Environmental Fate and Exposure Assessment of Water-Soluble Polymers

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PhD

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Environment and Geography

September 2023

Abstract

Polymers are a diverse group of materials with a wide range of properties, and many polymer types are likely be released to the environment. However, environmental risk assessment methods for polymers are lacking, and little is known about their environmental fate and exposure, particularly for water-soluble polymers. The aim of this thesis was to investigate and apply methods for environmental fate and exposure assessment of water-soluble polymers, and thus develop recommendations for how environmental exposure of water-soluble polymers could be better assessed in practice.

Current methods for environmental risk assessment of chemicals were first reviewed in the context of their applicability to both solid and water-soluble polymers. The need for adaptation of current methods for polymers was identified, as well as development of analytical methods, characterisation of environmental fate parameters for exposure modelling, and in-depth analysis of polymer transformation in the environment.

A lower-tier exposure modelling approach was then developed to identify, group, and prioritise water-soluble polymers released from household products. Preliminary estimates of environmental exposure and risk were obtained for several water-soluble polymer types. The results indicated that polyethers, polyquaterniums, and polyol ethoxylate esters have the potential to pose an unacceptable environmental risk and that these materials should be a priority for further research and risk assessment.

The environmental fate and behaviour of two prioritised polyethers (polyethylene glycol and polypropylene glycol) was then studied, as despite their low persistence and low toxicity, these polymers may be of concern due to their high usage volumes. An analytical method for quantitation of individual polymer chains was first developed, and used to obtain an in-depth understanding of environmental fate behaviour of different polymer chains within the polymer mixtures. Characterisation of soil sorption indicated dependence on polymer molecular weight and functional group, as well as mixture interactions which may impact fate testing. Analysis of environmental transformation mechanisms and kinetics confirmed biodegradation via sequential chain shortening for both polymers, and provided a basis for kinetics modelling of water-soluble polymers in which mixture components are simultaneously broken down and formed. Both sorption and biodegradation data indicated that shorter polyether chains are likely to persist for longer in surface water than larger chains. Overall, these studies provide crucial information on both polymer environmental risk assessment and method development, and current environmental exposure and potential risk of water-soluble polymers.

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List of Abbreviations

a_0	Initial value of degradation rate constant
AE	Alcohol ethoxylate
AES	Alcohol ethoxysulphate
a_{max}	Maximum value of degradation rate constant
α	Attachment efficiency
BAF	Bioaccumulation factor
BCF	Bioconcentration factor
C_S	Concentration of polymer in soil at equilibrium
C_W	Concentration of polymer in water at equilibrium
%C	Soil organic carbon
DOC	Dissolved organic carbon
EC50	Half maximal effect concentration
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemicals Agency
EMA	European Medicines Agency
EP&C	European Parliament and Council
EPI Suite	Estimation Program Interface
ERA	Environmental risk assessment
FGEW	Functional group equivalent weight
FOCUS	FOrum for the Co-ordination of pesticide fate models and their USe
FTIR	Fourier-transform infra-red
HERA	Human and Environmental Risk Assessment on ingredients in household cleaning products
HMW	High molecular weight
(HP)LC-MS	(High performance) liquid chromatography mass spectrometry
K_d	Soil/water partition coefficient
k_{deg}	(Bio)degradation rate constant
K_F	Freundlich sorption coefficient
K_{oc}	Soil organic carbon/water partition coefficient
K_{ow}	Octanol/water partition coefficient
LMW	Low molecular weight
LoD	Limit of detection
LoQ	Limit of quantitation
M	Amount of polymer present at time *t*
M_0	Amount of polymer present at time 0
MEC	Measured environmental concentration

MS	Mass spectrometry
MW	Molecular weight
MWD	Molecular weight distribution
MW_N	Number average molecular weight
MW_W	Weight average molecular weight
NICNAS	Australian National Industrial Chemicals Notification and Assessment Scheme
NOEC	No observed effect concentration
OECD	Organisation for Economic Co-operation and Development
P-AA	Homopolymer of acrylic acid
P-AA/MA	Copolymer of acrylic acid and maleic acid
P-AM/AA	Copolymer of acrylamide and acrylic acid
PEC	Predicted environmental concentration
PEC_{SOIL}	Predicted environmental concentration in soil
PEC_{SW}	Predicted environmental concentration in surface water
PEG	Polyethylene glycol
PLC	Polymer of low concern
P-MAA/EA	Copolymer of methacrylic acid and ethyl acrylate
PNEC	Predicted no-effect concentration
PPG	Polypropylene glycol
PSD	Particle size distribution
QSAR	Quantitative structure-activity relationship
r	Microbial growth rate
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RFG	Reactive functional group
R_h	Hydrodynamic radius
RQ	Risk quotient
S_A	Surface area
SAR	Structure-activity relationship
SIM	Selected ion monitoring
$t_{1/2}$	(Bio)degradation half-life
TSCA	Toxic Substances Control Act
USEPA	United States Environmental Protection Agency
WSP	Water-soluble polymer
WWT	Wastewater treatment
WWTP	Wastewater treatment plant

Acknowledgements

First and foremost I would like to thank my main supervisor Alistair Boxall, for his invaluable advice and continued support throughout the PhD. His guidance and encouragement were vital to completion of this thesis and my development as a researcher. I would also like to thank my co-supervisor at the university, Brett Sallach, for his consistent support, advice, and positive outlook, for which I am very grateful.

I would also like to acknowledge NERC and Reckitt for co-funding my PhD, and I would like to thank my co-supervisors and collaborators at Reckitt: Oliver Price, Victor Zanchi, and Tom Hutchinson, for their helpful feedback and interesting discussions about my research.

I would also like to thank the lab technicians at the University of York for their assistance, particularly Matt Pickering for his help with LC-MS analysis and method development, as well as technical support upon the many instances of instrument failure, which was much appreciated. I would also like to thank Mat Evans for his help with modelling of kinetic formation and degradation processes which provided an essential starting point for my final chapter.

I would like to thank my parents, Jane and Chris, and my brother Wolf, for their unwavering love and support and for giving me a reason to keep going. I especially want to thank my mum, for her endless support and for being there for me without fail, without whom completion of this thesis would not have been possible.

I would also like to thank my best friends, Rachel and Michael, for always knowing how to put a smile on my face.

Last but not least, I extend my utmost thanks to my cat Koski, whose generous bestowment of cuddles and scratches in equal measure kept me true until the very end.

Author's declaration

The work in this thesis comprises original work completed by the candidate as a PhD student at the University of York under the supervision of Professor Alistair Boxall. The research was funded by the Natural Environment Research Council (NERC) as part of the Adapting to the Challenges of a Changing Environment Doctoral Training Partnership (ACCE DTP) and by Reckitt as part of a collaborative partnership (Collaborative Awards in Science and Engineering (CASE) partner). This work has not been previously submitted for any degree or other qualification at the university or elsewhere.

All research presented in the thesis is original work and was carried out by the candidate, with the exception of measurements of river water element, ion, and DOC content (*Chapter 5*), which were carried out by technicians at the university (Matt Pickering and Blaine Hancock).

Thesis chapters 2-5 have been written for publication in peer-reviewed journals by the candidate as lead author, however, these chapters have gained through suggestions and advice from co-authors and supervisors. The main text body of *Chapter 2* has been published and has benefitted through comments from co-authors at the University of York (Alistair Boxall and Brett Sallach) and at Reckitt (Oliver Price and Victor Zanchi), as well as through suggestions from anonymous peer-reviewers. The publication status of the presented chapters is summarised in Table 0.1.

All sources are acknowledged as references.

Table 0.1: Status of the chapters presented in this thesis with respect to the publication process.

Chapter	Authors	Title	Status	Journal
Chapter 2	Brunning H, Sallach JB, Zanchi V, Price O, Boxall A	Toward a Framework for Environmental Fate and Exposure Assessment of Polymers	Published	*Environmental Toxicology and Chemistry* 41:515-540
Chapter 3	Brunning H, Sallach JB, Boxall A	Environmental Risks of Water-Soluble Polymers in Household Products: Identification, Grouping, and Prioritisation	Submitted	*Environmental Toxicology and Chemistry*
Chapter 4	Brunning H, Boxall A	Environmental Fate and Sorption Behaviour of Water-Soluble Polyethers in Soil	In preparation	
Chapter 5	Brunning H, Boxall A	Biodegradation and Transformation of Water-Soluble Polyethers in Freshwater	In preparation	

Chapter 1

Introduction

1.1. Polymers and their applications

Polymers are a broad class of substances which includes synthetic, semi-synthetic, and natural compounds unified by their broader structure: they are macromolecules made up of smaller repeating subunits ("monomers") covalently bonded together. Natural polymers including starch, cellulose, proteins, and DNA are fundamental to key biological processes, and human use and processing of natural rubber (a latex polymer) can be dated back thousands of years (Tarkanian and Hosler 2011). Several semi-synthetic polymers such as nitrocellulose were developed in the 19th century (Saunders and Taylor 1990), and the first fully synthetic plastic polymer (Bakelite) was patented by Leo Baekeland in 1907 (Baekeland 1907; Crespy *et al.* 2008), paving the way for rapid innovation in polymer science in the 20th century. The theory that polymers exist as high molecular weight molecules formed by covalent bonding of smaller subunits was first postulated in 1920 by Hermann Staudinger, and eventually accepted in the 1930s (Mülhaupt 2004).

Today, hundreds of millions of tonnes of synthetic polymers are produced globally each year (Danso *et al.* 2019), with variation of monomer type, additives, and methods of synthesis allowing a vast array of properties and applications to be achieved. Solid plastic polymers are now ubiquitous in packaging, construction, automotive and electrical equipment, biomedical devices, and agriculture (Lambert *et al.* 2014), with the most common synthetic polymers produced worldwide being polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polyurethane, polystyrene, and polyamide (Danso *et al.* 2019; Table 1.1).

Water-soluble polymers (which will typically be dissolved in aqueous solution, unlike the solid plastics) are also used abundantly, with applications in wastewater treatment, agriculture, household cleaning and personal care products, pharmaceuticals, and industrial products such as paints and coatings, again with annual usage in the range of millions of tonnes (Arp and Knutsen 2020; Huppertsberg *et al.* 2020). Key water-soluble

polymers in current use include polyethylene glycol, polypropylene glycol, polyacrylic acid, polyacrylamide, polyethylene imide, and polyvinylpyrrolidone (Huppertsberg *et al.* 2020; Table 1.2). A single polymer substance, whether solid, liquid, or soluble, also contains a complex mixture of individual compounds, with polymer chains distributed across a range of molecular weights and potentially residual monomer units and additives being present.

Table 1.1: Structures and broad use categories of some of the most commonly produced synthetic polymers worldwide (Lambert *et al.*, 2014, Danso *et al.*, 2019). Repeating units (derived from monomers) are shown, which are repeated n times via covalent bonding in the bulk structure.

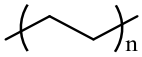
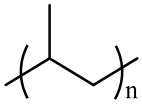
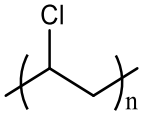
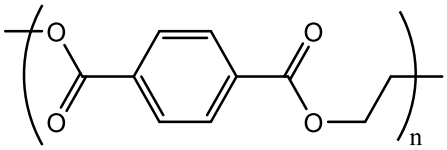
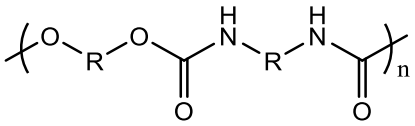
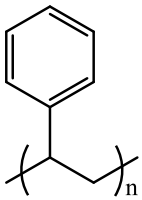
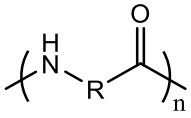
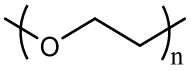
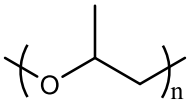
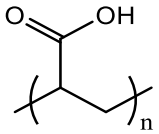
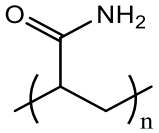
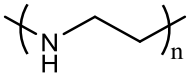
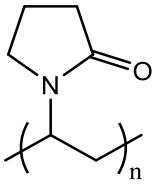
Polymer	**Structure**	**Uses**
Polyethylene		Packaging, containers, construction, electrical equipment, household objects
Polypropylene		Containers, automotive industry
Polyvinyl chloride		Packaging, construction, transport, electronic equipment, healthcare
Polyethylene terephthalate		Containers, packaging, electrical equipment, textiles
Polyurethane		Automotive industry, construction, biomedical applications, textile coatings
Polystyrene		Containers, packaging, household objects
Polyamide		Textiles (e.g. nylon), automotive industry

Table 1.2: Structures and broad use categories of widely used water-soluble polymers (Huppertsberg *et al.* 2020). Repeating units (derived from monomers) are shown, which are repeated n times via covalent bonding in the bulk structure.

