Sean Corrigan (National Federation of Group Water Schemes) and Carmel Ramwell (Fera Science, UK) for their valued input, expertise and support. The authors thank Jerome Sheahan for his expertise and assistance with the statistical component of this project. The authors acknowledge the support of Brian MacDomhnaill, Brendan Harhen, Peter Croot, Liam Morrison, John Murnane, Martin Lavelle, John McMyler, Sean Quinn, Declan Mannion, Peadar McGuiness, Dermot Baxter, Joe Griffen, Pamela Bartley, Flint Walter, John Gallagher, Patrick Veale, Michael O'Driscoll, Seamus O'Malley, Jose Ledesma, Martyn Futter, John Coll, Eva Mockler and the landowners in the study catchments. The authors wish to acknowledge the opportunity that was provided by George Mathers and Graeme Campbell (College of Agriculture, Food and Rural Enterprise and Department of Agriculture, Food and Rural Affairs, NI) to utilise their bracken study plots in Northern Ireland. The authors also acknowledge the provision of datasets from the EPA, Irish Water, the Geological Survey of Ireland, the Geological Survey of Northern Ireland, the Office of Public Works and Met Éireann.

DISCLAIMER

Although every effort has been made to ensure the accuracy of the material contained in this publication, complete accuracy cannot be guaranteed. The Environmental Protection Agency, the authors and the steering committee members do not accept any responsibility whatsoever for loss or damage occasioned, or claimed to have been occasioned, in part or in full, as a consequence of any person acting, or refraining from acting, as a result of a matter contained in this publication. All or part of this publication may be reproduced without further permission, provided the source is acknowledged.

The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA RESEARCH PROGRAMME 2014–2020
Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-84095-751-8 November 2017

Price: Free Online version

Project Partners

Connie O'Driscoll, Project Manager and Postdoctoral Researcher
Department of Civil, Structural and Environmental Engineering
Trinity College Dublin
Dublin 2
Ireland
Tel: +353 877 435 669
Email: connieodriscoll@gmail.com

Liwen Xiao, Principal Investigator
Department of Civil, Structural and Environmental Engineering
Trinity College Dublin
Dublin 2
Ireland
Tel: +353 18 963 741
Email: liwen.xiao@tcd.ie

Xinmin Zhan, Co-investigator
Department of Civil Engineering
National University of Ireland, Galway
Galway
Ireland
Tel: +353 91 495 239
Email: xinmin.zhan@nuigalway.ie

Bruce Misstear, Co-investigator
Department of Civil, Structural and Environmental Engineering
Trinity College Dublin
Dublin 2
Ireland
Tel: +353 18 962 800
Email: bmisster@tcd.ie

Francesco Pilla, Co-investigator
Department of Civil, Structural and Environmental Engineering
Trinity College Dublin
Dublin 2
Ireland
Email: fpilla@tcd.ie

Carmel Ramwell
Centre for Chemical Safety and Stewardship
Fera Science Ltd
Sand Hutton
York YO41 1LZ
United Kingdom
Tel: +44 1904 462 485
Email: carmel.ramwell@fera.co.uk

Sean Corrigan
National Federation of Group Water Schemes
24 Old Cross Square
Monaghan
Ireland
Tel: +353 429 742 228
Email: ruralwaternews@gmail.com

Contents

List of Figures

List of Tables

Executive Summary

This research project focused on assessing toxins in surface water and groundwater drinking supplies in Ireland. Specifically, it focused on the assessment of (1) natural organic matter (NOM), the precursor for disinfection by-products (DBPs) and trihalomethanes (THMs), and (2) the naturally occurring organic toxin ptaquiloside from bracken. THMs are the only DBP regulated by the European Union and, along with ptaquiloside, are listed as "a *possible* carcinogen" by the International Agency for Research on Cancer (IARC). While the presence of THMs in drinking water is a national concern, the World Health Organization (WHO) states that "efficient disinfection must never be compromised in attempt to meet the guidelines for DBPs and that the microbiological quality of the water must always take precedence".

High-risk catchments for public and private water supplies in relation to NOM across Ireland were identified. Catchment characteristics such as peat presence, high rainfall and mild slopes highlighted areas that were at greater risk for increased NOM and THMs. Statistical analysis of the national THM dataset from 2006 to 2013 further differentiated between water supplies that had (1) no NOM treatment and (2) treatment with some degree of NOM removal such that supplies with "treatment with some degree of NOM removal" had higher THMs with increasing percentages of peat and pasture land in the catchment.

Three case study water supplies with raw water fed from catchments with peat and pasture were selected for further assessment of NOM quantity and quality, and THMs. The findings highlighted that:

1. For a public water supply (PWS) abstracting from a spring in a karst area, ozone and granular activated carbon treatment was inadequate to remove the NOM present in the raw water resulting in THM exceedances. The average raw and treated water dissolved organic carbon (DOC) concentrations (a measure of individual NOM compounds in the dissolved state) were 5.95 and 5.39 mg L^{-1}, respectively. Specific ultraviolet absorbance (SUVA) values in the treated water were indicative of low to moderate aromaticity. A humic-like, terrestrial-delivered reprocessed organic matter fluorescent component was most prominent in the treated water. The average total THM (TTHM) concentration over the study period was 109 µg L^{-1}. Chloroform was the most prominent THM (72%), followed by bromodichloromethane (20%), dibromochloromethane (6%) and bromoform (< 1%). For all three humic-like components, ultraviolet absorbance at 254 nm (UVA_{254}) and total nitrogen were significantly correlated to chloroform as determined by Spearman's rank correlations. A zone of contribution had not previously been defined for this supply, making the drinking water safety plan approach to drinking water problematic.
2. For a PWS abstracting from the lower reaches of the Boyne catchment, coagulation, flocculation and clarification treatment followed by rapid gravity filtration was inadequate to remove the NOM present in the raw water. The average raw and treated water DOC concentrations were 7.90 and 4.52 mg L^{-1}, respectively. As with the spring supply, the SUVA values present in the treated water were indicative of low to moderate aromaticity, and a humic-like, terrestrially delivered organic matter fluorescent component was most prominent in the treated water. TTHMs exceeded the parametric value on one occasion, highlighting the episodic nature of riverine NOM and that routine monitoring not timed with episodic rainfall events does not adequately assess NOM trends.
3. For a private group water scheme abstracting from a lowland lake, ultrafiltration membrane treatment was inadequate to remove the NOM present in the water, resulting in THM exceedances. The average raw and treated water DOC concentrations were 9.38 and 7.54 mg L^{-1}, respectively. SUVA values present in the treated water were indicative of moderate aromaticity, and a humic-like, terrestrially delivered organic matter fluorescent component was most prominent in the treated water.

In additional, temporal variation in NOM was evident in all three case study raw waters, with autumnal peaks.

Hydrological, empirical and process-based biogeochemical models coupled with an ensemble of downscaled regional climate models allowed the determination of scenarios for local-scale effects of forest climate change on surface water DOC concentrations and fluxes. DOC concentrations were estimated for a PWS abstracting from the River Boyne using high-resolution (frequency) online DOC raw water monitoring data. Predicted mean annual temperatures are set to increase in the Boyne catchment by ~1°C. Total annual precipitation will remain generally the same, and results show projected monthly average decreases in spring through to late summer. Predicted daily flows, averaged monthly to demonstrate seasonal impacts, show an overall decrease, and predicted DOC mean monthly concentrations show an overall increase. Simulated mean annual DOC export from the Boyne catchment ($5.8 \pm 1.3\,\mathrm{g\,C\,m^{-2}}$ per year) is in the higher reported range for agricultural catchments and was strongly linked to patterns in discharge and timing of vegetation senescence at the end of the growing season. The modelling approach adopted here suggests that, while biogeochemical mechanisms controlling carbon within a watershed are complex, representation of such interdependent processes in a process-based model is possible, even for a catchment with a low percentage of peat and high use of pastures, using online high-resolution water treatment plant (WTP) data and routinely monitored parameters (i.e. temperature, precipitation and flow). The authors believe that this is the first modelling study to simulate the effects of a changing climate on raw drinking water DOC using routine monitoring data from a WTP for a large, predominantly agricultural catchment. The results highlight the unexplored resource of high-resolution routine WTP monitoring data, together with routine catchment monitoring data, coupled with high-resolution climate models to predict NOM trends.

Initial bracken vegetation survey data collation highlighted an overriding lack of bracken abundance data for Ireland without which it was impossible to determine the national risk. However, three private drinking water sources with one or two domestic houses and bracken in the surrounding catchment were selected for investigation. Ptaquiloside concentrations were quantified in the bracken fronds from frond emergence to plant die-off. Ptaquiloside was detected in the drinking water on only one sampling occasion. Bracken ferns are classified by the IARC as “possibly carcinogenic to humans”.

From a review of the limited research literature and from the limited sampling carried out as part of this research project, we do not believe that there is a large-scale national risk from bracken ferns to drinking water quality. However, areas have been identified for further research such as (1) the need for a bracken abundance map for Ireland; (2) a study of spatial and temporal variations in ptaquiloside concentrations; (3) a more intensive study with an increased number of sampling sites and higher temporal resolution, specifically targeting episodic rainfall events during the plant die-off period; and (4) the effect of various treatments on ptaquiloside.

The findings suggest that there is a need for stakeholder awareness, with regard to ensuring bracken-free zones close to water abstraction sources, especially for supplies with short water residence times. Investigation into the ptaquiloside concentrations of bracken subjected to different management treatments indicated that spraying was the most effective means of control for reducing ptaquiloside load, whereas cutting bracken may increase the production of ptaquiloside in the short term and hence the potential risk to drinking water quality. However, asulam is a banned substance and is itself potentially harmful in drinking water.

Historically, drinking water in Ireland was managed at a local scale with a lack of connectivity between one management unit and the next. With the establishment of a new national water utility, Irish Water, there is significant opportunity for improving THM compliance through systematic connectivity and viewing each abstraction source as a function of its catchment rather than of its management boundaries. This research project served as an exploratory study assessing TTHM data collected through routine monitoring from 2006 to 2013, prior to the establishment of Irish Water, and case studies of water treatment supplies with treatment plants designed prior to the establishment of Irish Water.

1 Introduction

1.1 Context and Background of the Project

1.1.1 *Natural organic matter*

Successive Environmental Protection Agency (EPA) reports have shown that Ireland has an unacceptably high number of drinking water supplies exceeding the parametric value of 100 μg L^{-1} for average total trihalomethanes (TTHMs). In fact, Ireland has been reporting the highest non-compliance with respect to TTHMs in drinking water across the 27 EU Member States (Figure 1.1).

THMs are the most well-known class of disinfection by-products (DBPs) in treated water and the only one currently regulated by the European Union (Drinking Water) Regulations 2014 (S.I. 122 of 2014), although more than 600 different DBPs have been acknowledged. DBPs are formed when natural water is treated to control microbial presence during the drinking water treatment process. THMs are used as an indicator for the presence of DBPs and do not give a true representation of the extent of DBP presence in drinking water. DBPs consist of halogenated and/or non-halogenated compounds, depending on the nature of disinfectants used and precursors present. THMs are typically formed when chlorine reacts with aromatic structures in natural organic matter (NOM); however, non-aromatic NOM can also form THMs. In Ireland, water suppliers add sufficient chlorine to ensure a 0.1 mg L^{-1} level of residual chlorine at the end of the network (EPA, 2012).

An upward trend in aquatic NOM concentrations has been observed at an international scale and will augment the challenges for Irish drinking water suppliers in meeting the parametric value for THMs. Increases in NOM from peaty catchments have been attributed to global warming (Freeman *et al*., 2001; De Wit *et al*., 2007; Evans *et al*., 2016). This has been amplified by decreasing atmospheric sulfur deposition, the implication being that reductions in soil solution sulfur cause significant increases in soil solution and surface water dissolved organic carbon (DOC) concentrations (Evans *et al*., 2012). In this post-acidification period, the focus has shifted to the impacts of land management practices, such as peat harvesting, peatland forestry and agriculture, on changing aquatic NOM quantity and character (Jones *et al*., 2001).

Ireland has a large number of public and private water supplies (3664) for a relatively small population

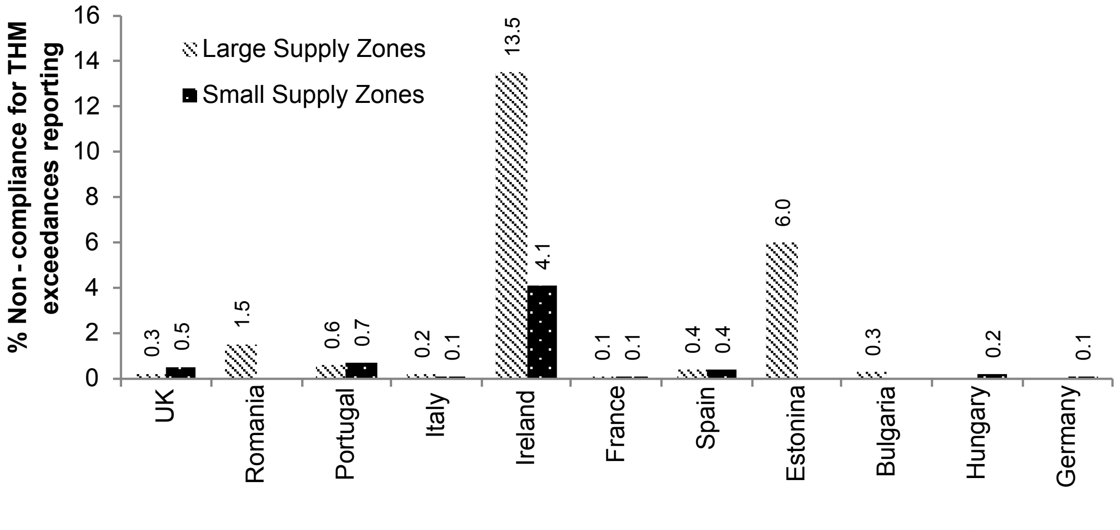


Figure 1.1. Non-compliance for THM exceedances in EU Member States reporting ≥0.1% non-compliance for 2010. Large water supply zones refer to zones supplying more than 5000 people and small supply zones to those supplying fewer than 5000 (EC, 2014).

compared with other EU countries (EPA, 2016). For example, in comparison with Scotland's 242 supplies (DWQR, 2015), Ireland has 973 public water supplies (PWSs) for a similar population size (EPA, 2016). Management of Ireland's water supplies is complex owing to a suite of identified factors: (1) the variation in supply types, i.e. groundwater/surface water source; (2) geographical location; (3) size; (4) treatment processes; (5) management; (6) consumers; (7) ownership issues; (8) distribution networks; and (9) a lack of investment in water infrastructure over many years (EPA, 2016).

A national-scale assessment of the catchment characteristics driving THMs is necessary to support an evidence-based approach in dealing with the THM issue. NOM characterisation of raw waters forms a critical component of the work required to understand how different treatment processes will perform in removing NOM and to understand how land management practices upstream of abstraction can impact on treatment performance. The drinking water safety plan (DWSP) approach is based on a risk assessment from source to tap and, while water suppliers take the lead in incorporating DWSPs, it is a key objective of the DWSP to identify that others have responsibilities towards ensuring the safety of water and for them to work with the water supplier on risk reduction, i.e. agriculture and forestry workers, landowners, other utilities, local government and consumers (WHO, 2011).

1.1.2 Ptaquiloside

In addition to concerns over NOM giving rise to DBP toxins, there is increased recognition and concern around toxins that occur naturally, such as the phytochemical ptaquiloside produced by bracken [*Pteridium aquilinum* (L.) Kuhn], and whether or not they can make their way to raw drinking water (Clauson-Kaas *et al*., 2016; O'Driscoll *et al*., 2016).

Bracken ferns have a vast array of diverse phytochemical armaments, which contain a substantial number of potentially harmful substances, including ptaquiloside (Figure 1.2). Phytochemical armament is an effective and widespread defence strategy in promoting direct vegetative survival, and it is a relatively new area of scientific interest that has become known only in the last 40 years. Ptaquiloside, a highly water soluble phytotoxin, was first isolated in 1983 and has been identified as having carcinogenic, mutagenic and clastogenic properties. Along with other natural phytotoxins, ptaquiloside is receiving increased attention from scientists and land use managers.

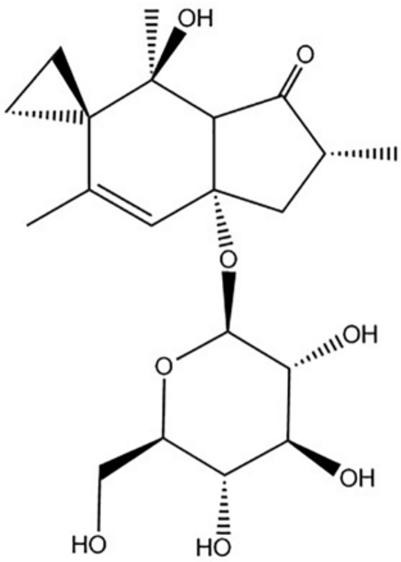


Figure 1.2. Chemical structure of ptaquiloside.

There is an urgent need to increase empirical evidence to understand the scale of phytotoxin mobilisation and its potential to enter the environment. Bracken ferns are classified by the International Agency for Research on Cancer (IARC) as "possibly carcinogenic to humans" and there has been limited evidence available to be able to adopt a health-based risk assessment approach.

1.2 Overall Project Aims and Objectives

The overall aim of the project was to quantify more accurately the risk of NOM, including the naturally occurring (organic) toxin, ptaquiloside, to surface water and groundwater supplies in Ireland. The main objectives of the project were to:

- identify high-risk catchments for public and private water supplies in relation to NOM across Ireland;
- undertake a surveying and monitoring programme in three high-risk catchments;
- estimate likely NOM concentrations in raw water sources in the selected catchments using predictive modelling under different climate change scenarios for the next 30 years;
- assess the risk of ptaquiloside to drinking water supplies;

- develop guidelines to reduce risk of NOM and ptaquiloside in drinking waters.

1.3 Literature Review

1.3.1 Natural organic matter and THMs

The term "natural organic matter" refers to a wide spectrum of carbon-based compounds that result from natural processes in the environment. It originates from living and dead plants, animals and microorganisms and from the degradation products of these sources (Chow *et al*., 1999). The presence of NOM causes many problems in drinking water treatment processes. In addition to aesthetic problems such as colour, taste and odour, it contributes to the fouling of membranes, serves as a precursor for the formation of DBPs, increases the exhaustion and usage rate of coagulant and disinfectant doses, and increases levels of complex heavy metals, adsorbed organic pollutants and possible toxins. In addition, certain fractions of NOM can promote microbial growth and corrosion in the distribution system.

The degree to which NOM affects water treatment processes is determined by its quality or character and quantity. NOM rich in aromatic structures has been found to be highly reactive with chlorine, with a higher potential to form DBPs (Reckhow *et al*., 1990). However, non-aromatic NOM can also form THMs (Fram *et al*., 1999). Large molecular hydrophobic humic substances are enriched with aromatic structures and are easily removed by conventional drinking water treatment consisting of coagulation, flocculation, clarification (CFC) and filtration. Low molecular weight hydrophilic and less aromatic NOM is more problematic to remove and is a major contributor of easily biodegradable organic carbon, which promotes microbiological regrowth in the distribution system. An understanding of the behaviour of different fractions or constituents of NOM present in water is crucial to understanding their fate and impact during water treatment and in water distribution systems. Therefore, accurate characterisation of NOM in raw water and along the treatment process would be an important basis for the selection of water treatment processes, monitoring of the performance of different treatment steps, and assessing distribution system water quality.

The structural composition of NOM is highly variable and depends mainly on the origin of the precursor material and the degree of modification it has undergone (Lankes *et al*., 2008). NOM, measured as DOC concentration and colour in stream water, has been shown to be positively correlated with catchment characteristics such as increasing percentage peat, presence of forestry and discharge being significant (Grieve and Marsden, 2001; Billett *et al*., 2004; Kortelainen *et al*., 2006; Austnes *et al*., 2010; Cool *et al*., 2014). Slope has been shown to be negatively correlated and, specifically, slopes of less than 5° significantly predicted stream water colour in catchments with multiple soil types (Mitchell and McDonald, 1995). This has been attributed to the slower rate of runoff and the extended period that the soil water has to dissolve organic matter on milder slopes. In addition, Parry *et al*. (2015) elaborated on this, adding that the majority of peatlands form the deepest and most well-developed deposits in flat terrain where the peatland is able to spread unimpeded over extended areas.

Temporal variation has also been reported, with significantly lower DOC concentrations from late winter and early spring to higher concentrations in autumn and early winter (Liu *et al*., 2014). However, high-resolution monitoring at an individual catchment scale demonstrated a higher level of complexity of the interactions between climate and land management (Ryder *et al*., 2014).

Apart from spatial and seasonal variability, a long-term upward trend in increases of riverine DOC concentrations has been identified and reported on an international scale (Fabris *et al*., 2008). International research collated over the past decade has indicated an increase in surface water DOC concentrations linked to global warming (Worrall *et al*., 2003; Freeman *et al*., 2004), which is amplified by decreasing atmospheric sulfur. Anthropogenic land management change can also significantly alter river carbon delivery and composition, potentially increasing organic material inputs to streams (Jones *et al*., 2001). In Scotland, DOC concentrations from wind farms established on peatland ranged from 2.9 $mg\,L^{-1}$ to 57.1 $mg\,L^{-1}$, with flux rates of 9.0 $g\,m^{-2}$ per year and 42.3 $g\,m^{-2}$ per year (Murray, 2012). Application of organic slurries to agricultural soils can also result in increased carbon losses to groundwater and surface waters (Murnane *et al*., 2016). The great seasonal variability and the trend towards elevated NOM concentrations present challenges for the water industry and water treatment facilities in terms of operational optimisation and proper process control (Fabris *et al*., 2008).

The operational classification of NOM present in raw water intended for drinking (i.e. humic/non-polar and non-humic/polar; Krasner *et al*., 1996) based on what is adsorbed (or not) on XAD resins (Malcolm and MacCarthy, 1992) is not widely accepted. Non-humic/hydrophilic fractions of NOM show some of the properties typically observed for classic humic fractions (Barret *et al*., 2000). Operationally defined aquatic humic substances can be divided into two main fractions: humic acids (insoluble at pH < 1) and fulvic acids (soluble at all pH levels). Aquatic humic substances typically account for ~50% of the DOC present in natural waters. Non-humic NOM consists of hydrophilic acids, proteins, amino acids, amino sugars and carbohydrates (Figure 1.3).

In addition, NOM can be characterised based on its source (Sharma *et al*., 2011):

1. allochthonous NOM – originating from decay of biomass (vegetative debris) and soil leaching (runoff) in the catchment and primary derivation of NOM (Brooks *et al*., 1999);
2. autochthonous NOM – originating from *in situ* sources (algae, phytoplankton and macrophytes) and related to photosynthetic activity and decay products of algal matter;
3. effluent organic matter – composed of drinking water NOM not removed during wastewater treatment in addition to soluble microbial products formed during biological treatment of wastewater.

NOM is initially characterised via the fractionation of total organic carbon (TOC) into operationally derived fractions of particulate organic carbon (POC) (≥0.45 μm particle size) and DOC (<0.45 μm) prior to direct measurement. Real-time NOM monitoring is possible via online UVA_{254}/UVT (ultraviolet absorbance at wavelength 254 nm/ultraviolet transmission)

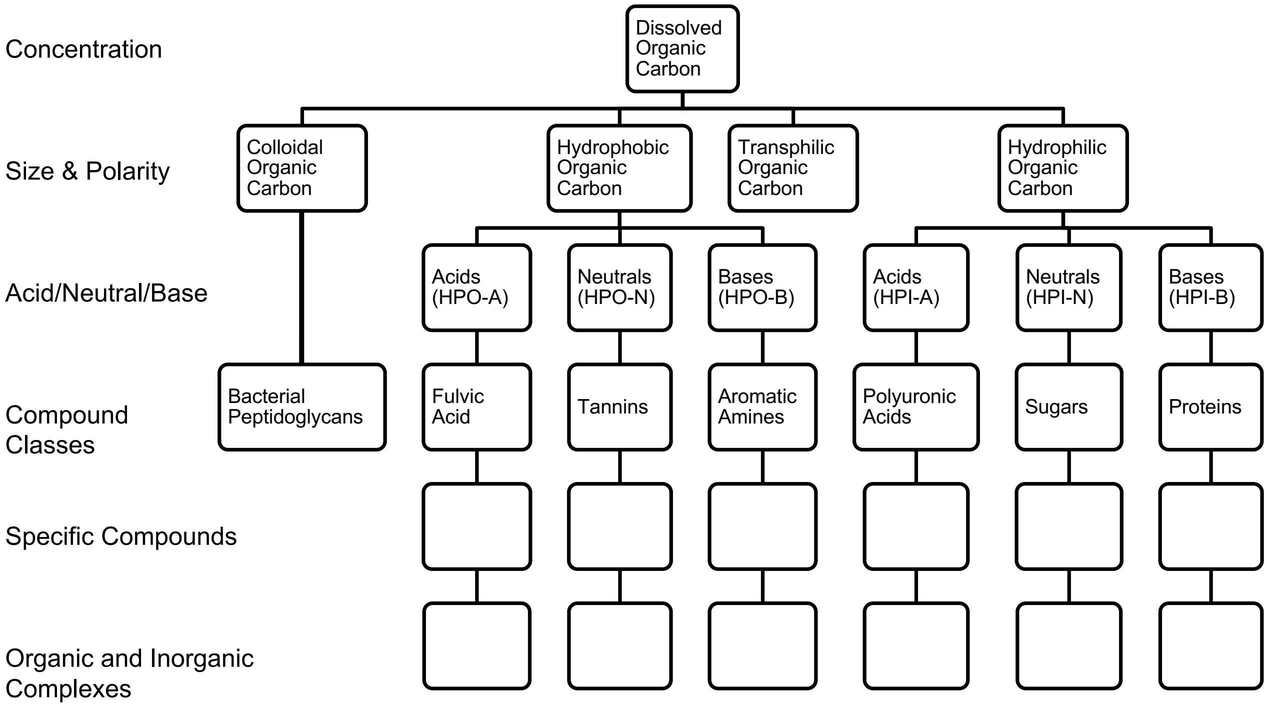


Figure 1.3. DOC fractionation diagram classifies DOC based on polarity (hydrophobic/hydrophilic), acid/neutral/base properties, compound class characteristics, specific compound characteristics and compound complex characteristics (Leenheer and Croue, 2003).

analysers. UVA_{254} provides an indication of the amount of aromatic and/or reactive NOM in water. Specific ultraviolet absorbance (SUVA) is defined as the ratio of UVA_{254} to DOC in a sample. SUVA of $\leq 2\,L\,mg^{-1}\,m^{-1}$ is indicative of non-humic NOM that has relatively low hydrophobicity, is less aromatic and is of lower molecular weight; SUVA of $2–4\,L\,mg^{-1}\,m^{-1}$ indicates a mixture of aquatic humics, hydrophobic and hydrophilic NOM and a mixture of molecular weights (Edzwald and Tobiason, 1999). Organic nitrogen, representing a small fraction of NOM in natural waters (Westerhoff and Mash, 2002), may also react with disinfectants to form carcinogenic nitrogenous DBPs (Richardson *et al.*, 1999).

Fluorescence excitation–emission matrix (F-EEM) spectroscopy has been used to distinguish different types and sources of DOC in natural waters and has gained popularity in recent years as a simple and relatively inexpensive, yet sensitive, approach (Baghoth *et al.*, 2011). F-EEM spectroscopy has been used to characterise DOC and identify humic- and protein-like fluorescent signals in water samples from different aquatic environments (Coble, 1996). F-EEMs coupled with PARAFAC (multi-way data analysis using parallel factor analysis; Stedmon *et al.*, 2003) can provide even more detailed information about NOM character. PARAFAC has been employed successfully to track the fate of problematic NOM fractions and to optimise the design and operation of drinking water treatment processes for their removal (Shutova *et al.*, 2014) as well as to indicate DOC source (Kraus *et al.*, 2010).

An understanding of the behaviour of different fractions or constituents of NOM present in water is crucial to understanding their fate and impact during water treatment and in water distribution systems. Furthermore, treatment processes are capable of changing the composition of NOM (Matilainen, 2007; Gonsior *et al.*, 2014).

Treatment methods used to remove NOM with varying degrees of success include but are not limited to (Baghoth, 2012):

1. Enhanced coagulation. Enhanced coagulation/optimisation of the conventional (CFC) treatment process by selection of appropriate types of coagulant, coagulant dosage and pH adjustment as determined by jar testing is recommended for hydrophobic and relatively high molecular weight NOM, as indicated by moderate to high SUVA values. Enhanced coagulation is less effective for the removal of intermediate and lower molecular weight organic matter (Volk *et al.*, 2000).
2. Ozonation and granular activated carbon (GAC). Ozonation degrades intermediate molecular weight organic carbon to low molecular weight organic carbon and is efficient when followed with an activated carbon filter (Matilainen, 2007). GAC filters remove NOM through adsorption and biological degradation. Ozonation oxidises organic carbon and, when placed upstream of GAC, extends the life of the activated carbon; since both processes have high capital and operating costs, careful economic analysis is required (Parsons and Jefferson, 2006).
3. Membrane filtration. Membrane filtration systems, i.e. ultrafiltration and nanofiltration, can be used to remove larger organic matter components left after coagulation, and certain dissolved NOM components. Ultrafiltration may be used to effectively remove larger molecular weight organic compounds but is limited by its molecular weight cut-off in effectively removing a significant fraction of lower molecular weight organic matter. Nanofiltration membranes could be used effectively for removal of NOM fractions that cannot be removed by ultrafiltration (Frimmel *et al.*, 2006). Nanofiltration following conventional treatment has been shown to be 100% efficient in removing high molecular weight organic carbon and the reduction in intermediate molecular weight was 52–100% depending on the membrane type. Reduction in low molecular weight organic carbon ranged between 43 and 79% (Matilainen, 2007).

THMs are the most prominent class of halogenated DBPs in treated water (Krasner *et al.*, 1989) and the only one regulated by the European Union (Drinking Water) Regulations (S.I. 122 of 2014). THMs are used as a surrogate for DBPs in many countries but do not give a true representation of the extent of DBPs present in drinking water (Krasner, 2009). Exposure pathways include oral, inhalation and dermal contact (Basu *et al.*, 2011). It has been estimated that prominent identifiable DBPs constitute only 50% of the total organic halogen formed during chlorination (Zhang *et al*., 2000). THMs have both genotoxic and carcinogenic effects, particularly in the liver and kidney (WHO, 2011). A parametric limit of 100 µg L^{-1} has been adopted in Europe and 80 µg L^{-1} in the United States.

In a joint position statement, the Health Service Executive (HSE) and the EPA echo the IARC's stance on chlorinated drinking water, which states that "chloroform and bromodichloromethane, two individual THMs, were classified as *possibly carcinogenic to humans* (Group 2B carcinogen – inadequate evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals)" (HSE and EPA, 2011). Risk evaluation must be balanced between disabling pathogens and creating harmful by-products. The European Union (Drinking Water) Regulations state that "any contamination from disinfection by-products is kept as low as possible without compromising the disinfection" (EU, 2014).

In Ireland, NOM is one of the main sources of environmental pollution of drinking water supplies. Concentrations of TTHMs exceeded 100 µg L^{-1}, the parametric value set by the Drinking Water Regulations (S.I. 278 of 2007), in 13% of all PWSs during 2012, where the figure for the public group water schemes was 39.7% (EPA, 2013). The majority of THM failures identified by the EPA were caused by either the absence of adequate treatment to remove organic matter or the presence of treatment that is incapable of removing high levels of organic matter (EPA, 2013). The highest TOC concentrations in raw water have been identified downstream of forestry catchments and lowland lakes (Ryan Hanley, 2012).

With numerous studies publishing results on DOC concentrations across much of northern and north-western Europe, process-based biogeochemical models of DOC are required to understand and predict the complex dynamics of organic carbon in soils and surface waters (Evans *et al*., 2005; Palmer *et al*., 2005; Futter *et al*., 2007). The Integrated Catchments Model for Carbon (INCA-C) (Futter *et al*., 2007) was the first model of DOC cycling to explicitly include the effects of different land cover types, hydrological flow paths, in-soil carbon biogeochemistry and surface water processes on in-stream DOC concentrations. Naden *et al*. (2010) combined the Generalised Watershed Loading Function hydrological model with a DOC model. Most DOC flux and modelling studies have been carried out in the context of catchment carbon balance and DOC concentrations, as opposed to fractions and composition of NOM.

1.3.2 Bracken and ptaquiloside

There is increased recognition of and concern about toxins occurring naturally in the environment. Bracken fern is the fifth most common weed species in the world. Bracken contains a diverse array of phytochemical armaments, present as a large number of potentially harmful substances, including ptaquiloside, illudane and protoilludane glycosides (Page, 2002). Bracken ferns are classified by the IARC as "possibly carcinogenic to humans". The majority of research into bracken toxins has focused on ptaquiloside (Ramwell *et al*., 2010). Human and animal populations are exposed to ptaquiloside through multiple routes (Vetter, 2009). Ptaquiloside – bracken's carcinogenic metabolite – is very soluble in water. It has been reported that bracken's contamination of local water supplies and cow's milk could cause gastric cancer (Vetter, 2009).

The percentage of land covered by bracken is reported to be trending upwards, with an average annual increase estimated at 1% of total land mass in the UK (Gil da Costa *et al*., 2012). The invasion of bracken is anticipated to be more aggressive considering that a ban on asulam, the mostly effective herbicide in bracken control used in the EU, came into effect in 2012 (Viney, 2012). In Ireland, percentage bracken coverage and its historical trend has not been researched or quantified. Holland and Alpin (2012) presented a super-resolution image analysis approach to monitoring bracken distributions in the UK incorporating 4 m IKONOS imagery and considering temporal changes and hard classifications using the freely available 30 m Landsat sensor imager (Woodcock *et al*., 2008).

In the UK, existing ptaquiloside data is limited (Ramwell *et al*., 2010) and there are no ptaquiloside data available for Ireland. There are only two reports quantifying ptaquiloside in UK bracken. Rasmussen (2003a) reported levels of ptaquiloside of between 50 µg g^{-1} fronds and 5900 µg g−1 fronds (average value of 1142 µg g^{-1} fronds) throughout the growing season in Scottish bracken. Smith *et al.* (1994) quantified the ptaquiloside content of bracken and found that the ptaquiloside content of British bracken was in the range of 447–1211 μg g^{-1}. There is limited empirical knowledge relating to the quantity of ptaquiloside that is available for leaching.

Rasmussen *et al*. (2003b) showed for the first time that ptaquiloside can be found in the soil layers beneath bracken stands, indicating that ptaquiloside is transferred from bracken to the underlying soil from where it may leach to surface- and groundwaters, impairing the quality of drinking water. Rasmussen *et al*. (2005) characterised the solubility, degradation and retention of ptaquiloside, reporting that leaching to the aqueous environment will be most extensive on sandy soils, which have pH > 4 and poor organic matter content and are exposed to high precipitation rates during cold seasons.

Clauson-Kaas *et al*. (2014) revealed unequivocally the presence of ptaquiloside and its degradation product pterosin B in groundwater and surface water. While ptaquiloside is regarded as "possibly carcinogenic to humans", pterosin B is not believed to be harmful. While concern has been raised about the ptaquiloside content in bracken spores and exposure via inhalation (Galpin *et al*., 1990; Alonso-Amelot and Avendaño, 2001; Tubridy, 2013), Rasmussen *et al*. (2013) reported a considerably low abundance of spores in breathing air under normal conditions and recommended that this exposure route is secondary to the milk and drinking water ingestion route.

Advances in testing methods have allowed the detection of low concentrations of ptaquiloside in groundwater and drinking water. In particular, a combination of methodologies from Jensen *et al*. (2008) and Fletcher *et al*. (2011) provides a robust and successful method for the detection of ptaquiloside and its degradation product pterosin B. The liquid chromatography–mass spectrometry/mass spectrometry (LC-MS/MS) method presented by Jensen *et al*. (2008) allows quantification of ptaquiloside and pterosin B in soil and groundwater samples at environmentally relevant concentrations and gives reliable identification because of the structure-specific detection method. Fletcher *et al*. (2011) showed that including a step that hydrolysises the ptaquiloside to pterosin B is essential for recoveries.

Furthermore, the gap in our knowledge of long-term effects makes rational decisions with regard to allowable levels of these substances a major problem. Recently, Ramwell *et al*. (2010) carried out a desk study to quantify the risk that ptaquiloside and other bracken toxins may pose to the quality of drinking water supplies in England and Wales using the PEARL model to predict the concentration of ptaquiloside in raw water. In Ireland, while bracken is included in the Habitat Survey Guidelines (Smith *et al*., 2011), limited abundance data exist and empirical knowledge is needed to quantify ptaquiloside and related bracken toxins in Irish surface- and groundwaters.

Ramwell *et al*. (2015) undertook a monitoring programme in eight water supplies in England and Wales (four private supplies and four public supplies). The catchments were selected based on the findings of a preliminary high-risk catchment study (Ramwell *et al*., 2010). The key findings of the monitoring programme were that there was no positive detection of ptaquiloside in any of the PWSs, although they had been identified as potentially high risk because of the dense bracken coverage in the catchment, the proximity of the bracken to the abstraction point and the pH of the water; ptaquiloside was expected to be stable because the water was in the range of pH 4 to < 8. Similarly, no positive ptaquiloside detections were identified at any of the four private water supplies, although they had also been identified as high risk because of the aforementioned factors and because of the absence of any water treatment. Ptaquiloside was detected in a feeder stream to a reservoir at one of the study sites; the maximum concentration per rain event was < 0.05–0.35 μg L^{-1} in three episodic rain events sampled in the autumn period. The presence of ptaquiloside in the small feeder stream, albeit absent in the raw water of the reservoir, was reported to demonstrate that in-stream dynamics, storage conditions and dilution may be important factors to consider in the absence of ptaquiloside in the reservoir.

2 High-risk NOM Catchment Maps

2.1 Approach

A desk study was carried out investigating the drivers of TTHM exceedances using routinely collected monitoring data for the period 2006 to 2013. Geographical information system (GIS) coordinates for the abstraction sources were obtained and further GIS datasets included soil data from the National Soil Dataset (from the EPA); the Derived Irish Peat Map (DIPM) (Connolly and Holden, 2009); long-term rainfall averages (LTAs) for Ireland (Walsh, 2012); the Digital Elevation Map for Ireland (from the EPA); and Irish Rivers and Lakes Segments (from the EPA). Groundwater vulnerability, derived by combining the two GIS layers of subsoil thickness and permeability, plus karst features where present, was obtained from www.gsi.ie (Misstear *et al*., 2009; Hunter Williams *et al*., 2013).

Four THMs – chloroform ($CHCl_3$), bromodichloromethane ($CHBr_2Cl$), dibrochloromethane ($CHBrCl_2$) and bromoform ($CHBr_3$) – were routinely measured in water samples taken from randomly selected taps in each water scheme by Irish local authorities or water suppliers in each county. The sum of the concentrations of the four individual THMs is the TTHM concentration. Only TTHM data were available for this study. The statutory limit for TTHMs for drinking water in Ireland is 100 $\mu g\,L^{-1}$ (EU, 2014). Water schemes differ by area, population size and volume of water supplied. Not all schemes are accounted for in the final dataset owing to lack of abstraction information. Repeated measurements from each scheme were averaged between and within years. Only schemes for which the water source did not change over the study period were included. For statistical analysis this left 684 water schemes serving 1,062,700.91 m^3 of water daily to a population of 2,289,539 (Figure 2.1). Of these, 270 schemes abstracted from surface water (serving 1,777,888) and 414 from groundwater (serving 511,651). The number of samples taken per scheme is determined by the amount of water provided and the size of the population served, in accordance with the European (Drinking Water) Regulations (EU, 2014). There are four supply types in Ireland, which for the purposes of this study were combined to form two levels: (1) private group water schemes (PGWSs) and private schemes form the level PRI; and (2) public group water schemes and PWSs form the level PUB.

2.1.1 High-risk catchment maps

The high-risk catchment maps were created by integrating geo-located data from three layers, which detailed information about presence of peat, yearly average rainfall and slope.

1. Extracted peat areas were combined with the rainfall layer to identify the peat areas with annual average rainfall greater than 1400 mm.
2. Mean slope has been reported to be a strong (and negative) determinant of DOC in high-NOM riverine systems (Cool *et al*., 2014; Parry *et al*., 2015). Defra (2005) classifies > 5.25% as moderate to high slope and catchments with slope < 5.25% were considered higher risk.
3. Schemes abstracting water from groundwater vulnerability classes extreme (E) and high (H), located in peat areas with annual average rainfall greater than 1400 mm and slope < 5.25% were considered high risk.

2.1.2 Statistical analysis

Further layers used in the statistical analysis were generated using the “tabulate intersection” tool in ArcGIS. The sub-catchment of each abstraction point was used to calculate the percentage area upstream of the abstraction point (Table 2.1). A general linear mixed model (GLMM) was fitted to study the effects on the response average TTHM of certain explanatory or input variables and possible interaction effects among these. As the number of observations was not the same for all schemes and as the variance of a sample mean depends on the sample size used, care must be taken to account for the heterogeneity of variance of the response for the various combinations of input variables used in the experiment; typically, this is achieved by using a weighted least squares analysis (e.g. with weights inversely proportional to the variances).

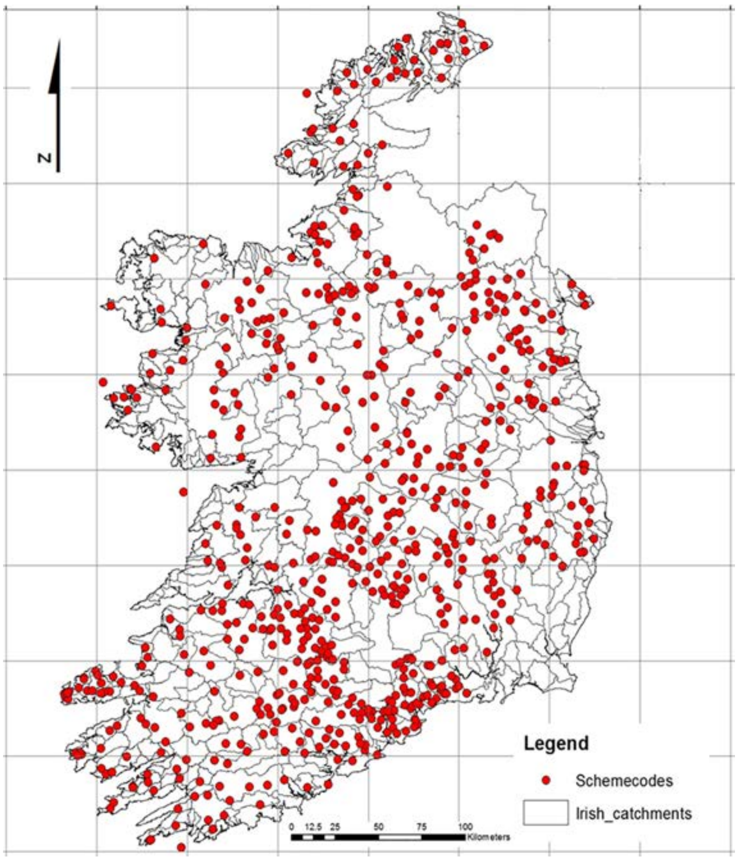


Figure 2.1. Map of Irish water schemes with the catchment boundaries used in the statistical analysis.

Table 2.1. Variables used to identify the drivers of TTHM concentrations

TTHM (μg L^{-1})	EPA
Treatment code	1 – no NOM treatment
	2 – treatment with some degree of NOM removal
Vulnerability	Surface water[a]
	High vulnerability (E and H)[a]
	Low vulnerability (M and L)[a]
Peat (%)	DIPM[b]
Forest (%)	CLC12[c]
Upland (%)	Land > 150 m[d]
Artificial surfaces (%)	CLC12[c]
Arable land (%)	CLC12[c]
Crops (%)	CLC12[c]
Pastures (%)	CLC12[c]
Heterogeneous (%)	CLC12[c]

[a] **Lee *et al.* (2008) and Hunter Williams *et al.* (2013).**

[b] **Connolly *et al.* (2009).**

[c] **Lydon and Smith (2014).**

[d] **Perrin *et al.* (2014).**

CLC12, Corine Land Cover Class 12.

Residual diagnostics were conducted to examine any violations of assumptions underlying the linear model that are needed to justify the analysis. These assumptions include the linearity of the model (relating the response to the explanatory variables), the normality of the response at each combination of values of the input variables, the homogeneity of variances of these responses and the independence of the responses. While normality was not crucial in the present study because of the reasonably large sample size available ($n = 684$), where other violations occurred, transformations of the response were conducted in addition to the possible weighting alluded to above.

The choice of transformations of average TTHM applied were guided by a Box–Cox procedure. Statistical analyses were conducted with IBM SPSS Statistics v22.0 software (IBM Corp., 2013) and Minitab 17 Statistical Software (2010), and graphical representations were conducted in R (R Core Team, 2008).

At each stage of the model-fitting process diagnostics were performed on the adequacy of the fitted model.

Addressing violations of assumptions, along with large variance inflation factors (VIFs) caused by high correlation among many pairs of input variables, while endeavouring to produce a parsimonious model, resulted in many competing fitted models. These models varied according to the input variables included, and differed according to a number of criteria commonly used to assess the appropriateness of a model and to compare various competing models. The choice of variables to include in a model was initially guided by best subset regression followed by various stepwise regression routines. Criteria for the evaluation of the resulting model included a variety of residual plots (including a plot of residuals versus fitted values for each potential model), statistical tests including a test of homogeneity of variances, and various criteria such as R^2, R^2 adjusted for degrees of freedom (R^2-adj), R^2 predicted (R^2-pred), Mallow's C_p, VIFs and p-values associated with each input variable included in the model.

A GLMM allowed the response to be modelled as a function of covariates along with fixed and random factors. In this study, most river basins in Ireland were sampled and “Basin” was not included as a random factor directly because of loss of degrees of freedom. It was not our objective to compare basins, only to adjust the analysis for possible within-basin correlation period.

2.2 Findings

2.2.1 High-risk catchment maps

The results of the high-risk catchment exercise demonstrated that surface water and groundwater drinking water sources most at risk of TTHM exceedances occur on the west coast of Ireland (Figure 2.2). In Ireland, peat soils cover 20% of the national land area (Connolly and Holden, 2009) and contain more than 75% of the national soil organic

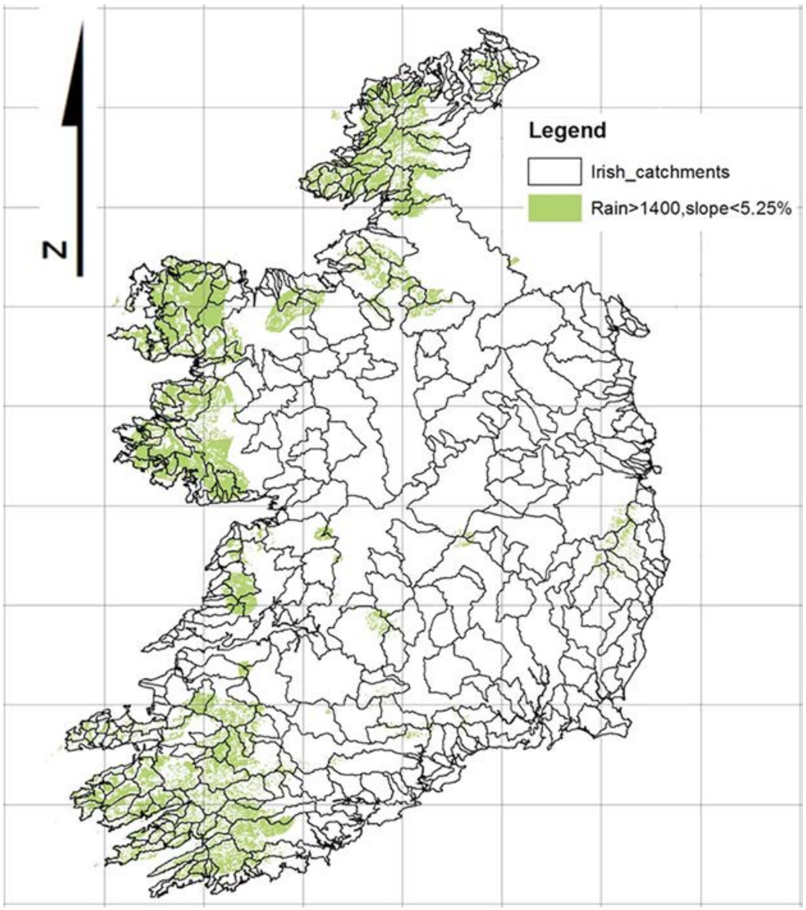


Figure 2.2. Surface water and groundwater sources in peat areas with slope < 5.25% (O’Driscoll *et al.*, 2017a).

carbon (SOC). The association between peat soils and TTHMs, as highlighted by the high-risk catchment maps, is in agreement with the general consensus that water draining upland catchments with organic-rich soils receive large quantities of NOM (Mitchell, 1991).

When the TTHM results were overlaid on top of this high-risk catchment map, a correspondence between TTHM results and the high-risk catchments was observed (Figure 2.3).

This output suggests that this desk-based GIS approach can be used to indicate the spatiality of TTHM exceedances. Some select areas, i.e. the south-east and the mid-north-west, were highlighted by the TTHM map and showed no correspondence with the high-risk catchment map. This highlights to a degree that, while rainfall and peat are important contributory factors in explaining higher national TTHM values, variables other than those selected for the high-risk categories are driving TTHM concentrations.

2.2.2 *Statistical analysis*

A total of 684 schemes were included in the statistical analysis. The average TTHM concentration was 32.66 ± 35.74 µg L^{-1}. Taking all possible input variables into consideration, the chosen fitted model included main effects of Peat_perc, Pastures_perc, Treatment type (Treatment 1 and 2), Vulnerability (set at High, Low and Surface water) and interaction terms Peat*Pastures_perc, Pastures*Forest_perc and Peat_perc*Treatment type. This model is shown in Table 2.2 and, for clarity, gives the fit separately for each combination of the Treatment type and Vulnerability. This model explained 62.9% of the variation in the data (R^2), with only slight deviations for R^2-adj (62.42%) and

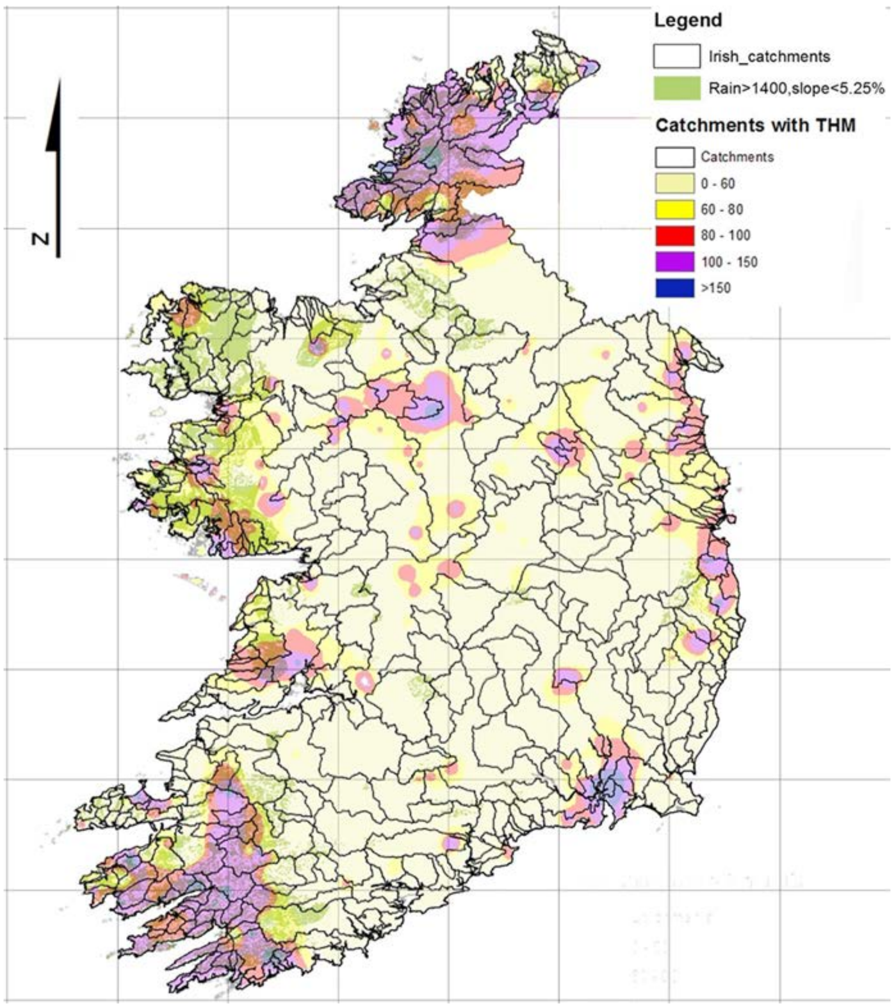


Figure 2.3. Surface water and groundwater sources in peat areas with slope < 5.25% and annual average rainfall > 1400 mm and with corresponding TTHM concentrations overlaid (O'Driscoll *et al.*, 2017a).

Table 2.2. Model of TTHM concentration (µg L^{-1}) for each level of treatment (*p*-values associated with each coefficient in the model are significant at the 5% level of significance)

Factor combinations	Equation
Treatment 1 and High vulnerability	$TTHM_{0.2} = 1.4575 + 0.001956 \times Peat\_perc - 0.001193 \times Pastures\_perc + 0.000055 \times Peat\_perc*Pastures\_perc - 0.000103 \times Pastures\_perc*Forest\_perc$
Treatment 1 and Low vulnerability	$TTHM_{0.2} = 1.4931 + 0.001956 \times Peat\_perc - 0.001193 \times Pastures\_perc + 0.000055 \times Peat\_perc*Pastures\_perc - 0.000103 \times Pastures\_perc*Forest\_perc$
Treatment 1 and Surface water	$TTHM_{0.2} = 1.9740 + 0.001956 \times Peat\_perc - 0.001193 \times Pastures\_perc + 0.000055 \times Peat\_perc*Pastures\_perc - 0.000103 \times Pastures\_perc*Forest\_perc$
Treatment 2 and High vulnerability	$TTHM_{0.2} = 1.7766 - 0.000332 \times Peat\_perc - 0.001193 \times Pastures\_perc + 0.000055 \times Peat\_perc*Pastures\_perc - 0.000103 \times Pastures\_perc*Forest\_perc$
Treatment 2 and Low vulnerability	$TTHM_{0.2} = 1.8122 - 0.000332 \times Peat\_perc - 0.001193 \times Pastures\_perc + 0.000055 \times Peat\_perc*Pastures\_perc - 0.000103 \times Pastures\_perc*Forest\_perc$
Treatment 2 and Surface Water	$TTHM_{0.2} = 2.2931 - 0.000332 \times Peat\_perc - 0.001193 \times Pastures\_perc + 0.000055 \times Peat\_perc*Pastures\_perc - 0.000103 \times Pastures\_perc*Forest\_perc$

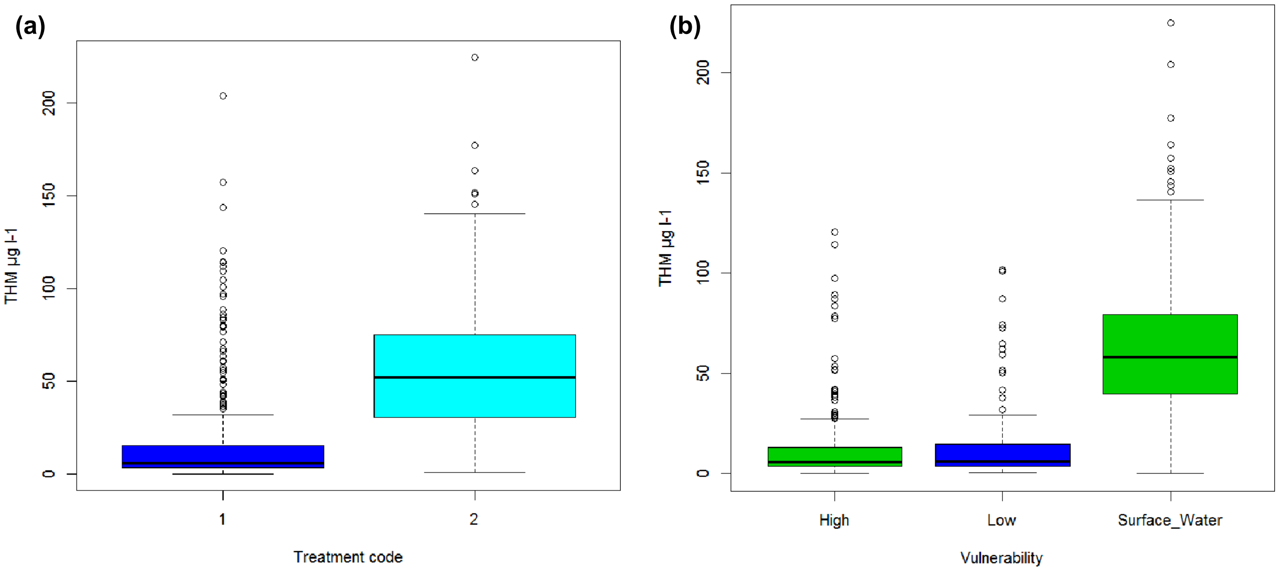


Figure 2.4. Comparison of average THM concentrations (µg L^{-1}) at each level of (a) treatment code (level 1 – absence of adequate treatment to remove organic matter; level 2 – treatment with some degree of NOM removal) and (b) vulnerability (high, low and surface water) before the effects of other variables were removed.

R^2-pred (61.72%). Mallow's C_p (7.6) was very close to the number of included variables in the model (i.e. seven variables).

Treatment type was highly significant in explaining variation in the data. Four hundred schemes had treatment plants that could be defined by "absence of treatment to remove organic matter" (Treatment code – level 1) and 284 schemes were defined by "treatment with some degree of NOM removal" (Treatment code – level 2). Treatment 2 gave significantly higher average TTHMs than Treatment 1, suggesting that a greater proportion of schemes have treatment, but the designs did not consider the quantity or character of NOM in the raw water (Figure 2.4a). Two hundred and seventy schemes abstracted water from surface water, 296 from groundwater with High vulnerability and 118 from groundwater with Low vulnerability. Schemes with surface water sources had significantly higher average TTHM concentrations than schemes with High or Low vulnerability sources (Figure 2.4b). Surface water is susceptible to runoff from land management activities with typically higher NOM and consequently higher TTHM concentrations than groundwater (Keegan *et al*., 2001).

Statistical analysis showed that Peat_per cent in the catchment above the abstraction point was a strong (and positive) determinant of average TTHMs at Treatment code level 1. These water supplies essentially chlorinate abstracted water for disinfection purposes. Numerous studies have demonstrated that DOC concentrations are positively correlated with the size of the soil carbon pool and are highest in organic soil pore waters and freshwaters draining wetlands and peatlands, especially where runoff is low (Eckhardt and Moore, 1990; Evans *et al*., 2005). Kothawala *et al*. (2015) showed that land cover alone explained 49% of the variability in dissolved organic matter (DOM) composition in comparison with 8% seasonal fluctuations in a study in north-central Sweden. POC exports from peatlands are considered small, but exceptions occur in areas with steep topography, high precipitation and bare peat (Worrall *et al*., 2011; Evans *et al*., 2016). DOC is a measure of individual organic compounds in the dissolved state and is chemically more reactive than POC. In general POC represents a minor fraction (< 10%) of TOC (Thurman, 1985). In agreement with Liu *et al*. (2014) the variable Forest did not show any significant effects; however, historically forests in Ireland were for the most part planted on peat (44% of all state-owned forestry).

Pastures_per cent was shown to be a strong (and negative) determinant of average TTHMs for all combinations of treatment type and vulnerability (Table 2.2). Well-drained soils have been shown to be negatively related to DOC concentrations (Liu *et al*., 2014). Aitkenhead-Peterson *et al*. (2007) observed that spring DOC export was negatively correlated with both the percentage cover of arable land and the sum of improved and rough grass in stream catchments in Scotland. Similarly, the interaction term Pastures_perc × Forest_perc was also shown to be a negative (and weak) determinant of average TTHMs for all combinations of treatment type and vulnerability (Table 2.2). In Ireland, 90% of forests were planted during the late 20th century and sites were cultivated by ploughing (O'Driscoll *et al*., 2014), thus increasing the rate of runoff and reducing the potential for DOC leaching.

The interaction Peat_per cent × Pastures_perc was a positive (and weak) determinant of average TTHMs for all combinations of treatment type and vulnerability (Table 2.2). This finding highlights the importance of agricultural catchments in considering sources of NOM. Land disposal is the primary and traditional method of recycling animal manures. Manure spreading can produce an excess of nitrate and phosphate (Jardé *et al*., 2007), and nitrogen enrichment is a likely mechanism for increased autochthonous activity in agricultural streams (Wilson and Xenopoulos, 2009), ultimately contaminating receiving waters. Intensification of agricultural practices to meet government food production goals has led to an over-application of animal manures to soils (Wilson and Xenopoulos, 2009).

3 NOM Case Studies

3.1 Overview

Three study sites were selected using a multi-criteria approach to further examine TTHM exceedances in schemes that had some level of NOM removal (treatment level 2 as opposed to treatment level 1, where the raw water received no pre-treatment and was disinfected only). The selection of catchments aimed to cover the range of geological, climate, geology, land use and pressures, accessibility, availability of data, existing instrumentation and any prior research undertaken in the catchments. The final schemes selected included two water treatment plants (WTPs) from PWSs in Counties Louth and Galway and a PGWS in County Mayo.

3.1.1 Study sites

Galway PWS

A PWS abstracting from a spring source was chosen as it is located in a vulnerable karst area with a history of TTHM exceedances (Figure 3.1). The zone of contribution (ZoC) for this source had been mapped as part of a desk study, although cautions were highlighted (EPA, 2011). In order to estimate a potential ZoC a staff gauge was installed at the sister spring in December 2014. A rating curve was developed using spot flow measurements at a range of flows. This exercise established that, while the PWS spring had a discharge of ~600 m^3 per day, the sister spring adjacent to the abstraction spring had a

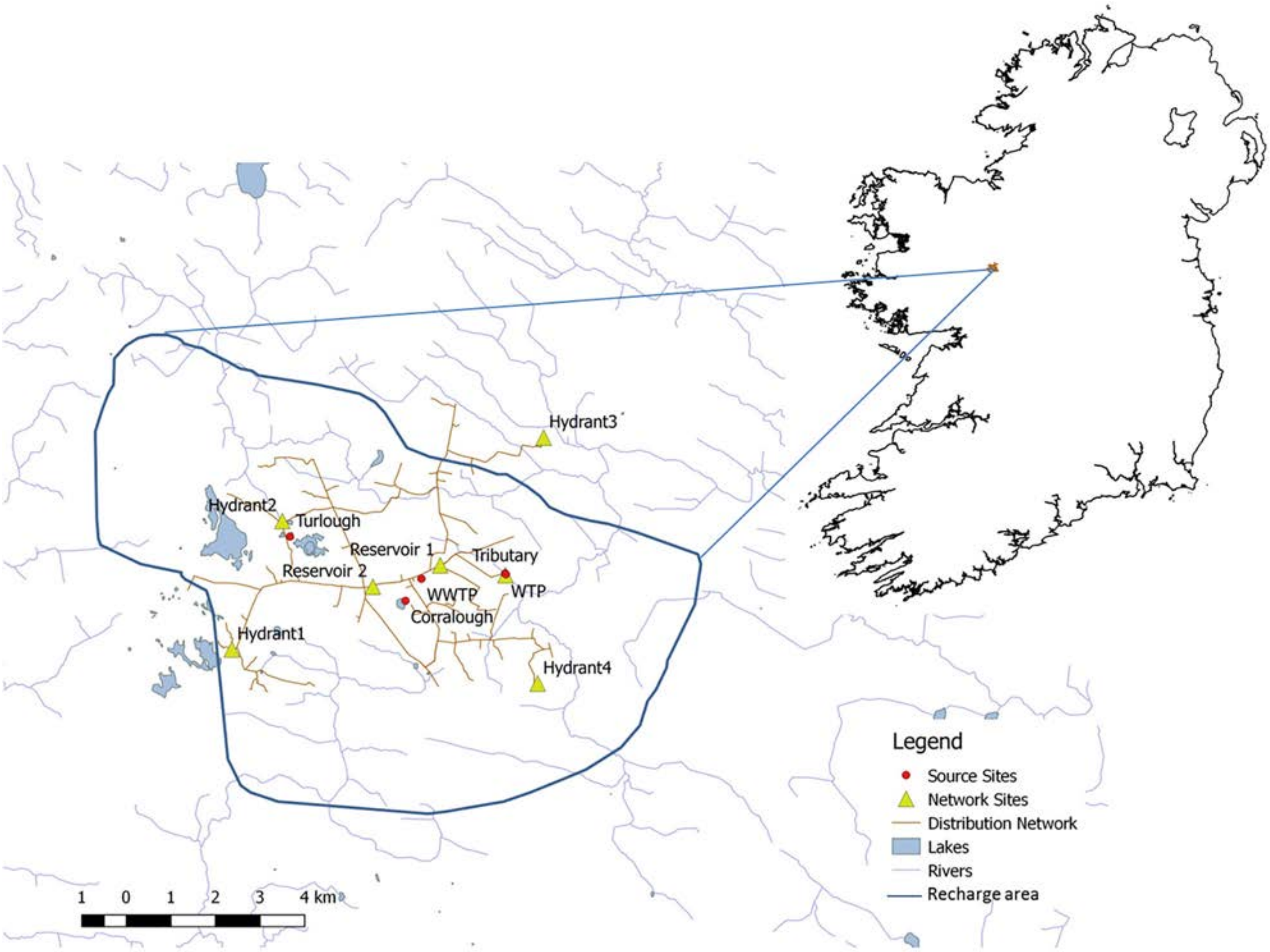


Figure 3.1. Sampling locations for Galway PWS.

discharge of ~19,000 m^3 per day. Using topography, nutrient and metal concentrations and the integration of recharge coefficients, a reasonable and justifiable catchment size was estimated to be ~24 km^2. Water samples were collected at five locations within a 4 km^2 vicinity of the spring: a wetland, a turlough, a small stream, a sister spring and the outlet of a sewage treatment plant. Water samples were also taken from different points along the treatment process and at eight locations along the distribution network (raw, post ozone and post GAC), before and after both reservoirs and at four of the network extremities (Figure 3.1). The treatment train consisted of ozonation, GAC, UV and chlorination. The GAC, which was installed in late 2011, had never been replaced or reconditioned.

Mayo PGWS

A PGWS abstracting from a lowland lake was chosen, as it has a combination of peat presence and agricultural land use in the catchment and has a history of TTHM exceedances. Treatment is by ultrafiltration membranes followed by chlorination. Samples were collected from nine locations in the catchment and three points along the treatment train (i.e. raw water, treated water and one location in the network) (Figure 3.2). The catchment is approximately 17 km^2 in size with approximately 80% agricultural land and 14% peatland. Annual rainfall is typically 1300 mm.

Louth PWS

A PWS abstracting from a low-lying river was chosen, as it has multiple pressures, i.e. peat extraction, municipal WTPs and intensive agriculture. This supply also has a history of TTHM exceedances. Treatment is by alum sulfate coagulation, clarifiers, rapid gravity filter and chlorination. Samples were collected from 12 locations in the catchment and four points along the treatment train (i.e. raw water, settled water following clarification, treated water and at one location further down the network) (Figure 3.2). The catchment

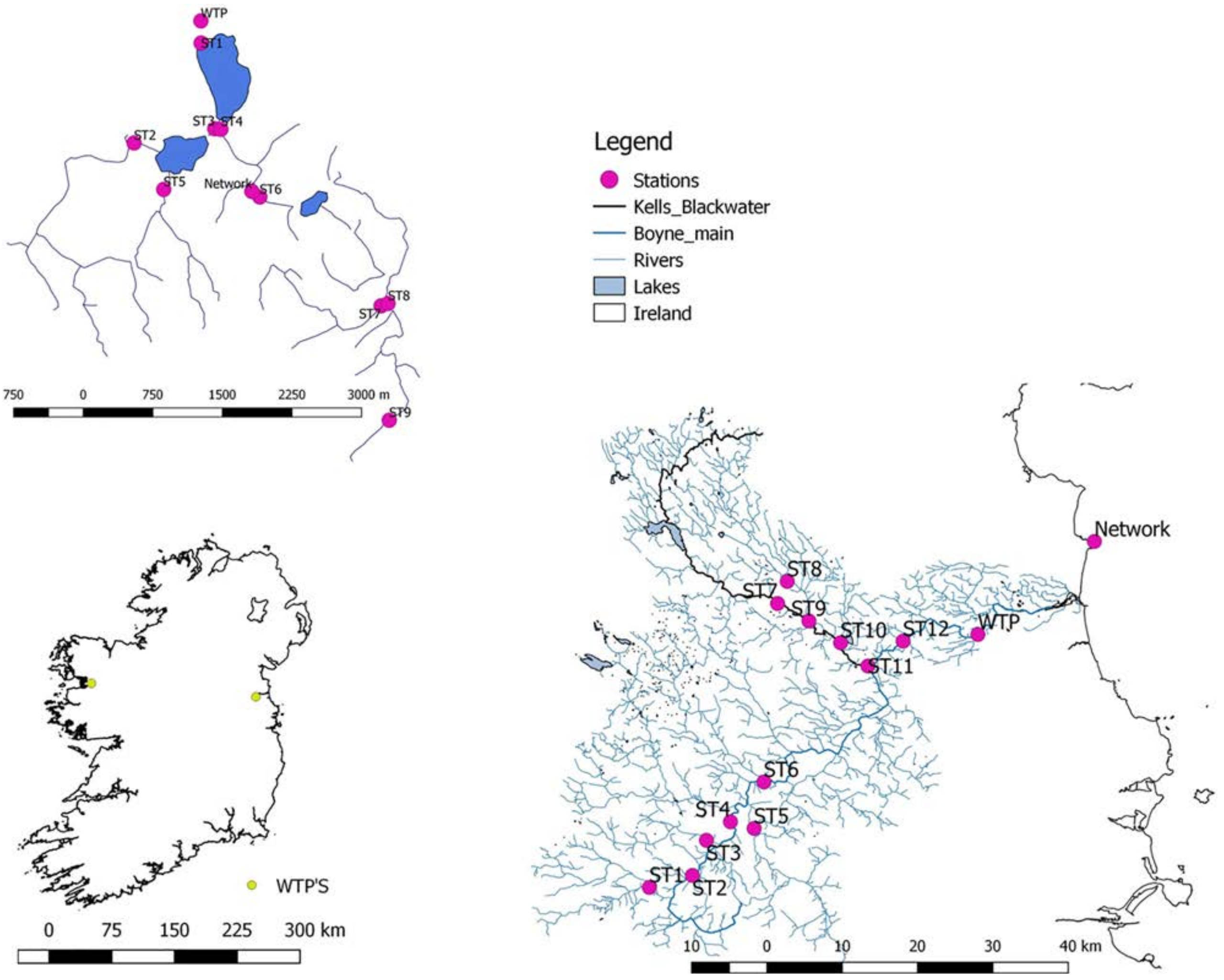


Figure 3.2. Sampling locations for Mayo PGWS (top left) and Louth PWS (bottom right).

is approximately 2480 km^2 in size with about 80% agricultural land and 6% peatland. Annual rainfall is typically 800 mm.