Polymer	Structure	Uses
Polyethylene glycol		Paints and coatings, construction, agriculture, manufacturing, oil recovery, cosmetics, pharmaceuticals
Polypropylene glycol		Paints and coatings, construction, agriculture, manufacturing, oil recovery, cosmetics
Polyacrylic acid		Paints and coatings, construction, agriculture, manufacturing, oil recovery, detergents and cleaning agents, agriculture
Polyacrylamide		Wastewater treatment, cosmetics, agriculture
Polyethylenimine		Paints and coatings, construction, agriculture, manufacturing, oil recovery, wastewater treatment, cosmetics
Polyvinylpyrrolidone		Detergents and cleaning agents, pharmaceuticals

1.2. Environmental risk assessment of polymers

Environmental risk assessment of a chemical or substance incorporates estimates of the chemical's hazard (i.e. ecotoxicological effects on organisms) and exposure (i.e. presence and concentration in the environment, as well as fate behaviour such as biodegradation and transport) to evaluate the potential to cause ecological harm, and is essential in identifying and mitigating adverse effects from chemical pollution. Legislation such as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) in the European Union (European Parliament and Council (EP&C) 2006) and the United States TSCA (Toxic Substances Control Act 1976) is key in driving risk assessment and restricting use of chemicals found to cause environmental harm.

However, historically polymers have been exempt from such legislation (United States Environmental Protection Agency (USEPA) 1997; EP&C 2006) based on the assumption that their high molecular weights mean they are unlikely to pose a hazard.

In recent years, pressure to regulate and assess the environmental risks of polymers has increased, due to the substantial quantities of polymers in use, and there have been moves towards incorporating certain polymer types under REACH (European Commission *et al.* 2020). Many applications of polymers, including in agriculture, wastewater treatment, and chemical products, involve direct routes of emission to the environment, and the pervasiveness of plastics in ocean, river, and terrestrial environments has long been a cause for concern (Derraik 2002; Thompson *et al.* 2009; Li *et al.* 2021). Despite extensive research into environmental plastic pollution, definitive assessments of risk are somewhat lacking (Koelmans *et al.* 2017; Burns and Boxall 2018). The occurrence, fate and effects of non-plastic polymer types, such as water-soluble polymers, have received considerably less attention (Huppertsberg *et al.* 2020), despite the fact that they are likely to be present in the environment due to their high usage quantities, and that dissolved polymer molecules may be an important stage in the lifecycle of solid plastic polymers following their biodegradation in the environment. Microplastics and nanoplastics may also transition to liquids and soluble molecules via colloids, and both nanoplastics and water-soluble polymers may exist as colloids in the environment. Existing methods for environmental exposure and hazard assessment are also likely to need adjustment for application to polymers due to their unique properties as high molecular weight complex mixtures (European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) 2019), and analytical methods for polymer characterisation require development (Burns and Boxall 2018; Huppertsberg *et al.* 2020), particularly for in-depth study of the environmental fate and behaviour of these materials.

Thus, we are now in a situation in which we know that a multitude of polymers are present in the environment, that a vast range of polymers are continuing to be used and emitted, and that they are currently poorly regulated, but we are not certain of their potential risks and lack methods to accurately assess these risks. Therefore, there is a pressing need to both develop environmental risk assessment methods for polymers, and apply them in practise to determine and mitigate potential environmental impacts. The work described in this thesis begins to address this large gap in risk assessment science.

1.3. Thesis aims and objectives

The overall aim of the work described in this thesis was to develop and apply methods for environmental fate and exposure assessment of water-soluble polymers, and thus provide recommendations for how environmental exposure of water-soluble polymers could be better assessed in practice. The specific objectives were to:

1) Assess current environmental exposure assessment methods for chemicals in terms of their applicability to polymers, along with key considerations for polymer exposure assessment, in the form of a critical review of the literature;
2) Prioritise water-soluble polymers in current use in terms of their potential environmental exposure and risks;
3) Characterise the sorption behaviour of two prioritised water-soluble polymers (polyethylene glycol and polypropylene glycol) and their constituents in soil, along with key implications for fate assessment;
4) Characterise biodegradation of the two prioritised polyether mixtures and their constituents in river water, along with key implications for fate assessment.

Note that the initial literature review was broadly focussed on polymers in general, however following identification of research needs and knowledge gaps in the literature review, subsequent research and objectives were refined to focus specifically on water-soluble polymers.

1.4. Thesis overview

This thesis comprises six chapters, which are summarised below:

Chapter 2 is a critical literature review of current environmental exposure assessment methods established for low molecular weight chemical compounds, along with a discussion of how these methods can be applied to different types of polymers, with a particular focus on key environmental fate parameters. This chapter highlights the key knowledge gaps and research needs in polymer exposure assessment, and outlines a framework detailing the key considerations for development of polymer exposure assessment approaches.

In *Chapter 3*, usage and product ingredient data are used with a lower-tier environmental exposure model to identify water-soluble polymers in current use in household products, providing preliminary estimates of exposure in terrestrial and

aquatic environments, as well as potential risk of key polymer types to organisms. These preliminary exposure and risk estimates are used to prioritise polymer groups of highest potential concern to focus future risk assessments, as well as to select polymers for application of test methods in chapters *4* and *5*.

Chapter 4 describes the development of an analytical method for two prioritised case study polymers (polyethylene glycol and polypropylene glycol) and describes the application of a standard test method to explore the sorption of the polymers to soil. The results of this study provide both key environmental fate data for these water-soluble polymers, which is relevant in environmental risk assessment, and further analyses of the key considerations identified in *Chapter 2* for application of exposure assessment methods to polymers.

Chapter 5 explores the biodegradation of the two prioritised water-soluble polymers in a range of water types, again providing key environmental fate data, along with a discussion of the application and interpretation of biodegradation test methods for polymers and their mixture components. This chapter along with *Chapter 4* also characterises fate and behaviour in aquatic and terrestrial environments as initially modelled in *Chapter 3* and determines values for key environmental fate parameters and in-depth polymer biodegradation mechanisms as identified in *Chapter 2*.

In *Chapter 6*, key findings of the thesis are synthesised and discussed along with their broader implications for further efforts to better assess environmental exposure and risk of water-soluble polymers.

Chapter 2

Literature Review: Towards a Framework for Environmental Fate and Exposure Assessment of Polymers

2.1. Introduction

The prevalence and persistence of polymers in the environment has resulted in heightened concern in public, scientific and regulatory communities. Polymers have previously been subject to reduced regulatory requirements compared to low molecular weight (LMW) chemicals, for example under REACH (European Parliament and Council (EP&C) 2006), and there have increasingly been calls for regulation and efforts to develop risk assessment approaches for polymers (European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) 2019). In particular, the potential risks of plastics and microplastics have been the focus of a vast amount of research due to their widespread release into, and persistence in, the environment (Derraik 2002; Thompson *et al.* 2009; Ivleva *et al.* 2017; Koelmans *et al.* 2017; Burns and Boxall 2018), with a number of risk assessment strategies being suggested for microplastics (Syberg *et al.* 2015; Hüffer *et al.* 2017; Gouin *et al.* 2019). However, microplastics represent a single group of polymeric material, and in contrast, the environmental impacts of other groups including water-soluble polymers have been given considerably less attention (e.g. Xiong *et al.* 2018a; Arp and Knutsen 2020). Water-soluble materials were excluded from the definition of microplastics in the recent European Chemicals Agency (ECHA) report for restriction of intentionally added microplastics (ECHA 2019), which could lead to the potential environmental impacts of water-soluble polymers being overlooked. This is despite the fact that water-soluble polymers have many applications, including in agriculture, wastewater treatment, consumer products, and detergents (Arp and Knutsen 2020), and it is inevitable that they will be released to the environment. Additionally, standard exposure and risk assessment protocols for polymers are only just being developed (ECETOC 2019), and technical limitations exist in the tools and methods necessary to support such assessments (ECETOC 2020).

Typically, environmental exposure to chemical substances is assessed using a combination of data on chemical emissions, physicochemical properties, and fate which are then used to inform computational modelling (Di Guardo *et al.* 2018). However, some of the physicochemical descriptors used to assess the distribution and mobility of LMW chemical substances are not necessarily appropriate for polymers. Moreover, the analytical methods to determine concentrations and properties of LMW chemicals in fate studies may not be suitable for characterisation of polymers. Polymers may also fall outside the applicability domain of many of the models used to support environmental exposure assessment.

Given the previous lack of regulation of polymers, there is a pressing need to establish robust methodologies and procedures in order to evaluate and mitigate potential environmental impacts of polymers. In the present review, environmental exposure assessment of polymers will be discussed in the context of established chemical risk assessment methodologies, in response to increasing urgency to regulate polymers and develop risk assessment approaches. Current approaches to prospective environmental risk assessment of chemicals, which include key fate parameters (describing basic physicochemical properties, partition coefficients, bioconcentration and bioaccumulation, and abiotic and biotic degradation), will first be discussed in the context of their applicability to polymers. The significance of these parameters in development of an environmental exposure assessment framework for polymers will then be assessed, before highlighting key challenges and considerations and identifying future research needs.

2.2. Current approaches to environmental exposure assessment

Exposure assessment is key in environmental risk assessment (ERA), with exposure predictions being combined with ecotoxicity data to determine risk, often by calculation of a risk quotient (RQ) using predicted environmental concentration (PEC) and predicted no-effect concentration (PNEC) (Amiard and Amiard-Triquet 2015).

Key to exposure assessment is the generation of information on the physicochemical properties and fate of a substance. These fate parameters include basic physicochemical properties such as water solubility, partition coefficients, bioconcentration and bioaccumulation factors, and biotic and abiotic degradation rates, with standard

Organisation for Economic Co-operation and Development (OECD) test methods for their measurement.

As experimental fate and property data are sometimes only available for a small proportion of chemical substances in use, structure-activity relationships (SARs) and quantitative structure-activity relationships (QSARs) are often utilised where the data are insufficient or unavailable. QSAR models such as those in the EPI Suite (USEPA 2012) have been established for prediction of physicochemical properties (e.g. water solubility, vapour pressure, Henry's Law Constant, octanol-water partition coefficient) and environmental fate parameters (e.g. degradation half-lives and sorption coefficients) of chemicals.

Both experimental and predicted property and fate parameters can ultimately be used as input parameters in exposure models. A multitude of exposure models exist for chemical compounds including very simple lower tier models through to complex higher tier models. Examples include The OECD Tool, a consensus model for ranking overall persistence and long-range transport potential of organic chemicals (Wegmann *et al.* 2009), EUSES (Vermeire *et al.* 1997), which may be used to quantify exposure and risk of chemicals (e.g. under REACH), and the FOCUS (FOrum for the Co-ordination of pesticide fate models and their USe) models for estimating concentrations of plant protection products (FOCUS 2001). Lower tier models are often very simplistic and provide 'worst-case' concentrations in the environment, often ignoring dissipation processes. Higher tier exposure models typically may rely on a large number of input parameters including partition coefficients and degradation half-lives in different media, and aim to characterise transport and transformation of a chemical before its ultimate degradation, uptake, or sequestration (Di Guardo *et al.* 2018).

These different methods for measuring or estimating the properties and fate of molecules and for modelling exposure concentrations may however not be appropriate for polymeric substances. In the following sections, we therefore discuss why polymers are different and assess the validity of these existing methods for exposure assessment of polymers, before then proposing strategies that could be used for polymer exposure assessment.

2.3. What are polymers and why do they require a different approach?

Polymers are typically high molecular weight (HMW) molecules made up of repeating subunits ('monomers'). Fundamentally, they have been defined by the OECD as having a simple weight majority of molecules comprising at least three monomer units bound to another reactant or monomer unit, and a distribution of molecular weights (MW) with less than a simple weight majority of molecules of the same MW, where differences in MW are primarily due to differences in the number of monomer units (OECD 1991). Polymer MW is therefore typically defined in terms of number and weight average molecular weight (MW_N and MW_W, respectively) and molecular weight distribution (MWD). Polymers have widespread usage and are released to the environment both in solid form (e.g. plastics; Kawecki and Nowack 2019) and dissolved form (e.g. water-soluble polymers from water treatment and agriculture; Arp and Knutsen 2020).

There are a number of unique characteristics of polymers that require additional consideration in exposure assessment compared to LMW chemicals. Polymers often comprise multiple components (including residual monomer, oligomers, polymer chains of varying MW, and chemical additives) and are poorly defined compared to most simple LMW chemical compounds. For example, for polymers (alcohol ethoxylates, alcohol ethoxysulfates, and polycarboxylates) incorporated in the Human & Environmental Risk Assessment on ingredients of European household cleaning products (HERA), in addition to molecular weight distribution for each MW_N, polymers of a wide range of MW_N were in use, with different fate properties (such as degradation and sorption) requiring separate incorporation or consideration in risk assessment (HERA 2004, 2009, 2014a, 2014b). Identification of polymers is complex; names and CAS numbers (which are based on incorporated monomers) are insufficient to differentiate polymers, since the same name and CAS number may apply to two polymers with vastly different properties. For example, poly(methylmethacrylate) (PMMA) is assigned a single CAS number, but may be used in a range of forms from thermoplastic sheets to resin in solution, with different molecular weights, methods of manufacture, and additives, meaning that the associated CAS (9011-14-7) does not give sufficient information or differentiation between these different forms of the polymeric material or the relevant environmental fate properties (ECETOC 2019). Additionally, compared with LMW chemicals, polymers may form a more complex mixture of products when they transform in the

environment, including cross-linked polymer chains, micro- and nano-scale particles, oligomers, and LMW chemical compounds (e.g. Saad *et al.* 2010; Lambert *et al.* 2013a, 2013b; Ter Halle *et al.* 2016; Weinstein *et al.* 2016).

It is likely that for lower tier, worst-case ERA scenarios, existing exposure assessment methods will be generally sufficient for polymers, with only information on usage/production volumes and emissions estimates being necessary, although the availability of this data for many current-use polymers may limit characterisation of exposure (Cumming 2008; Duis *et al.* 2021). However, for more complex, higher tier environmental exposure assessment studies which incorporate data on fate behaviour, additional considerations are likely to be necessary for polymers. Only a limited number of environmental exposure and risk assessments have been performed for polymers to date, including for polyethoxylated surfactants, polycarboxylates, and polyquaterniums (e.g. HERA 2004; Cumming 2008; HERA 2009, 2014a, 2014b; DeLeo *et al.* 2020), with detailed information on polymer characteristics often being limited (Duis *et al.* 2021). For example, broad estimates of usage data for polyquaterniums used in the assessment conducted by Cumming (2008) were available only for five polyquaterniums from the Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS), with a further 18 polyquaterniums on the Australian Inventory of Chemical Substances (AICS) lacking in usage data. No further information was available to determine the actual mixture and relative quantities of polyquaterniums likely to be present in the environment, or their range of charge densities and molecular weight, thus limiting the resultant exposure assessment to being conducted for a theoretical representative polyquaternium (Cumming 2008).

A primary concern for higher tier environmental exposure assessment is the establishment of key parameters to measure the behaviour and fate processes of polymers in the environment. In the present review, a detailed analysis of the relevance and applicability of fate parameters to polymers has been performed, exemplifying the need for additional considerations in higher tier exposure assessment of polymers and application of fate parameters in exposure modelling. The applicability of established fate parameters for LMW chemical compounds to polymers is first discussed below, and summarised in Table 2.1.

Table 2.1: Summary of key parameters used in exposure assessment of low molecular weight chemical compounds and their applicability to polymers.

Key para-meters	Information given	Relevance to dissolved polymers?	Relevance to bulk solid polymers?	Rationalisation and comments
Basic physicochemical properties				
Water solubility	Extent of dissolution in water	Applicable	Applicable	Water solubility and dissociation constants give useful information on likely environmental compartment, and reactivity and charge distribution; both have been applied to polymers. Vapour pressure of dissolved polymers will likely be driven by LMW content (oligomers and monomers). The high molecular weights of polymers mean most will decompose before a boiling point is reached.
pK_a	Acidity (thus behaviour at environmental pH)			
T_m	Whether substance will exist as solid or liquid in environment			
P	Partitioning between air and liquid/solid phase		Not applicable	
T_b	Whether substance exists as solid/liquid or gas in environment	Not applicable		
Partition coefficients				
K_d	Partitioning between soil and water	Applicable	Not applicable	Dissolved polymers will behave similarly to LMW chemicals, meaning K_d, K_{oc}, and K_{ow} can be applied (however applicability should be assessed for those in nano-size range). Equilibrium constants are not applicable to particulate matter or colloidal solutions, for which partitioning is controlled by kinetic factors and thermodynamic equilibrium is not reached, and so application of thermodynamic parameters to bulk solid polymers is not appropriate.
K_{oc}				
K_{ow}	Partitioning between lipid (octanol) and water			
Bioconcentration and bioaccumulation				
k_u and k_d	Uptake and depuration rates	Applicable	Applicable	The concept of BCF assumes passive diffusion and is thus not relevant for polymer molecules or particles (for which active processes will play a major role in organism uptake). BAF may be applicable in some soil/sediment systems, however specific parameters for polymer accumulation should be developed and current tests should be interpreted to reflect uptake/depuration rates.
BCF	Partitioning into organisms	Not applicable	Not applicable	
BAF				
Biotic and abiotic degradation				
$t_{1/2}$	Time taken for concentration to reduce by half	Applicable	Applicable	Rate constants and half-lives can be applied to both dissolved and solid polymers as they provide a simple measure of degradation rate.
k_{deg}	Rate constant for (bio)degradation			

T_m = melting point; P = vapour pressure; T_b = boiling point; LMW = low molecular weight; K_d = soil/water partition coefficient; K_{oc} = soil organic carbon/water partition coefficient; K_{ow} = octanol/water partition coefficient; k_u = uptake rate constant; k_d = depuration rate constant; BCF = bioconcentration factor; BAF = bioaccumulation factor; $t_{1/2}$ = half-life; k_{deg} = degradation rate constant

We suggest that both homo- and co-polymers can be grouped either as solid polymers (including bulk macroscopic solids and particles) or dissolved polymers (defined in the present review to cover polymers which are dissolved in solution, such as water-soluble polymers in an aqueous environment, and polymers which exist in the liquid state (which may be water-insoluble)), based on applicability of both established fate parameters and suggested polymer-specific parameters. This grouping underpins the following discussion.

2.3.1. Basic physicochemical properties

Boiling points (T_b) are typically not relevant for most polymers, since, by definition, polymers exist as macromolecules with high molecular weights, and typically decompose before boiling (e.g. Schupp *et al.* 2018). Similarly, vapour pressure (P) will generally remain low for dissolved polymers due to their high molecular weight. Whilst vapour pressure can be measured for some liquid polymers, it is likely that it is LMW and oligomeric components that contribute most to the vapour pressure (Schupp *et al.* 2018); P may therefore be a relevant parameter for some LMW polymers and substances containing high levels of oligomers or residual monomer (RPA/GnoSys/Milieu 2012).

Conversely, melting points (T_m) are applicable to both LMW and HMW polymers. In the context of polymers, the melting temperature refers to the transition between crystalline and amorphous states, and applies only to semi-crystalline polymers (Alsleben and Schick 1994). The physical properties of the polymer matrix in a solid polymer may play an important role in environmental fate and effects. For example, LMW constituents may leach more readily from a flexible polymer compared to a rigid one (Hoekstra *et al.* 2015), and amorphous polymers or polymer regions may undergo preferential (bio)degradation before those that are crystalline structured (Khatiwala *et al.* 2008; Fukushima *et al.* 2013).

Reactive functional groups (RFGs) also influence environmental fate; these are often oxygen or nitrogen-containing molecular groups such as e.g. carboxylic acid, amide, or hydroxyl groups (present in e.g. the water-soluble polymers polyacrylic acid, polyacrylamide, and polyvinyl alcohol and polyethylene glycol, respectively) and which may be susceptible to chemical transformation or ionisation under certain conditions. In contrast to LMW chemical compounds, the functional group equivalent weight (FGEW) is important for polymers, as it describes the relative proportion of RFGs within the

polymer (ECETOC 2019). Anionic and cationic polymers are analogous to acidic and basic polymers, respectively (e.g. Guiney *et al.* 1998; Ostolska and Wiśniewska 2014; Hennecke *et al.* 2018) and measurement of their pK_a(s) can enable prediction of their charge or charge distribution (q) at environmental pH (e.g. Schupp *et al.* 2018). Water-soluble ionic polymers have multiple applications, including in household products (Pecquet *et al.* 2019) and wastewater treatment (e.g. Shen *et al.* 2013), and there has been concern over the ecological hazard potential of cationic polymers (e.g. Goodrich *et al.* 1991; USEPA 1997; Cumming *et al.* 2008; Costa *et al.* 2014). Charge also influences environmental fate processes such as sorption (Galvão *et al.* 2007; Blachier *et al.* 2009). Surface tension (γ) is relevant for dissolved and colloidal polymers with surfactant properties, with surfactant behaviour being recognised as significant for environmental fate and effects (e.g. Jardak *et al.* 2016).

2.3.2. Partition coefficients

Parameters such as the soil/water and soil organic carbon/water partition coefficients (K_d and K_{oc}, respectively; Kookana *et al.* 2014), are used to assess the partitioning of chemicals between soil/sediment/sludge and water (Amiard and Amiard-Triquet 2015), and are useful in predicting the concentrations of a chemical in these environmental compartments. Although terrestrial environments and soils are an important receiving compartment of both solid and dissolved polymers (due to application of, for example, sludge, mulch, agrochemicals, and soil conditioners; Felsot *et al.* 2011; Horton *et al.* 2017; Arp and Knutsen 2020), the use of K_d and K_{oc} in the context of bulk solid polymers is not appropriate. As has been highlighted in the literature, colloidal dispersions (which consist of one phase distributed as nano-sized particles or droplets in another phase, e.g. solid nanoplastics suspended (but not dissolved) in water) do not reach thermodynamic equilibrium. Instead, processes such as sorption to soils are kinetically controlled, and are dependent on time, concentration, and system conditions (Kookana *et al.* 2014; Praetorius *et al.* 2014). It therefore follows that application of K_{oc} and K_d, as well as other commonly used equilibrium-based partition coefficients such as the octanol-water partition coefficient (K_{ow}) to partitioning of nano-sized polymer particles, as well as micro-scale particles and larger solids which can undergo sedimentation, is not appropriate and may lead to erroneous results (Praetorius *et al.* 2014). Such equilibrium-based partitioning parameters should only be applied to polymer molecules, not bulk solids (e.g. Min *et al.* 2020).

These parameters may therefore be applied to dissolved and water-soluble polymers, as these will follow equilibrium partitioning behaviour. Equilibrium partition coefficients have been previously applied to polymer macromolecules (Gorbunov and Skvortsov 1995; Tong and Anderson 1996; White and Deen 2000; Lazzara and Deen 2004), usually in the context of partitioning between a gel and solution, but also in an environmental context, albeit rarely (Cumming *et al.* 2011a; Cumming *et al.* 2011b). However, use of K_{ow} to indicate potential for bioaccumulation may be insufficient for HMW polymers due to uptake by non-partitioning processes (see later discussion of bioconcentration and bioaccumulation). Given that polymer molecules in solution can also exist in the nano-size range (Armstrong *et al.* 2004; Xiong *et al.* 2018b; Arp and Knutsen 2020), it may also be relevant to test and verify the applicability domain of equilibrium-based parameters to such polymers, as colloidal properties may influence observed partitioning as described above and thus limit the validity of partition coefficients. Furthermore, as has been discussed by Cumming (2008) and Duis *et al.* (2021) in the context of environmental fate of the water-soluble polyquaterniums, polyethylene glycols, and acrylic acid polymers, conformation of polymer chains is likely to play a role in sorption and desorption, which will affect partitioning to soils and sediment in the environment for dissolved polymers. Polymer chain conformation describes how polymer molecules are arranged in three-dimensional space, with the number of available conformations of a molecule reflected in the number of conformational degrees of freedom.