3.1.2 *Sampling and analyses*

Samples were collected in pre-labelled, sterilised polypropylene bottles and kept cold and in the dark during overnight delivery to the National University of Ireland, Galway, where they were analysed within 72 hours or filtered through 0.2 µm sterilised syringe filters and stored at –20°C until further analysis. Subsamples taken in glass vials with septa lids and sodium thiosulfate, and were sent to an external accredited laboratory (CLS Connemara, Galway, Ireland) for analysis of THMs. Each of the water samples was analysed using fluorescence spectroscopy, UV absorbance spectroscopy, soluble reactive phosphorus (SRP), total nitrogen (TN) and DOC analysis as follows: DOC and TN concentrations were determined using a TOC Analyser (BioTector Analytical Systems Ltd, Cork, Ireland). UV absorption data were obtained for UVA$_{254}$ absorbance measured using a UV-visible spectrophotometer (Cary 50, Agilent Technologies) using a quartz sample cell with a path length of 10 mm. SRP was measured using a Konelab 20 Analyser (Konelab Ltd, Finland). Major cation and trace metal analyses were performed using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer ELAN DRCe, Waltham, USA) in a Class 1000 (ISO Class 6) cleanroom in the Chemical Monitoring Facility at the National University of Ireland, Galway.

Principal components analysis (PCA) was used to investigate the relationships between the hydrochemical indicators. PCA is a method of data reduction. It attempts to replace the original variables (typically standardised, see Reimann *et al*., 2008) with a smaller set of principal components (PCs), each of which is a linear combination of the original variables. These PCs are constructed to have decreasing variance, to be mutually orthogonal and to be such that the sum of their variances is equal to the sum of the variances of the original variables. The sample PCs extracted are estimates of the corresponding population PCs. The relationship of the variables with a given direction of maximum variance (i.e. a PC) can be visualised with a biplot. The length of the arrows represents the variability explained in two PCs and the angle between two arrays indicates their correlation (Reimann *et al*., 2008). PCA was conducted with IBM SPSS Statistics v22.0 software (IBM Corporation, 2013) and graphical representation was performed using CANOCO 4.1 (ter Braak and Šmilauer, 1998).

F-EEMs were obtained using a 1-cm path length quartz cuvette (Starna, Australia) and a Horiba Aqualog (Kyoto, Japan). A 0.1 s integration time was used during the measurement of emission at 200–625 nm and excitation at 240–600 nm. The CCD gain was set to medium. Inner filter effects (IFE) and first- and second-order Rayleigh scattering were removed using the included Aqualog software (v3.6.10) . The area of the Raman peak (350 nm excitation) was used to normalise the fluorescence intensity of all spectra, which are expressed in Raman units (RU) (Lawaetz and Stedmon, 2009; Murphy *et al*., 2010).

PARAFAC modelling

Analysis of the spectra was carried out using the drEEM toolbox (Murphy *et al*., 2013) for MATLAB (Mathworks) software for PARAFAC. The methodology presented by Murphy *et al*. (2013) was followed to determine an adequate PARAFAC model. The processed data (blank subtraction, Rayleigh and Raman scatter regions removed, Raman normalisation and IFE corrections) were imported into MATLAB. Regions were smoothed using the drEEM interpolation functions. The fluorescence signals were then normalised to reduce the leverage of extreme values for the purposes of developing a PARAFAC model and the normalisation process was reversed after validation. To establish a robust PARAFAC model, several samples were identified as outliers through observation of sample leverages on the model. The validity of the PARAFAC model was established through several approaches. Spectral loadings of the components were observed to conform to general guidelines of how organic fluorophore signals appear (e.g. only one emission peak and no abrupt changes in loadings with wavelength). Residuals, calculated as the difference between the modelled and measured spectra, were generally random with few minor peaks. Split-half validation was also carried out based on a randomised split of the dataset into six equal parts to form three unique comparisons of dataset halves. For each unique half (combination of two splits), an independent PARAFAC model was developed and the components were found to be identical for all combinations as well as for the overall model. Finally comparison of the resulting PARAFAC components with the OpenFluor database (Murphy *et al.*, 2014) also provides some indication of model validity. After reversal of the fluorescence normalisation, results from the model were reported as F_{max} values in RU.

3.2 Findings

3.2.1 Galway PWS

Meteorological observations

The mean air temperature from a nearby Met Éireann weather station (circa 12 km south of the study site) was 8.7°C during the study period, varying from a daily minimum of 1.1°C to a daily maximum of 18.5°C.

Average monthly precipitation was 100 mm with two extremely dry months observed in September 2014 and June 2015 and one extremely wet month in December 2015 (Figure 3.3). The number of wet days [> 1 mm of precipitation/day (Hundecha and Bárdossy, 2005)] recorded over the study period was 342 (1/8/2014 to 30/4/2016; 689 days) and the mean daily precipitation was 3.3 mm (Figure 3.3).

Raw water observations

Mean estimated stream discharge over the observation period (12/11/2014 to 22/07/2015) was 20,559 m^3 per day, with a minimum of 11,163 m^3 per day and a maximum of 34,497 m^3 per day (Figure 3.4). The maximum change in recorded water level over the observation period was ~100 mm throughout the winter and 50 mm throughout the summer.

DOC concentrations in the raw water varied between 3.84 mg L^{-1} and 11.40 mg L^{-1} with an average of 5.95 mg L^{-1} (Figure 3.5). In general a seasonal trend could be observed, with DOC concentrations increasing by 2 mg L^{-1} from summer to winter with the exception of July and August 2015. The highest DOC concentrations were observed in July and August 2015 following the drought period in June 2015. DOC concentrations plotted against temperature showed no correlation. DOC concentrations plotted against precipitation gave a strong positive correlation ($R^2 = 0.7611$).

DOC concentrations from around the potential catchment varied. The wetland site showed the highest concentrations (max. 20.46 mg L^{-1} in September 2015) and the raw water site had the lowest concentrations overall (Figure 3.6). There was temporal variation at sites also between sampling occasions demonstrated by the high standard deviations at the wetland and tributary sites (Figure 3.6).

The metals analysed in this study were Ca, K, Mg, Na, Si, Sr, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Pb, Sb, Se, Sn, Ti, V and Zn (Table 3.1). All concentrations detected in the water samples were lower than the World Health Organization (WHO) permissible limits. PCA ordination results showed that 62.4% of water chemistry variance was explained (21.4% on axis 1, with a further 17.4% explained on

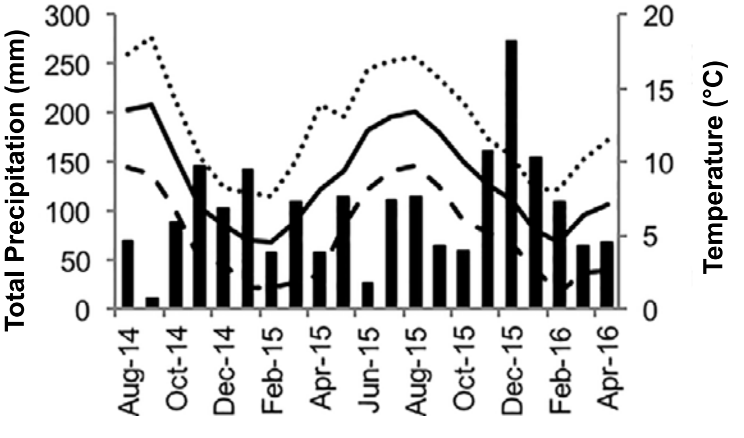


Figure 3.3. Precipitation (*y*-axis) and temperature (*z*-axis). Mean temperature, continuous black line; maximum temperature, dotted line; and minimum temperature, dashed line.

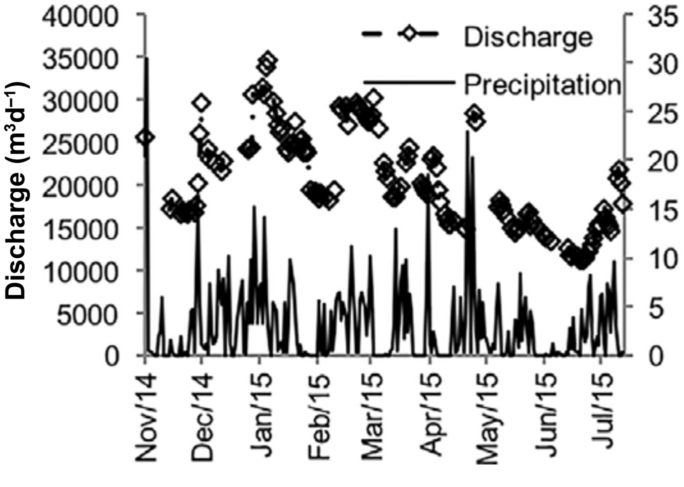


Figure 3.4. Discharge and precipitation.

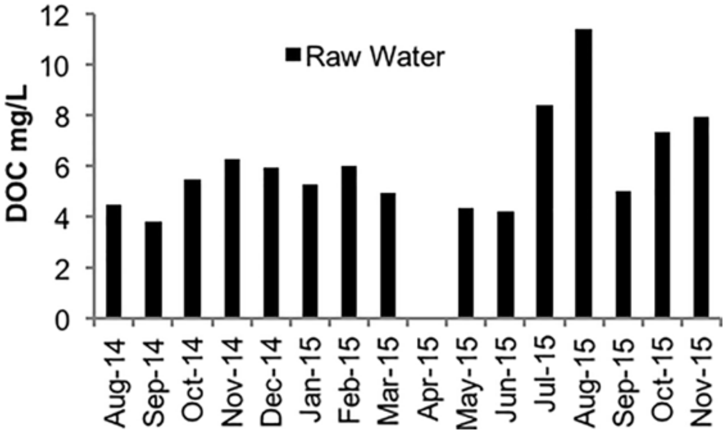


Figure 3.5. Raw water DOC for the study duration.

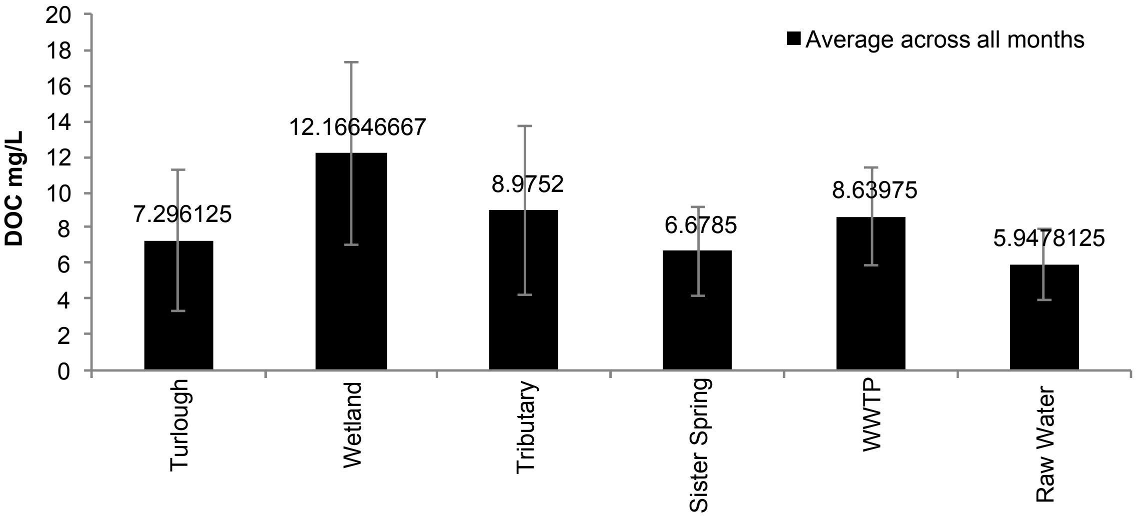


Figure 3.6. Average DOC across all months. WWTP, wastewater treatment plant.

Table 3.1. Concentrations of metals during study duration (*mg L–1; **µg L–1)

	TIC*	TOC*	TN*	UVA_{254}	Ca*	K*	Mg*	Na*	Si*	Sr*
Turlough	46.2	7.30	0.72	0.1646	0.816	0.019	0.065	0.080	0.016	0.004
Wetland	36.0	12.2	0.69	0.3798	0.765	0.048	0.046	0.117	0.021	0.004
Tributary	67.4	10.2	1.38	0.3674	0.851	0.021	0.037	0.075	0.014	0.003
Sister spring	65.1	6.68	1.28	0.2144	0.841	0.020	0.049	0.073	0.014	0.003
WWTP	56.4	8.64	5.08	0.1913	0.626	0.062	0.036	0.255	0.017	0.003
Raw	65.3	5.95	1.62	0.2040	0.832	0.020	0.050	0.081	0.014	0.003
	Al**	**As****	**B****	**Ba****	**Cd****	**Co****	**Cr****	**Cu****	**Fe****	**Mn****
Turlough	0.0741	0.0051	0.1071	0.0739	0.0004	0.0018	0.0011	0.0105	0.3483	0.2264
Wetland	0.0593	0.0047	0.0672	0.0731	0.0002	0.0012	0.0015	0.0129	0.2510	0.4047
Tributary	0.0850	0.0040	0.0649	0.0490	0.0002	0.0015	0.0015	0.0056	0.5311	0.1856
Sister spring	0.0707	0.0068	0.1206	0.0911	0.0003	0.0020	0.0019	0.0113	0.4766	0.1017
WWTP	0.0412	0.0046	0.1183	0.0286	0.0001	0.0012	0.0009	0.0148	0.3497	0.1979
Raw	0.0817	0.0070	0.1167	0.0814	0.0003	0.0019	0.0034	0.0187	0.4707	0.0625
	Mo**	**Nb****	**Ni****	**Pb****	**Sb****	**Se****	**Sn****	**Ti****	**V****	**Zn****
Turlough	0.0064	0.0005	0.0352	0.0007	0.0003	0.0020	0.0058	0.0040	0.0024	0.0941
Wetland	0.0049	0.0004	0.0227	0.0004	0.0005	0.0015	0.0105	0.0047	0.0042	0.0744
Tributary	0.0031	0.0002	0.0261	0.0004	0.0002	0.0017	0.0037	0.0032	0.0032	0.0298
Sister spring	0.0074	0.0004	0.0459	0.0008	0.0004	0.0023	0.0049	0.0045	0.0033	0.0470
WWTP	0.0058	0.0004	0.0195	0.0005	0.0008	0.0014	0.0035	0.0243	0.0028	0.1837
Raw	0.0065	0.0004	0.0467	0.0013	0.0004	0.0024	0.0047	0.0047	0.0034	0.0851

WWTP, wastewater treatment plant.

axis 2, 13.8% on axis 3 and 9.8% on axis 4) (Figure 3.7).

There are three main groupings of samples, the first at the top of the graph (dominated by wetland samples), the second on the left hand side (dominated by raw water, turlough and sister spring samples) and the third on the right hand side of the graph (dominated by the WTP samples), indicating that the qualities of the raw and sister spring water samples are most similar to those of the turlough samples, with lower DOC. In lowland karst regions underground water flow occurs through the epikarst and consequently discharges to springs, turloughs and streams and, as a result, surface and underground flow systems are highly connected (Hickey, 2009). As can be seen from the PCA biplot, the first PC (*x*-axis) is determined by DOC, Ba, Mn, Si and Mg. On the other hand, the second PC axis (*y*-axis) is determined by Ca and Mg, which have an internal origin (bedrock dissolution) and by elements related to anthropogenic activities such as Na and Se, which mostly have external origins. With regard to the sites, the raw water is most similar to the adjacent sister spring and the turlough except for on three occasions following high rainfall when all sites become quite similar as the water table rose and land became flooded.

Fluorescence analysis

Exploratory analysis highlighted outliers, which were removed from the dataset in order to facilitate the modelling process and the model validation using the split-half method; otherwise, the dataset would need to contain a sufficient number of the unique samples, which are evenly divided between the split halves. An outlier contained either instrument error or was for some reason very different from the others. PARAFAC was applied to a dataset of 203, encompassing 15 sampling dates and 17 sampling locations (five in the potential ZoC, three along the treatment process train and nine along the distribution network). A four-component model (C1–C4) was established based on several diagnostic criteria and random split validation. The loading values for the four components are shown in Figure 3.8.

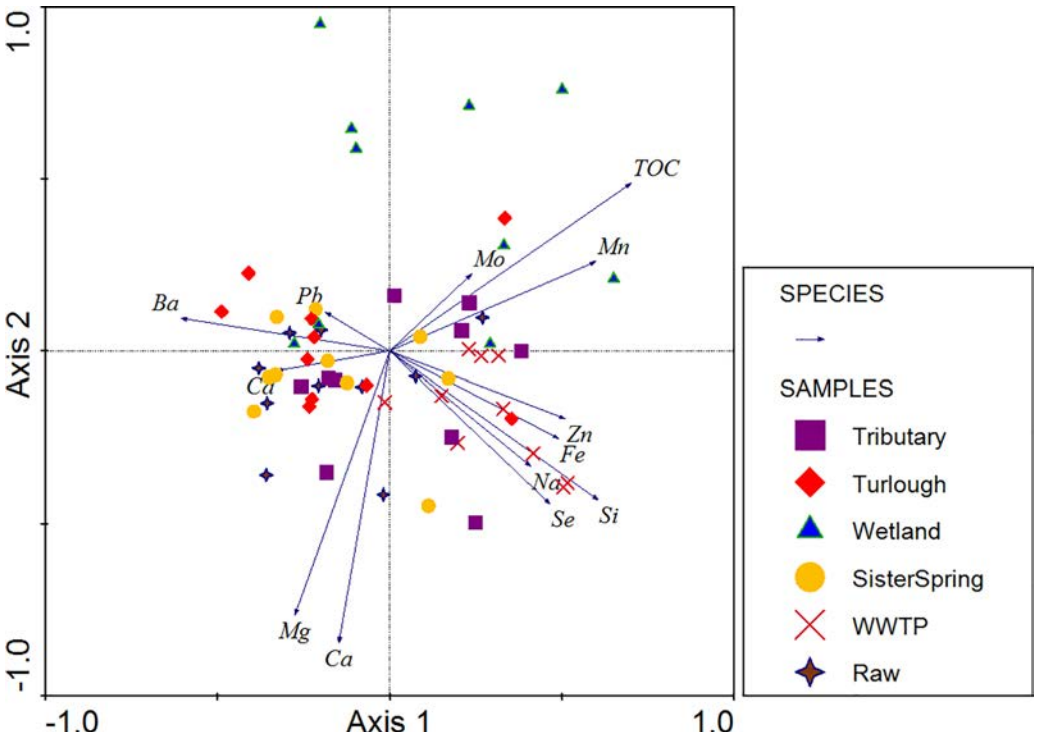


Figure 3.7. PCA ordinations of chemicals. WWTP, wastewater treatment plant.

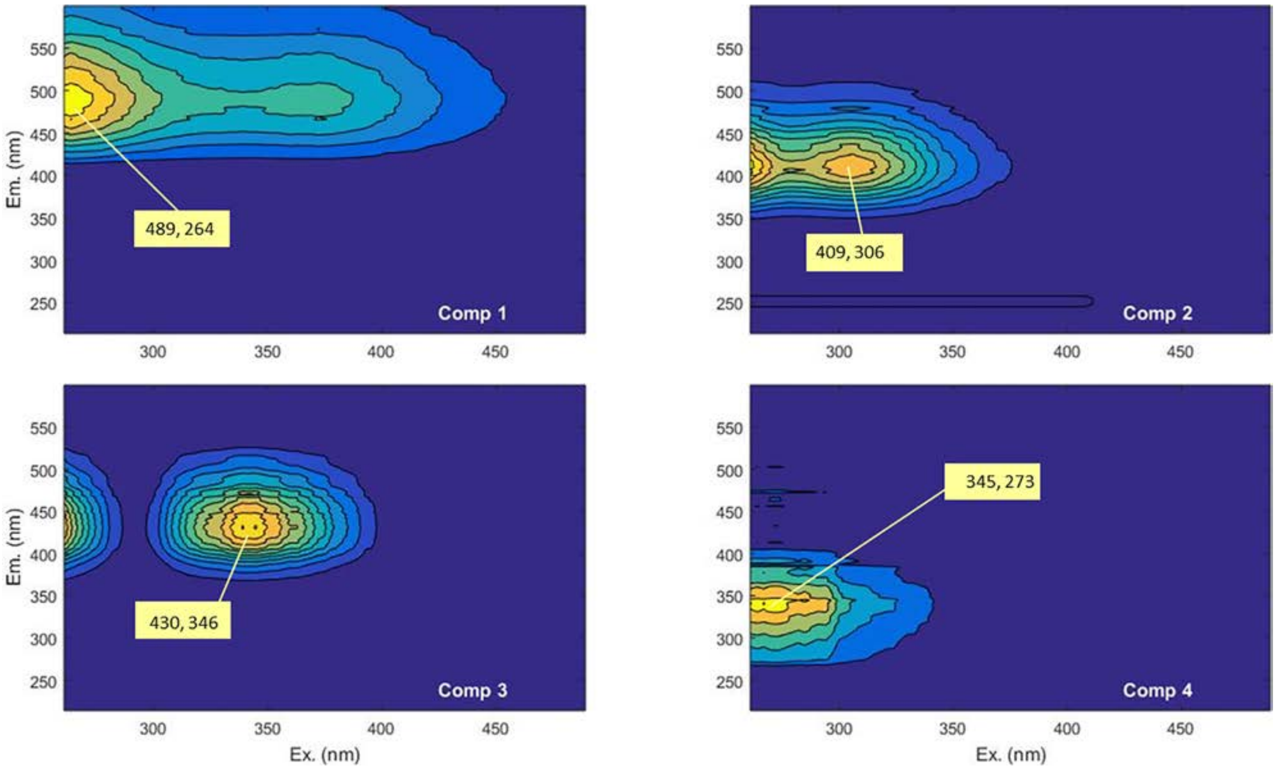


Figure 3.8. Loading values for the three PARAFAC components with excitation (nm) on the *x*-axis and emission (nm) on the *y*-axis.

Derived fluorescent components were cross-referenced with the OpenFluor database (Murphy *et al.*, 2014), which provided context for the similarities between these organic fluorophores and those reported globally from other studies. A total of 42 studies were found with at least one of the three derived components with a high similarity score (> 0.95) (Table 3.2). According to previous classifications, C1 consisted of humic-like terrestrial organic matter, ubiquitous to freshwater, composed of high molecular weight and aromatic organic compounds; C2 consisted of humic-like, terrestrially delivered reprocessed organic matter; C3 consisted of humic-like terrestrially delivered organic matter; and C4 consisted of protein-like microbially delivered organic matter.

All four components are commonly reported in surface and treated water (Shutova *et al*., 2014). In all source water, C1 and C2 had higher fluorescence intensities than C3 and C4 (Figure 3.9). All sites exhibited contrasting organic matter. Specifically, the turlough samples showed the highest variability of C1 and C2 (0.99 ± 0.28 RU and 0.97 ± 0.19 RU, respectively) in contrast to the raw water samples, which tended to be stable for all components (Figure 3.9). The two surface-water-fed sources (i.e. the wetland and the tributary sources) had greater median values of C1 and lower median values of C2 compared with the four groundwater sampling locations, which had similar medians for C1 and C2 (Figure 3.9).

Treatment: DOC, UVA$_{254}$ and SUVA

Raw water DOC concentrations ranged between 3.84 mg L^{-1} and 11.40 mg L^{-1} with an average of 5.95 mg L^{-1} (Figure 3.10).

Water samples taken after the GAC filter had DOC concentrations of between 3.30 mg L^{-1} and 10.37 mg L^{-1} with an average of 5.39 mg L^{-1}. Removal by the GAC varied between 2.6 mg L^{-1} and 0.19 mg L^{-1} with a mean removal of 0.56 mg L^{-1}. On three occasions the GAC water had higher DOC than the raw water samples, illustrating that the GAC filter itself was a source of NOM of up to 1.51 mg L^{-1} DOC. A seasonal trend can be observed, with low DOC concentrations observed in August and September 2014 and higher concentrations in the late autumn to winter period. However, July and August 2015 had exceptionally high

Table 3.2. Identities and related references for similar components using the OpenFluor database

Score[a]	Component identity	References
Component 1		
1	Humic-like terrestrial delivered	Shutova *et al*., 2014
0.99	Terrestrial humic-like OM	Walker *et al*., 2009
0.99	Humic-like fluorescence	Catalá *et al*., 2015.
0.99	Humic-like fluorescence	Murphy *et al*., 2006
0.98	Terrestrial humic-like	Lambert *et al*., 2016
Component 2		
0.99	Humic-like, terrestrial delivered reprocessed OM	Shutova *et al*., 2014
0.99	Terrestrial humic-like	Stedmon *et al*., 2007
0.99	Terrestrial humic-like	Lambert *et al*., 2016
0.98	Terrestrial humic-like	Cawley *et al*., 2012
0.98	Terrestrial humic-like	Williams *et al*., 2013
0.95	Humic-like terrestrial delivered	Shutova *et al*., 2014
Component 3		
0.97	Protein-like – microbial delivered	Shutova *et al*., 2014
Component 4		
0.96	Protein-like – microbial delivered	Walker *et al*., 2013
0.96	Protein-like	Cawley *et al*., 2012
0.96	Autochthonous DOM	Kowalczuk *et al*., 2009
0.96	Protein-like	Williams *et al*., 2013

[a]A total of 70 studies were found with at least one component with > 0.95 similarity score. The top five highest similarity scores are shown where available.

OM, organic matter.

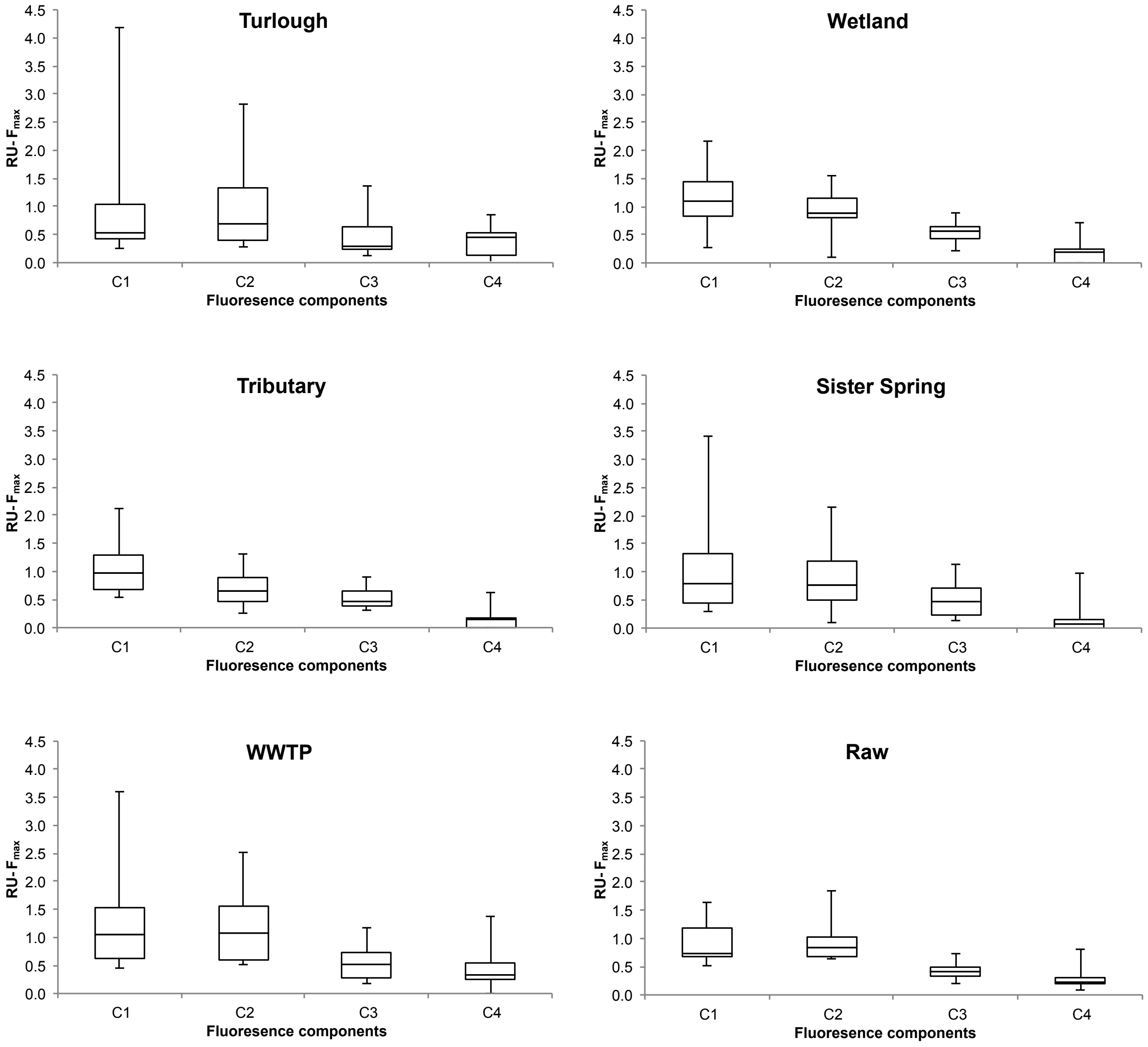


Figure 3.9. ***F*$_{max}$ of fluorescence components at the catchment sites.**

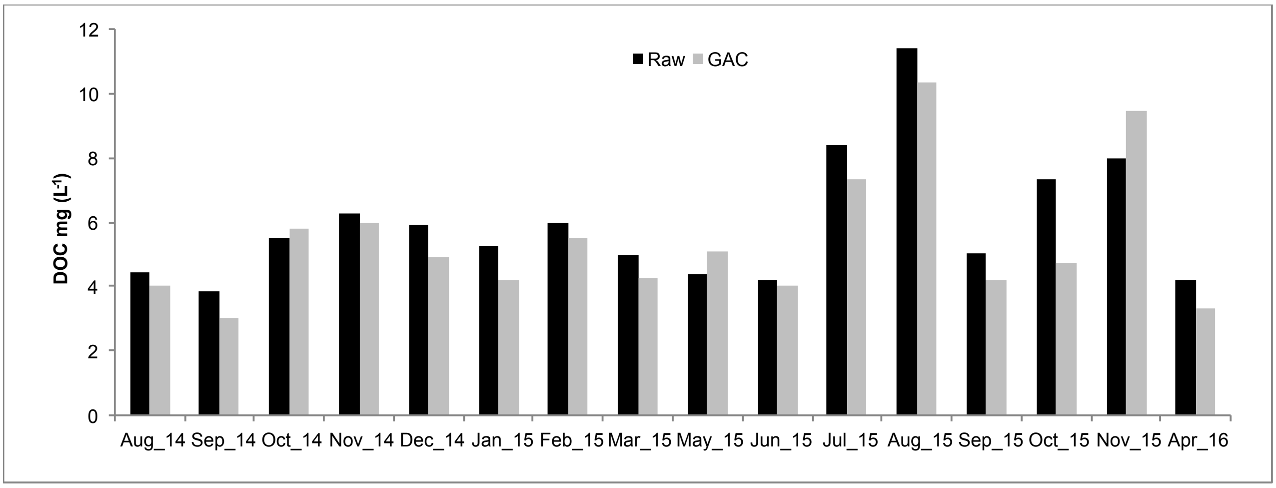


Figure 3.10. DOC concentrations in the raw and treated water.

DOC, which was not in line with the seasonal trend and was owing to high rainfall after a drought period (Figure 3.3).

Raw water UVA_{254} values ranged between 0.0567 cm^{-1} and 0.4756 cm^{-1} with an average of 0.1995 cm^{-1}. Post-ozone water had UVA_{254} values of 0.0340 cm^{-1} and 0.3861 cm^{-1} with an average of 0.1333 cm^{-1}. Following GAC filtration, UVA_{254} values ranged between 0.0264 cm^{-1} and 0.2654 cm^{-1} with an average of 0.0987 cm^{-1}. Reduction in UVA_{254} value by the ozone treatment ranged between 0.0040 cm^{-1} and 0.1486 cm^{-1} with an average of 0.0662 cm^{-1}. Further reduction was observed with the GAC filter with an average of 0.0461 cm^{-1} except for three occasions when an increase in UVA_{254} was observed (August and December 2014 and February 2015) (Figure 3.11).

The average SUVA for raw water was 3.2 $L mg^{-1} m^{-1}$, an indication of NOM of moderate aromaticity, while that of finished water was 1.8 $L mg^{-1} m^{-1}$, which is typical of NOM with low aromaticity (SUVA < 2 $L mg^{-1} m^{-1}$). On five occasions SUVA was greater than 2 $L mg^{-1} m^{-1}$, indicating that the higher/intermediate NOM was not removed on these occasions.

Treatment: PARAFAC components

F_{max} was higher for terrestrial and ubiquitous humic-like component C1 in the raw water followed by C2, C3 and C4. Samples taken after ozone treatment had similar values of C1 and C2 (humic-like, terrestrially delivered reprocessed organic matter). Samples taken after the GAC filter had slightly higher values for C2 than for C1, C3 or C4 (Figure 3.12).

To evaluate the effect of water treatment on the fluorescence characteristics of NOM, the percentage reduction of F_{max} across each treatment process was calculated (Figure 3.13). Ozone reduced C1 by an average of 69% (± 7%) across all sampling occasions. C2, C3 and C4 were reduced by 64% (± 11%), 64% (± 8%) and 46% (± 17%), respectively. The GAC filter increased C1 by an average of –4% (± 96%), C2 by –61% (± 172%), C3 by –4% (± 80%) and C4 by 41% (± 56%).

Distribution network: DOC, UVA_{254}, SUVA and THMs

The average DOC concentration in the distribution network was 5.59 ± 1.76 $mg L^{-1}$. Average UVA_{254} values ranged between 0.0519 cm^{-1} and 0.2654 cm^{-1} with an average of 0.0972 cm^{-1}. SUVA values ranged between 0.84 $L mg^{-1} m^{-1}$ and 2.87 $L mg^{-1} m^{-1}$ with an average of 1.7 $L mg^{-1} m^{-1}$. C2 had higher fluorescence intensities than C1, C3 and C4 in the distribution network (Figure 3.14). Average free and total chorine concentrations were 0.98 $mg L^{-1}$ and 1.22 $mg L^{-1}$.

TTHM concentrations ranged between 22.4 $\mu g L^{-1}$ and 251 $\mu g L^{-1}$ with an average concentration of

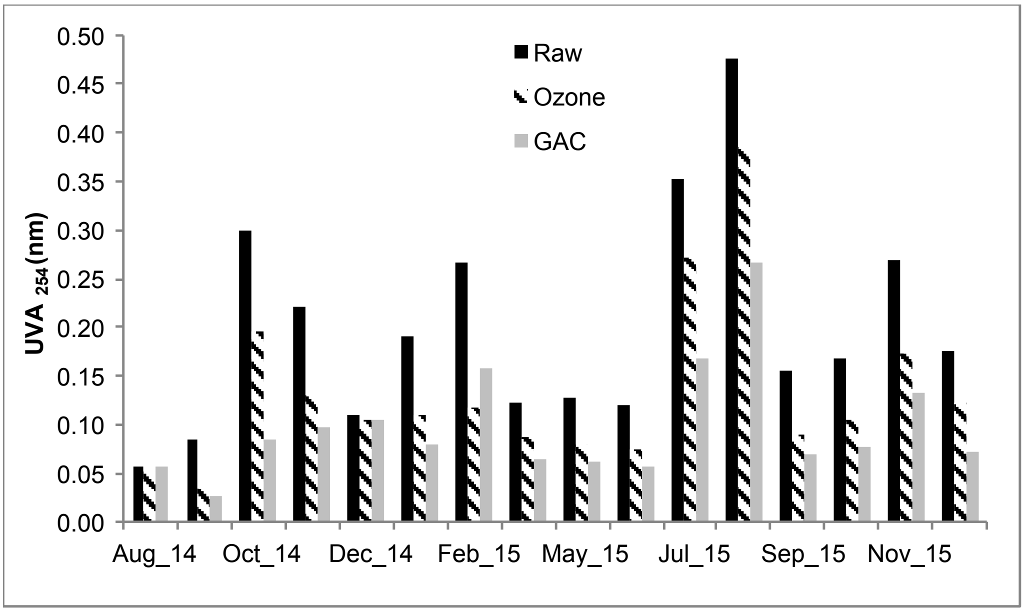


Figure 3.11. UVA_{254} values for the raw, post-ozone and post-GAC water samples.

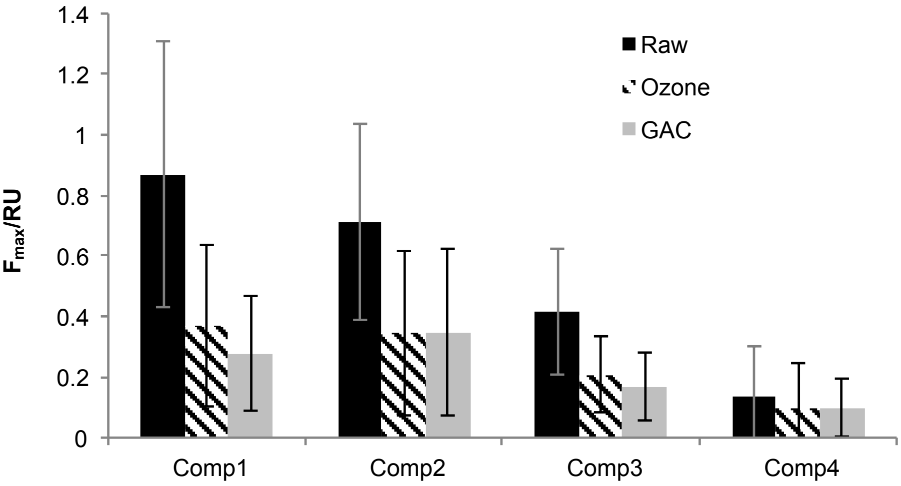


Figure 3.12. F_{max} concentrations from the raw, ozone and GAC stations.

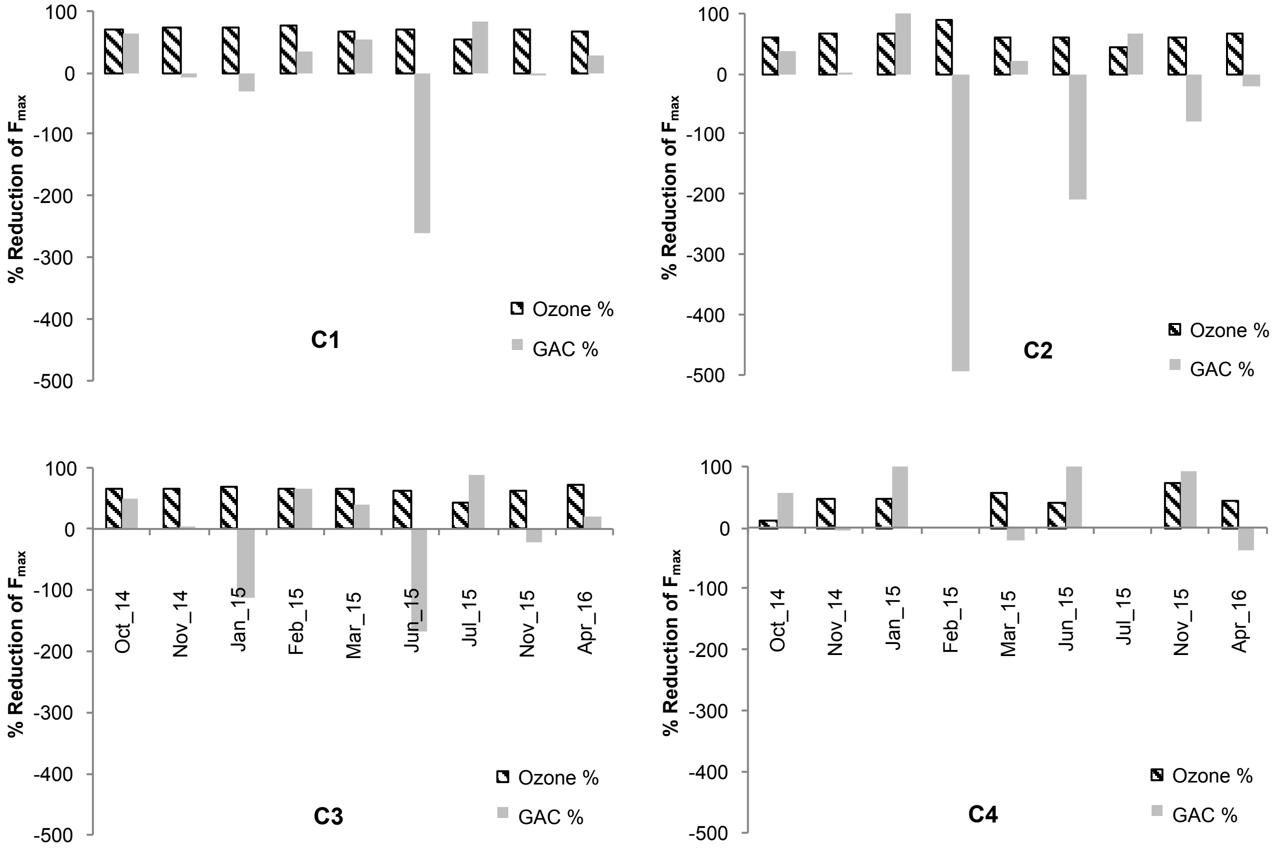


Figure 3.13. Reduction of F_{max} from the four components following ozone and GAC treatment.

109 µg L^{-1}. Chloroform was the most prominent THM (average ~72%) across all samples taken, followed by bromodichloromethane (~20%), dibromochloromethane (~6%) and bromoform (< 1%). Average TTHMs across the distribution network displayed similar temporal changes as DOC with ambient temperature and local rainfall.

It was observed while speaking to customers whose taps were being sampled over the duration of the study period in the distribution network that there was a lack of public awareness of the TTHM exceedances for the supply.

Spearman's correlation coefficients were calculated to assess how well the relationship

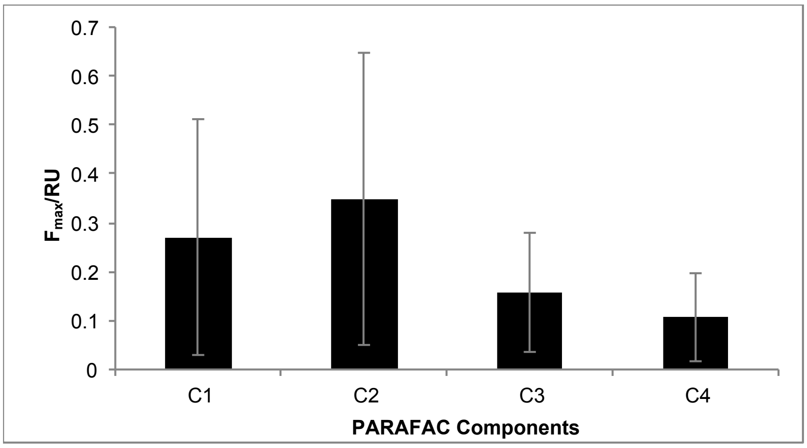


Figure 3.14. F_{max} concentrations of the four components in the distribution network.

Table 3.3. Spearman's rank correlation coefficients between DOC concentrations, UVA_{254} absorbance, SUVA, total nitrogen, chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHBr_2Cl$), dibromochloromethane ($CHBrCl_2$), TTHMs and PARAFAC component scores.

	DOC	UVA_{254}	SUVA	C1	C2	C3	C4	TN	$CHCl_3$	$CHBr_3$	$CHBr_2Cl$	$CHBrCl_2$	TTHMs
DOC	1	0.72^a		0.72^a	0.49^a	0.67^a					-0.53^a		
UVA_{254}		1	0.62^a	0.82^a	0.56^a	0.69^a		0.52^a	0.64^a		-0.52^a		0.61^a
SUVA			1						0.48^a				
C1				1	0.56^a	0.77^a			0.57^a		-0.65^a		0.56^a
C2					1				0.53^a		-0.49^a		0.49^a
C3						1			0.52^a		-0.49^a		
C4							1						
TN								1	0.62^a				0.63^a
$CHCl_3$									1			0.62^a	0.93^a
$CHBr_3$										1			
$CHBr_2Cl$											1		
$CHBrCl_2$												1	0.71^a
TTHMs													1

[a]Correlations are significant, $p < 0.05$.

between two variables could be described. All samples post treatment and from the distribution network were included in the determination of Spearman's correlation coefficients (Table 3.3). There were significant correlations among DOC, UVA_{254} SUVA, PARAFAC components C1, C2 and C3, TN, chloroform, bromodichloromethane, dibromochloromethane and TTHMs. UVA_{254} and C1 had equal correlation scores (0.72) to DOC. TN was significantly correlated with UVA_{254} and chloroform. C1, C2 and C3 were significantly correlated with UVA_{254} and chloroform. SUVA was not significantly correlated with any of the PARAFAC components.

3.2.2 Louth PWS and Mayo PGWS

Meteorological observations

Mean air temperatures from nearby Met Éireann weather stations were 8.6°C (max. 18.0°C and min. 0.65°C) and 9.6°C (max. 20.6°C and min. –2.7°C) for the Louth and Mayo WTPs, respectively, during the study period (Figure 3.15). Average monthly precipitation was 82 mm and 140 mm for the Louth and Mayo WTPs, respectively. The number of wet days [> 1 mm of precipitation/day (Hundecha and Bárdossy, 2005)] recorded over the study period was 261 and 367 out of 639 for the Louth and Mayo WTPs,

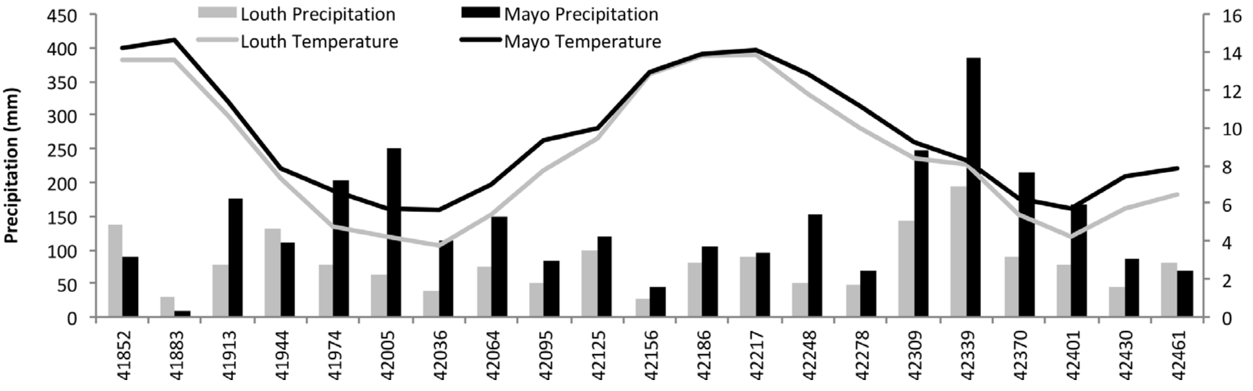


Figure 3.15. Precipitation and temperature at the Louth and Mayo WTPs for the duration of the study period.

respectively. The mean daily precipitation was 2.7 mm and 4.6 mm, respectively (Figure 3.15).

Raw water observations

DOC concentrations in stations around the catchment supplying the Louth PWS (i.e. the Boyne catchment) varied between 3.43 mg L^{-1} and 26.1 mg L^{-1} with an average of 10.3 mg L^{-1}. DOC concentrations in the Mayo catchment ranged between 2.15 mg L^{-1} and 21.1 mg L^{-1} with an average of 9.98 mg L^{-1}. Seasonal trends were evident peaking typically in late autumn (Figure 3.16).

The Boyne river DOC concentrations in general decreased along the river gradient (Figure 3.16). Station 1 (ST1), a tributary to the main Boyne river, drained a peat extraction site and had the highest median DOC value. ST 7, ST 8, ST 9, ST 10 and ST 11 drained the Kells Blackwater part of the Boyne. The highest DOC concentration was observed at ST8, which drained a site downstream of intensive pig rearing farms. ST7, ST8 and ST9 all showed higher nutrient inputs (Table 3.4). The maximum phosphate values observed for ST7, ST8 and ST9 were 0.10, 0.30 and 0.39 mg L^{-1}, respectively (Table 3.4).

Maximum total nitrogen values in the catchment were also relatively high, with ST8 and ST10 observing the highest at 6.81 mg L^{-1} and 10.5 mg L^{-1}, respectively (Table 3.4). SUVA decreased downstream with the highest values observed in the upper reaches of the catchment, indicative of high molecular weight DOC and with intermediate molecular weight DOC lower down the catchment (Table 3.4).

Downstream gradients were not as evident in the Mayo catchment with regard to DOC concentrations (Figure 3.16). ST1 and the raw water station were located in the lake and very little variation can be seen over the sampling period (Figure 3.16). With respect to land use in the catchment, there was some cut peat in the catchment upstream of ST9 and this station had one of the highest median values for DOC (Figure 3.16). The highest concentrations, however, were observed coming from the intensively farmed land upstream of ST7. In general, mean phosphate concentrations over the study period were 0.01 mg L^{-1} apart from ST7 for which it was 0.02 mg L^{-1} (Table 3.4). SUVA concentrations were all high in the Mayo catchment, higher than 4 L mg m^{-1}, which are indicative of high molecular weight organic matter that is highly reactive with chlorine (Table 3.4).

Fluorescence analysis

Exploratory analysis highlighted outliers, which were removed from the dataset. An outlier contained either instrument error or was for some reason very different from the others. They were removed in order to facilitate the modelling process as well as the model validation using the split-half method; otherwise, the datasets would need to contain a sufficient number of the unique samples, which were evenly divided between the split halves. PARAFAC was applied to two datasets of 234 (Louth) and 174 (Mayo) samples encompassing 15 sampling dates and 16 (Louth) and 12 (Mayo) sampling locations (encompassing source, treatment process train and the distribution network). A four-component model was established based on

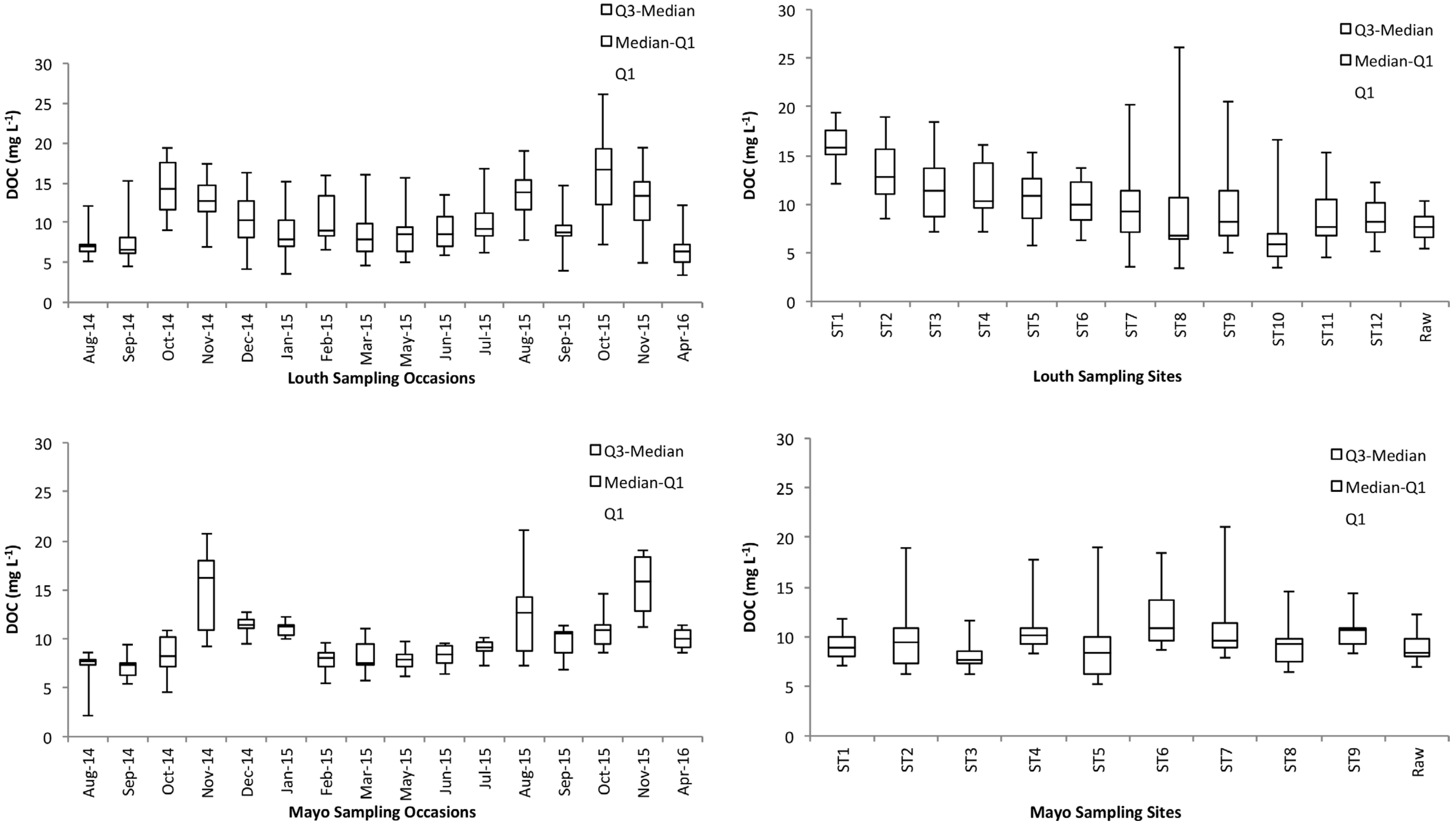


Figure 3.16. DOC concentrations for the Louth and Mayo study catchments over the study duration. The top of each box plot refers to Q3 and the bottom to Q1.

Table 3.4. PO_4, TN and SUVA values for the Louth and Mayo catchments

Louth sites													
	ST1	**ST2**	**ST3**	**ST4**	**ST5**	**ST6**	**ST7**	**ST8**	**ST9**	**ST10**	**ST11**	**ST12**	**Raw**
PO_4													
Max	0.02	0.03	0.05	0.07	0.05	0.02	0.10	0.30	0.39	0.08	0.10	0.05	0.44
Min	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01
Mean	0.01	0.01	0.02	0.02	0.02	0.01	0.04	0.05	0.06	0.02	0.03	0.02	0.05
TN													
Max	3.81	4.10	3.61	3.92	3.37	3.46	5.02	3.96	3.31	5.34	3.69	3.44	3.40
Min	1.60	2.15	1.71	1.83	2.24	1.71	1.38	1.96	1.71	1.81	1.84	2.00	1.93
Mean	2.89	3.23	2.75	2.91	2.82	2.65	2.39	2.96	2.60	3.96	2.74	2.69	2.59
SUVA													
Max	5.37	5.76	4.97	5.36	5.14	5.30	4.66	6.81	5.92	10.51	4.43	3.89	4.05
Min	2.65	2.45	2.28	2.85	2.12	2.55	2.25	2.08	2.26	1.62	1.76	2.23	1.30
Mean	3.90	3.74	3.49	3.79	3.59	3.72	3.18	3.11	3.20	3.10	3.17	3.13	2.99
Mayo sites													
	ST1	**ST2**	**ST3**	**ST4**	**ST5**	**ST6**	**ST7**	**ST8**	**ST9**				**Raw**
PO_4													
Max	0.09	0.04	0.01	0.04	0.02	0.04	0.07	0.04	0.04	–	–	–	0.08
Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–	–	–	0.00
Mean	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	–	–	–	0.01
TN													
Max	1.11	1.18	0.94	1.48	1.40	1.57	3.81	2.07	1.87	–	–	–	1.13
Min	0.21	0.23	0.15	0.42	0.20	0.23	0.41	0.58	0.35	–	–	–	0.25
Mean	0.73	0.71	0.54	1.06	0.69	1.16	1.36	1.26	1.21				0.80
SUVA													
Max	4.98	5.41	5.02	7.39	6.07	5.67	5.27	4.32	4.56	–	–	–	4.42
Min	1.69	2.97	2.91	3.05	2.10	2.70	1.26	2.51	2.71	–	–	–	2.86
Mean	3.58	3.81	3.53	3.92	3.68	3.73	3.39	3.62	3.88	–	–	–	3.66

several diagnostic criteria and random split validation. The loading values for the four components are shown in Figure 3.17.

Derived fluorescent components were cross-referenced with the OpenFluor database (Murphy *et al.*, 2014), which provided context for the similarities between these organic fluorophores to those reported globally from other studies. A total of 42 studies were found with at least one of the three derived components with a high similarity score (>0.95) (Table 3.5).

According to previous classifications, C1 consisted of humic-like terrestrial organic matter, ubiquitous to freshwater, composed of high molecular weight and aromatic organic compounds; C2 consisted of humic-like, fulvic-like terrestrially derived organic matter associated with high molecular weight compounds; C3 consisted of microbial humic-like, terrestrially delivered reprocessed organic matter; and C4 consisted of protein-like organic matter that is microbially/algally derived and associated with biological production in surface waters (Table 3.5). All four components are commonly reported in surface and treated water (Shutova *et al.*, 2014). In all source water, C1 and C2 had higher fluorescence intensities than C3 and C4 (Figures 3.18 and 3.19). All sites exhibited contrasting organic matter properties.

Specifically, ST1 draining the peat workings in the Boyne catchment experienced the highest concentrations of C1 and C2 (3.90 ± 0.78 RU and 2.06 ± 0.45 RU, respectively). Similar trends in components were observed in all tributaries, with

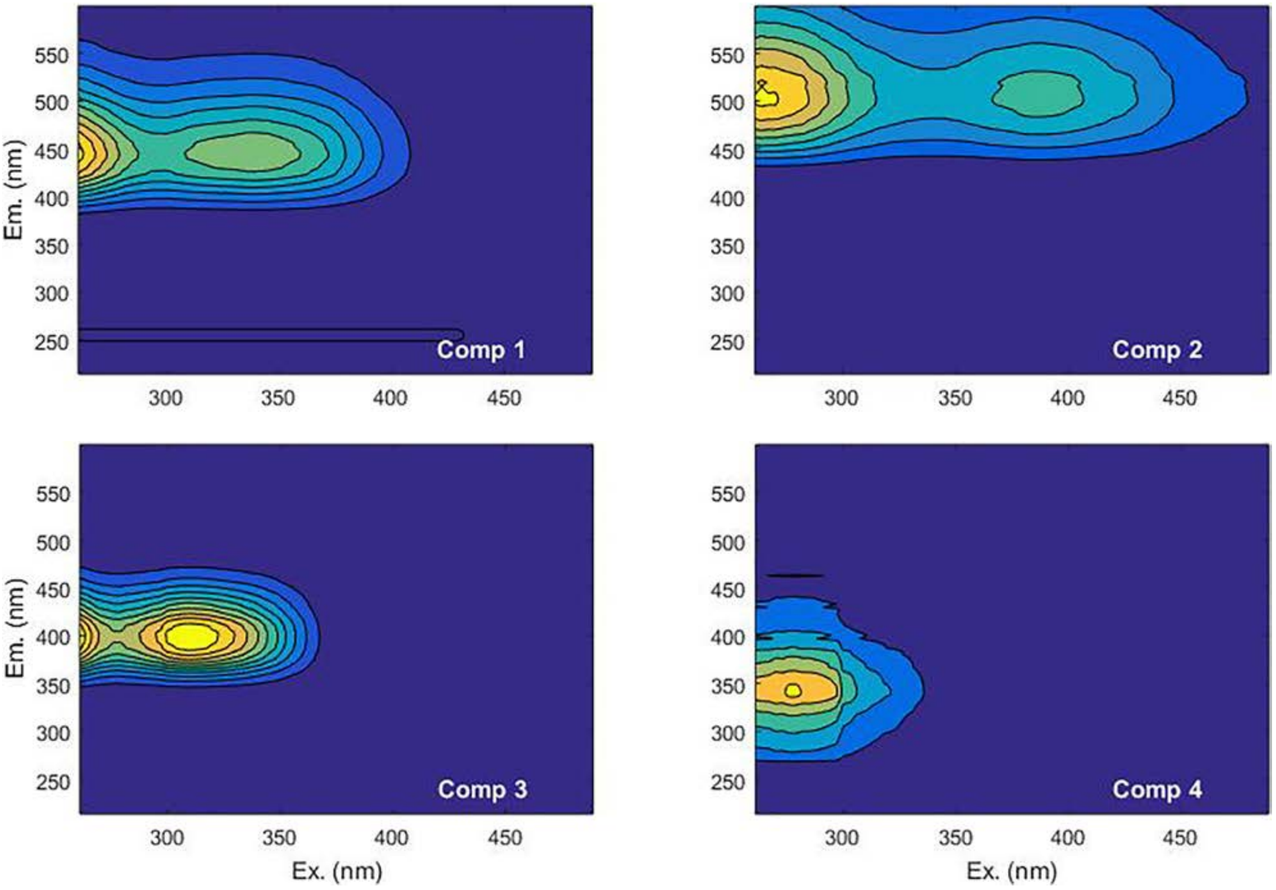


Figure 3.17. Loading values for the three PARAFAC components with excitation (nm) on the *x*-axis and emission (nm) on the *y*-axis.

highest concentrations of C1, followed by C2, C3 and lowest concentrations of C4 (Figure 3.18). Similarly, in the Mayo catchment, there was some cut peat in the catchment upstream of ST9, which had the highest concentration of C1 (Figure 3.19). C1 and C2 had the highest concentrations at most sites. At the raw water site C2 and C3 concentrations were similar (Figure 3.19).

Raw water DOC concentrations ranged between 5.42 mg L^{-1} and 10.3 mg L^{-1} with an average of 7.90 mg L^{-1} in the Louth WTP (Figure 3.20). Samples taken after coagulation and clarification had an average of 2.94 ± 1.0 mg L^{-1} DOC removed over the duration of the study period (Figure 3.20). Following the rapid gravity filters, a further average of 0.44 ± 0.7 mg L^{-1} was removed over the duration of the study period (Figure 3.20). On three occasions the rapid gravity filters were observed to be releasing higher levels of DOC. The treated water had an average of 4.52 ± 1.2 mg L^{-1}. This County Louth WTP has been on the EPA Remedial Action List (RAL) since 2009 because of poor turbidity removal. It is likely, owing to the nature of river sources, that during periods of high rainfall the current treatment process is incapable of removing adequate NOM.

In the Mayo WTP, raw water DOC concentrations ranged between 7.26 and 12.6 mg L^{-1} with an average of 9.38 mg L^{-1} (Figure 3.21). Samples taken after the ultrafiltration membranes had an average of 1.84 ± 1.1 mg L^{-1} DOC removed over the duration of the study period (Figure 3.21). The treated water had an average of 7.54 ± 2.0 mg L^{-1}.

Raw water UVA$_{254}$ values ranged between 0.1339 cm^{-1} and 0.4159 cm^{-1} in the Louth WTP with an average of 0.2374 cm^{-1}. Post coagulation and clarification, water had an average UVA$_{254}$ value of 0.1045 cm^{-1}. Following rapid gravity filtration UVA$_{254}$ was on average 0.0848 cm^{-1}.

Raw water UVA$_{254}$ values ranged between 0.2627 cm^{-1} and 0.4610 cm^{-1} in the Mayo WTP with an average of 0.3391 cm^{-1}. Post ultrafiltration membrane filtration, water had an average UVA$_{254}$ value of 0.2217 cm^{-1}. The average SUVA for raw water in

Table 3.5. Identities and related references for similar components using the OpenFluor database

Score[a]	Component identity	References
Component 1		
0.99	Derivatives of terrestrial OM	Stedmon *et al*., 2007
0.99	Humic-like	Guéguen *et al*., 2014
0.98	Terrestrial humic-like; photolabile	Osburn *et al*., 2011
0.98	Humic-like	Jørgensen *et al*., 2011
0.98	Humic-like	Murphy *et al*., 2014
Component 2		
1.00	Derivatives of terrestrial OM	Stedmon *et al*., 2007
0.99	Terrestrial humic	Murphy *et al*., 2014
0.99	Humic-like fluorophore; terrestrial or autochthonous, fulvic acid-like, present in all environments; reduced terrestrial semi-quinone fluorophore; positively related to agriculture and bacterial production	Graeber *et al*., 2012
0.99	Terrestrially derived fulvic acid	Stedmon *et al*., 2005
0.98	Terrestrial humic-like; humic-like components C1 and C2 are among the most common in freshwaters and are associated with high molecular weight and aromatic compounds of terrestrial origin	Lambert *et al*., 2016
Component 3		
0.99	Humic-like; microbial humic-like fluorescence	Murphy *et al*., 2011
0.99	Humic-like	Murphy *et al*., 2014
0.98	Humic-like	Tanaka *et al*., 2014
0.98	Marine and terrestrial humic materials, possible microbial reprocessing	Kowalczuk *et al*., 2009.
0.98	Humic-like, terrestrially delivered reprocessed OM	Shutova *et al*., 2014.
Component 4		
0.98	Associated with tryptophan, autochthonous FDOM source	Walker *et al*., 2013
0.98	Amino acids, free or bound in proteins	Murphy *et al*., 2008
0.98	Protein-like fluorescence, including tryptophan-like C5, is associated with biological production in surface waters	Murphy *et al*., 2014

[a] A total of 70 studies were found with at least one component with >0.95 similarity score. The top five highest similarity scores are shown where available.

FDOM, fluorescent dissolved organic matter; OM, organic matter.

the Louth WTP was 3.02 $\mathrm{L\,mg^{-1}\,m^{-1}}$, an indication of NOM of moderate aromaticity, while that of finished water was 1.9 $\mathrm{L\,mg^{-1}\,m^{-1}}$, which is typical of NOM with low aromaticity (SUVA $< 2\,\mathrm{L\,mg^{-1}\,m^{-1}}$). On four occasions SUVA was greater than 2 $\mathrm{L\,mg^{-1}\,m^{-1}}$. The average SUVA for raw water in the Mayo WTP was 3.7 $\mathrm{L\,mg^{-1}\,m^{-1}}$, an indication of NOM of moderate aromaticity, while that of finished water was 3.0 $\mathrm{L\,mg^{-1}\,m^{-1}}$.

PARAFAC components

C1, the humic-like terrestrially derived organic matter of high aromaticity, was the prominent component at each sampling point along the treatment processes (Figures 3.22 and 3.23). Similarly, C3, the humic-like terrestrially delivered reprocessed organic matter, had the second highest concentration at each point along both treatment processes, followed by C2 (humic-like, fulvic-like and terrestrially derived organic matter) and C4 (protein-like autochthonous produced) (Figure 3.22 and Figure 3.23).

Clarification removed C2 most efficiently, followed by C1, C3 and C4 (Louth WTP) (Figure 3.23). Rapid gravity filtration was most efficient at removing C1, followed by C2, C3 and C4. Ultrafiltration membranes were the most inefficient treatment process (Figure 3.23) removing only 20% of C2 and C4 and 10–15% of C1 and C3 (Figure 3.24).