2.3.3. Bioconcentration and bioaccumulation

Bioconcentration and bioaccumulation factors (BCF and BAF, respectively) are often used in fate and hazard assessment of chemicals (e.g. Berrojalbiz *et al.* 2009; Wu *et al.* 2011; Castro *et al.* 2019) to characterise uptake and accumulation into organisms in the environment. Values of BCF and BAF reflect the concentration of a chemical in biota relative to the exposure concentration, and are typically determined based on partition coefficients or the ratio of rate constants for biotic chemical uptake and depuration. Whilst BCF accounts for uptake of a chemical substance only via dermal and respiratory absorption, BAF accounts for additional uptake via ingestion (Arnot and Gobas 2006; Mackay *et al.* 2013). Since the concept of BCF assumes passive diffusion, it is known to be inapplicable to nanoparticles (Kookana *et al.* 2014; Kühnel and Nickel 2014), as equilibrium partitioning does not apply (discussed in Section 2.3.2) and active processes such as endocytosis play a significant role in nanoparticle uptake due to their size

(Fröhlich 2012; Kookana *et al.* 2014; Utembe *et al.* 2018). This is also the case for larger solids such as microplastics (von Moos *et al.* 2012). The role of active processes in nanoparticle uptake also means that BCF and BAF may be dependent on exposure concentration (contrary to low molecular weight organic chemicals, for which BCF values will be independent of exposure concentration if uptake occurs via passive diffusion; Utembe *et al.* 2018). Therefore, multiple BCF or BAF values accounting for different exposure concentrations may be required to describe uptake of a single nanomaterial (Utembe *et al.* 2018), or a polymer in the context of the present work. It has been highlighted that parameters such as uptake and internalisation rates and attachment efficiencies (α) should be identified and developed for nanoparticle bioaccumulation to replace BCF (Kühnel and Nickel 2014; Praetorius *et al.* 2014). Test methods based on concentrations and rate constants may need to be modified and should be interpreted such that they reflect uptake/depuration rates rather than BCF (Kookana *et al.* 2014). Uptake and depuration rate constants (k_u and k_d, respectively), as well as assimilation efficiency (AE), have been applied to nanoparticles previously (Zhao and Wang 2010; Dai *et al.* 2015).

Knowledge from medicinal chemistry shows that endocytosis also plays a role in cell uptake of polymer molecules (Apostolovic *et al.* 2011) due to their large size, suggesting that BCF and BAF are also likely to be insufficient to describe uptake of dissolved and water-soluble polymers. Polymer and particle properties that influence cell membrane interactions and uptake have been identified from medicinal applications of polymers and nanoparticles in drug delivery, and include size, shape, composition, hydrophobicity, surface charge, and distribution of functional groups (Liechty *et al.* 2010; Fröhlich 2012). These properties may therefore be important for characterisation of biological fate processes of both solid and dissolved polymers.

2.3.4. Abiotic and biotic degradation

Degradation rates have been often assessed for polymers (e.g. Gómez and Michel Jr. 2013; Lambert *et al.* 2013a; Auta *et al.* 2018; Hennecke *et al.* 2018), and the degradation parameters half-life and degradation rate constant ($t_{1/2}$ and k_{deg}, respectively) remain applicable; however, the increased complexity of polymer degradation mechanisms and products should also be considered. Whilst degradation products of LMW chemicals are routinely incorporated into environmental risk assessments, the number and variety of

products formed from polymer degradation may be far greater, potentially including HMW molecules, micro- and nano-scale particles, and oligomers and LMW chemical compounds (e.g. Saad *et al.* 2010; Lambert *et al.* 2013a, 2013b; Ter Halle *et al.* 2016; Weinstein *et al.* 2016). The complexity of the transformation pathways and products from degradation of solid (e.g. plastic) and dissolved (e.g. water-soluble) polymers, along with implications for polymer properties and key fate parameters, is illustrated in Figure 2.1.

Degradation mechanisms and $t_{1/2}$ and k_{deg} values depend on both polymer properties (including the presence of certain RFGs, hydrophobicity, molecular weight, glass transition temperature (T_g), and fragment size, among others; Ter Halle *et al.* 2017; Min *et al.* 2020), and environmental factors (including light and oxygen availability, temperature, pH, salinity, and biofilm formation; Lambert *et al.* 2013a; Da Costa *et al.* 2018; Morohoshi *et al.* 2018). Polymer transformation products are likely to have different fate and degradation characteristics compared to one another and to the parent material, which will itself be altered, presenting challenges for characterising potential risk. Standard test methods will require modification and additional analytical techniques to characterise these products and corresponding degradation pathways.

Polymer particles may be formed from breakdown of a solid polymer; in addition, whilst water-soluble polymers will already exist in the environment as discrete dissolved molecules and are thus most likely to degrade into transformed polymer chains, oligomers, and chemical compounds rather than particles, there has been speculation over the potential for soluble polymers to form insoluble material in the environment (Arp and Knutsen 2020), and it should be noted that polymer solubility does not preclude non-biodegradability and environmental persistence (Swift 1998; Hennecke *et al.* 2018; Arp and Knutsen 2020). In addition, soluble polymer molecules could potentially be formed from degradation of some solid polymers and plastics, with overlap between the transformation pathways of solid and dissolved polymers (Figure 2.1) and a cross-over of the relevant fate parameters and exposure assessment methods.

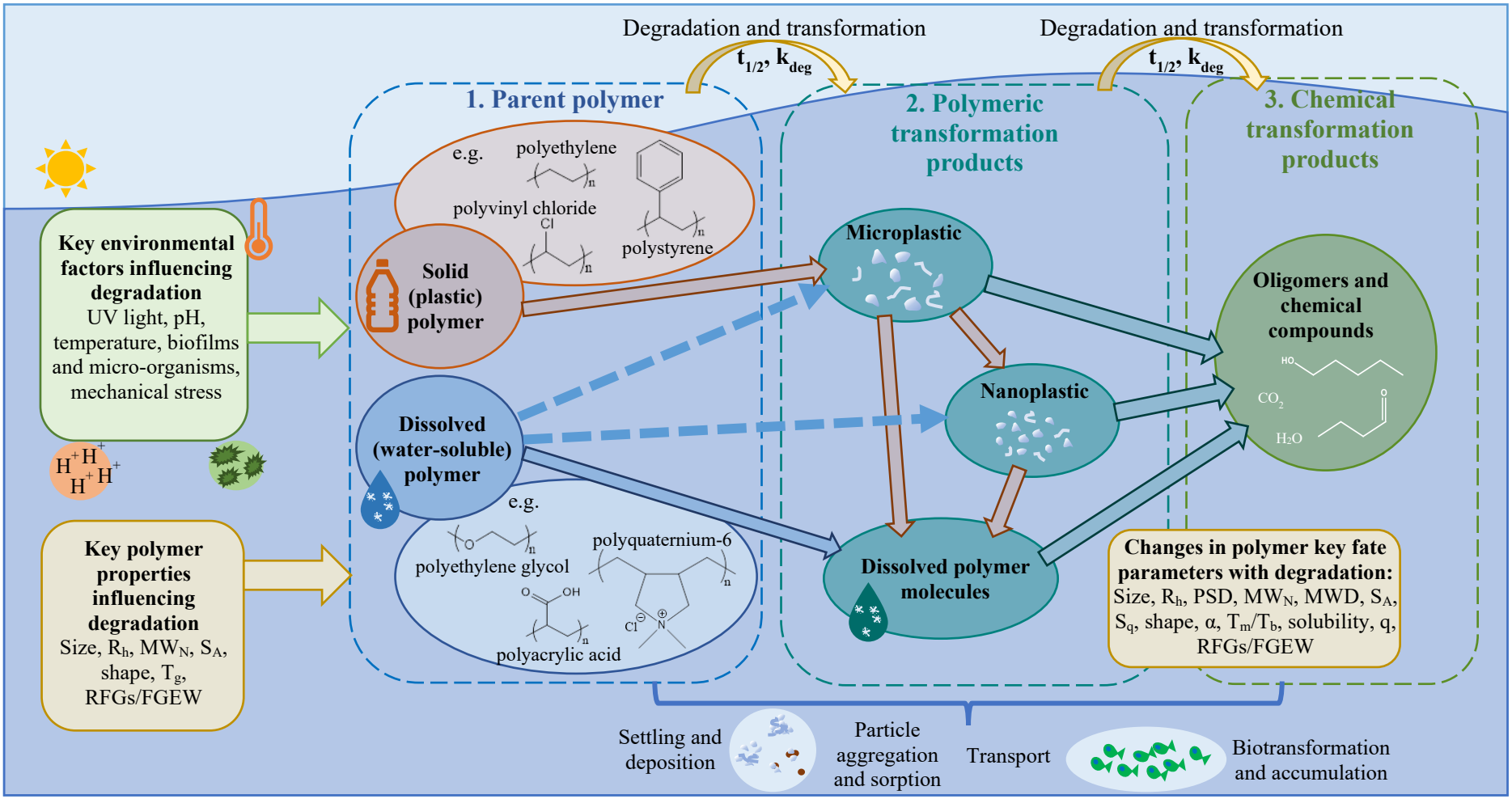


Figure 2.1: Summary of degradation and fate processes, including changes in key fate parameters, for solid (e.g. plastic) and dissolved (e.g. water-soluble) polymers in an aquatic environment.

MW_N = number average molecular weight; R_h = hydrodynamic radius, T_g = glass transition temperature; S_A = surface area; RFG = reactive functional group; FGEW = functional group equivalent weight; $t_{1/2}$ = degradation half-life; k_{deg} = degradation rate constant; PSD = particle size distribution; S_q = surface charge; α = attachment efficiency; MWD = molecular weight distribution; q = charge or charge distribution; T_m = melting point; T_b = boiling point.

Particles formed from polymer degradation can further fragment or aggregate (Liu *et al.* 2019); importantly, these secondary particles formed by polymer fragmentation are likely to differ from primary emitted particles such as primary microplastics. They will be more irregular in shape (e.g. Frydkjær *et al.* 2017), and both primary and secondary particles which have been exposed to the environment may have altered density (Morét-Ferguson *et al.* 2010; Chubarenko *et al.* 2016) and surface properties (Waldman and Rillig 2020), with different RFGs, charge (S_q), and topography (Fotopoulou and Karapanagioti 2012). These changes will influence fate; for example, the surfaces of UV-degraded polystyrene nanoparticles have been shown to be more oxygen-rich, potentially influencing aggregation behaviour compared to non-degraded particles (Liu *et al.* 2019). Ultimately, chemical products will form from polymer degradation (or can leach from the parent polymer); several LMW chemical products have been identified from plastic degradation (reviewed by Bond *et al.* 2018), and other solid polymers such as latex (Lambert *et al.* 2013b). Most prioritisation methodologies classify polymers of high average molecular weight (≥ 1,000 Da) as low concern (PLC) due to the expectation that they may be less able to cross organism membranes (OECD 2009). However, all polymers have the potential to degrade into LMW species following emission to the environment, with many PLC exclusion criteria acknowledging 'substantial' (bio)degradation as indicating potential concern (ECETOC 2019).

2.3.5. Additional parameters for polymer exposure assessment

In addition to the established parameters for LMW chemicals discussed above and summarised in Table 2.1, it is clear that there are a number of properties of polymers that are not applicable to LMW chemicals, but which may be instrumental in polymer exposure assessment. Suitable parameters and descriptors for such properties are suggested in the present review. A combination of established and novel parameters to describe polymer environmental fate is likely to be necessary, and will again be facilitated by classification of polymers as solid or dissolved. The overall picture is complex, with different sets of parameters likely being key for LMW chemical compounds, solid polymers (such as plastics), and dissolved polymers (such as water-soluble polymers). This has been summarised and illustrated in Figure 2.2.