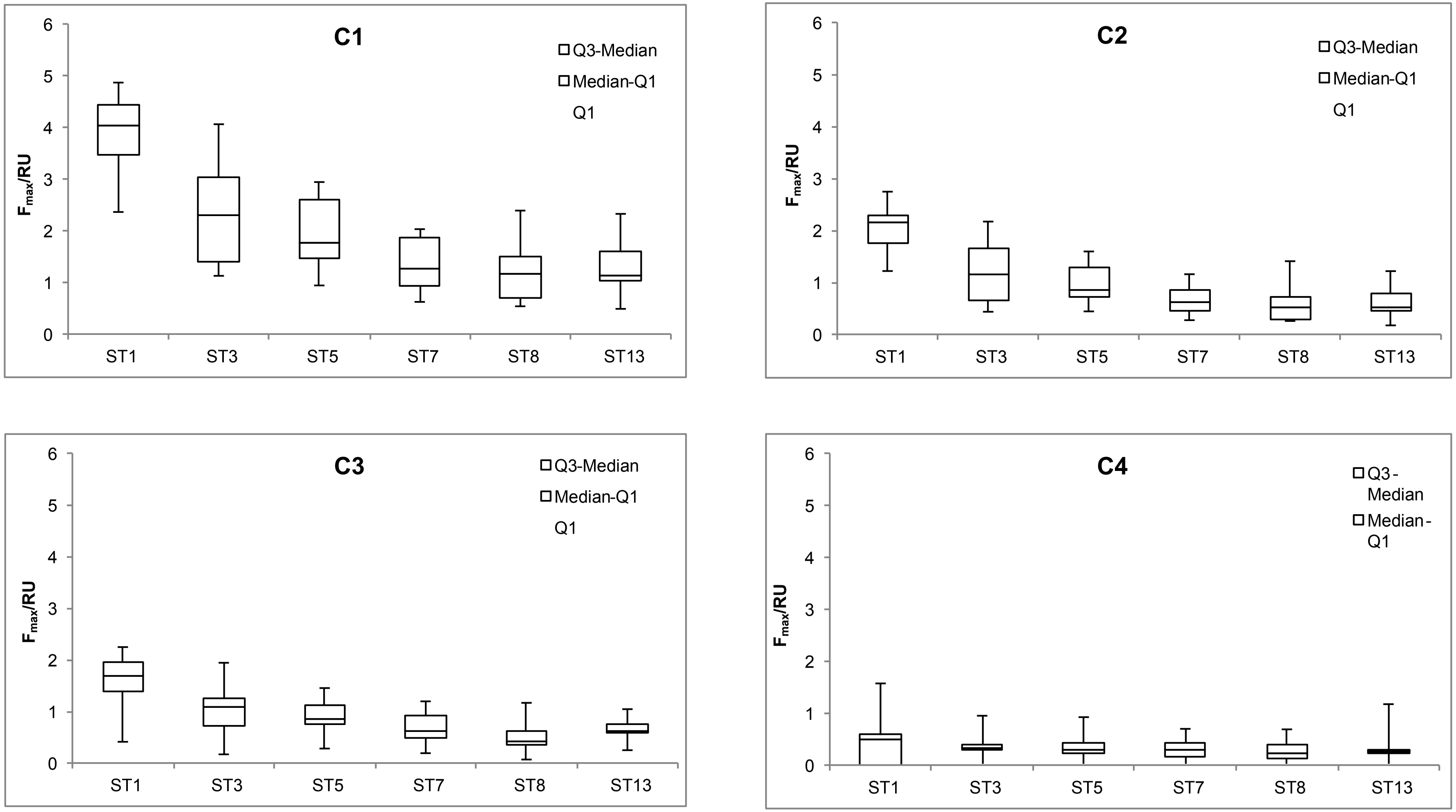


Figure 3.18. F_{max} of fluorescence components for the Louth catchment sites. The top of each box plot refers to Q3 and the bottom to Q1.

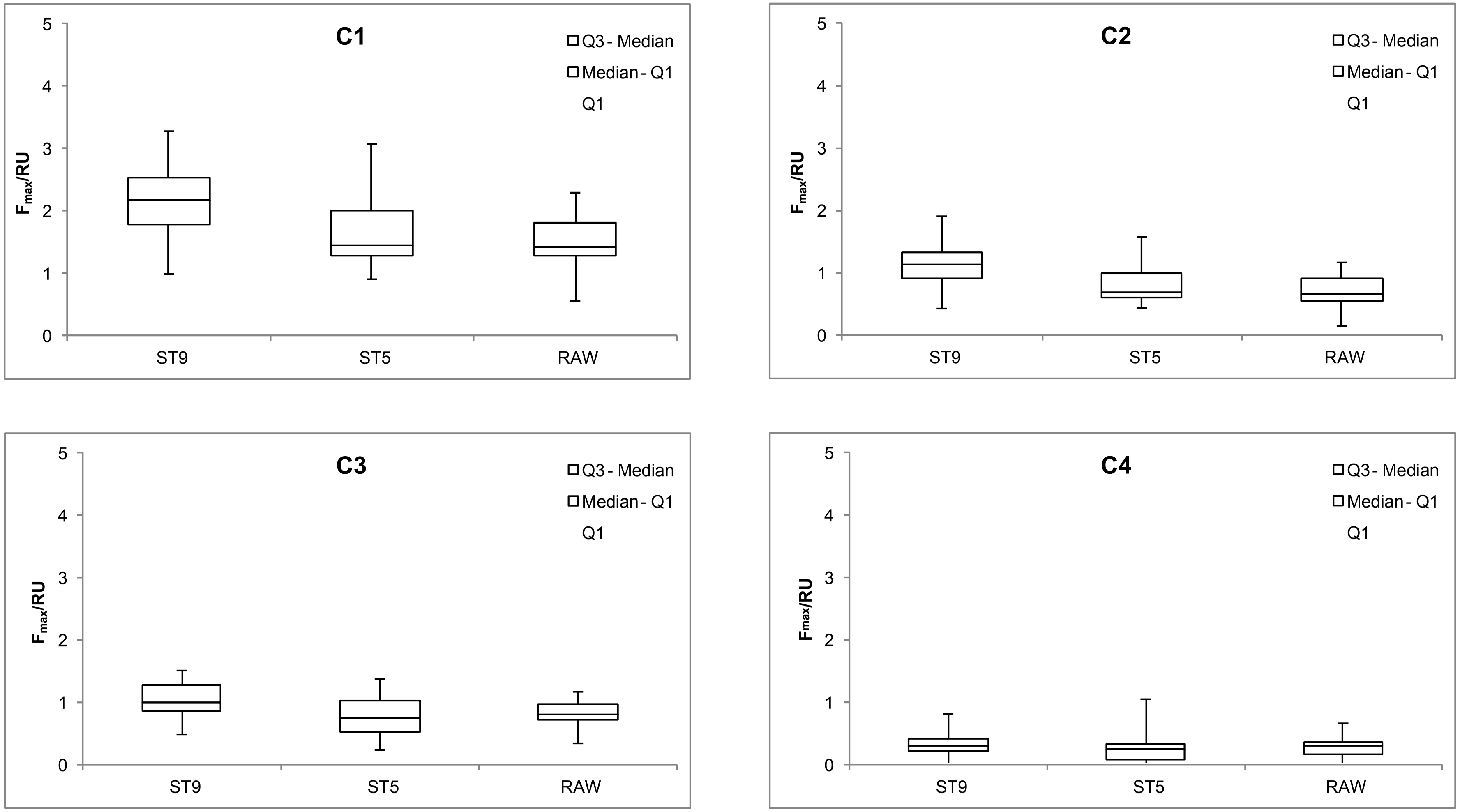


Figure 3.19. F_{max} **of fluorescence components for the Mayo catchment sites. The top of each box plot refers to Q3 and the bottom to Q1.**

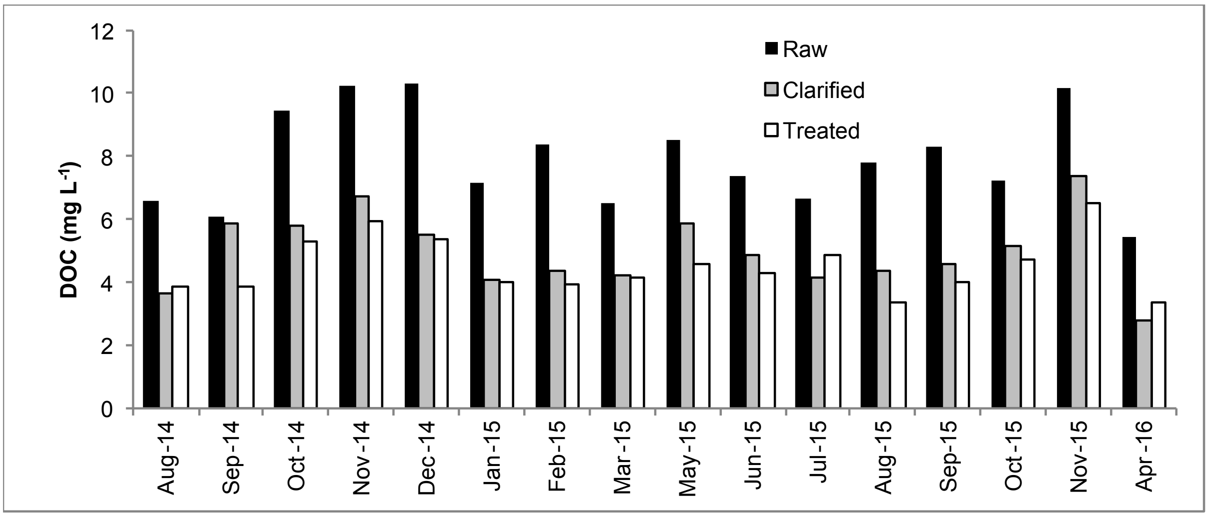


Figure 3.20. DOC concentrations along the treatment train in the Louth WTP.

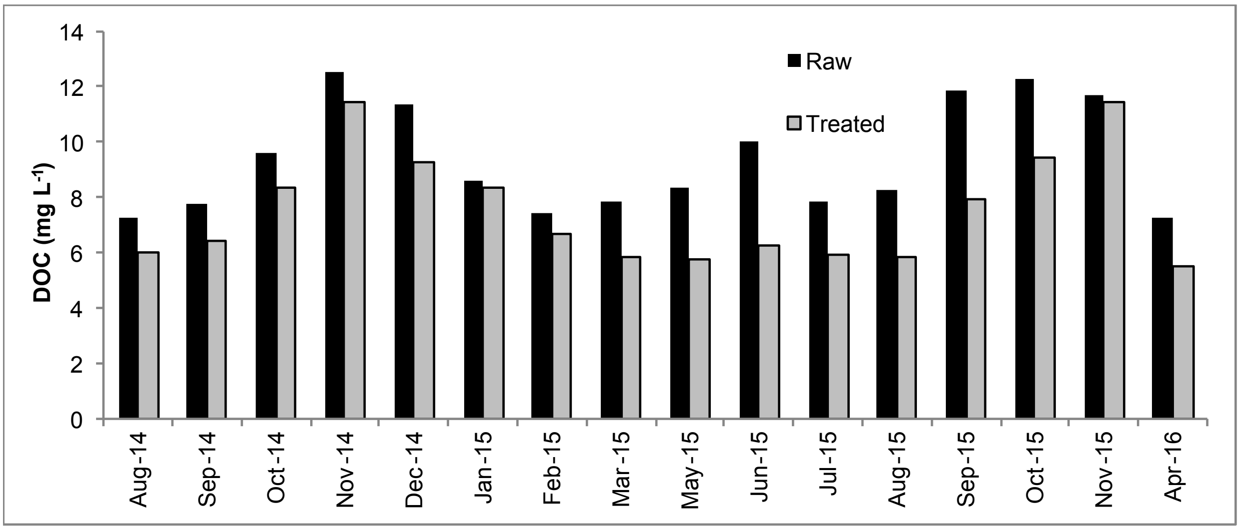


Figure 3.21. DOC concentrations along the treatment train in the Mayo WTP.

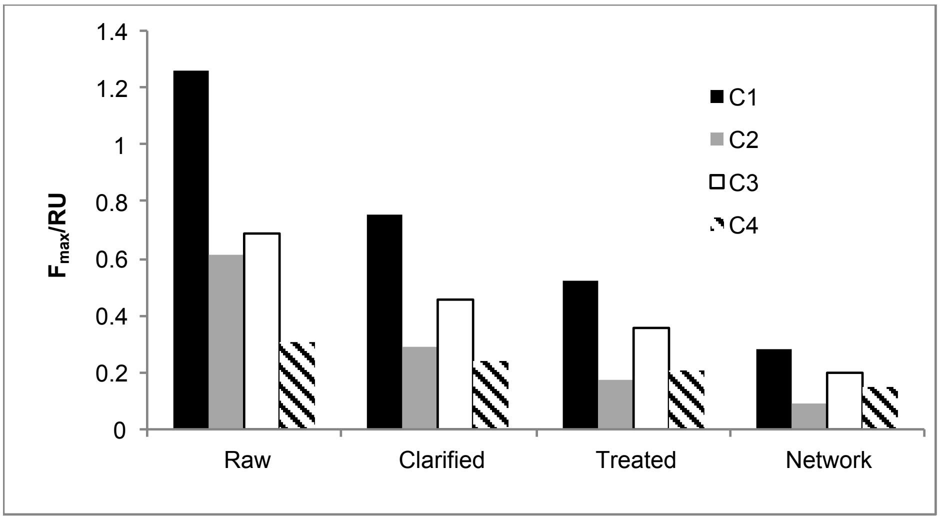


Figure 3.22. *F*$_{max}$ concentrations along the treatment train in the Louth WTP.

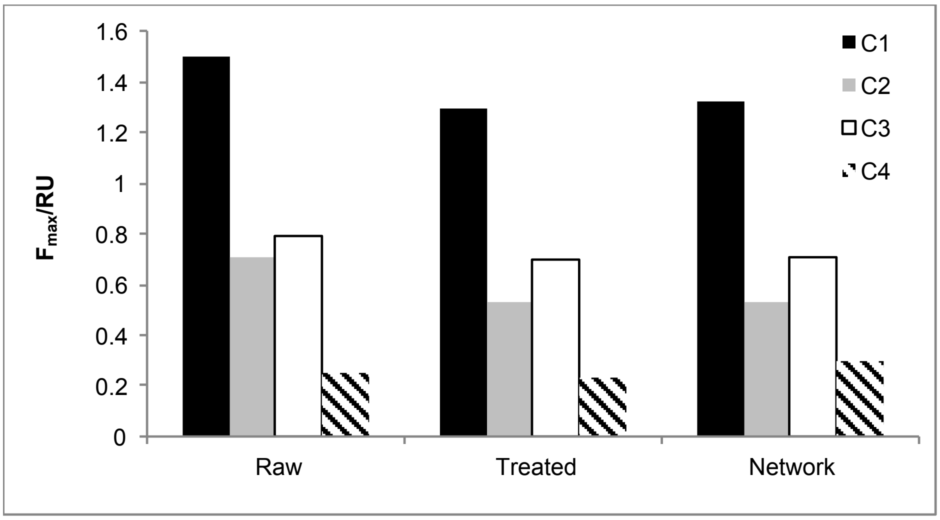


Figure 3.23. ***F*$_{max}$ concentrations along the treatment train in the Mayo WTP.**

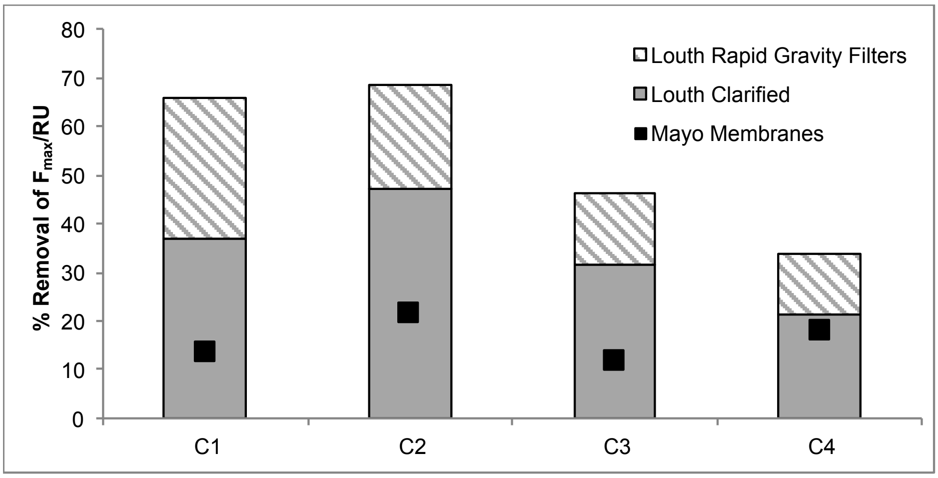


Figure 3.24. Removal of *F*$_{max}$ for C1, C2, C3 and C4 for each treatment type.

Distribution network: DOC, UVA$_{254}$, SUVA and THMs

The average DOC concentrations in the distribution network were 3.39 ± 0.7 mg L^{-1} and 7.19 ± 1.9 mg L^{-1} in the Louth and Mayo WTPs, respectively. Average UVA$_{254}$ values were 0.1027 cm^{-1} and 0.2093 cm^{-1} in the Louth and Mayo WTPs, respectively. The average SUVA values were 2.65 L mg^{-1} m^{-1} and 3.01 L mg^{-1} m^{-1} in the Louth and Mayo WTPs, respectively. C1 had higher fluorescence intensities followed by C3 in the distribution network (Figure 3.22 and Figure 3.23). C4 was higher than C2 in the Louth distribution network, whereas C2 was higher than C4 in the Mayo distribution network. C2 was associated with terrestrially derived humic-like organic matter with high aromaticity that was more likely to produce THMs.

At the Louth WTP, TTHM concentrations ranged between 24 µg L^{-1} and 76 µg L^{-1} with an average concentration of 46 µg L^{-1}. At the location further down the network the concentrations ranged between 53 µg L^{-1} and 164 µg L^{-1} with an average of 74 µg L^{-1} over the duration of the study period. Chloroform was the most prominent THM (average ~68%) across all samples taken, followed by bromodichloromethane (~23%), dibromochloromethane (~8%) and bromoform (< 1%). The Louth WTP only exceeded the parametric value for TTHMs (100 µg L^{-1}) on one occasion during the study period.

TTHM concentrations ranged between 40 µg L^{-1} and 225 µg L^{-1} with an average concentration of 124 µg L^{-1} at the Mayo WTP. At the location further down the network the concentrations ranged between 91 µg L^{-1}

and 250 µg L^{-1} with an average of 165 µg L^{-1} over the duration of the study period. Chloroform was the most prominent THM (average ~82%) across all samples taken, followed by bromodichloromethane (~16%), dibromochloromethane (~2%) and bromoform (< 1%). The Mayo WTP exceeded the parametric value for TTHMs (100 µg L^{-1}) on all but one occasion during the study period. TTHM concentrations across the distribution network displayed similar temporal changes to DOC with ambient temperature and local rainfall. The presence of a domestic GAC filter reduced the TTHM concentration by 80%.

As with the Galway PWS, it was observed while speaking to customers whose taps were being sampled over the duration of the study period in the distribution networks in County Louth and County Mayo, that there was a lack of public awareness of the TTHM exceedances for the supply.

All samples from the post-treatment and post-distribution network were included in the determination of Spearman's correlation coefficients (Table 3.6). There were significant correlations among DOC, UVA_{254} SUVA, PARAFAC components C1, C2 and C3, TN, chloroform, bromodichloromethane, dibromochloromethane and TTHMs. PARAFAC components C1, C2 and C3 had higher correlation scores than UVA_{254} to DOC. C1, C2 and C3 were significantly correlated with UVA_{254} and chloroform. SUVA was significantly correlated with C1, C2 and C3 of the PARAFAC components. Similarly PARAFAC components C1, C2 and C3 had higher correlations with TTHMs than UVA_{254} or SUVA.

Table 3.6. Summary of Spearman's rank correlation coefficients between DOC concentrations, UVA_{254} absorbance, SUVA, chloroform ($CHCl_3$), bromodichloromethane ($CHBr_2Cl$), TTHMs and PARAFAC component scores

	TOC	UVA_{254}	SUVA	C1	C2	C3	C4	$CHCl_3$	$CHBr_2Cl$	TTHM
TOC	1									
UVA_{254}	0.72	1.00								
SUVA	0.27	0.68	1.00							
C1	0.82	0.75	0.61	1.00						
C2	0.82	0.75	0.64	0.98	1.00					
C3	0.79	0.70	0.52	0.91	0.92	1.00				
C4	0.20	0.15	0.13	0.29	0.28	0.49	1.00			
$CHCl_3$	0.71	0.66	0.50	0.68	0.69	0.66	0.22	1.00		
$CHBr_2Cl$	0.27	0.30	0.41	0.33	0.32	0.32	0.07	0.71	1.00	
TTHM	0.65	0.61	0.52	0.64	0.65	0.62	0.20	0.99	0.78	1.00

4 NOM Predictions

4.1 Overview

4.1.1 Introduction

Climate change effects on drinking water include changes in the quantity and the timing of water availability, changes in water quality (including NOM) and reductions in the reliability of the relevant infrastructures and will need to be addressed with operative decisions at the level of the WTPs (Boholm and Prutzer, 2017). Potential explanations for increasing NOM concentrations include a number of drivers, e.g. increased precipitation and increased runoff from drainage areas, increased temperatures, increased primary production, increased biological activity and less acidic rain (summarised in Figure 4.1).

Increasing NOM due to climate change is expected to stimulate an increased use of disinfectants, which can in turn result in higher concentrations of DBPs (Kovacs *et al*., 2013). Raw water supplies will require integrated monitoring programmes, focusing on both water quality and availability (Karthe *et al*., 2016).

A chain of hydrological, empirical and process-based biogeochemical models coupled with an ensemble of downscaled regional climate model experiments was applied here to develop scenarios for the local-scale effects of climate change on surface water NOM concentrations and fluxes. INCA-C (Futter *et al*., 2007) has been developed to simulate climate controls on surface water DOC concentrations and export DOC parameters for NOM. INCA-C is based on previous versions of INCA, which were originally designed to model nutrient patterns in both aquatic and terrestrial environments (Whitehead *et al*., 1998; Wade *et al*., 2002a,b). The model is process based and simulates soil organic matter cycling controlled by temperature, soil moisture and chemistry, in addition to vertical and lateral hydrological transport of DOC. INCA-C has been used for simulating DOC under current (Futter *et al*., 2007; Futter and de Wit, 2008; Lepisto

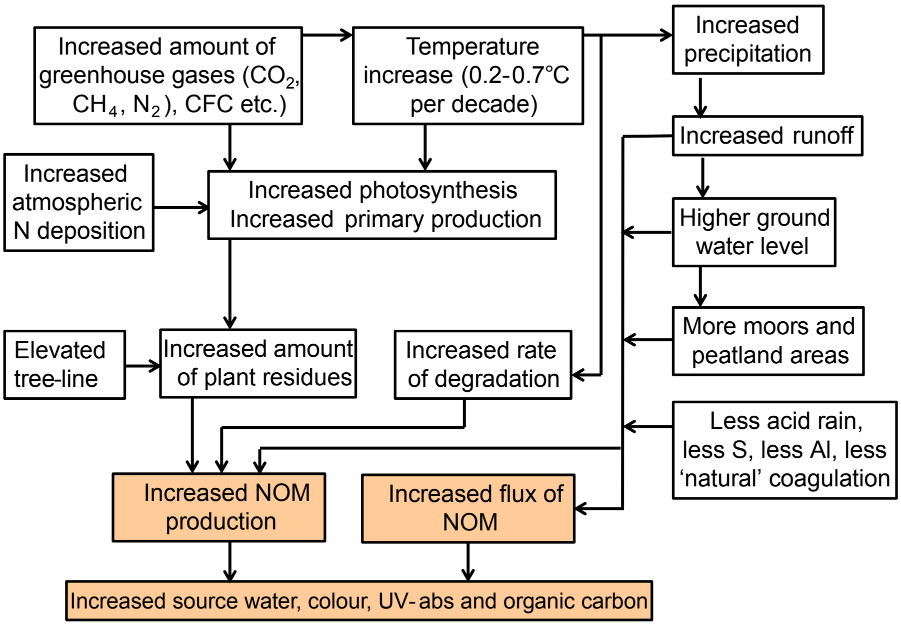


Figure 4.1. Potential explanations for increasing NOM concentrations associated with climate change effects (Eikebrokk *et al*., 2004).

et al., 2014) and future (Futter *et al.*, 2009; Oni *et al.*, 2014) conditions at a range of headwater and larger catchments in Fennoscandia and Canada.

4.1.2 Methodology

Study catchment

The County Louth WTP abstracts water from the Boyne catchment at Roughgrange, County Meath. Treatment includes pumping raw water through drum filters and then to the WTP. Alum is dosed as a coagulant and flocculated using polyelectrolyte as a coagulant aid upstream of six clarification tanks fitted with inclined lamella tube settlers within a building. Aluminium sulfate is used both to depress the high pH of the raw water and to flocculate it. Settled water is then filtered using rapid gravity filters prior to final pH adjustment, fluoridation and primary disinfection using chlorine gas.

The Boyne catchment (Figure 3.2) drains an area of approximately 2693 km^2 with a main channel length of 113 km. A characteristic of the catchment is the limited average gradient of 1.24 m km^{-1}, representing a 140 m fall from the headwaters of the main channel in north Kildare to the sea at Drogheda. There are two main river systems in the Boyne catchment: the Boyne itself drains the southern part of the catchment and the Kells Blackwater drains the northern part of the catchment. Both rivers combine at Navan with the Boyne continuing eastwards to the sea at Drogheda via Slane. The main pressures in the catchment are agricultural runoff, effluent from municipal WTPs and the impact of peat harvesting in the upper catchment.

The Boyne catchment shows significant distinction between the southern/central and northern areas of the catchment. The former are principally covered by grey–brown podzolics and gleys with significant peat deposits, whereas the soils in Cavan and Louth are more typically acid brown earths and gleys. The Boyne catchment typically receives 900 mm annual average rainfall. Land use types in the catchments have been identified from the Corine Land Cover Dataset 2012. "Arable agriculture land used for crop cultivation" accounts for 11% of total area in the Boyne catchment, and "Pasture" is the dominant agricultural form, accounting for 80% of the Boyne catchment area. Forest, including semi-natural areas (includes forest and semi-natural areas with moors and heathland) and transitional woodland/scrub accounts for 3% of the Boyne catchment.

Model input data

Daily flows at Roughgrange were obtained from www.epa.ie/hydronet/#07059 for the period 22 January 2005 to 2 February 2015. An online submersible spectrophotometer, spectro::lyser, from s::can Messtechnik, installed at the WTP abstraction on the raw water and equipped with a 35 mm measuring cell, was used to estimate daily values for DOC for the period 7 September 2014 to 2 December 2015.

Daily time series of temperature and precipitation measurements were obtained from meteorological (Met Éireann) stations located at Mullingar and Kilskyre, respectively, for the period 1 January 2005 to 30 April 2016. Daily time series of agricultural manure spreading (kg DOC ha^{-1} per day) were based on typical manure concentrations (Murnane *et al.*, 2016) applied at rates limited by the European Union (Good Agricultural Practice for the Protection of Waters) Regulations 2014 (S.I. No. 31 of 2014).

Hydrological modelling

The rainfall–runoff model PERSiST (Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport; Futter *et al.*, 2014) was used to simulate daily stream flow. PERSiST is a semi-distributed bucket-type model within a flexible framework that allows the modeller to specify the perceptual representation of the runoff generation process. PERSiST generates the daily time series of soil moisture deficits (SMDs) and hydrologically effective rainfall (HER; precipitation net of evapotranspiration) required to run INCA-C. In order to generate these, PERSiST requires daily time series of air temperature and precipitation as inputs. In the model configuration, precipitation is directed to the stream by direct runoff or into the soil; this is then further divided into four layers/boxes: a quick box for overland flow, an upper box for fast responses, a lower box for slow responses and a groundwater box for base flow simulations. Evapotranspiration leads to lowering of water storage, while water is transported either vertically (to the lower soil layer) or horizontally (to the stream). Key model parameters controlling soil hydrology in PERSiST are hydrological conductivity, soil depth, and runoff time constants.

The Boyne catchment was divided into six land use classes: pasture (75%), agriculture (13%), peatland (4%), forest (5%), urban (2%) and lake (1%). The PERSiST model was calibrated using long-term (April 2005 to April 2016) observed streamflow data from Roughgrange and precipitation and temperature from Kilskyre and Mullingar, respectively, to simulate present-day runoff conditions. Manual calibration was first performed by fine tuning model parameters relating to temperature, soil moisture and chemistry, in addition to vertical and lateral hydrological transport of DOC, to minimise the difference between the simulated and observed runoff (Futter *et al*., 2007). Model performance was assessed using the Nash–Sutcliffe (N-S) efficiency test (Nash and Sutcliffe, 1970) of observed and log-transformed flows. To assess parameter sensitivity and potentially improve model performance, a Monte Carlo analysis was performed, consisting of 100 iterations with 700 runs each. Model runs with better fits guided decision-making about the upper and lower limits of each parameter for the next Monte Carlo iteration. This process was repeated until no further improvement in the model's N-S efficiency was achieved.

DOC modelling

The INCA-C model required the daily time series of precipitation, temperature, SMD and HER (outputs from PERSiST) to simulate daily stream flow (hydrological sub-model, a simplified version of PERSiST) and daily DOC concentrations (biogeochemical sub-model) (Futter *et al*. 2007, 2009). INCA-C represents a number of processes in two soil layers. The most important processes for the purpose of this study include (1) SOC production from manure additions; (2) temperature, moisture and soil solution chemistry-dependent organic carbon sorption and desorption; and (3) hydrologic controls on transport from soils to stream waters. A "direct runoff" layer representing overland flow is also present. Carbon pools for dynamic transformation include DOC, SOC, potentially dissolved carbon (PDC) and dissolved inorganic carbon (DIC).

The same land use classes and simulation period (April 2005 to April 2016) as applied in the PERSiST model were applied for INCA-C. An initial catchment flow ($70\,m^3\,s^{-1}$) and DOC concentration ($7\,mg\,L^{-1}$) in the river were used, based on average known conditions for 1 January 2005. Initial conditions for SOC pools in the upper and lower soil layers, and DOC soil solution concentrations for the different land use types were estimated from Wellock *et al*. (2011a,b). Typically, upper soil horizons (peatlands and forest floors) have higher SOC and DOC concentrations and so higher values were given to peatlands and forests compared with pasture and agriculture.

A manual calibration was carried out to achieve a good approximation to the observed values prior to applying the Monte Carlo simulations. The calibration strategy first established operational values for the sensitive hydrological parameters, including the base flow index (BFI), soil volumes and residence times, until simulated flow was in the range of the PERSiST simulation and DOC simulations were in the range of the observed values. On achieving an acceptable fit to observed flows, hydrological parameters were set. Finally, the parameters describing carbon transformations in the soil were adjusted.

The Monte Carlo strategy described by Futter *et al*. (2014) was used for an exploration of the INCA-C parameter space. The following SOC process rate parameters were allowed to vary in the upper and lower soil layers during the Monte Carlo analysis: PDC → SOC; PDC → DOC; SOC → DOC; DOC → SOC; DOC → DIC (arrow indicates the direction of transformation between the different fractions of carbon). In addition, the critical soil moisture threshold and process rate response to a soil temperature change were allowed to vary.

During the Monte Carlo analysis, 100 iterations with 500 runs each were performed. In all cases, the initial boundaries were defined as ±20% of the parameter value for the best performing manual calibration. After each iteration of the Monte Carlo analysis, parameter sensitivity was assessed using the 100 best performing parameter sets, which were defined by ranking the N-S statistics comparing modelled and observed DOC. Parameter sensitivity was assessed by comparing the cumulative parameter distributions derived from the best performing parameter sets with rectangular distributions and, if non-rectangular, the parameter range was adjusted prior to the next Monte Carlo iteration. This routine terminated when the Monte Carlo analysis failed to provide any improvement in N-S values over the preceding set of model runs. A final manual tuning of the sensitive parameters was carried out to correct the major mismatches and to improve the model efficiency.

4.1.3 Climate change data

Regional climate modelling

The impact of increasing greenhouse gas concentrations on climate change can be simulated using global climate models (GCMs). However, long-term climate simulations using GCMs are currently feasible only with horizontal resolutions of ~50 km or coarser.

Climate parameters such as precipitation and temperature are closely correlated to the local topography. However, these scale-dependent local controls of topography are not adequately captured in GCMs because of the relatively coarse resolution of the model grids (Coll, 2010; Coll *et al*., 2010). These limitations can be addressed through the use of regional climate models (RCMs). An RCM is a numerical climate prediction model forced by lateral and ocean conditions from the GCM that simulates atmospheric and land surface processes, while accounting for high-resolution topographical data, land–sea contrasts, surface characteristics and other components of the Earth system. The Intergovernmental Panel on Climate Change (IPCC) has concluded that there is "high confidence that downscaling via RCMs adds value to the simulation of spatial climate detail in regions with highly variable topography (e.g. distinct orography, coastlines) and for mesoscale phenomena and extremes" (Flato *et al*., 2013).

Emission scenarios

The representative concentration pathways (RCPs) are four greenhouse gas concentration trajectories adopted by the IPCC to simulate climate change due to changes in land use and global emissions of greenhouse gasses (Moss *et al*., 2010). Four such scenarios (RCP2.6, RCP4.5, RCP6.0 and RCP8.5) are named with reference to a range of radiative forcing values for 2100 or later, i.e. 2.6, 4.5, 6.0 and 8.5 W m^{-2}, respectively (Moss *et al*., 2010; van Vuuren *et al*., 2011). RCPs supersede the Special Report on Emissions Scenarios (SRES) projections (Nakićenović *et al*., 2000).

Previous RCM temperature and precipitation projections for Ireland

The Community Climate Consortium for Ireland (C4I) research group used RCMs to downscale data from five GCMs over Ireland and the UK, using all SRES emission scenarios, achieving a finest horizontal resolution of 14 km. These indicated that mean seasonal temperatures for 2021–2060 are projected to increase by 1.1–1.4°C, with the largest increases occurring during summer and autumn (1.2–1.4°C) and with the greatest in the south and east of the country (McGrath and Lynch, 2008). Seasonal projections for 2021–2060 indicated that precipitation is projected to increase for winter and decrease for summer (McGrath and Lynch, 2008). Nolan *et al*. (2013, 2015) analysed mid-21st century projected temperature and precipitation changes using the output of three high-resolution (up to 4 km grid spacing) RCMs over Ireland, driven by four GCMs under five different future emission scenarios (SRES and RCP). The period 2041–2060 was compared with the past period 1981–2000. The projections indicate a rise of 1.0–1.6°C in mean annual temperatures, with the largest changes seen in the east of the country (O'Sullivan *et al*., 2015; Nolan, 2015). Results indicated significant projected decreases in mean annual spring and summer precipitation amounts by mid-century. The projected drying was largest for summer, with "likely" reductions in precipitation ranging from 0% to 20%. The frequency of heavy precipitation events showed notable increases (approximately 20%) during the winter and autumn months. The number of extended dry periods is projected to increase substantially during autumn and summer with values ranging from 0% to 40% (Nolan, 2015).

Projections for precipitation and temperature were obtained from Nolan (2015) for locations corresponding to the Kilskyre and Mullingar Met Éireann stations. The projections were generated by downscaling the EC-Earth consortium GCM (Hazeleger *et al*., 2011). To account for the uncertainty arising from the estimation of future global emission of greenhouse gases, two IPCC RCP (4.5 and 8.5) emission scenarios were used to simulate the future climate of Ireland. The RCMs used were the Consortium for Small-scale Modelling – Climate Limited-area Model (COSMO-CLM, version 4.0; Rockel *et al*., 2008) and the Weather Research and Forecasting (WRF) model (Skamarock *et al*., 2008). The COSMO-CLM regional climate model is the COSMO weather forecasting model in climate mode. It has been applied and further developed by members of the CLM Community (www.clm-community.eu). The COSMO model (www.cosmo-model.org) is the non-hydrostatic operational weather prediction model used by the German Weather Service (DWD) (Doms and Schattler, 2002; Steppeler *et al*., 2003). The WRF model (https://www.mmm.ucar.edu/weather-research-and-forecasting-model) is a numerical weather prediction system designed to serve atmospheric research, climate and operational forecasting needs. The WRF simulations of the present study adopted the Advanced Research WRF (ARW) dynamical core, developed by the US National Centre for Atmospheric Research (NCAR) Mesoscale and Microscale Meteorology Division (Skamarock *et al*., 2008).

The RCMs were initially driven by GCM boundary conditions (achieving a ~50 km grid size) and were then nested twice in succession to achieve grid spacings of 18 km and 6 km (WRF) and 4 km (COSMO-CLM). For the current study, only 4 km and 6 km grid spacing RCM data are considered. The higher resolution data allows finer scaled estimates of the regional variations of climate projections. The RCMs were validated using 20-year simulations of the past Irish climate, driven both by the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-40 global re-analysis and GCM datasets, and by comparing the output with Met Éireann observational data. Extensive validations were carried out to test the ability of the RCMs to accurately model the climate of Ireland. Results confirm that the output of the RCMs exhibits reasonable and realistic features as documented in the historical data record (Nolan, 2015).

An overview of the simulations used in the current study is presented in Table 4.1. This includes information on the RCM, the downscaled GCM, the number of GCM realisations and RCP used for future simulations, together with the periods analysed and the grid spacing of the RCM. The GCM realisations result from running the same GCM with slightly different conditions, i.e. the start date of historical simulations (O'Sullivan *et al*., 2015). Data from two time-slices, 1981–2009 (the control) and 2031–2059, were used for analysis of projected changes in the mid-21st-century Irish climate.

The daily total precipitation (mm) and mean daily temperature (°C) fields of the RCMs were interpolated to the latitude/longitude locations of the Kilskyre and Mullingar Met Éireann stations. These time series datasets were used to prime the calibrated PERSiST hydrological model to obtain the four output variables of precipitation, temperature, SMD and HER required for INCA-C. INCA-C was run with these simulated output variables to generate new simulations for DOC mobilisation and flow for Roughgrange.

Projections of future climate were compared with each historical dataset and the corresponding future dataset for each simulation within the same group and realisation. These produced projected changes for each model run, that is, the difference between future and past. This reduced the possibility that the biases of particular models will skew the results and allowed each projected change to be meaningfully compared with the other groups.

Table 4.1. Details of the ensemble RCM simulations

RCM	GCM	Scenario (number of realisations)	Number of climate projections	Time period	Grid spacing
Group 1					
CLM4	EC-Earth	Historical (3)	–	1981–2009	4 km
CLM4	EC-Earth	RCP4.5 (3)	3	2031–2059	4 km
CLM4	EC-Earth	RCP8.5 (3)	3	2031–2059	4 km
Group 2					
WRF	EC-Earth	Historical (3)	–	1981–2009	6 km
WRF	EC-Earth	RCP4.5 (3)	3	2031–2059	6 km
WRF	EC-Earth	RCP8.5 (3)	3	2031–2059	6 km

Projections of the future climate were analysed by comparing each historical dataset with the corresponding future dataset for each simulation within the same group and realisation. This resulted in future anomalies for each model run, that is, the difference between future and past. In this way, biases of particular models will not skew results and each anomaly can be meaningfully compared with the other groups. This process generated an ensemble of six RCP4.5 and six RCP8.5 projections corresponding to each station location. The number and spread of results generated and the comparisons between them allows the uncertainty of the projections to be partially quantified, providing a greater measure of confidence in the predictions.

4.2 Findings

4.2.1 Observed baseline climate and catchment flow regimes

Mean annual temperature between 2005 and 2015 (9.3°C) varied between 8.2°C and 9.9°C (Figure 4.2). The lowest and highest average temperature for the non-growing season was 2.4°C in 2010 and 6.3°C in 2007, respectively, whereas the lowest and highest average temperature for the growing season was 11.2°C and 12.9°C in 2015 and 2006, respectively. On average, December was the coldest month (4.6 ± 2.3°C) and July the warmest (15.0 ± 1.3°C). Annual precipitation varied between 773 mm and 1120 mm with a mean of 993 mm and was usually lowest from February to June and highest in November and December. The average number of wet days [≥ 1 mm/day (Hundecha and Bárdossy, 2005)] per year over the study period (January 2005 to December 2015) was 161.

Measured discharge (December 2005 to February 2015) ranged from average high flows (Q_{05}) of 113.4 $m^3 s^{-1}$ to average low flows (Q_{95}) of 8.4 $m^3 s^{-1}$ (Figure 4.3). Average daily flows were highest for January (75.95 $m^3 s^{-1}$) and lowest in June (12.85 $m^3 s^{-1}$) for the observed period.

The average measured DOC concentration (8.2 mg L^{-1}) ranged between 5.7 and 13.4 mg L^{-1} during the observation period September 2014 to December 2015. DOC showed a seasonal pattern with highest concentrations occurring during autumn (Figure 4.4).

4.2.2 Model-simulated flow and DOC for the baseline period

Calibration results from the model resulted in highly correlated simulations for both modelled flow ($R^2 = 0.83$, N-S = 0.80) and modelled DOC ($R^2 = 0.80$,

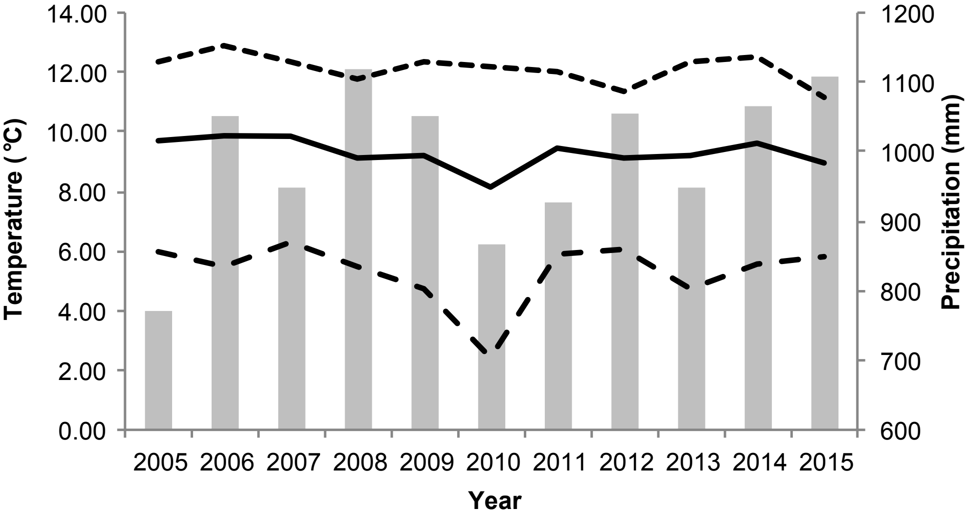


Figure 4.2. Annual meteorological records in the Boyne catchment. Temperatures were recorded at Mullingar station and precipitation at Kilskyre. Bars denote total precipitation; the solid line denotes the mean temperature. Mean temperature in the growing season (April to October) is denoted by the upper dashed line, and the lower dashed line denotes the mean temperature in the non-growing season (January to March and November to March).

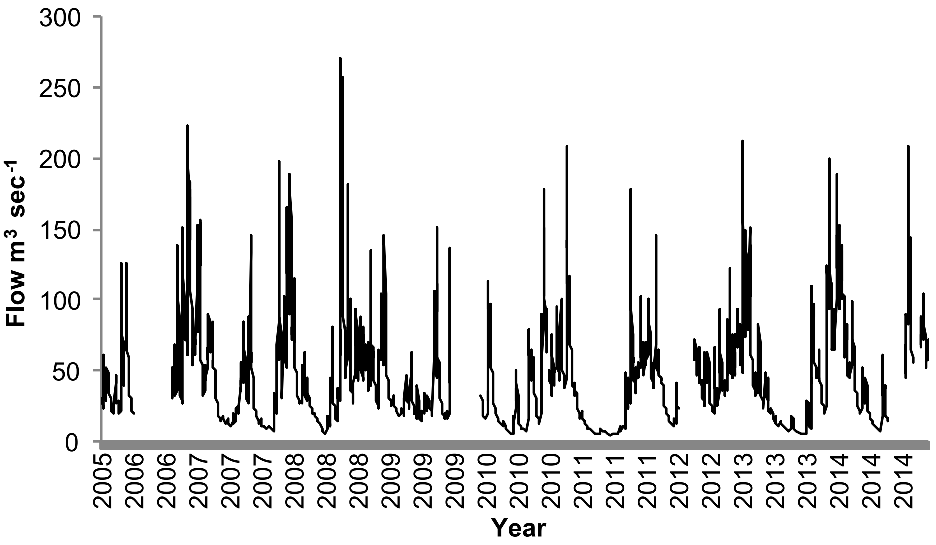


Figure 4.3. Time series of flow in the Boyne catchment measured at Roughgrange, the abstraction location for the Louth WTP.

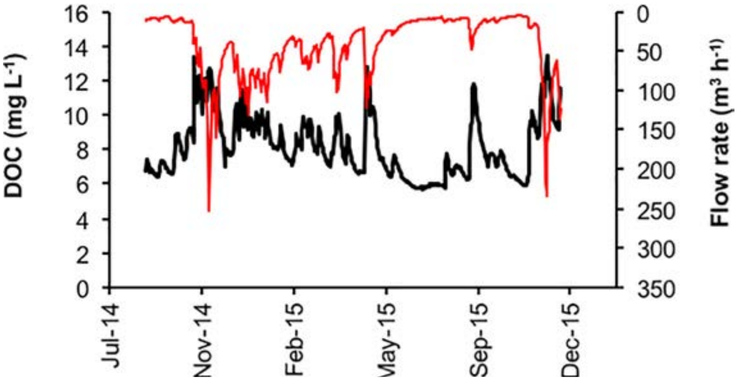


Figure 4.4. Daily DOC concentrations and River Boyne flow rates at the abstraction point for the Louth WTP. The range of DOC concentrations (mg L^{-1}) and flow (m^3 h^{-1}) are denoted by the black and red solid lines, respectively.

N-S = 0.75). The most sensitive parameters ($p < 0.01$) identified by the Monte Carlo analysis of PERSiST included “residence time” (a proxy for the hydrological connectivity of that particular soil box) and the “flow velocity exponent”, which controls water residence times in the streams. The most sensitive parameters ($p < 0.01$) identified by the Monte Carlo analysis of INCA-C included “lower layer residence time”, “base flow index”, “upper layer fast pool fraction”, “response to a 10°C soil temperature change” and “flow velocity exponent”. There was a strong seasonal signal in both observed and simulated discharge, with higher flows in the winter period and lower flows in the spring and summer (Figure 4.5). Overall PERSiST and INCA-C predicted mean monthly flow well, with slight overestimates in late summer and early autumn (Figure 4.5).

Mean monthly simulated DOC concentrations (2005–2015) averaged 8.5 mg L^{-1}, had a strong seasonal signal and varied between 6.6 mg L^{-1} in July and 10.9 mg L^{-1} in November (Figure 4.6).

The simulated daily DOC export pattern realistically matched the observed pattern in discharge and DOC concentrations. In November, December and January, DOC export increased, following a similar trend to that of DOC concentrations. Mean annual DOC export between 2005 and 2015, simulated based on the best

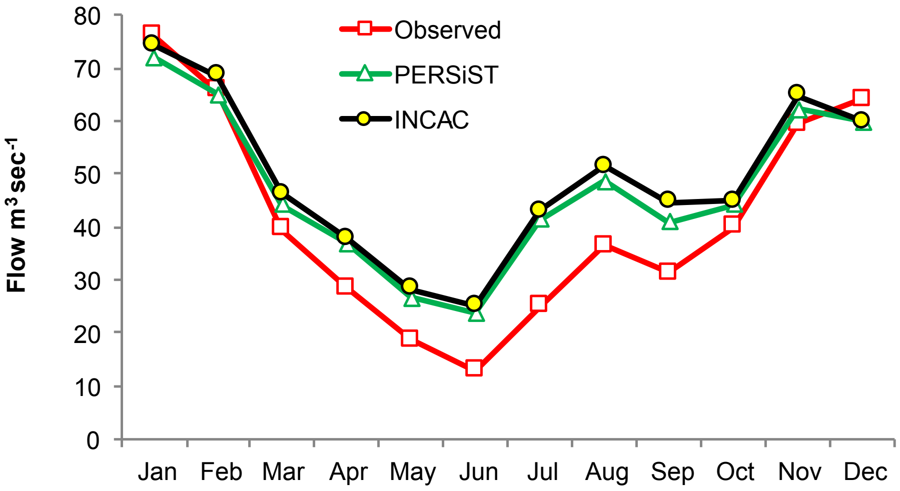


Figure 4.5. Average monthly observed and simulated flow in the Boyne catchment.

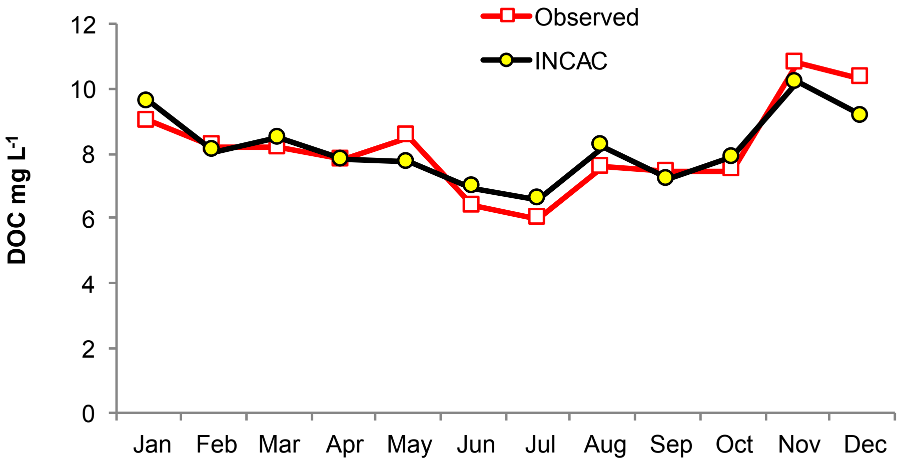


Figure 4.6. Average monthly observed and simulated DOC in the Boyne catchment.

parameter set, was 5.8 ± 1.3 g C m^{-2} per year, with a maximum of 7.8 g C m^{-2} in 2008 and a minimum of 3.7 g C m^{-2} in 2005 (Figure 4.7).

Projected future climate outputs from the 12 downscaled RCM experiments suggested warmer (1.1°C difference) conditions in 2031–2059 compared with simulated present-day conditions (Figure 4.8). Monthly average temperatures show even increases across all months with little variation between RCP emission scenarios.

Annual total precipitation conditions will remain largely the same (< 0.1% difference). However, results indicate projected monthly average decreases in spring through to late summer, with greater decreases associated with the WRF projections compared with the COSMO projections for the corresponding scenarios (Figure 4.9).

4.2.3 Model-simulated flow and DOC with projected future climate

Reflecting the overall projected changes in precipitation, the daily flows averaged over each month show decreases in 2031–2059 compared with the present day (Figure 4.10). Highest flows in January decrease from 77.3 m^3 s^{-1} to 71.3 m^3 s^{-1} and are lowest, 32.1 m^3 s^{-1} to 24.8 m^3 s^{-1}, in June (simulated present day) and July (2031–2059), respectively.

Applying the downscaled projections resulted in an increase in mean annual DOC concentration from 8.5 mg L^{-1} to 9.3 mg L^{-1}. Mean monthly DOC

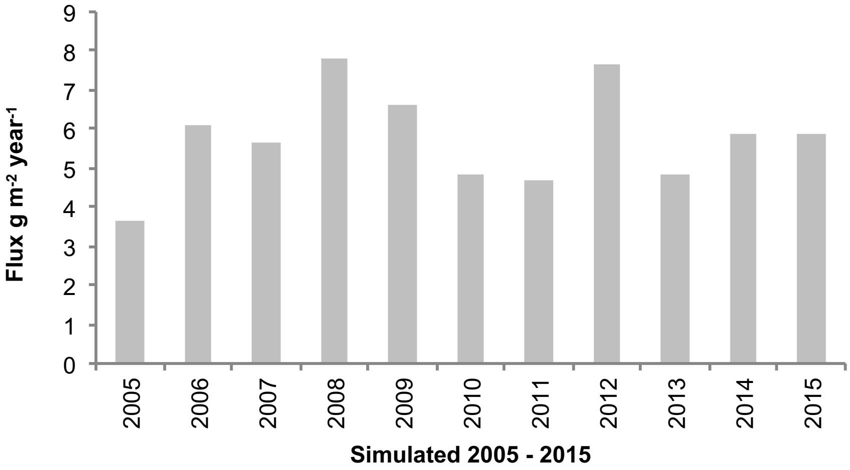


Figure 4.7. DOC export over the simulated period (2005–2015). Annual flux (g m^{-2} per year) is represented by grey bars.

concentrations (2031–2055) had a strong seasonal signal and varied between 7.5 mg L^{-1} in June and 11.6 mg L^{-1} in November (Figure 4.11). This increase in DOC concentration could be attributed to the increase in temperatures and resulting increased DOC production through increased microbial activity (Evans *et al.*, 2006).

Mean annual DOC export showed no change between present day and future projections based on WRF and COSMO low- and high-emission scenarios, respectively (Figure 4.12).

The modelling approach adopted here suggests that, while biogeochemical mechanisms controlling carbon within a watershed are complex, representation of such interdependent processes in a process-based model is possible even for a catchment with a low percentage of peat and high use of pastures.

The simulated mean annual DOC export from the Boyne catchment of 5.8 ± 1.3 g C m^{-2} per year is in the lower range of reported values for peatland catchments (de Wit *et al.*, 2016) and for carbon-rich temperate and boreal catchments with high rainfall (Barry *et al.*, 2016). However, the Boyne catchment has approximately 4% peatland; therefore, with respect to agricultural catchments, it is placed in the higher range (Kronholm and Capel, 2012). The simulated daily DOC export pattern was strongly linked to patterns in discharge. Years with higher precipitation (2008, 2012, 2014 and 2015) showed greater DOC export. DOC export was elevated during vegetation senescence and at the end of the growing season.

Mean annual temperatures are set to increase in the Boyne catchment by 1.0–1.1°C. These changes represent the largest so far projected to occur for the country (Nolan, 2015). Total annual precipitation will remain largely the same, and results show projected monthly average decreases in spring through to late summer. However, frequencies of heavy precipitation events are set to increase (Nolan, 2015). Extreme meteorological events are the primary cause for at-risk situations with regard to trends in the degradation of drinking water quality (Delpla *et al.*, 2009). In addition to increases in DOC concentration observed following rainfall events, organic matter reactivity can also be altered with an increase in THM formation potential (Delpla and Rodriguez, 2016).

Monthly averages of daily flows show overall decreases, and DOC mean monthly concentrations show an overall increase. This increase in DOC concentration could be attributed to the increase in temperature and resulting increased DOC production through increased microbial activity (Evans *et al.*, 2006). In addition, at lower flows there is minimal dilution and increased residence time for the water in contact with organic matter and so greater DOC concentrations (Evans *et al.*, 2006). Mean annual DOC export showed no change in the future with any of the climate and emission scenarios (Figure 4.12). With regard to water suppliers, the concentration of DOC should be given more importance than river loads, as the WTP abstracts the same amount of water each year and therefore loads of DOC are set to increase with concentrations.

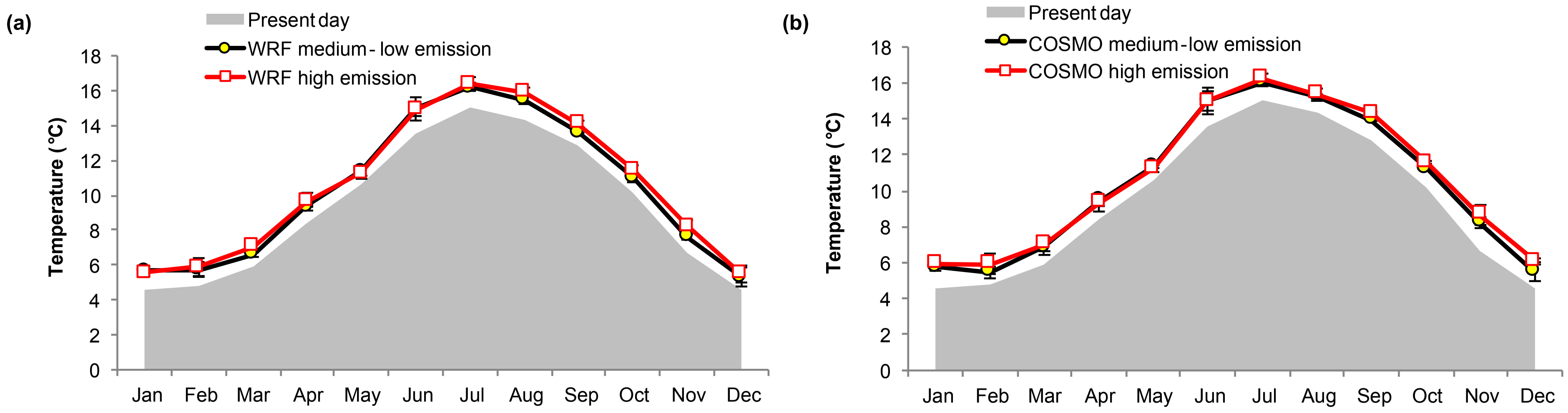


Figure 4.8. Temperature under present/future, high-/low-emission scenarios for (a) WRF projections and (b) COSMO projections.

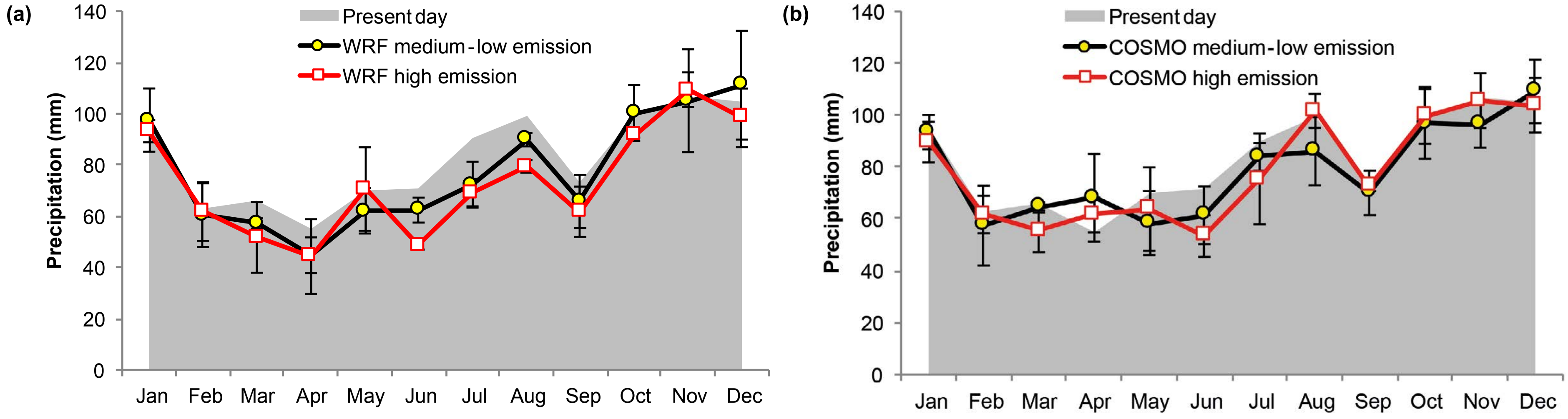


Figure 4.9. Precipitation under present/future, high-/low-emission scenarios for (a) WRF projections and (b) COSMO projections (O'Driscoll *et al.*, 2017b).

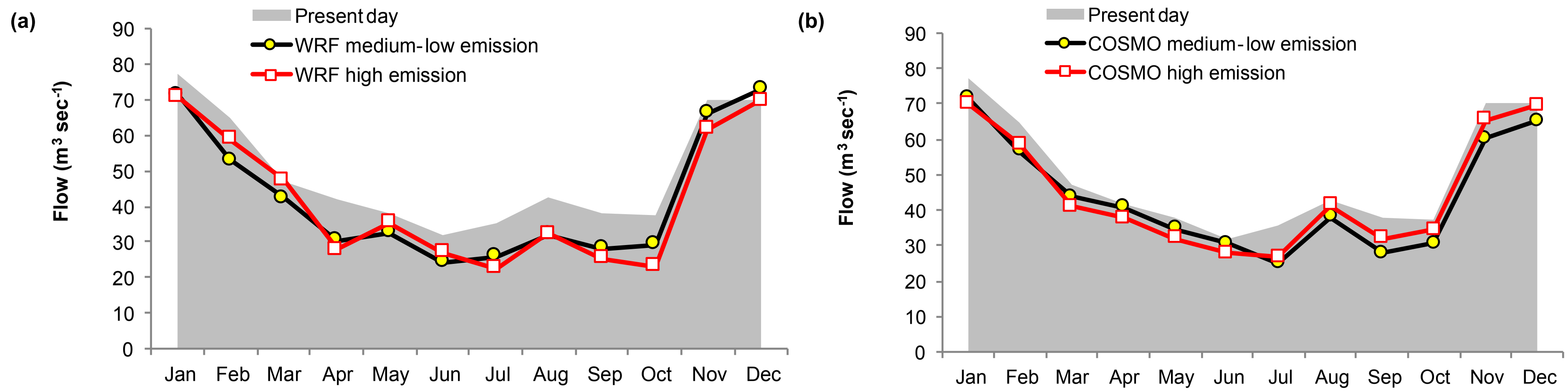


Figure 4.10. Flow under present/future, high-/low-emission scenarios for (a) WRF projections and (b) COSMO projections.

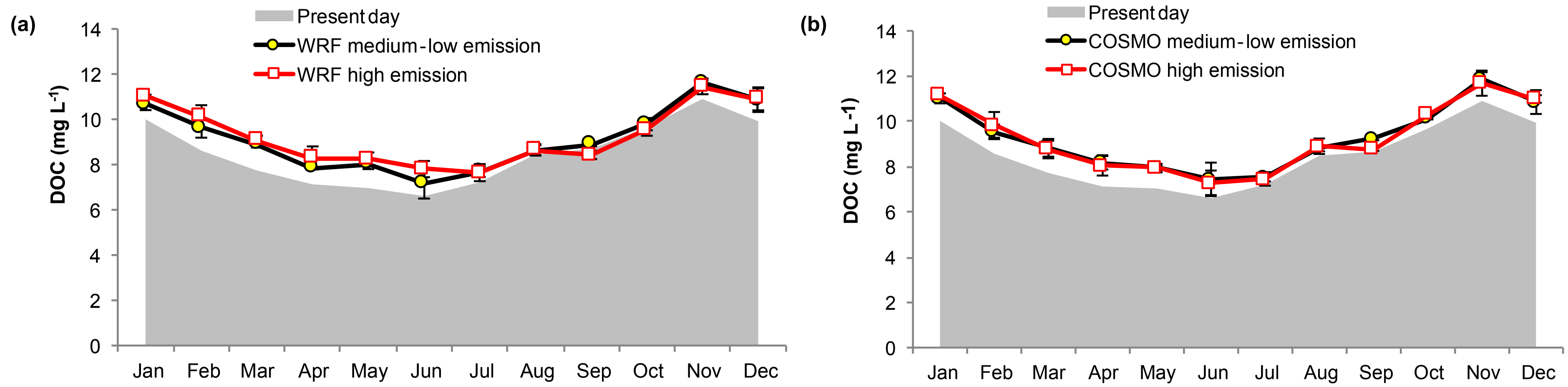


Figure 4.11. DOC under present/future, high-/low-emission scenarios for (a) WRF projections and (b) COSMO projections (O’Driscoll *et al.*, 2017b).

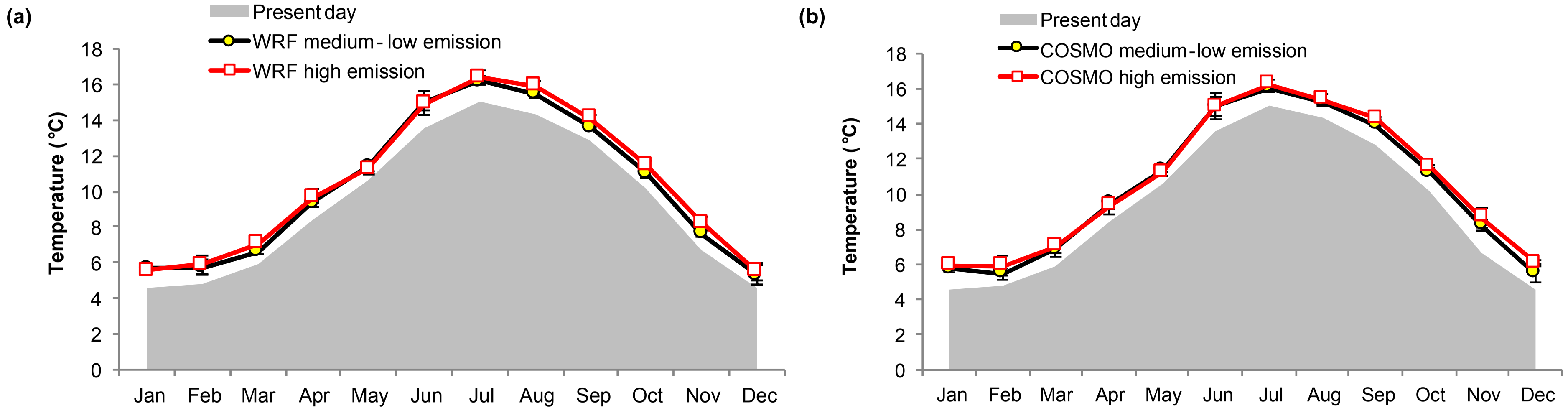


Figure 4.12 DOC export under present/future, high-/low-emission scenarios for (a) WRF projections and (b) COSMO projections.

5 Ptaquiloside in Irish Drinking Water

5.1 Overview

It was anticipated that we would follow the approach used by Ramwell *et al*. (2010) to create a high-risk catchment map for bracken in Ireland. However, owing to a lack of spatial data on national bracken percentage cover and a lack of time and expertise in remote sensing technology, this task was not feasible within the project timeframe. A field study was carried out on nine bracken stands, six in Northern Ireland, two on the west coast of Ireland and one on the east coast of Ireland (Figure 5.1; Table 5.1).

The three sites in Ireland were selected following consultation with the National Parks and Wildlife Service, based on local knowledge. The six sites in Northern Ireland were selected following collaboration with the College of Agriculture, Food and Rural Enterprise (CAFRE) and Department of Agriculture, Environment and Rural Affairs, Northern Ireland. CAFRE set up six demonstration sites to compare the effectiveness, against an untreated area, of three different treatments for bracken – cutting, rolling and spraying with asulam – in the summer of 2014, which coincided with the project timeline.

In this study the risk of ptaquiloside to drinking water was assessed by quantifying ptaquiloside in the receiving waters at three drinking water abstraction sites across Ireland and in bracken fronds surrounding the abstraction sites. We also investigated the impact of different management regimes (spraying, cutting

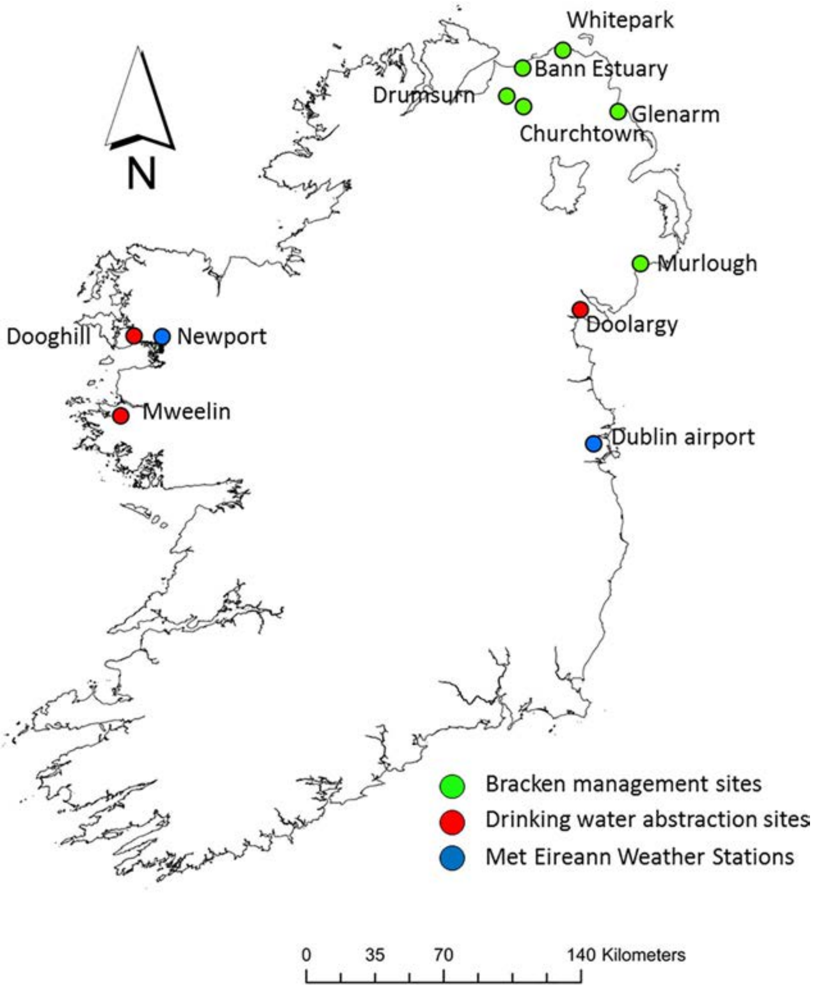


Figure 5.1. Map of Ireland with locations of bracken study sites (O'Driscoll *et al.*, 2016).