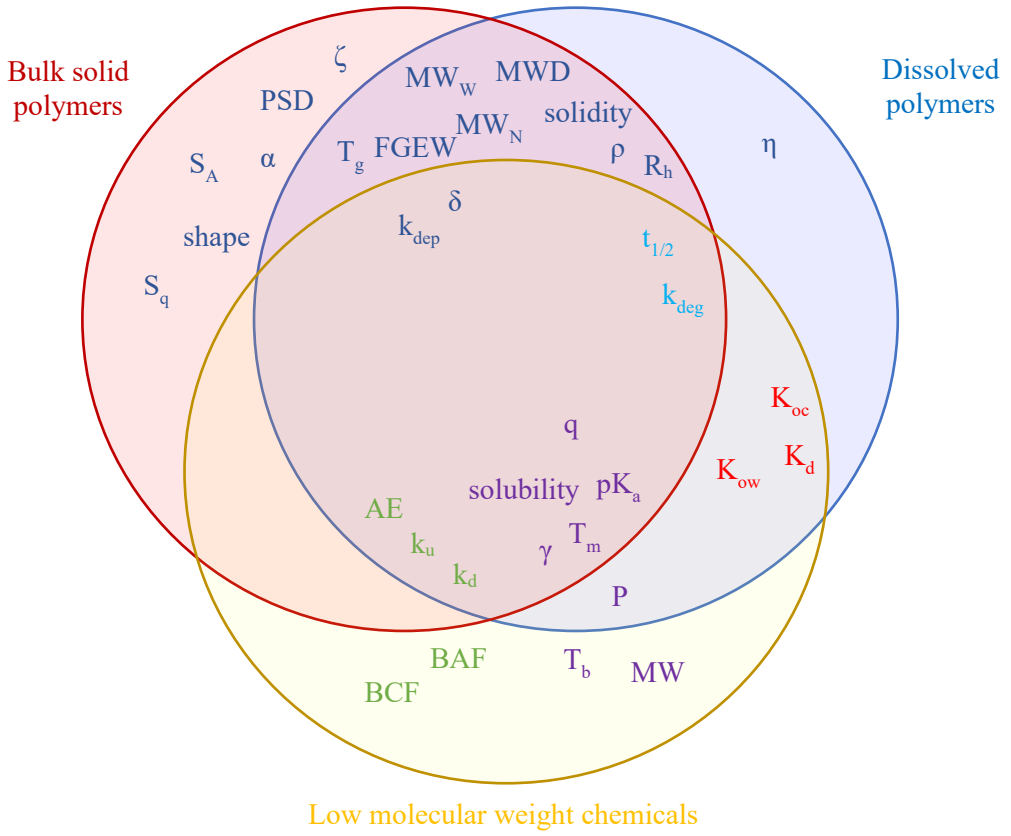


Figure 2.2: Summary of the applicability of various fate parameters and key properties to low molecular weight chemical compounds, bulk solid polymers (including particles), and dissolved polymers.
Parameters that are typically used in environmental exposure assessment of low molecular weight chemicals are further categorised in terms of basic physicochemical properties (purple), partition coefficients (red), bioconcentration and bioaccumulation (green), and biotic and abiotic degradation (light blue). Additional and polymer-specific parameters suggested in the present review, which may be useful in polymer exposure assessment, are also shown (dark blue).
AE = assimilation efficiency; k_{dep} = deposition rate constant; MW = molecular weight; MW_W = weight average molecular weight; R_h = hydrodynamic radius; γ = surface tension; δ = Hildebrand and Hansen solubility parameters; ζ = zeta potential; η = viscosity; ρ = density. Other abbreviations: see Figure 2.1 and Table 2.1.

An obvious distinction of polymers is their distributed MW (OECD 1991), which can be measured in terms of MW_N, MW_W, and MWD. The presence of leachable LMW compounds or oligomers in a polymer is also important, as these may be more bioavailable (e.g. Bejgarn *et al.* 2015). MW_N, MW_W, MWD, and LMW content of polymers can be characterised using size exclusion chromatography (OECD 1996a, 1996b).

An important property determining fate is solubility. Hildebrand and Hansen solubility parameters (δ) (Miller-Chou and Koenig 2003) have been used to predict polymer solubility in various solvents (Venkatram *et al.* 2019); however, there are a number of limitations of such methods, and they should be considered only predictive (Venkatram *et al.* 2019). Experimental determination of a polymer's concentration in solution is critical (OECD 2000b; Hartmann *et al.* 2019). Polymer solubility is also key for their classification within the framework of the present review, along with polymer solidity or hardness; solidity is also significant for the ECHA definition of microplastics as solid (ECHA 2019) and may influence environmental fate (for example by influencing biofilm formation; Muthukumar *et al.* 2011). Solid polymers also have several properties which are not shared with dissolved polymers but which are likely to be key for environmental fate, including particle size distribution (PSD), shape, surface properties, and aggregation characteristics.

Particle size, for example, will influence environmental fate and may dominate over other parameters such as density. Density (ρ) can be assessed via a number of methods (OECD 2012a) and can influence position in the water column and settling into sediment in an aqueous environment (Chubarenko *et al.* 2016). However, in a modelling study, Besseling *et al.* (2017) found that whilst retention of 1 – 200 μm plastic particles in a river stretch increased with polymer density, retention of 0.1 – 1 μm particles was almost density-independent, instead being driven by particle size. Similarly, some plastic types that are denser than seawater have been found in the form of micro- and nano-particles on the sea surface, suggesting that smaller debris may have different floatation behaviour despite density considerations (Ter Halle *et al.* 2017). This phenomenon highlights the complexity that can arise through the overlapping influence of multiple fate parameters.

Standard methods for measurement of PSD are based on sedimentation, centrifugation or Coulter Counter, or microscopic techniques for fibres (OECD 1981). Whilst size is most commonly used to refer to solid particles, dissolved polymer molecules may exist in the nano-size range, and thus measurement of hydrodynamic radius (R_h) may be important in characterising their fate. As well as influencing transport and vertical distribution as discussed above, particle size may also influence polymer degradation rate, along with particle shape (Ter Halle *et al.* 2016). Particle shape may also influence residence time in organisms (Frydkjær *et al.* 2017), as well as surface area (S_A) and therefore degree of biofouling, which can in turn influence settling time,

heteroaggregation, and degradation (Chubarenko *et al.* 2016; Michels *et al.* 2018; Morohoshi *et al.* 2018). Shape and S_A are thus potentially important fate parameters for particles. The "shape" of polymer molecules as described by their molecular conformation may also be significant in governing the fate of dissolved and water-soluble polymers.

Other surface characteristics of particles such as surface charge (S_q) may be important (e.g. Fotopoulou and Karapanagioti 2012). Surface charge of nano-scale polymer particles in colloidal suspensions can be assessed by measurement of the zeta potential (ζ), which influences stability and therefore aggregation behaviour (Cai *et al.* 2018; Oriekhova and Stoll 2018; Liu *et al.* 2019; Saavedra *et al.* 2019; Wu *et al.* 2019). Aggregate formation is also key, and may influence vertical transport of polymer particles in the environment (Michels *et al.* 2018). As described previously, the use of partition coefficients is not relevant to describe partitioning of solid particles via aggregation and deposition. Instead, kinetic parameters such as attachment efficiency (α) can be used; this is an empirical parameter which must be determined experimentally, given the multiple complex processes and properties which contribute to nanoparticle aggregation and attachment, including particle size, repulsion between particles (characterised by the zeta potential), and the suspension composition, all of which will influence the energy barrier for nanoparticles to reach short enough separation distances to aggregate (Praetorius *et al.* 2014). Attachment efficiency has been determined experimentally for analysis of heteroaggregation between microplastics, nanoplastics, and clays (Besseling *et al.* 2017).

The deposition rate constant (k_{dep}) may also be relevant (along with α) to assess settling times in an aquatic environment when equilibrium partitioning to sediment does not apply. Deposition of airborne polymeric particles in the micro- and nano-range (Bergmann *et al.* 2019; Kawecki and Nowack 2019; Wright *et al.* 2020), and dissolved polymers present in aerosols, for example in agricultural sprays (e.g. Felsot *et al.* 2011; Lewis *et al.* 2016), may also be significant. The deposition rate constant has been used to describe deposition of engineered nanoparticles both to soil and water from the atmosphere, and to sediment from an aqueous environment (Meesters *et al.* 2014).

There are other fate properties that may be key to polymer exposure assessment. For example, viscosity (η) (OECD 2012b), also used in environmental fate analyses of oil spills (Sebastião and Soares 1995), may be important for liquid polymers. In addition to

T_m, T_g is useful in polymer matrix characterisation as it describes the transition from rigid and glassy to rubbery, and has been found to influence sorption and desorption of organic contaminants (Teuten *et al.* 2009) as well as polymer degradation rate (Min *et al.* 2020).

In addition, metrics for quantifying exposure are key; whilst mass concentration remains sufficient for dissolved polymers, for solid polymers and particles, number concentration and particle size distribution (PSD) are likely to also be significant (Kookana *et al.* 2014). This is illustrated by the fact that larger particles may dominate in terms of mass, but smaller particles may dominate in terms of number (Ter Halle *et al.* 2016; Schwaferts *et al.* 2019), meaning the metric measured may influence conclusions drawn about relative environmental impacts.

2.3.6. Analytical techniques for polymer characterisation

It has been recognised that standard test methods may need to be adapted for application to polymers (ECETOC 2020). Whilst some methods do exist that are specifically tailored to polymers or solids, such as for assessment of solubility, MWD, and PSD (OECD 1981, 1996a, 2000b), an array of additional techniques may be required for full characterisation of a polymer. The traditional methodologies used for chemical analysis, including chromatography and mass spectrometry, may need to be adapted or replaced to characterise parameters such as shape, aggregation behaviour, and topography. Additionally, the existence of a 'methodological gap' in the nano-size range has been highlighted (Schwaferts *et al.* 2019), and it has been recognised multiple times in the literature that there is a lack of both standardisation and adequate validation of some techniques for plastic particle analysis (Hidalgo-Ruz *et al.* 2012; Ivleva *et al.* 2017; Burns and Boxall 2018; Pico *et al.* 2019). Methods for analysis of dissolved and water-soluble polymers also require development (Huppertsberg *et al.* 2020), and may utilise chemical identification methods such as mass spectrometry, or methods to characterise size and molecular weight such as size exclusion chromatography or scattering techniques. Knowledge from nanoparticle and microplastic analysis will be invaluable in further developing techniques for polymer analysis in exposure and risk assessment. Importantly, given the potentially massive range of products that may be formed from polymer degradation, use of a wide array of techniques will most likely be necessary for a single environmental degradation study if all products are to be characterised. Fully characterising the rate, route and products of polymer degradation may therefore be

difficult to achieve in a time and cost-effective manner, despite the importance of such studies for environmental risk assessment.

2.3.7. Structure-activity relationships and exposure models for polymers

Given that most QSAR models have been developed specifically for LMW organic compounds, many will be insufficient for application to polymers (ECHA 2016), and prediction of polymer environmental fate should also address additional influences as a result of polymer size, molecular weight, and macromolecular properties. A lack of data on polymer environmental fate will also limit development of polymer QSARs. Although models such as ECOSAR include recommendations for assessing the aquatic hazard of polymers (Mayo-Bean *et al.* 2017), they are limited by availability of data and have been developed only for specific polymer classes, meaning they are often not applicable to new polymers (Nolte *et al.* 2017b).

Given the added complexity of polymers compared to LMW compounds and the additional parameters influencing polymer fate, complex exposure models for polymer ERA may also require additional considerations. Whilst many simple, lower tier models are likely to be appropriate for polymers, higher tier models which require fate parameters as inputs may need to be adapted to account for the polymer-specific processes described above. For example, models such as the FOCUS models for pesticides (FOCUS 2001), and the ePiE model developed for pharmaceuticals, incorporate partition coefficients and loss processes such as degradation (Oldenkamp *et al.* 2018). However, for a solid polymer particle, partition coefficients are not applicable and degradation processes may not indicate a decrease in exposure, since initial degradation may simply form a larger number of smaller particles. This may also be true for degradation of water-soluble polymers, as transformation may initially yield shorter chain molecules of the same polymer type, or a chemically transformed derivative. Parameters such as size, shape, density, and attachment efficiencies, among others, will dictate transport and fate of particles (Kooi *et al.* 2018) in place of partition coefficients. Similarly, given the general lack of fate analyses of dissolved and water-soluble polymers, assessment of the applicability of fate models for LMW chemicals may be necessary, given that parameters such as size, molecular weight, and macromolecular properties such as chain conformation are likely to influence dissolved polymer fate.

2.4. Towards a framework for polymer exposure assessment

To move towards a framework for polymer environmental exposure assessment, we have identified key fate parameters and descriptors that are likely to be most significant (Figure 2.3). These include key physicochemical properties required for identification and characterisation of polymers, which can also facilitate polymer grouping and prioritisation. Approaches to polymer grouping have been discussed in detail by ECETOC (2019); in the present review we highlight key parameters for polymer characterisation for exposure assessment based on the discussion of fate parameters above, including properties such as molecular weight parameters, solubility, presence of functional groups, and transition temperatures.

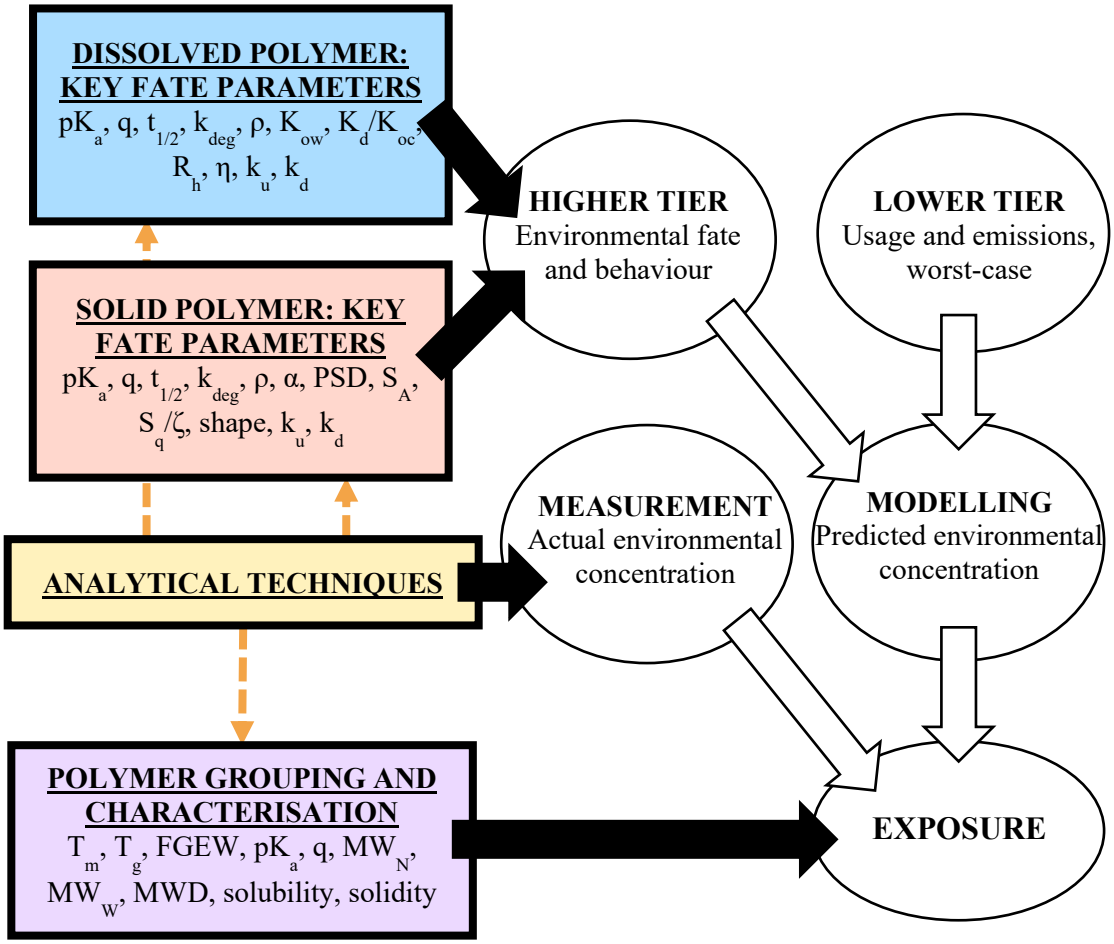


Figure 2.3: Impact of polymer properties, analytical techniques, and fate parameters for solid and dissolved polymers in development of an environmental exposure assessment framework.
Abbreviations: see Figures 2.1 and 2.2, and Table 2.1.

We have also identified the most relevant parameters for higher tier exposure modelling (Figure 2.3), and recommend that classification of polymers in terms of whether they will be in dissolved or solid form is likely to be useful in environmental risk assessment, since this will define the relevance of all other fate parameters to the polymer in question. This is particularly relevant for in-depth exposure assessment, to focus assessment efforts and avoid incorrect application of parameters. Whilst parameters such as k_{deg}, $t_{1/2}$, and many of the key physicochemical properties identified previously will be relevant to both groups, properties such as PSD, attachment efficiencies, and surface properties are unique to solid materials, and equilibrium partition coefficients are only applicable to dissolved polymers. However, the potential overlap of polymer components and transformation products (Section 2.3.4) means that an integrated approach with parameters from multiple categories may be necessary in some cases. It is important to note that development of analytical techniques is key moving forward, both for monitoring studies and in characterisation of key parameters for polymers.

From this framework (Figure 2.3), key considerations to address the knowledge gaps discussed previously can be identified, including: the most important parameters for polymer identification, grouping, prioritisation, and fate analysis; complex degradation processes and byproducts of polymers; available analytical techniques for polymer analysis; and fate and exposure modelling of polymers. These considerations are addressed in the context of the exposure assessment framework (Figure 2.3) below.

2.5. Considerations and key research needs for polymer exposure and risk assessment

2.5.1. Key parameters for polymer identification, grouping, and environmental fate

There is a clear need to develop standard identifiers for polymers to avoid ambiguity in risk assessment; identifiers based on the key physicochemical properties summarised in Figure 2.2 may be useful in differentiating polymers formed from the same monomer units, which would otherwise not be distinguishable from just, for example, name and CAS number. A number of these descriptors have also been highlighted by ECETOC

(2019), including molecular weight (MW_N, MW_W, MWD), T_m, T_g, and solubility, among others.

However, it is still unclear which parameters may be most important for polymer grouping and exposure assessment, given the complexity and potential overlap of factors in influencing environmental behaviour. Development of grouping approaches based on correlation between key parameters and environmental behaviour is necessary, which will likely require data from experimental fate and ecotoxicology studies for a wide range of polymers. Assessing the ability of key parameters to predict environmental behaviour of polymers is likely to be achieved through a combination of experimental fate studies and modelling; for example, Min *et al.* (2020) established key predictors for surface erosion and degradation of marine plastic debris based on physical properties and molecular structure. Similar analyses for other polymers and endpoints, based on use of experimental data, intrinsic properties, and key parameters to inform predictive modelling, are likely to be extremely useful in environmental exposure assessment and grouping. Further research into the relative extent that certain properties may influence hazard and fate, with establishment of a hierarchy of features to predict environmental behaviour (Min *et al.* 2020), as well as how these properties may interact to mitigate or exacerbate hazard, is warranted. Filling this research gap would also supplement development of QSARs and read-across approaches, as well as prioritisation efforts for polymers and identification of data needs for risk assessment. Development of QSARs for polymers will also further consolidate grouping approaches and establishment of key parameters for environmental exposure assessment of polymers.

Research into cut-off points for solidity and solubility is also warranted given the potential ambiguity that may arise for polymers which are not clearly either solid or dissolved (e.g. waxes). For polymers of sufficiently low molecular weight, parameters that would normally only be relevant for LMW chemical substances and oligomers (such as P and BCF) may become relevant, and so it may be important to define molecular weight cut-off points for such parameters. Additionally, as knowledge develops of which properties of particles may confer hazard, such as shape and surface properties (e.g. Della Torre *et al.* 2014; Frydkjær *et al.* 2017), the relative importance of these parameters for grouping of micro- and nano-polymers may become apparent.

2.5.2. Polymer degradation and implications for fate

Many of the current standard test methods for degradation study different transformation pathways in isolation or under specific sets of conditions (e.g. OECD 2004b, 2008); however, it is likely that in the environment these processes will occur in tandem and may interact. Therefore, use of simulation tests which closely mimic environmental conditions (e.g. OECD 2004a) are likely to be more useful in characterising complex polymer degradation. Such tests are frequently employed in environmental exposure assessment, and have been applied to a number of polymer classes. In particular, environmental exposure and risk assessments have been conducted for alcohol ethoxylates, alcohol ethoxysulfates, and polycarboxylate homo- and co-polymers as part of the HERA project (HERA 2004, 2009, 2014a, 2014b), with degradation data for these classes of polymers being summarised as part of these risk assessments. In addition, Duis *et al.* (2021) gathered available data for several water-soluble polymers: polycarboxylates, polyethylene glycols, and polyquaterniums.

In the present review, we have further summarised the aforementioned collated degradation data for these polymer types, in order to provide a comprehensive overview of the available degradation data and test results for these polymers, presented in Table 2.2. Full details are presented in the Appendix. We have here focussed on available data relevant to environmental exposure assessment for water-soluble polymers, due to the relative scarcity of environmental fate and exposure data for water-soluble polymers compared with plastics (Arp and Knutsen 2020; Huppertsberg *et al.* 2020) and thus the need to further assess available data and research needs.

Whilst there are degradation data in a range of media available for many of these polymer groups (Table 2.2), it should be noted that these groups cover only a small fraction of the polymer types in current use, and degradation data for environmental matrices (surface waters, soils, and sediments) are limited. There are also few data available for polyquaterniums as a class (Duis *et al.* 2021), despite potential concerns relating to environmental hazard of cationic polymers (e.g. USEPA 1997). In addition, a lack of availability of information on experimental methods limits assessment of the quality of some results (Duis *et al.* 2021) as well as comparison and verification between studies, highlighting the need for transparency and standardisation of methods for adequate risk assessment, as well as the need for further study of water-soluble polymers alongside plastics and microplastics.

Table 2.2: Summary of degradation data for several types of water-soluble polymers (alcohol ethoxylates, alcohol ethoxysulfates, polycarboxylates, polyethylene glycol, and polyquaterniums) obtained from a meta-review of previously collated data from the literature.

Polymer class	Polymers covered	Methods	Results	References
		Ready biodegradability		
Alcohol ethoxylates	C: 8-18 EO[a]: 2-30	OECD 301D, 301F; Closed bottle test; BOD; Sapromat	60-92 % ThOD	HERA 2009
	C: 10-18 EO: 3 to >20	OECD 301B; CO_2 evolution test; Modified Sturm	60-95.4 % CO_2 formation/ThCO_2	
	C: 11-15 EO: 3-20	Die away screening test; modified OECD screening test	65-100 % DOC	
	C: 13 EO: 9	OECD 301E	80 % primary biodegradation	
Alcohol ethoxysulfates	C: 14-15 EO: 2.25	Modified Sturm	0.18 day^{-1} (mineralisation rate, CO_2 evolution) 3.9 days ($t_{1/2}$, CO_2 evolution)	Federle *et al.* 1997; HERA 2004
Polycarboxylates	P-AA, mean MW 4 kDa or not specified; P-MAA/EA, MW approx. 500 kDa; P-AM/AA, MW 10,000 kDa (25% sodium acrylate (w/w))	Modified MITI tests, closed bottle tests	<20 % biodegradation or not indicated. All polymers found to be not readily biodegradable.	Duis *et al.* 2021
Polyethylene glycol	Mean MW 0.2-57.8 kDa	OECD 301B, 310; Combined CO_2/DOC test	-5 to 95 % CO_2 evolution	Duis *et al.* 2021
	Mean MW 0.2-57.8 kDa (MW_W 0.251-57.8 kDa or not specified, MW_N 0.120-25.1 kDa or not specified)	OECD 301A; Combined CO_2/DOC test	>70 to >90 % DOC reduction/ removal	
	Mean MW 350 Da	ISO 14593	77 % CO_2 production (total inorganic carbon)	
	Mean MW 0.2-4,000 kDa	OECD 301B, 301E, 301F; modified OECD screening test; DIN 38412	4.1 to >95 % (endpoints not specified)	

(Table 2.2 continued)

Polymer class	Polymers covered	Methods	Results	References
		Ready biodegradability (*continued*)		
Polyquaterniums	PQ-10, MW approx. 30,000 kDa, 1.0 meq g^{-1}	Not specified	1 % BOD (not readily biodegradable)	Duis *et al.* 2021
	PQ-16, MW approx. 100 and 400 kDa, 2.0 and 3.0 meq g^{-1} (pH 7)	OECD 301F	< 10 % ThOD (mineralisation rate)	
	PG-6, MW_N > 10 kDa; PQ-10, MW_N approx. 240 kDa, MW approx. 400 kDa, 1.2 meq g^{-1}; PQ-7, MW 4,300-5,200 kDa, 1.6 meq g^{-1}	Not specified	General and ready biodegradability, qualitative data only: "not readily biodegradable", "poorly biodegradable"	
	Removal in wastewater treatment (including data for inherent biodegradability, batch, and simulation tests)			
Alcohol ethoxylates	C: 12-16 EO: 1-9	Activated sludge die away test, radiolabelled polymer	0.28-2.32 minutes ($t_{1/2}$) 18-146 $hour^{-1}$ (k_1)	HERA 2009
Alcohol ethoxysulfates	C: 12-18 EO: 2-12	SCAS and OECD CAS confirmatory test	95.4-100 % removal	Federle *et al.* 1997; HERA 2004
	C: 14-15 EO: 2.25	$^{14}CO_2$ evolution, activated sludge system	1.79 day^{-1} (mineralisation rate) 0.39 days ($t_{1/2}$)	
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	$^{14}CO_2$ evolution, water (domestic activated sludge); CO_2 production coupled with SCAS or batch activated sludge, adapted WWTP inocula	8-43 % CO_2 evolution	HERA 2014a, 2014b; Duis *et al.* 2021
	P-AA (and sodium salts), mean MW 1-15 kDa or not specified; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa; P-MAA/EA, mean MW approx. 500 kDa	OECD 302A, 302B, 303A; ISO 18749; ISO 9888, 88/302/EEC, part C	9-100 % DOC reduction	
	P-AA, mean molecular weights 1 and 2 kDa	OECD 303A	9-24 % DOC or ^{14}C removal (no clear information on test endpoint)	
	P-AA (and sodium salts), mean MW 4.5 kDa	Wastewater treatment simulation test, domestic; OECD 303A	55 and 76 % (removal of radiolabelled material)	