Table 5.1. Study site locations and charactistics

Site Name	x-coordinate	y-coordinate	Altitude (m.a.s.l.)	Soil type	Land use	Soil available P (mg L^{-1})	Soil available K (mg L^{-1})	Soil available Mg (mg L^{-1})	Groundwater vulnerability	Average annual precipitation (mm)	Soil pH
Murlough[a]	740704	835420	15	Poorly drained gleys	Cattle grazing	27	113	178	n/a	900–1000	5.3
Glenarm[a]	729329	913040	52	Poorly drained gleys	Cattle grazing	7	452	356	n/a	1250–1500	6
Whitepark Bay[a]	701135	944416	14	Poorly drained gleys	Cattle grazing	7	114	227	n/a	1000–1250	7.5
Drumsurn[a]	672517	920998	86	Poorly drained gleys	Cattle grazing	11	417	285	n/a	1000–1250	5.4
Bann Estuary[a]	680615	935318	6	Poorly drained gleys	Cattle grazing	27	110	159	n/a	1000–1250	5.5
Churchtown[a]	681061	915631	84	Poorly drained gleys	Cattle grazing	9	353	246	n/a	1000–1250	5.3
Dooghill[b]	482372	798514	25	Peaty podzols	Sheep grazing	6	93	216	Extreme	1600–2000	5.64
Doolargy[b]	710012	811895	148	Peaty podzols	Sheep grazing	4	272	310	Extreme	1000–1200	5.82
Mweelin[b]	475591	757708	68	Peaty podzols	Sheep grazing	<1	96	267	Extreme	1600–2000	6.86

Soil-available P and K were determined by a flow injection analysis system and Mg was determined by atomic absorption spectrophotometry for the upper 300 mm soil layer.

[a] Bracken management plots in Northern Ireland.

[b] Water abstraction sites.

Source: O'Driscoll *et al.*, 2016.

and rolling) on ptaquiloside concentrations at plot scale in six locations in Northern Ireland.

5.1.1 Drinking water abstraction sites

Three drinking water abstraction sites were selected for the study (Mweelin well, Dooghill, Doolargy; Figure 5.1). The Mweelin well and Doolargy sites had groundwater (spring well) abstractions and Dooghill had a surface water abstraction from a first-order stream. Sampling was undertaken at all sites within two consecutive days in the last week of each month between June 2015 and November 2015, yielding a total of six water samples and six vegetation samples.

5.1.2 Bracken management plots

Six bracken stands located across Northern Ireland were selected for this investigation (Whitepark Bay, Glenarm, Churchtown, Drumsurn, Bann Estuary, Murlough; Figure 5.1 and Table 5.1). At all sites, bracken coverage was dominant. Plots of approximately 20 × 40 m were established at each site. Four treatments were applied in July 2014. The treatment design was as follows: control (no treatment), roll, cut and chemical (spraying with the herbicide asulam). Asulox (a soluble concentrate containing 400 g L^{-1} (33.6% w/w) of the sodium salt of asulam) was applied at a rate of 11 L ha^{-1} in 400–500 L ha^{-1} of water using an all-terrain vehicle (ATV) with a mounted boom sprayer. Bracken was cut using a flail cutter mounted on an ATV and rolled with a Cambridge-type roller. Debris was not removed.

Fronds were counted in eight 0.25 m^2 quadrats in each plot before treatment (July 2014) and after treatment (July 2015) to estimate the frond density. The average height of the fronds in each treatment was also noted. Cutting and rolling were repeated in July 2015 following frond density measurements. Bracken was collected for analysis of ptaquiloside content on one occasion on 23 July 2015 at all six sites, 2 weeks after the repeat treatments (cutting and rolling) had been applied. Ten whole fronds were harvested for analysis at the soil surface from each treatment at each site. All 10 fronds were pooled to give a single, composite sample for each treatment at each site ($n = 24$).

5.1.3 Sampling and extraction protocol

The sampling and extraction protocols used the most recent developments from other researchers investigating ptaquiloside (Cáceres-Peña et al., 2013; Clauson-Kaas *et al*., 2014). Water samples were collected in 100 mL amber bottles and buffered with 2.5 mL of 0.3 M ammonium acetate buffer, adjusted to pH 5 with glacial acetic acid (Clauson-Kaas *et al*., 2014). Buffered samples were chilled on ice packs in the dark until further analyses were performed, with a maximum storage time of 1 day. Vegetation samples comprised 10 randomly harvested fronds, cut at the soil surface, from the dense bracken stand surrounding the drinking water abstraction point. Each composite vegetation sample was placed in an opaque polyethylene bag and placed in a cooler box. The following day, pinnulae were stripped off and hard rachis were discarded (Cáceres-Peña et al., 2013). Samples were mixed to homogenise them and a subsample of fresh blades (6 g) was extracted twice with 90°C MilliQ water (200 mL) in a fast rotating blender for 5 minutes. After filtration through cheesecloth (unbleached food grade) and immediate cooling of filtrates in an ice-water bath (5–8°C), extracts were combined and centrifuged at 503 × *g* for 5 minutes. After separation of the solids, the volume was adjusted to 500 mL with 5°C MilliQ water, from which a 20 mL aliquot was drawn. Aliquots of the extracts were analysed on the same day. Three replicate 300-mm deep soil cores were collected from each of the study sites using a 30-mm diameter gouge auger. The vegetation layer was removed and the samples were homogenised. Three subsamples were obtained from each.

5.1.4 Chemical analysis

Samples (water and vegetation extracts) were pre-concentrated by a factor of 20. A solid-phase extraction (SPE) 150 mg Oasis MAX column (Waters Corporation, Milford, MA) was conditioned with 2 mL of methanol followed by 2 mL of MilliQ water (Jenson *et al*., 2008). A total of 20 mL water/vegetation extract sample was loaded on the column for cleaning and pre-concentration. The column was rinsed with 2 mL of MilliQ water followed by 2 mL of 15% (v/v) methanol.

Elution was performed using 2 × 0.25 mL of 80% (v/v) methanol. Prior to analysis, the eluate was diluted 1:1 with MilliQ water to obtain better performance on the liquid chromatography (LC) column (Jenson *et al.*, 2008). An external standard of ptaquiloside was isolated and purified from dried bracken material using the procedure described in Aranha *et al.* (2014). To evaluate the recovery efficiency of the method, 20 mL of MilliQ water was spiked with ptaquiloside at concentrations of 1 μg L^{-1} for quality control (QC) Low and 10 μg L^{-1} for QC High samples.

A 6460 Triple Quad liquid chromatography–mass spectroscopy (LC-MS) system (Agilent Technologies, Santa Clara, CA) coupled with an Agilent 1200 high-pressure liquid chromatography (HPLC) system and interfaced with jetstream ionisation was used for the chromatographic separation and detection of ptaquiloside. The limit of detection for the overall method including SPE pre-concentration was 0.01 μg L^{-1}. The linear range of the LC-MS/MS method was determined by triplicate injections of seven standards in the range of 1–300 μg L^{-1}. Recovery for ptaquiloside was 70% for QC Low and 57% for QC High.

5.2 Findings

5.2.1 Ptaquiloside in bracken fronds collected from the drinking water abstraction sites

Above-ground frond growth began in late May to early June 2015. Ptaquiloside was detected in all bracken frond samples analysed between June and November 2015 (Table 5.2).

The highest ptaquiloside concentration was observed at Doolargy in June 2015 (297 μg g^{-1}). A temporal pattern was observed in ptaquiloside concentrations from bracken fronds at the three drinking water abstraction sites (Figure 5.2).

The highest frond concentrations were reported in June 2015. Concentrations began to decrease in September 2015 with a rapid reduction in ptaquiloside (to < 0.01 μg g^{-1}) in November 2015. Collated data on ptaquiloside concentrations in bracken fronds from the three abstraction sites and the six bracken management plots in Northern Ireland revealed spatial variation, with lower concentrations of ptaquiloside in the west than in the east of Ireland. Similarly lower

Table 5.2. Ptaquiloside concentrations in bracken fronds and water samples from the drinking water abstraction sites, and total rainfall and average temperature in the 4 hours preceding sample collection (taken from nearby Met Éireann weather stations) (O'Driscoll *et al.*, 2016)

	Month (2015)					
Site	**June**	**July**	**August**	**September**	**October**	**November**
Vegetation ptaquiloside (μg g^{-1})						
Mweelin	14.1	33.1	0.27	0.88	1.34	< 0.01
Dooghill	88.4	52.7	95.1	30	3.33	0.03
Doolargy	297	140	148	32	27.6	0.01
Water ptaquiloside (μg L^{-1})						
Mweelin	0	0	0	0	0.57	0
Dooghill	0	0	0	0	0.67	0
Doolargy	0	0	0	0	0.01	0
Rain (cm)						
Mweelin	1.6	0	1.1	0	0	2.2
Dooghill	0	1.2	2.6	0	3.8	2.2
Doolargy	0	0	5.3	0	0	0.1
Temperature (°C)						
Mweelin	16.5	14.2	14.4	16.2	13	9.85
Dooghill	17.1	13.7	13.6	18.1	12.2	9.85
Doolargy	23.7	15.3	13.5	16.1	12.7	9.85

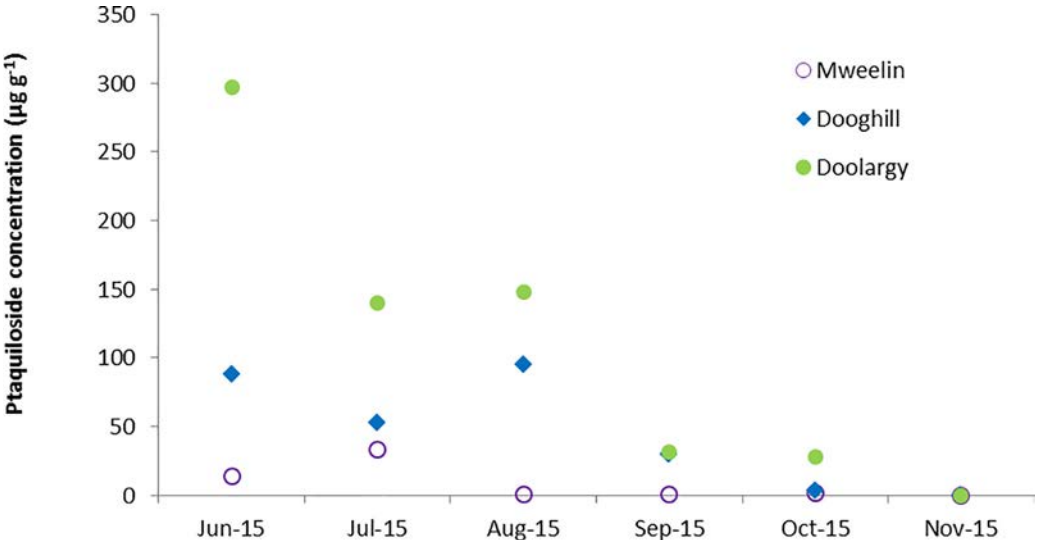


Figure 5.2. Trends in average ptaquiloside concentrations in bracken fronds from Mweelin, Dooghill and Doolargy sites (O'Driscoll *et al.*, 2016).

concentrations were observed in the south than in the north of the country (Figure 5.3).

5.2.2 *Ptaquiloside in surface water and groundwater abstractions*

Ptaquiloside was observed in samples from all three drinking water abstraction sites (Mweelin well, Dooghill and Doolargy) in October 2015. The highest ptaquiloside concentration, 0.67 μg L^{-1}, was detected in Dooghill in the surface water stream, followed by 0.57 μg L^{-1} in Mweelin and 0.01 μg L^{-1} in Doolargy.

Bracken management plot study

Ptaquiloside was detected in all frond samples analysed from the six treatment plots in Northern Ireland in July 2015. Ptaquiloside concentrations were 30.2–787 μg g^{-1}. The highest concentrations of ptaquiloside in fronds were observed in Churchtown and Bann Estuary. The Bann Estuary site was most sensitive to the treatments, possibly because it had previously being subjected to spraying. Overall, concentrations of ptaquiloside were markedly elevated in the plots subjected to cutting compared with the control plots, with the notable exceptions of Glenarm, where the different treatments had very little impact on ptaquiloside concentrations, and Churchtown, where spraying had a much larger impact on the ptaquiloside concentrations in the fronds.

The environmental load of ptaquiloside is a function of the frond concentration and the mass of bracken. In this study the frond height and density were used as an indicative measure of the amount of bracken to provide an indicative ptaquiloside load. When the quantity of bracken is considered in conjunction with the ptaquiloside concentration, spraying has the largest effect on reducing ptaquiloside load (Figure 5.4).

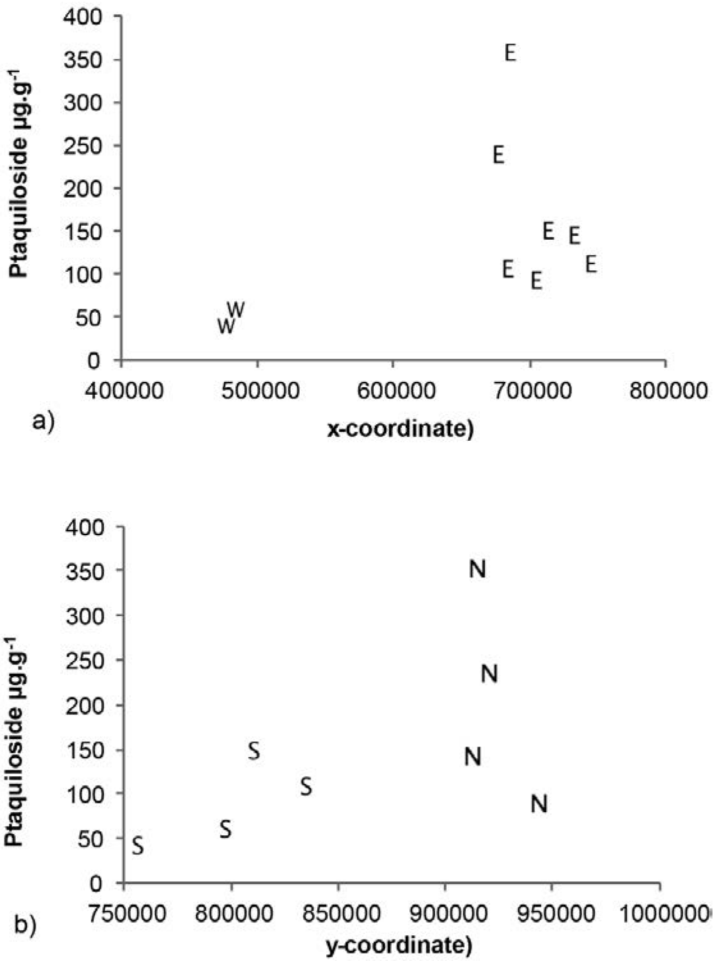


Figure 5.3. Ptaquiloside concentrations plotted against (a) *x*-coordinates and (b) *y*-coordinates (N – north; S – south; E – east; W – west) for fronds sampled in July 2015 at Mweelin, Dooghill, Doolargy, Whitepark Bay, Glenarm, Churchtown, Drumsurn, Bann Estuary and Murlough (O'Driscoll *et al*., 2016).

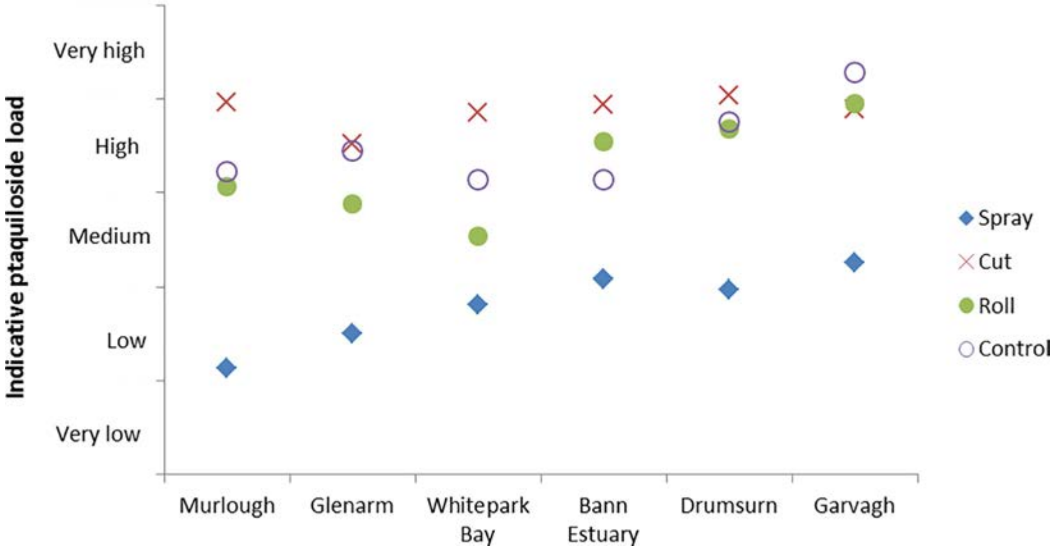


Figure 5.4. Effect of treatment regime on ptaquiloside load for the six experimental plots (O'Driscoll *et al*., 2016).

6 Conclusions and Recommendations

6.1 Conclusions

- The results of the high-risk catchment exercise demonstrated that raw surface water and groundwater sources most at risk of TTHM exceedances occur on the west coast of Ireland and were associated with the selected criteria, i.e. peat presence, high rainfall and low slopes, in addition to groundwater vulnerability.
- All 684 water supplies included in the statistical analysis were assigned to Treatment type 1 (no NOM removal) or Treatment type 2 (some degree of NOM removal). Statistical analysis of TTHM (as the response variable) at treatment plants with Treatment types 1 and 2, for surface water and groundwater sources with respect to catchment characteristics (percentage area of peat, pastures and forestry), indicated that for water supplies:
    - with no NOM treatment (type 1), TTHM concentrations significantly increased with percentage of peat;
    - with treatment giving some degree of NOM removal, TTHM concentrations were significantly higher when the peat percentage and the pastures percentage were both higher;
    - with surface water sources, there were significantly higher average TTHM concentrations than in schemes with high or low vulnerability groundwater sources.
- Raw water DOC concentrations plotted against precipitation for the spring-fed supply in the Galway PWS gave a strong positive correlation, indicating that the surface and underground flow systems were highly connected.
- PCA ordination of chemicals was successful in revealing relationships among catchment sites in the Galway PWS.
- TTHMs exceeded the parametric value on the majority of sampling occasions in the groundwater spring supply and DOC concentrations monitored in the raw and treated water indicated that NOM was not adequately removed in the Galway PWS.
- NOM, characteristic of compounds with moderate aromaticity that originate from humic-like terrestrially derived reprocessed organic matter, was the most prevalent form following treatment in the Galway PWS. Higher and intermediate molecular weight NOM has a higher potential to form THMs.
- Measurements of fluorescent components and TN performed similarly to UVA_{254} in predicting levels of chloroform in the Galway PWS as highlighted by the Spearman's rank coefficient analysis.
- Following assessment of ozone and GAC treatment of NOM in a groundwater spring water supply where (1) the ZoC has not been adequately mapped, (2) the supply is prone to surface water infiltration, and (3) it has not been previous practice to regenerate the GAC, it can be concluded that this is not a suitable treatment design for NOM.
- Fluorescence spectroscopy was successful in tracking changes in NOM character downstream in the Boyne river and highlighted the different catchment land uses.
- Seasonal trends in NOM concentrations were identified in both Mayo and Louth raw water, with NOM increasing from late autumn and through the winter, which is consistent with vegetation senescence and decreasing soil temperatures.
- The Louth WTP reduced the greatest amount of NOM in comparison with the other treatment types; however, the treated water had an average DOC concentration of $4.52 \pm 1.2\,\text{mg}\,\text{L}^{-1}$ and DOC $> 2\,\text{mg}\,\text{L}^{-1}$ can cause THM formation. Higher proportions of higher and moderate molecular weight NOM were removed and smaller percentages of low molecular weight NOM were removed.
- TTHMs exceeded the parametric value on one occasion in the Louth WTP during the study period.
- The Mayo WTP, using ultrafiltration membranes, was not adequate to remove the concentrations of NOM it was receiving. It was most inefficient at removing higher molecular weight humic-like terrestrially derived organic matter and only slightly more efficient at removing humic-like

terrestrially derived reprocessed and protein-like organic matter. Higher and intermediate molecular weight NOM have a higher potential to form THMs.

- TTHMs exceeded the parametric value on all but one occasions in the Mayo WTP. Fluorescent components performed slightly better than UVA_{254} and SUVA for predicting chloroform as indicated by the Spearman's rank correlation.
- Mean annual temperatures are predicted to increase in the Boyne catchment by 1.0–1.1°C. Total annual precipitation will remain largely the same, and results show projected monthly average decreases in spring through to late summer.
- Monthly averages of daily flow show projected overall decreases and DOC mean monthly concentrations show an overall increase.
- Simulated mean annual DOC export from the Boyne catchment ($5.8 \pm 1.3\,\mathrm{g\,C\,m^{-2}}$ per year) is in the higher range for agricultural catchments and was strongly linked to the timing of vegetation senescence/at the end of the growing season.
- The modelling approach adopted here suggests that while biogeochemical mechanisms controlling carbon within a watershed are complex, representation of such interdependent processes in a process-based model is possible even for a catchment with a low percentage of peat and high use of pastures using online high resolution WTP data and routinely monitored parameters (i.e. temperature, precipitation and flow).
- While the presence of THMs in drinking water is a national concern, the WHO states that "efficient disinfection must never be compromised in attempt to meet the guidelines for DBPs and that the microbiological quality of the water must always take precedence".
- Ptaquiloside is present in bracken fronds in Ireland from frond emergence (14.1–$297\,\mu\mathrm{g\,g^{-1}}$) to plant die-off (0.03 to less than $0.01\,\mu\mathrm{g\,g^{-1}}$).
- There is a suggestion that spatial and temporal variation exists; however, further research with an increased number of sites and a higher temporal resolution is warranted to confirm this.
- Spraying was the most effective means of control for reducing ptaquiloside load, whereas cutting bracken may increase the production of ptaquiloside in the short term and hence the potential risk to drinking water quality. However, asulam is a banned substance and is itself potentially harmful in drinking water.
- Ptaquiloside was detected in drinking water on only one sampling occasion in concentrations as high as $0.67\,\mu\mathrm{g\,L^{-1}}$ in drinking water from abstraction sites.
- Bracken ferns are classified by the IARC as "possibly carcinogenic to humans". From a review of the limited research literature and from the limited sampling carried out as part of this research project, it is not believed that there is a large-scale national risk from bracken ferns to drinking water; however, further research is warranted.

6.2 Recommendations for Policy

Recommendation	Target
Use of a high-risk catchment map tool such as that trialled here in establishing monitoring programmes for collation of baseline data on NOM quantity and character for the design of new/upgraded WTPs	EPA, IW, NFGWS, LA, PGWSs
Audit monitoring of THMs to comply with the Drinking Water Regulations should consider the nature of the source water accounting for both the seasonal flush of NOM in the autumn period and episodic rainfall events where supplies are influenced by such events	IW, NFGWS, LA, PGWSs, HSE
Accurate mapping of ZoC should be a prerequisite for drinking water supplies	NFGWS, IW, PGWSs
Consideration given to the localised predicted effects of climate change on NOM concentrations in water supplies and monitoring of high-resolution DOC data	NFGWS, IW, PGWSs
Establish the extent of bracken invasion in Ireland with the use of remote sensing and ground-truthing to accurately determine the extent of the bracken problem in Ireland	DAFM, EPA, DEHCLG
Increase the level of awareness of the possible risks of bracken and ptaquiloside to private drinking water wells	DAFM, EPA, HSE, DoH, NFGWS

DAFM, Department of Agriculture, Food and the Marine; DoH, Department of Health; HSE, Health Service Executive; IW, Irish Water; NFGWS, National Federation of Group Water Schemes; NPWS, National Parks and Wildlife Service; DEHCLG, Department of Housing, Planning and Local Government; PGWS, private group water scheme managers.

References

Aitkenhead-Peterson, J.A., Smart, R.P., Aitkenhead, M.J., Cresser, M.S. and McDowell, W.H., 2007. Spatial and temporal variation of dissolved organic carbon export from gauged and ungauged watersheds of Dee Valley, Scotland: effect of land cover and C:N. *Water Resources Research* 43: W05442. DOI: 10.1029/2006WR004999.

Alonso-Amelot, M.E. and Avendaño, M., 2001. Possible association between gastric cancer and bracken fern in Venezuela: an epidemiologic study. *International Journal of Cancer* 91: 252–259.

Aranha, P.C.R., Hansen, H.C.B., Rasmussen, L.H., Strobel, B.W. and Friis, C., 2014. Determination of ptaquiloside and pterosin B derived from bracken (*Pteridium aquilinum*) in cattle plasma, urine and milk. *Journal of chromatography. B, Analytical Technologies in the Biomedical and Life Sciences* 951–952: 44–51.

Austnes, K., Evans, C., Eliot-Laize, C., Naden, P. and Old, G., 2010. Effects of storm events on mobilisation and instream processing of dissolved organic matter (DOM) in a Welsh peatland catchment. *Biogeochemistry* 99: 157–173.

Baghoth, S.A. 2012. Characterizing natural organic matter in drinking water treatment processes and trains. PhD Thesis, UNESCO-IHE.

Baghoth, S.A., Sharma, S.K. and Amy, G.L., 2011. Tracking natural organic matter (NOM) in a drinking water treatment plant using fluorescence excitation-emission matrices and PARAFAC. Water *Research* 45(2): 797–809.

Barret, S.E., Krasner, S.W. and Amy, G.L., 2000. *Natural Organic Matter and Disinfection By-products Characterization And Control In Drinking Water*. American Chemical Society, Washington, DC.

Barry, C.D., Renou-Wilson, F., Wilson, D., Müller, C. and Foy, R.H., 2016. Magnitude, form and bioavailability of fluvial carbon exports from Irish organic soils under pasture. *Aquatic Sciences* 78: 541–560. DOI: 10.1007/s00027-015-0464-x.

Basu, M., Gupta, S.K., Singh, G. and Mukhopadhyay, U., 2011. Multi-route risk assessment from trihalomethanes in drinking water supplies. *Environmental Monitoring and Assessment* 178(1): 121–134.

Billett, M., Palmer, S., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K., Flechard, C. and Fowler, D. 2004. Linking land–atmosphere–stream carbon fluxes in a lowland peatland system. *Global Biogeochemical Cycles* 18. DOI: 10.1029/2003GB002058.

Boholm, A. and Prutzer, M., 2017. Experts' understanding of drinking water risk management in a climate change scenario. *Climate Risk Management* 16: 133–144. DOI: 10.1016/j.crm.2017.01.003.

Brooks, P., McKnight, D.M. and Bencala, K.E., 1999. The relationship between soil heterotrophic activity, soil dissolved organic carbon (DOC) leachate, and catchment-scale DOC export in headwater catchments. *Water Resources Research* 35: 1895–1902.

Cáceres-Peña, Y.C., Naya, M., Calcagno-Pissarelli, M.P. and Alonso-Amelot, M.E., 2013. Influence of bracken fern (*Pteridium caudatum* L. Maxon) pre-treatment on extraction yield of illudane glycosides and pterosins. *Phytochemical Analysis* 24: 290–295.

Casey, T., Kearney, P. and Kerr, H., 2012. *The Chlorine Demand Characteristics of Irish Water Supplies: Process Design Implications for Disinfection and THM Formation*. Engineers Ireland. Available online: https://www.engineersireland.ie/EngineersIreland/media/SiteMedia/groups/societies/water-enviro/Chlorine-Demand-Characteristics-of-Irish-Water-Supplies.pdf?ext=.pdf (accessed 21 September 2017.

Catalá, T.S., Reche, I., Fuentes-Lema, A., Romera-Castillo, C., Nieto-Cid, M., Ortega-Retuerta, E., Calvo, E., Álvarez, M., Marrasé, C., Stedmon, C.A. and Álvarez-Salgado, X.A., 2015. Turnover time of fluorescent dissolved organic matter in the dark global ocean. *Nature Communications* 6: 5986. DOI: 10.1038/ncomms6986.

Cawley, K.M., Ding, Y., Fourqurean, J. and Jaffé, R., 2012. Characterising the sources and fate of dissolved organic matter in Shark Bay, Australia: a preliminary study using optical properties and stable carbon isotopes. *Marine and Freshwater Research* 63: 1098–1107. DOI: 10.1071/MF12028.

Chow, C.W.K., van Leeuwen, J.A., Drikas, M., Fabris, R., Spark, K.M. and Page, D.W., 1999. The impact of the character of natural organic matter in conventional treatment with alum. *Water Science and Technology* 40: 97–104.

Clauson-Kaas, F., Jensen, P.H., Jacobsen, O.S., Juhler, R.K. and Hansen, H.C.B., 2014. The naturally occurring carcinogen ptaquiloside (pta) is present in groundwater below bracken vegetation. *Environmental Toxicology and Chemistry* 33: 1030–1034. DOI: 10.1002/etc.2533.

Clauson-Kaas, F., Ramwell, C., Hansen, H.C.B. and Strobel, B.W., 2016. Ptaquiloside from bracken in stream water at base flow and during storm events. *Water Research* 106: 155–162.

Coble, P.G. 1996 Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Marine Chemistry* 51: 325–346.

Coll, J., 2010. Climate change and Europe's mountains. In Price, M.F. (ed.), *Europe's Ecological Backbone: Recognising the True Value of Our Mountains*. EEA Report No. 6/2010. European Environment Agency, Copenhagen, pp. 74−84.

Coll, J., Gibb, S.W., Price, M.F., McClatchey, J. and Harrison, J., 2010. Developing site scale projections of climate change in the Scottish Highlands. *Climate Research* 45: 71−85.

Connolly, J. and Holden, N.M., 2009. Mapping peat soils in Ireland: updating the derived Irish peat map. *Irish Geography* 42(3): 343–352.

Cool, G., Lebel, A., Sadiq, R. and Rodriguez, M.J., 2014. Impact of catchment geophysical characteristics and climate on regional variability of dissolved organic carbon (DOC) in surface water. *Science of the Total Environment* 490: 947–956.

de Wit, H.A., Mulder, J., Hindar, A. and Hole, L., 2007. Long-term increase in dissolved organic carbon in streamwaters in Norway in response to reduced acid deposition. *Environmental Science & Technology* 41: 7706–7713.

de Wit, H.A., Valinia, S., Weyhenmeyer, G.A., Futter, M.N., Kortelainen, P., Austnes, K., Hessen, D.O., Raike, A., Laudon, H. and Vuorenmaa, J., 2016. Current browning of surface waters will be further promoted by wetter climate. *Environmental Science & Technology Letters* 3: 430–435.

Defra, 2005. *Controlling Soil Erosion: a Manual for the Assessment and Management of Agricultural Land at Risk of Water Erosion in Lowland England*. Revised September 2005. Department for Environment, Food and Rural Affairs, London.

Delpla, I., Rodriguez, M.J., 2016. Experimental disinfection by-product formation potential following rainfall events. *Water Research* 104: 340–348. DOI: 10.1016/j.watres.2016.08.031.

Delpla, I., Jung, A.-V., Baures, E., Clement, M. and Thomas, O., 2009. Impacts of climate change on surface water quality in relation to drinking water production. *Environment International* 35: 1225–1233.

Doms, G. and Schättler, U., 2002. *A Description of the Nonhydrostatic Regional Model LM. Part I: Dynamics and Numerics*. Deutscher Wetterdienst, Offenbach.

DWQR (Drinking Water Quality Regulator), 2015. *Drinking Water Quality in Scotland 2014: Annual Report by the Drinking Water Quality Regulator*. Available online: http://dwqr.scot/media/13775/dwqr-annual-report-2013-public-water-supplies.pdf (accessed 25 September 2017).

Eckhardt, B.W. and Moore, T.R., 1990. Controls on dissolved organic carbon concentrations in streams, southern Quebec. *Canadian Journal of Fisheries and Aquatic Sciences* 47: 1537–1544.

Edzwald, J.K. and Tobiason, J.E., 1999. Enhanced coagulation: US requirements and a broader view. *Water Science and Technology* 40(9): 63–70.

Eikebrokk, B., Vogt, R.D. and Liltved, H., 2004. NOM increase in northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Science and Technology: Water Supply* 4(4): 47–54.

EPA (Environmental Protection Agency), 2011. *Site Information Report – Williamstown PS*. Available online: https://www.epa.ie/pubs/reports/water/ground/gwmpinfo/EPA_DWZOC_Williamstown%20PS.pdf (accessed 13 February 2017).

EPA (Environmental Protection Agency), 2012. *Disinfection By-products in Drinking Water*. Advice Note No. 4, Version 2. Available online: http://www.epa.ie/pubs/advice/drinkingwater/DrinkingWaterGuide4_v8.pdf (accessed 25 September 2017).

EPA (Environmental Protection Agency), 2013. *The Provision and Quality of Drinking Water in Ireland – A Report for the Year 2012*. Available online: http://www.epa.ie/pubs/reports/water/drinking/drinkingwaterreport2012.html (accessed 25 September 2017).

EPA (Environmental Protection Agency), 2016. *Drinking Water Report for Public Supplies 2015*. Available online: http://www.epa.ie/pubs/reports/water/drinking/dwreport2015.html (accessed 25 September 2017).

Evans, C., Monteith, D. and Cooper, D., 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environmental Pollution* 137: 55–71.

Evans, C.D., Chapman, P.J., Clark J.M., Monteith, D.T. and Cresser, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology* 12: 2044–2053.

Evans, C.D., Page, S.E., Jones, T., Moore, S., Gauci, V., Laiho, R., Hruška, J., Allott, T.E.H., Billett, M.F., Tipping, E., Freeman, C. and Garnett, M.H., 2012. Acidity controls on dissolved organic carbon mobility in organic soils. *Global Change Biology* 18: 3317–3331.

Evans, C.D., Renou-Wilson, F. and Strack, M., 2016. The role of waterborne carbon in the greenhouse gas balance of drained and re-wetted peatlands. *Aquatic Sciences* 78: 573–590.

Fabris, R., Chow, C.W.K., Drikas, M. and Eikebrokk, B., 2008. Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Research* 42(15): 4188– 4196.

Flato, G., Marotzke, J., Abiodun, B., Braconnot, P., Chou, S.C., Collins, W., Cox, P., Driouech, F., Emori, S., Eyring, V., Forest, C., Gleckler, P., Guilyardi, E., Jakob, C., Kattsov, V., Reason, C. and Rummukainen, M., 2013. Evaluation of climate models. In Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V. and Midgley, P.M. (eds), *Climate Change 2013: The Physical Science Basis*. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge.

Fletcher, M.T., Brock, I.J., Reichmann, K.G., McKenzie, R.A. and Blaney, B.J., 2011. Norsesquiterpene glycosides in bracken ferns (*Pteridium esculentum* and *Pteridium aquilinum* subsp. *wightianum*) from eastern Australia: reassessed poisoning risk to animals. *Journal of Agricultural and Food Chemistry* 59: 5133–5138.

Fram, M.S., Fujii, R., Weishaar, J.L., Bergamaschi, B.A. and Aiken, G.R., 1999. How DOC composition may explain the poor correlation between specific trihalomethane formation potential and specific UV absorbance. Report 99-4018B. *Proceedings of the Technical Meeting, USGS Toxic Substances Hydrology Program*. Charleston, SC.