(Table 2.2 continued)

Polymer class	Polymers covered	Methods	Results	References
Removal in wastewater treatment (including data for inherent biodegradability, batch, and simulation tests) (*continued*)				
Polycarboxylates (*continued*)	P-AA, MW 4.5-215 kDa or not specified	OECD 303A; various simulation and activated sludge tests, including SCAS, CAS, treatment with $FeCl_3$	16-98 % overall removal	HERA 2014a, 2014b; Duis *et al.* 2021
	P-AA, mean MW 4.5 kDa	Series of batch experiments (^{14}C-labelled polymer); Primary treatment simulation	13-98 % removal	
Polyethylene glycol	Mean MW 0.2-20 kDa	OECD 302A, 303A/ISO 11733; batch system, adapted or non-adapted sludge	41-102 % DOC removal	Duis *et al.* 2021
	Mean MW 350 Da	ISO 9888 (modified)	>80 % COD reduction	
	Mean MW 1-20 kDa	CO_2 production test; various batch experiments, adapted or non-adapted sludge; OECD confirmatory test (^{14}C-labelled polymer)	40 to >90 % CO_2 evolution/ mineralisation	
	Mean MW 0.3-6 kDa	OECD 302B; DIN 38412 L 24	<20 to >95 % (endpoint not specified)	
	Mean MW 4.6 kDa.	Sealed vessel test	79-86 % mineralisation (inorganic carbon production) at test end	
	Mean MW 0.6-20 kDa	Batch experiment, microorganisms from terylene plant	77-88 % primary degradation based on chemical analysis	
Polyquaterniums	PQ-7 (MW not specified).	OECD 302B	30-50 % DOC or COD elimination	Duis *et al.* 2021
	PQ-16, MW approx. 40-100 kDa, 2.0-6.1 meq g^{-1} (pH 7)	OECD 302B	20-70 % DOC elimination	
	PQ-6, MW_N > 10 kDa; PQ-16, MW approx. 40-400 kDa/ unspecified, 2.0-6.1 meq g^{-1} (pH 7)/ unspecified	OECD 302 (no further information); not specified	Qualitative data only: "not inherently biodegradable"; "Moderately/partly eliminated from water; virtually eliminated from water by e.g. sorption to activated sludge"; "Removed from waste water by e.g. strong sorption on activated sludge"	

(Table 2.2 continued)

Polymer class	Polymers covered	Methods	Results	References
		Fate in wastewater treatment (anaerobic)		
Alcohol ethoxylates	C: 9-11 EO: 8	Measurement of gas production, digested sludge	60-83 % $ThCH_4$	HERA 2009
	C: 9-11 EO: 8	Measurement of gas production, digested sludge	79 % ThGP	
	C: 18 EO: 7	$^{14}CH_4$ and $^{14}CO_2$ evolution, digested sludge	84 % $ThCH_4$ + $ThCO_2$	
Polycarboxylates	P-AA/MA (and sodium salts), 70 kDa	Incubation in mixture of digester sludge and nutrient solution, radiolabelled polymer	Biodegradability extent between 11 and 16 %	HERA 2014b
Polyethylene glycol	Mean MW 0.4-10 kDa (included tests on mixtures of 0.4/0.6/1 kDa, and of 1.5/3/10 kDa)	Batch experiments (adapted and non-adapted digested activated sludge)	Approx. 85-92 % TOC removal	Duis *et al.* 2021
	Mean MW 0.6-20 kDa	Batch experiment, adapted micro-organisms	40-70 % primary degradation	
		Degradation in river water		
Alcohol ethoxylates	C: 8-18 EO: 1-20	Rate of removal of some AE homologues, extrapolation to other chain lengths	4-24 hours ($t_{1/2}$)	HERA 2009
Alcohol ethoxysulfates	C: 14-15 or not specified EO: 2.25 or not specified	$^{14}CO_2$ evolution, river water and settled sludge supernatant; unspecified methods	0.48 day^{-1} and 0.7 $hour^{-1}$ (mineralisation/ degradation rate). 1.4 days and approx. 1 hour ($t_{1/2}$). Approx. 16.6 day^{-1} (rate constant).	Federle *et al.* 1997; HERA 2004
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	$^{14}CO_2$ evolution, river water or water and sediment, adapted or non-adapted water	6-63 % CO_2 evolution	HERA 2014a, 2014b; Duis *et al.* 2021
Polyethylene glycol	Mean MW 0.3 kDa	River water die-away test	99 % primary biodegradation	Duis *et al.* 2021

(Table 2.2 continued)

Polymer class	Polymers covered	Methods	Results	References
		Degradation in seawater		
Polyethylene glycol	MW_W 0.251-57.8 kDa, MW_N 0.120-25.1 kDa	Combined CO_2/DOC test, artificial seawater and marine micro-organisms	No biodegradation to >90 % (DOC removal)	Duis *et al.* 2021
	Mean MW 0.6 kDa	OECD 306	55 % (endpoint not specified)	
		Degradation in sediment		
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	$^{14}CO_2$ evolution test, sediment (river water and sediment)	6-58 % CO_2 evolution	HERA 2014a, 2014b
		Degradation in sediment (anaerobic)		
Alcohol ethoxylates	C: 9-11 EO: 8	Gas production, freshwater swamp material and marine sediment	66-77 % ThGP	HERA 2009
	C: 10-12 EO: 7.5-23	CH_4 production, polluted creek mud	70-80 % ThCH_4	
	C: 12 EO: 8-9	$^{14}CH_4$ and $^{14}CO_2$ evolution, pond sediment, wastewater pond sediment	13-40 % ThCH_4 + ThCO_2	
Polyethylene glycol	Mean MW 0.4 kDa	Anaerobic water-sediment test, marine sediments and seawater	92 % (primary degradation) 18 days ($t_{1/2}$)	Duis *et al.* 2021
		Degradation in soil		
Alcohol ethoxysulfates	C: 14-15 EO: 2.25	$^{14}CO_2$ evolution, sludge-amended soil test system	0.29 day^{-1} (mineralisation rate) 2.4 days ($t_{1/2}$)	Federle *et al.* 1997; HERA 2004
Polycarboxylates	P-AA (and sodium salts), mean MW 1-530.4 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa; P-AM/AA	$^{14}CO_2$ evolution test, sludge treated soil; biodegradation (^{13}C), agricultural soil; biodegradation (^{14}C), flask or tube reactors	0.91-35 % mineralisation/ CO_2 evolution	HERA 2014a, 2014b; Duis *et al.* 2021

(Table 2.2 continued)

Polymer class	Polymers covered	Methods	Results	References
		Degradation in soil (*continued*)		
Polycarboxylates (*continued*)	P-AM/AA, approx. 80% acrylamide and approx. 20% acrylic acid, mean MW 12,000-15,000 kDa (18% negative charge density)	Field study (8 years), agricultural site, polymer degradation (^{13}C)	13-74 % degradation relative to total amount of polymer added over 3 or 6 years 9.8% per year (mean degradation rate)	HERA 2014a, 2014b; Duis *et al.* 2021
Polyethylene glycol	Mean molecular weight 4 kDa (^{14}C labelled).	Biodegradation in three tropical soils	approx. 5-10 % mineralisation/ $^{14}CO_2$ production (read from graph)	Duis *et al.* 2021

[a] Data for EO=0 (i.e. for corresponding fatty alcohols) has not been included in the present summary due to the absence of monomer units.

C = number of carbons in alcohol, EO = average number of ethoxy monomer units, ThOD = theoretical oxygen demand, $ThCO_2$ = theoretical carbon dioxide, DOC = dissolved organic carbon, $t_{1/2}$ = half-life, P-AA = homopolymer of acrylic acid, MW = molecular weight, P-MAA/EA = copolymer of methacrylic acid and ethyl acrylate, P-AM/AA = copolymer of acrylamide and acrylic acid, MW_W = weight average molecular weight, MW_N = number average molecular weight, BOD = biochemical oxygen demand, PQ = polyquaternium, k_1 = first order rate constant, P-AA/MA = copolymer of acrylic acid and maleic acid, WWTP = wastewater treatment plant, COD = chemical oxygen demand, PEG = polyethylene glycol, $ThCH_4$ = theoretical methane, ThGP = theoretical gas production, TOC = total organic carbon, HRT = hydraulic retention time, AE = alcohol ethoxylate, LCMS = liquid chromatography mass spectrometry.

In general, it can be observed that alcohol ethoxylates, alcohol ethoxysulfates, and polyethylene glycols often exhibit higher rates or levels of degradation than polycarboxylates and polyquaterniums, although there are high levels of variation due to the wide ranges of polymers summarised together in the present review. Importantly, many studies focus on extent of degradation and associated biodegradability endpoints (Table 2.2), whereas full environmental exposure assessment will in many cases require treatment of degradation products formed. In addition, tests focussed on measures such as CO_2 evolution may underestimate degradation for some HMW polymers which may undergo extensive fragmentation into lower MW polymer chains before complete mineralisation; similarly, measurement of loss of a parent material may overlook the presence of persistent polymer chains of lower MW. Analysis of degradation products will likely require additional parameters and a wide array of analytical techniques to describe their fate. However, it may not always be feasible to characterise the full range of polymer degradation products, particularly given the constraints of current analytical methodologies for analysis of nano-scale polymer particles; therefore, further research into optimum methods by which polymer degradation can be characterised, which product types are most significant in terms of environmental risk, and how polymer properties can be predictive of degradation products (e.g. Min *et al.* 2020), is warranted.

2.5.3. Characterisation of polymers and degradation products

A further key consideration for polymer exposure assessment is the analytical tools available to characterise polymer fate and degradation processes. The applicability of existing standard test methods to analysis of polymer properties and fate parameters has been evaluated (ECETOC 2020), and thus in the present review we present a holistic overview of how analytical tools could be deployed and further developed to better characterise polymer specific fate properties and degradation products.

Fate and degradation studies may involve use of complex environmental matrices, which will often require extraction or separation prior to analysis. A number of methods exist for extraction of micro- and nano-plastics from soils, sediments, and biota, including density separation and chemical or enzymatic digestion (e.g. Karlsson *et al.* 2017; Hurley *et al.* 2018). However, these treatments may alter the particle analytes (Enders *et al.* 2017; Rist *et al.* 2017; Hurley *et al.* 2018), and thus methods should be tested and validated for the polymers in question. For analysis of LMW chemical

compounds in complex environmental matrices, various solvent extraction techniques are typically used (e.g. Basheer *et al.* 2005; Martínez-Parreño *et al.* 2008; Berlioz-Barbier *et al.* 2014), which may be developed and optimised for dissolved polymers (e.g. Antić *et al.* 2011).

A number of reviews of available techniques for analysis of micro- and nano-plastics in the environment are available (Li *et al.* 2018; Silva *et al.* 2018; Nguyen *et al.* 2019; Schwaferts *et al.* 2019; Fu *et al.* 2020). The advantages and limitations of some key analytical methods for solid polymers and their degradation products are summarised in Table 2.3 and further discussed below, along with relevant methods for characterisation of water-soluble polymers.

Microscopy, particularly light microscopy and scanning electron microscopy (SEM), is commonly used in visualisation of plastics, allowing characterisation of size and shape of particles (e.g. Ter Halle *et al.* 2016; Hernandez *et al.* 2017; Oriekhova and Stoll 2018) and surface degradation of macro-polymers (Gómez and Michel Jr. 2013; Musioł *et al.* 2017). However, unequivocal chemical identification of the analyte is essential, and relies on combination with spectroscopic methods such as Fourier-transform infra-red (FTIR) and Raman spectroscopy (Burns and Boxall 2018; Cabernard *et al.* 2018), which may also provide information on chemical changes with degradation (Da Costa *et al.* 2018). Automation can provide faster and more reliable results, and reduce issues with bias and sample representativeness, for example in focal plane array (FPA)-based micro-FTIR (Löder *et al.* 2015; Primpke *et al.* 2017). However, spectroscopic techniques are unable to give chemical information on particles below the micro-scale.

Table 2.3: Summary of the currently available techniques for analysis of polymer degradation in the environment.