Freeman, C., Evans, C.D., Monteith, D.T., Reynolds, B. and Fenner, N., 2001. Export of organic carbon from peat soils. *Nature* 412: 785.

Freeman, C., Fenner, N., Ostle, N.J., Kang, H., Dowrick, D.J., Reynolds, B., Lock, M.A., Sleep, D., Hughes, S. and Hudson, J., 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature* 430:195–198.

Frimmel, F.H., Saravia, F. and Gorenflo, A., 2006. NOM removal from different raw waters by membrane filtration. *Water Science & Technology Water Supply* 4(4): 165–174.

Futter, M.N. and de Wit, H.A., 2008. Testing seasonal and long-term controls of streamwater DOC using empirical and process based models. *Science of the Total Environment* 407(1): 698–707.

Futter, M.N., Butterfield, D., Cosby, B.J., Dillon, P.J., Wade, A.J. and Whitehead, P.G., 2007. Modelling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. *Water Resources Research* 43: W02424.

Futter, M.N., Forsius, M., Holmberg, M. and Starr, M., 2009. A long term simulation of the effects of acidic deposition and climate change on surface water dissolved organic carbon concentrations in a boreal catchment. *Hydrology Research* 40(2–3): 291–305.

Futter, M.N., Erlandsson, M.A., Butterfield, D., Whitehead, P.G., Oni, S.K. and Wade, A.J., 2014. PERSiST: a flexible rainfall–runoff modelling toolkit for use with the INCA family of models. *Hydrology and Earth System Sciences* 18(2): 855–873.

Galpin, O.P., Whitaker, C.J., Whitaker, R. and Kassab, J.Y., 1990. Gastric cancer in Gwynedd. Possible links with bracken. *British Journal of Cancer* 61: 737–740.

Gil da Costa, R.M., Bastos, M.M.S.M., Oliveira, P.A. and Lopes, C., 2012. Bracken-associated human and animal health hazards: chemical, biological and pathological evidence. *Journal of Hazardous Materials* 203–204: 1–12.

Gonsior, M., Schmitt-Koppin, P., Stavklint, H., Richardson, S.D., Hertkorn, N. and Bastviken, D., 2014. Changes in dissolved organic matter during the treatment processes of a drinking water plant in Sweden and formation of previously unknown disinfection byproducts. *Environmental Science & Technology* 48: 12,714–12,722.

Government of Ireland, 2014. European Union (Drinking Water) Regulations 2014. S.I. No. 122 of 2014. Government of Ireland, Dublin.

Government of Ireland, 2014. (Good Agricultural Practice for the Protection of Waters) Regulations 2014 (S.I. No. 31 of 2014). Government of Ireland, Dublin.

Graeber, D., Gelbrecht, J., Pusch, M.T., Anlanger, C. and von Schiller, D., 2012. Agriculture has changed the amount and composition of dissolved organic matter in central European headwater streams. *Science of the Total Environment* 438: 435–446.

Grieve, I.C. and Marsden, R.L., 2001. Effects of forest cover and topographic factors on TOC and associated metals at various scales in western Scotland. *Science of the Total Environment* 265: 143–151.

Guéguen, C., Cuss, C.W., Cassels, C.J. and Carmack, E.C., 2014. Absorption and fluorescence of dissolved organic matter in the waters of the Canadian Arctic Archipelago, Baffin Bay, and the Labrador Sea. *Journal of Geophysical Research Oceans* 119: 2034–2047. DOI: 10.1002/ 2013JC009173.

Hazeleger, W., Wang, X., Severijns, C., Ştefănescu, S., Bintanja, R., Sterl, A., Wyser, K., Semmler, T., Yang, S., van den Hurk, B., van Noije, T., van der Linden, E. and van der Wiel, K., 2011. EC-Earth V2.2: description and validation of a new seamless earth system prediction model. *Climate Dynamics* 39: 2611–2629.

Hickey, C., 2009. The use of multiple techniques for the conceptualisation of lowland karst, a case study from County Roscommon, Ireland. *Acta Carsologica* 39(2): 331–346.

Holland, J. and Alpin, P., 2012. Super-resolution image analysis as a means of monitoring bracken (*Pteridium aquilinum*) distributions. *ISPRS Journal of Photogrammetry and Remote Sensing* 75: 48–63.

Hundecha, Y. and Bárdossy, A., 2005. Trends in daily precipitation and temperature extremes across Western Germany in the second half of the 20th century. *International Journal of Climatology* 25: 1189–1202.

Hunter Williams, N.H., Misstear, B.D.R., Daly, D. and Lee, M., 2013. Development of a national groundwater recharge map for the Republic of Ireland. *Quarterly Journal of Engineering Geology & Hydrogeology* 46: 493–506.

HSE (Health Service Executive) and EPA (Environmental Protection Agency), 2011. *Joint Position Statement Trihalomethanes in Drinking Water*. Available online: http://www.epa.ie/pubs/advice/drinkingwater/trihalomethanesjointpositionstatement.html (accessed 21 September 2017).

IBM Corporation, 2013. IBM SPSS Statistics for Windows, Version 22.0. IBM Corporation, Armonk, NY.

Jardé, E., Gruau, G. and Mansuy-Huault, L., 2007. Detection of manure-derived organic compounds in rivers draining agricultural areas of intensive manure spreading. *Applied Geochemistry* 22: 1814–1824.

Jensen, P.H., Jacobsen, O.S., Hansen, H.C.B. and Juhler, R.K., 2008. Quantification of ptaquiloside and pterosin B in soil and groundwater using liquid chromatography–tandem mass spectrometry (LC-MS/MS). *Journal of Agricultural and Food Chemistry* 56: 9848–9854.

Jones, R., Grey, J., Quarmby, C. and Sleep, D., 2001. Sources and fluxes of inorganic carbon in a deep, oligotrophic lake (Loch Ness, Scotland). *Global Biogeochemical Cycles* 15: 863–870.

Jørgensen, L., Stedmon, C.A., Kragh, T., Markager, S., Middelboe, M. and Søndergaard, M., 2011. Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter. *Marine Chemistry* 126: 139–148. DOI: 10.1016/j.marchem.2011.05.002.

Karthe, D., Behrmann, O., Blättel, V., Elsässer, D., Heese, C., Ho, J., Hügle, M., Hufert, F., Kunze, A., Niessner, R., Scharaw, B., Spoo, M., Tiehm, A., Urban, G., Vosseler, S., Westerhoff, T., Dame, G. and Seidel, M., 2016. Modular development of an inline monitoring system for waterborne pathogens in raw and drinking water. *Environmental Earth Sciences* 75: 1481. DOI: 10.1007/s12665-016-6287-9.

Keegan, T., Whitaker, H., Nieuwenhuijsen, M.J., Toledano, M.B., Elliott, P., Fawell, J., Wilkinson, M. and Best, N., 2001. Use of routinely collected data on trihalomethane in drinking water for epidemiological purposes. *Occupational Environmental Medicine* 58: 447–452.

Kortelainen, P., Mattsson, T., Finér, L., Ahtiainen, M., Saukkonen, S. and Sallantaus, T., 2006. Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland. *Aquatic Sciences* 68: 453–468.

Kothawala, D.N., Ji, X., Laudon, H., Ågren, M., Futter, M.N., Köhler, S.J. and Tranvik, L.J., 2015. The relative influence of land cover, hydrology, and in-stream processing on the composition of dissolved organic matter in boreal streams. *Journal of Geophysical Research Biogeosciences* 120(8): 1491–1505.

Kovacs, M.H., Ristoiu, D., Voica, C. and Moldovan, Z., 2013, Climate change influence on drinking water quality. *Processes in isotopes and molecules (PIM 2013)* 1565(1): 298–303.

Kowalczuk, P., Durako, M.J., Young, H., Kahn, A.E., Cooper, W.J. and Gonsior, M.J., 2009. Characterization of dissolved organic matter fluorescence in the South Atlantic Bight with use of PARAFAC model: interannual variability. *Marine Chemistry* 113: 182–196.

Krasner, S.W., 2009. The formation and control of emerging disinfection by-products of health concern. *Philosophical Transactions of the Royal Society A* 367: 4077–4095.

Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M. and Aieta, E.M., 1989. The occurrence of disinfection by products in United States drinking water. *Journal of the American Water Works Association* 81: 41–53.

Krasner, S.W., Croué, J.-P., Buffle, J. and Perdue, E.M., 1996. Three approaches for characterizing NOM. *Journal of the American Water Works Association* 88(6): 66–79.

Kraus, T.E., Anderson, C.A., Morgenstern, K., Downing, B.D., Pellerin, B.A. and Bergamaschi, B.A., 2010. Determining sources of dissolved organic carbon and disinfection byproduct precursors to the McKenzie River, Oregon. *Journal of Environmental Quality* 39: 2100–2112.

Kronholm, S. and Capel, P.D., 2012. Concentrations, loads, and yields of organic carbon in streams of agricultural watersheds. *Journal of Environmental Quality* 41: 1874–1883. DOI: 10.2134/jeq2012.0045.

Lambert, T., Bouillon, S., Darchambeau, F., Massicotte, P. and Borges, A.V., 2016. Shift in the chemical composition of dissolved organic matter in the Congo River network. *Biogeosciences* 13: 5405–5420.

Lankes, U., Demann, H.-D.L. and Frimmel, F.H., 2008. Search for basic relationships between "molecular size" and "chemical structure" of aquatic natural organic matter – answers from 13C and 15N CPMAS NMR spectroscopy. *Water Research* 42: 1051–1060.

Lawaetz, A.J. and Stedmon, C.A., 2009. Fluorescence intensity calibration using the Raman scatter of water. *Applied Spectroscopy* 63: 936–940.

Lee, M., Hunter-Williams, N., Meehan, R., Kelly, C., Kabza, M., Murphy, O. and Spillane, M., 2008. Groundwater vulnerability mapping. Irish National Hydrology Conference, Tullamore, Ireland, pp. 34–43.

Leenheer, J.A. and Croue, J.-P., 2003. Characterizing dissolved aquatic organic matter: understanding the unknown structures is key to better treatment of drinking water. *Environmental Science & Technology* 37(1): 19A–26A.

Lepisto, A., Futter, M.N. and Kortelainen, P., 2014. Almost 50 years of monitoring shows that climate, not forestry, controls long term organic carbon fluxes in a large boreal watershed. *Global Change Biology* 20(4): 1225–1237.

Liu, W., Xu, X., McGoff, N.M., Eaton, J.M., Leahy, P., Foley, N. and Kiely, G., 2014. Spatial and seasonal variation of dissolved organic carbon (DOC) concentrations in Irish streams: importance of soil and topography characteristics. *Environmental Management* 53: 959–967.

Lydon, K. and Smith, G., 2014. *CORINE Land Cover 2012 Ireland Final Report*. Environmental Protection Agency, Johnstown Castle, Ireland.

Malcolm, R.L. and MacCarthy, P., 1992. Quantitative Evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water. *Environment International* 18: 597–607.

Matilainen, A., 2007. Removal of the natural organic matter in the different stages of the drinking water treatment process. PhD Thesis. Publication 651. Tampere University of Technology, Tampere.

McGrath, R. and Lynch, P., 2008. *Ireland in a Warmer World: Scientific Predictions of the Irish Climate in the Twenty First Century*. Met Éireann, Dublin.

Minitab, Inc., 2010. *Minitab 17 Statistical Software*. State College, PA. Available online: www.minitab.com (accessed 25 September 2017).

Misstear, B.D.R., Brown, L. and Daly, D., 2009. A methodology for making initial estimates of groundwater recharge from groundwater vulnerability mapping. *Hydrogeology Journal* 17(2): 275–285.

Mitchell, G.N., 1991. Water quality issues in the British uplands. *Applied Geography* 11: 201–214.

Mitchell, G. and McDonald, A.T., 1995. Catchment characterization as a tool for upland water quality management. *Journal of Environmental Management* 44: 83–95.

Moss, R.H., Edmonds, J.A., Hibbard, K.A., Manning, M.R., Rose, S.K., van Vuuren, D.P., Carter, T.R., Emori, S., Kainuma, M., Kram, T., Meehl, G.A., Mitchell, J.F.B., Nakićenović, N., Riahi, K., Smith, S.J., Stouffer, R.J., Thomson, A.M., Weyant, J.P. and Wilbanks, T.J., 2010. The next generation of scenarios for climate change research and assessment. *Nature* 463(7282): 747–756.

Murnane, J.G., Brennan, R.B., Fenton, O. and Healy, M.G., 2016. Zeolite combined with alum and polyaluminum chloride mixed with agricultural slurries reduces carbon losses in runoff from grassed soil boxes. *Journal of Environmental Quality* 45(6): 1941–1948.

Murphy, K.R., Ruiz, G.M., Dunsmuir, W.T.M. and Waite, T.D., 2006. Optimized parameters for fluorescence-based verification of ballast water exchange by ships. *Environmental Science & Technology* 40: 2357–2362.

Murphy, K.R., Butler, K.D., Spencer, R.G.M., Stedmon, C.A., Boehme, J.R. and Aiken, G.R., 2010. Measurement of dissolved organic matter fluorescence in aquatic environments: an interlaboratory comparison. *Environmental Science & Technology* 44: 9405–9412.

Murphy, K.R., Hambly, A., Singh, S., Henderson, R.K., Baker, A., Stuetz, R. and Khan, S.J., 2011. Organic matter fluorescence in municipal water recycling schemes: toward a Unified PARAFAC model. *Environmental Science and Technology* 45: 2909–2916.

Murphy, K.R., Stedmon, C.A., Graeber, D. and Bro, R., 2013. Fluorescence spectroscopy and multi-way techniques. *Analytical Methods* 5: 6557–6566.

Murphy, K.R., Stedmon, C.A., Wenig, P. and Bro, R., 2014. OpenFluor – an online spectral library of auto-fluorescence by organic compounds in the environment. *Analytical Methods* 6: 658–661.

Murray, H.S., 2012. Assessing the impact of windfarm-related disturbance on streamwater carbon, phosphorus and nitrogen dynamics: a case study of the Whitelee catchments. PhD thesis, University of Glasgow, Glasgow.

Naden, P., Allott, N., Arvola, L., Jarvinen, M., Jennings, E., Moore, K., Nic Aonghusa, C., Pierson, D. and Schneiderman, E. 2010. Modelling the effect of climate change on dissolved organic carbon. In George, D.G. (ed.), *The Impact of Climate Change of European Lakes*. Aquatic Ecology Series Vol. 4. Springer, Amsterdam, pp. 221–252.

Nakićenović, N., Alcamo, J., Davis, G., de Vries, B., Fenhann, J., Gaffin, S., Gregory, K., Grbler, A., Jung, T.Y., Kram, T., La Rovere, E.L., Michaelis, L., Mori, S., Morita, T., Pepper, W., Pitcher, H., Price, L., Raihi, K., Roehrl, A., Rogner, H.-H., Sankovski, A., Schlesinger, M., Shukla, P., Smith, S., Swart, R., van Rooijen, S., Victor, N. and Dadi, Z., 2000. *IPCC Special Report on Emissions Scenarios*. Cambridge University Press, Cambridge.

Nash, J.E. and Sutcliffe, J.V., 1970. River flow forecasting through conceptual models, part I – a discussion of principles. *Journal of Hydrology* 10: 282–290.

Nolan, P., 2015. *Ensemble of Regional Climate Model Projections for Ireland*. Environmental Protection Agency, Johnstown Castle, Dublin.

Nolan, P., Goodman, P., O'Sullivan, J., Sweeney, C., Gleeson, E. and McGrath, R., 2013. Climate change: impacts on Irish temperatures. In Gleeson, E., McGrath, R. and Treanor, M. (eds), *Ireland's Climate: The Road Ahead*. Met Éireann, Dublin, pp. 33–39. Available online: http://www.met.ie/UserMediaUpl/file/Irelands_Climate_25092013_LR.pdf (accessed 25 September 2017).

O'Driscoll, C., O'Connor, M., Asam, Z.-Z., de Eyto, E., Poole, R., Rodgers, M., Zhan, X., Nieminen, M. and Xiao, L., 2014. Whole-tree harvesting and grass seeding as potential mitigation methods for phosphorus export in peatland catchments. *Forest Ecology and Management* 319: 176–185.

O'Driscoll, C., Ramwell, C., Harhen, B., Morrison, L., Clauson-Kaas, F., Hansen, H.C.B., Campbell, G., Sheahan, J., Misstear, B. and Xiao, L., 2016. Ptaquiloside in Irish bracken ferns and receiving waters, with implications for land managers. *Molecules* 21: 543.

O'Driscoll, C., Sheahan, J., Renou-Wilson, F., Croot, P., Pilla, F., Misstear, B. and Xiao, L., 2017a. National scale assessment of total trihalomethanes in Irish drinking water. *Journal of Environmental Management*. Submitted.

O'Driscoll, C., Ledesma, J.L.J., Coll, J., Murnane, J.G., Nolan, P., Mockler, E.M., Futter, M.N. and Xiao, L., 2017b. Climate change is projected to have minimal effects on dissolved organic carbon (DOC) in an Irish drinking water basin. *Science of the Total Environment*. Submitted.

Oni, S.K., Futter, M.N., Teutschbein, C. and Laudon, H., 2014. Cross scale ensemble projections of dissolved organic carbon dynamics in boreal forest streams. *Climate Dynamics* 42(9–10): 2305–2321.

Osburn, C.L., Wigdahl, C.R., Fritz, S.C. and Saros, J.E., 2011. Dissolved organic matter composition and photoreactivity in prairie lakes of the U.S. Great Plains. *Limnology and Oceanography* 56(6): 2371-2390.

O'Sullivan, J., Sweeney, C., Nolan, P. and Gleeson, E., 2015. A high-resolution, multi-model analysis of Irish temperatures for the mid-21st century. *International Journal of Climatology* 36: 1256–1267.

Page, C.N., 2002. Ecological strategies in fern evolution: a neopteridological overview. *Review of Palaeobotany* 119: 1–33.

Palmer, S.M., Wellington, B.I., Johnson, C.E. and Driscoll, C.T., 2005. Landscape influences on aluminium and dissolved organic carbon in streams draining the Hubbard Brook valley, New Hampshire, USA. *Hydrological Processes* 19: 1751–1769.

Parry, L.E., Chapman, P.J., Palmer, S.M., Wallage, Z.E. and Wynne, H., 2015. The influence of slope and peatland vegetation type on riverine dissolved organic carbon and water colour at different scales. *Science of the Total Environment* 527–528: 530–539.

Parsons, S.A. and Jefferson, B., 2006. *Introduction to Potable Water Treatment Processes*. Blackwell Publishing, Oxford.

Perrin, P.M., Barron, S.J., Roche, J.R. and O'Hanrahan, B., 2014. *Guidelines for a National Survey and Conservation Assessment of Upland Vegetation and Habitats in Ireland. Version 2.0*. Irish Wildlife Manual No. 79. National Parks and Wildlife Service, Department of Arts, Heritage and the Gaeltacht, Dublin.

R Core Team, 2008. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna. Available online: http://www.R-project.org (accessed 25 September 2017).

Ramwell, C., van Beinum, W., Rowbotham, A., Parry, H., Parsons, S., Luo, W. and Evans, G., 2010. *Ptaquiloside & Other Bracken Toxins: a Preliminary Risk Assessment*. The Food and Environment Research Agency, York.

Ramwell, C., Anderson, W., Hansen H.C. and Egan, B., 2015. *Measurement of Ptaquiloside Concentrations at a Few of the Most Vulnerable Sources and Final Waters*. Defra Project WT1262 (DWI 70/2/271). Department for Environment, Food and Rural Affairs, London.

Rasmussen L.H., 2003, Ptaquiloside – an environmental hazard? PhD Thesis, The Royal Veterinary and Agricultural University, Denmark.

Rasmussen, L.H., Kroghsbo, S., Frisvad, J.C. and Hansen, H.C.B., 2003a. Occurrence of the carcinogenic bracken constituent ptaquiloside in fronds, topsoils and organic soil layers in Denmark. *Chemosphere* 51: 117–127.

Rasmussen, L.H., Jensen, L.S. and Hansen, H.C.B., 2003b. Distribution of the carcinogenic terpene ptaquiloside in bracken fronds, rhizomes (*Pteridium aquilinum*), and litter in Denmark. *Journal of Chemical Ecology* 29(3): 771–778.

Rasmussen, L.H., Hansen, H.C.B. and Lauren, D., 2005. Sorption, degradation and mobility of ptaquiloside, a carcinogenic bracken (*Pteridium* sp.) constituent, in the soil environment. *Chemosphere* 58: 823–835.

Rasmussen, L.H., Schmidt, B. and Sheffield, E., 2013. Ptaquiloside in bracken spores from Britain. *Chemosphere* 90: 2539–2541.

Reckhow, D.A., Singer, P.C. and Malcolm, R.L., 1990. Chlorination of humic materials: byproduct formation and chemical interpretations. *Environmental Science Technology* 24: 1655–1664.

Reimann, C., Filzmoser, P., Garrett, R.G. and Dutter, R., 2008. *Statistical Data Analysis Explained. Applied Environmental Statistics with R*. John Wiley & Sons, Chicester.

Richardson, S.D., Thruston, A.D., Caughran, T.V., Chen, P.H., Collette, T.W. and Floyd, T.L., 1999. Identification of new drinking water disinfection byproducts formed in the presence of bromide. *Environmental Science Technology* 33: 3378–3383.

Rockel, B., Will, A. and Hense, A., 2008. Special issue regional climate modelling with COSMO-CLM (CCLM). *Meteorologische Zeitschrift* 17: 347–348.

Ryan Hanley, 2012. Technical guidance document on trihalomethane formation in drinking water supplies. Unpublished report,

Ryder, E., de Eyto, E., Dillane, M., Poole, R. and Jennings, E., 2014. Identifying the role of environmental drivers in organic carbon export from a forested peat catchment. *Science of the Total Environment* 490: 28–36.

Sharma, S.K., Salinas Rodriguez, S.G., Baghoth, S.A., Maeng, S.K. and Amy, G., 2011. Natural Organic Matter (NOM): Characterizsation Profiling as a Basis for Treatment Process Selection and Performance Monitoring. In *Handbook on Particle Separation Processes*. IWA Publishing, UK, pp. 61–88.

Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B., 2006. Impact of fractional character on the coagulation of NOM. *Colloids and Surfaces A: Physicochemival Engineering Aspects* 286: 104–111.

Skamarock, W.C., Klemp, J.B., Dudhia, J., Gill, D.O., Barker, D.M., Duda, M.G., Huang, X.Y., Wang, W. and Powers, J.G., 2008. *A Description of the Advanced Research WRF Version 3 NCAR Tech. Note TN-475_STR*. Available online: www2.mmm.ucar.edu/wrf/users/docs/user_guide_V3.3/ARWUsersGuideV3.pdf (accessed 25 September 2017).

Smith, B.L., Seawright, A.A., Ng, J.C., Hertle, A.T., Thomson, J.A. and Bostock, P.D., 1994. Concentration of ptaquiloside, a major carcinogen in bracken fern (*Pteridium* spp.), from eastern Australia and from a cultivated worldwide collection held in Sydney, Australia. *Natural Toxins* 2: 347–353.

Smith, G.E., O'Donghue, P., O'Hara, K. and Delaney, E., 2011. *Best Practice Guidance for Habitat Survey and Mapping*. The Heritage Council, Kilkenny. http://www.heritagecouncil.ie/content/files/best_practice_guidance_habitat_survey_mapping_onscreen_version_2011_8mb.pdf (accessed 25 September 2017).

Stedmon, C.A. and Markager, S., 2005. Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis. *Limnology and Oceanography* 50(2): 686–697.

Stedmon, C.A., Markager, S. and Bro, R., 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry* 82: 239–254.

Stedmon, C.A., Thomas, D.N., Granskog, M., Kaartokallio, H., Papadimitriou, S. and Kuosa, H., 2007. Characteristics of dissolved organic matter in baltic coastal sea ice: allochthonous or autochthonous origins? *Environmental Science & Technology* 41: 7273–7279.

Steppeler, J., Doms, G., Schättler, U., Bitzer, H.W., Gassmann, A., Damrath, U. and Gregoric, G., 2003. Meso-gamma scale forecasts using the nonhydrostatic model LM. *Meteorology and Atmospheric Physics* 82: 75–96.

Tanaka, K., Kuma, K., Hamasaki, K., Yamashita, Y. and Yamashita, Y., 2014. Accumulation of humic-like fluorescent dissolved organic matter in the Japan Sea. *Scientific Reports* 4: 5292. DOI: 10.1038/srep05292.

ter Braak, C.J.F. and Šmilauer, P., 1998. CANOCO reference manual and user's guide to Canoco for Windows: software for canonical community ordination (version 4). Microcomputer Power, Ithaca, NY.

Thurman, E.M., 1985. *Organic Geochemistry of Natural Waters*. Martinus Nijhoff, Dordrecht.

Tubridy, M., 2013. *A Study to Identify Best Management of Upland Habitats in County Wicklow*. Wicklow Uplands Council Ltd, Ireland.

van Vuuren, D.P., Edmonds, J., Kainuma, M.L.T., Riahi, K., Thomson, A., Matsui, T., Hurtt, G.C., Lamarque, J.-F., Toshihiko, M., Meinshausen, M., Smith, S.J., Rose, S., Hibbard, K.A., Nakicenovic, N., Krey, V. and Kram, T., 2011. The representative concentration pathways: an overview. *Climatic Change* 109(11): 5–31.

Vetter, J., 2009. A biological hazard of our age: bracken fern [*Pteridium aquilinum* (L.) Kuhn] – a review. *Acta Veterinaria Hungarica* 57(1): 183–196.

Viney, M., 2012. Bracken's fern grip on our countryside unshakable for now. *The Irish Times,* 21 July 2012.

Volk, C., Bell, K., Ibrahim, E., Verges, D., Amy, G. and LeChevallier, M., 2000. Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water. *Water Research* 34: 3247–3257.

Wade, A.J., Durand, P., Beaujouan, V., Wessel, W.W., Raat, K.J., Whitehead, P.G., Butterfield, D., Rankinen, K. and Lepisto, A., 2002a. A nitrogen model for European catchments: INCA, new model structure and equations. *Hydrology and Earth System Sciences* 6: 559–582.

Wade, A.J., Whitehead, P.G., Butterfield, D., 2002b. The Integrated Catchments model of Phosphorus dynamics (INCA-P), a new approach for multiple source assessment in heterogeneous river systems: model structure and equations. *Hydrology and Earth System Sciences* 6: 583–606.

Walker, S.A., Rainer, M.W.A., Stedmon, C., Duan, S. and Louchouam, P., 2009. The use of PARAFAC modeling to trace terrestrial dissolved organic matter and fingerprint water masses in coastal Canadian Arctic surface waters. *Journal of Geophysical Research* 114: G00F06. DOI: 10.1029/2009JG000990.

Walker, S.A., Amon, R.M.W. and Stedmon, C.A., 2013. Variations in high-latitude riverine fluorescent dissolved organic matter: a comparison of large Arctic rivers. *Journal of Geophysical Research Biogeoscience* 118: 1689–1702. DOI: 10.1002/2013JG002320.

Walsh, S., 2012. New long-term rainfall averages for Ireland. National Hydrology Conference, Tullamore, Ireland, pp. 3–12.

Wellock, M.L., LaPerle, C.M. and Kiely, G., 2011a. What is the impact of afforestation on the carbon stocks of Irish mineral soils? *Forest Ecology and Management* 262: 1589–1596.

Wellock, M.L., Reidy, B., LaPerle, C.M., Bolger, T. and Kiely, G., 2011b. Soil organic carbon stocks of afforested peatlands in Ireland. *Forestry* 84(4): 441–451.

Westerhoff, P. and Mash, H., 2002. Dissolved organic nitrogen in drinking water supplies: a review. *Journal of Water Supply: Research and Technology AQUA* 51(8): 415–448.

Whitehead, P.G., Wilson, E.J. and Butterfield, D., 1998. A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchments (INCA): part I—model structure and process equations. *Science of the Total Environment* 210: 547–548.

Williams, C.J., Frost, P.C. and Xenopoulos, M.A., 2013. Beyond best management practices: pelagic biogeochemical dynamics in urban stormwater ponds. *Ecological Applications* 23: 1384–1395.

Wilson, H.F. and Xenopoulos, M.A., 2009. Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nature Geosciences* 2: 37–41.

WHO (World Health Organization), 2011. *Guidelines for Drinking-water Quality*. 4th Edition. World Health Organization, Geneva.

Woodcock, C.E., Allen, R., Anderson, M., Belward, A., Bindschadler, R., Cohen, W., Gao, F., Goward, S.N., Helder, D., Helmer, E., Nemani, R., Oreopulos, L., Schott, J., Thenkabail, P.S., Vermote, E.F., Vogelmann, J., Wulder, M.A. and Wynne, R., 2008. Free access to Landsat imagery. *Science* 320(5879): 1011.

Worrall, F., Burt, T. and Shedden, R., 2003. Long term records of riverine dissolved organic matter. *Biogeochemistry* 64: 165–178.

Worrall, F., Rowson, J.G., Evans, M.G. and Bonn, A., 2011. Carbon fluxes from eroding peatlands – the carbon benefit of revegetation. *Earth Surface Processes and Landforms* 36(11): 1487–1498.

Zhang, X., Echigo, S., Minear, R.A. and Plewa, M.J., 2000. Characterization and comparison of disinfection by-products of four major disinfectants. In Barrett, S.E., Krasner, S.W. and Amy, G.L. (eds), *Natural Organic Matter and Disinfection By-products: Characterization and Control in Drinking Water.* American Chemical Society, Washington, DC, pp. 299–314.

Abbreviations

ATV	All-terrain vehicle
CAFRE	College of Agriculture, Food and Rural Enterprise
CFC	Coagulation, flocculation, clarification
COSMO-CLM	Consortium for Small-scale Modelling–Climate Limited-area Modelling
DBP	Disinfection by-products
DIC	Dissolved inorganic carbon
DIPM	Derived Irish Peat Map
DOC	Dissolved organic carbon
DWSP	Drinking water safety plan
EPA	Environmental Protection Agency
EU	European Union
F-EEM	Fluorescence excitation–emission matrix
GAC	Granular activated carbon
GCM	Global climate models
GIS	Geographical information system
GLMM	General linear mixed model
HER	Hydrologically effective rainfall
IARC	International Agency for Research on Cancer
IFE	Inner filter effects
INCA-C	Integrated Catchments model for Carbon
IPCC	Intergovernmental Panel on Climate Change
LC-MS	Liquid chromatography–mass spectroscopy
N-S	Nash–Sutcliffe
NOM	Natural organic matter
PARAFAC	Multi-way data analysis using parallel factor analysis
PC	Principal components
PCA	Principal components analysis
PDC	Potentially dissolved carbon
PERSiST	Precipitation Evapotranspiration and Runoff Simulator for Solute Transport
PGWS	Private group water scheme
POC	Particulate organic carbon
PWS	Public water supply
QC	Quality control
RCM	Regional climate models
RCP	Representative concentration pathways
RU	Raman units
SMD	Soil moisture deficit
SOC	Soil organic carbon
SPE	Solid phase extraction
SRES	Special Report on Emissions Scenarios
SRP	Soluble reactive phosphorus
ST	Station
SUVA	Specific ultraviolet absorbance
THM	Trihalomethane
TN	Total nitrogen
TOC	Total organic carbon
TTHM	Total trihalomethanes
UVA_{254}	Ultraviolet absorbance at 254 nm
VIF	Variance inflation factor
WHO	World Health Organization
WRF	Weather Research and Forecasting
WTP	Water treatment plant
ZoC	Zone of contribution

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL
Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

EPA Research Report 231

Assessment of Natural Organic Matter (NOM) and Ptaquiloside in Irish Waters

epaResearch
Climate - Water - Sustainability
Identifying pressures • Informing policy • Developing solutions

Authors: Connie O'Driscoll, Liwen Xiao,
Xinmin Zhan, Bruce Misstear and Francesco Pilla

Ireland has an unacceptably high number of drinking water supplies that exceed the parametric value of 100 µg L-1 for total trihalomethanes (THMs) and has been reporting the highest non-compliance with respect to total THMs in drinking water across the 27 EU Member States. Trihalomethanes are a possible carcinogen formed when chlorine, used to disinfect drinking water reacts with natural organic matter (NOM) also present in the drinking water. Furthermore, there is no scientific evidence available for Ireland on the naturally occurring organic toxin, ptaquiloside, which is derived from bracken ferns. This report presents findings from a literature review and case studies on THMs and ptaquiloside in Irish drinking water.

Identifying pressures

This research identified high-risk catchments for public and private water supplies in relation to NOM across Ireland. This study highlighted that presence of peatland in the catchment is an important factor contributing to THMs in supplies where water has no pre-treatment and receives chlorine disinfection only. Furthermore, in supplies where there is removal, to some degree, of natural organic matter, presence of both peatland and pasture give rise to higher concentrations of THMs. The extent of bracken coverage in Ireland is not known. Ptaquiloside concentrations were detected in the bracken fronds from frond emergence to plant die-off and in the receiving drinking water supply on one sampling occasion at plant die-off.

Informing policy

The findings from this research suggest that there is a need for policy that recommends the use of a high-risk catchment map tool such as that trialled in this research in establishing monitoring programmes for collation of baseline data on NOM quantity and character for the design of new/upgraded WTPs. Audit monitoring of THMs to comply with the Drinking Water Regulations should consider the nature of the source water accounting for both the seasonal flush of NOM in the autumn period and episodic rainfall events where supplies are influenced by such events. Accurate mapping of zones of contribution should be a prerequisite for drinking water supplies. Consideration should be given to the localised predicted effects of climate change on NOM concentrations in water supplies and monitoring of high-resolution data. The extent of bracken coverage in Ireland should be established using remote sensing with ground-truthing to accurately determine the extent of the bracken problem in Ireland. There is a need for policy that can increase the level of awareness of the possible risks of bracken and ptaquiloside to private drinking water wells.

Developing solutions

The establishment of a national water utility in 2014 represents a significant opportunity for improving THM compliance through systematic connectivity and viewing each abstraction source as a function of its catchment rather than of its management boundaries. The findings of the ptaquiloside study from this research suggest that there is a need for stakeholder awareness, with regard to ensuring bracken-free zones close to water abstraction sources, especially for supplies with short water residence times. Investigation into the ptaquiloside concentrations of bracken subjected to different management treatments indicated that spraying with asulam was the most effective means of control for reducing ptaquiloside load. Asulam, the most effective herbicide for eradicating bracken is currently banned in the EU and can only be used with derogation. This finding indicates that cutting bracken may increase the production of ptaquiloside in the short term and hence the potential risk to drinking water quality. However, asulam is a pesticide and is itself potentially harmful to drinking water.

EPA Research: McCumiskey House,
Richiew, Clonskeagh, Dublin 14.

Phone: 01 268 0100
Twitter: @EPAResearchNews
Email: research@epa.ie

www.epa.ie

EPA Research Webpages
www.epa.ie/researchandeducation/research/