Method	Size range	Information obtained	Advantages	Limitations	References & examples of use
Mass loss	Mass based; > ca. 0.01 mg	Provides estimation of overall extent and rate of degradation, and can aid mass balance of products	- Fast, easy method giving overall indication of degradation - Non-destructive	- Other factors besides degradation may affect mass, including oxidation, biofilm formation, and oxygen absorption - High error rates - No information on degradation pathways or products	Lambert *et al.* 2013a, 2013b; Hintersteiner *et al.* 2015; Ter Halle *et al.* 2016; Balestri *et al.* 2017; Auta *et al.* 2018
Thermo-analytical methods (e.g. TGA, DSC)	Mass-based; 10-20 mg	Changes in thermal properties and stability	- Fast, simple methods giving indication of degree of degradation - Can combine with identification techniques such as FTIR and MS to provide information on thermal degradation products	- Cannot confirm possible degradation pathways - Cannot obtain information on environmental degradation products	Cheremisinoff 1996; Deroiné *et al.* 2014; Dümichen *et al.* 2014; Musioł *et al.* 2017
Light microscopy	> 500 µm	Imaging of degraded macro-polymer surface, visualisation and screening of single microplastic particles	- Simple method for visualisation and screening - Non-destructive	- Extremely high error rate for sample identification, so must couple with definitive chemical identification methods such as spectroscopy	Eriksen *et al.* 2013; Löder and Gerdts 2015; Musioł *et al.* 2017; Burns and Boxall 2018
ATR-FTIR	> 500 µm	Chemical identification and changes in chemical functionality due to degradation	- Well-established and widely used - Fast analysis time - Non-destructive	- Smaller samples may give too weak a signal - Spectral interferences from water may arise - Micro-polymer particles must be visually sorted which may introduce bias	Lambert and Wagner 2016b; Cabernard *et al.* 2018

(Table 2.3 continued)

GPC	Mass based; > ca. 20 mg	Molecular weight metrics and changes in molecular weight distribution with degradation	- Relatively fast and simple sample preparation - Can provide overall picture of molecular changes with degradation, as well as information on amount of polymer	- High temperature required for some plastic types – potential induced degradation - Potential lower accuracy and difficulties distinguishing polymers for certain polymer types	Hintersteiner *et al.* 2015; Musioł *et al.* 2017; Biver *et al.* 2018; Müller *et al.* 2018; Giacomucci *et al.* 2019
FPA-based micro-FTIR	> 10 µm	Simultaneous visualisation, mapping and chemical identification of polymer particles	- Wide area analysed, giving large numbers of spectra - No visual sorting required - Automation possible, removing bias in analysis and allowing detection of smaller particles - High resolution and non-destructive	- Spectral interferences from water may arise - Time consuming - If manual not automated, particle counts may be underestimated - Environmental matrix may cause problems for detection of smaller particles	Ivleva *et al.* 2017; Primpke *et al.* 2017; Cabernard *et al.* 2018
Raman micro-spectroscopy	> 1 µm	Simultaneous visualisation, mapping and chemical identification of polymer particles	- High resolution - Little interference from water - Fast, automatic data acquisition possible - Non-destructive - Higher resolution in identification compared with FTIR-based techniques	- Fluorescent interferences may occur - Visual sorting often used - May require sample purification - Very time consuming - Low signal-to-noise ratio - Sample heating may damage polymer	Frére *et al.* 2017; Ivleva *et al.* 2017; Araujo *et al.* 2018; Cabernard *et al.* 2018; Scheurer and Bigalke 2018
Coulter Counter	0.4 - 1200 µm	Particle concentration and size distribution	- Sensitive, consistent, high reproducibility - Large concentration range - Conductivity-based so orthogonal to optical techniques	- Spherical model may be used to calculate size - Particles must be suspended in electrolyte solution	Demuele *et al.* 2010; Rhyner 2011; Lambert and Wagner 2016b; Frydkjær *et al.* 2017

(Table 2.3 continued)

LD	20 nm – 3.5 mm	Particle size and size distribution	- Wide size range - Accurate and reproducible - High sensitivity - Can detect larger particles or agglomerates in a population of smaller particles, if pure LD used - Fast analysis time	- Spherical model - Inaccurate results if incorrect optical parameters used - Instruments may require additional methods and parameters for smaller particles - Possible trade-off between measurements of larger and smaller particles	Witt and Röthele 1996; Eshel *et al.* 2004; Keck and Müller 2008; Lee *et al.* 2014; Kokalj *et al.* 2018
MALS	50 – 1000 nm	Particle size	- Fast and reproducible - Can determine particle shape when coupled to other techniques such as FFF and DLS	- Matrix effects may influence results - Monodisperse samples required, therefore need coupling to separation techniques such as SEC or AF4	Brar and Verma 2011; Gigault *et al.* 2017; Mehn *et al.* 2017; Mintenig *et al.* 2018
NTA	30 - 2000 nm	Particle size and volume distributions, particle number	- Can apply to heterogeneous samples - Individual particles tracked, giving accurate sizing over broad range of distributions - Good size resolution - Some information on nature of particles from scattering intensity - Can give information on aggregation	- Spherical model - Particle concentration measurements may be imprecise - Method and sample concentration must be optimised before use - Possible instrument operation bias - Sample preparation and measurement may affect aggregation	Filipe *et al.* 2010; Lambert *et al.* 2013a; Lambert and Wagner 2016a, 2016b

(Table 2.3 continued)

AFM	> 10 nm	Visualisation of macro-polymer surface morphology and polymer particles	- Can combine with IR and Raman to obtain both morphological and chemical information as well as potential subsurface information - Can obtain force-interaction curves using colloidal probe AFM - Relatively simple sample preparation and no metal coating required	- Obtaining representative sample is difficult - Imaging artefacts can be problematic	Moons 2002; Yeo *et al.* 2009; Nolte *et al.* 2017a; Iñiguez *et al.* 2018; Merzel *et al.* 2019
DLS	3 nm – 6 µm	Particle size and size distribution	- Fast and straightforward - Accurate for monodisperse suspensions - Relatively wide concentration range - Can give information on aggregation	- Spherical model - Less suitable for heterogeneous samples, due to low size resolution and high sensitivity towards larger particles - Cannot determine particle concentration - Less applicable to complex or unknown samples	Jillavenkatesa *et al.* 2001; Filipe *et al.* 2010; Gigault *et al.* 2016; Besseling *et al.* 2017; Gigault *et al.* 2017; Ter Halle *et al.* 2017
SEM	> 3 nm	Visualisation of polymer surface morphology, and visualisation and characterisation of polymer particle shapes and sizes	- High resolution - Detailed mapping and visualisation - Elemental analysis possible if coupled to EDS	- Complex sample preparation which may alter nature of sample - Heavy metal staining usually required - Difficult to obtain representative sample - bias when determining size distributions of heterogeneous particle mixtures	Bootz *et al.* 2004; Brabazon and Raffer 2010; Oriekhova and Stoll 2018; Nazareth *et al.* 2019

(Table 2.3 continued)

TEM	> ca. 1 nm	Visualisation and characterisation of polymer particles	- Precise information on particle size and shape - Elemental analysis possible if coupled to EDS - Very high size resolution	- Complex sample preparation which may alter nature of sample - Heavy metal staining sometimes required - Obtaining representative sample may be difficult - Thin sample required	Michler 2008; Pyrz and Buttrey 2008; Velzeboer *et al.* 2014; Cole and Galloway 2015; Gigault *et al.* 2016
py-GCMS	Mass based; 3 ng – 0.5 mg	Identification of polymer type and associated additives	- Solvent not required, reducing background contamination - Reliable, good repeatability - Can identify complex samples such as co-polymers, polymer mixtures, polymers with additives - Spectral changes due to polymer degradation may be observable - Very low LoD for some polymers (3 ng for polystyrene)	- Difficulty in analysis of plastics in complex environmental matrix - LoD depends on polymer type - Require spectral database for accurate polymer identification - Hand-picking or pre-separation of particles required - Relatively small sample sizes - Contamination or tube blocking can be an issue	Fries *et al.* 2013; Dümichen *et al.* 2015; Dümichen *et al.* 2017; Ter Halle *et al.* 2017; Hermabessiere *et al.* 2018; Mintenig *et al.* 2018
TED-GCMS	Mass based; 200 ng – 100 mg	Identification of polymer type and determination of its mass fraction in an environmental sample	- Direct analysis of polymers in environmental matrix - Large sample sizes (up to 100 mg) and bulk analysis allow representative sampling - High repeatability, automation possible, and can identify complex samples such as polymer blends - Low LoD for some polymers (200 ng for polystyrene) - Most contaminants do not enter GCMS system	- LoD depends on polymer type - Comparison to database required for identification of polymer - Matrix effects may cause issues with adsorption during the analytical process - Smaller range of compound chain lengths can be measured compared to py-GCMS	Dümichen *et al.* 2014; Dümichen *et al.* 2015; Dümichen *et al.* 2017; Elert *et al.* 2017; Dümichen *et al.* 2019

(Table 2.3 continued)

Range of chroma-tography-mass spectrometry techniques	LMW chemical com-pounds	Characterisation and identification of chemical compounds in unknown mixtures	- Can identify compounds in complex mixtures - Robust, well-established methodology	- Often require database for comparisons of spectra and full species identification - Determination of compound structure may not be possible	Lambert *et al.* 2013b

TGA = thermogravimetric analysis; DSC = differential scanning calorimetry; FTIR = Fourier-transform infra-red; MS = mass spectrometry; ATR-FTIR = attenuated total reflection Fourier-transform infra-red; GPC = gel permeation chromatography; FPA = focal plane array; LD = laser diffraction; MALS = multi-angle light scattering; FFF = field-flow fractionation; DLS = dynamic light scattering; SEC = size-exclusion chromatography; AF4 = asymmetric flow field-flow fractionation; NTA = nanoparticle tracking analysis; AFM = atomic force microscopy; SEM = scanning electron microscopy; EDS = energy dispersive spectroscopy; TEM = transmission electron microscopy; LoD = limit of detection; py-GCMS = pyrolysis gas-chromatography mass-spectrometry; TED-GCMS = thermal extraction desorption gas-chromatography mass-spectrometry

Information on PSD can also be obtained from scattering or diffraction-based techniques, which can be applied to nano-scale particles (e.g. Gigault *et al.* 2016; Lambert and Wagner 2016a; Mintenig *et al.* 2018). Laser diffraction (LD) instruments in particular have the potential to cover a wide particle size range (Witt and Röthele 1996; Keck and Müller 2008), and dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA) are useful for characterising particle aggregation (e.g. Filipe *et al.* 2010; Besseling *et al.* 2017; Gigault *et al.* 2017). However, such techniques typically utilise spherical models to describe particles (e.g. Eshel *et al.* 2004; Lambert and Wagner 2016b; Frydkjær *et al.* 2017) which may influence analysis of irregularly-shaped secondary particles. Techniques such as DLS and multi-angle light scattering (MALS) may also require pre-separation of particles into specific size fractions, which can be achieved using asymmetric flow field-flow fractionation (AF4) (e.g. Filipe *et al.* 2010; Gigault *et al.* 2017; Mintenig *et al.* 2018); however, it has been highlighted that many AF4 techniques have been optimised using primary particles, and secondary particles may behave differently (Schwaferts *et al.* 2019). Chromatographic techniques utilised in nanoparticle separation and analysis that have the potential to be adapted for plastic particle analysis have also been highlighted by Schwaferts *et al.* (2019), including hydrodynamic chromatography (HDC) and high-performance liquid chromatography (HPLC).

For chemical analysis of nano-sized particles, mass spectrometry techniques are crucial. Pyrolysis gas-chromatography mass-spectrometry (py-GCMS) has been used to identify polymer types of plastic particles (Fries *et al.* 2013; Ter Halle *et al.* 2017; Hermabessiere *et al.* 2018), and may reveal changes resulting from degradation (Ter Halle *et al.* 2017). Thermal extraction desorption gas-chromatography mass-spectrometry (TED-GCMS) can be used to directly analyse and potentially quantify plastic particles in an environmental sample (Dümichen *et al.* 2014; Dümichen *et al.* 2015; Dümichen *et al.* 2017; Dümichen *et al.* 2019), making it a potentially powerful technique for analysis of polymers in environmental matrices in fate and degradation studies.

Other techniques are available to determine additional key properties for polymer fate analysis. For example, molecular weight information can be obtained using gel-permeation chromatography (GPC), which has been used in analysis of microplastics down to 10 μm (Hintersteiner *et al.* 2015). Differential scanning calorimetry (DSC) can

give information on thermal properties including T_m and T_g (Deroiné *et al.* 2014; Musioł *et al.* 2017).

Whilst most studies have focussed on analysis of solid plastic polymers, particularly microplastics, most chemical identification techniques (such as infra-red and Raman spectroscopy, and mass spectrometry) will also be generally suitable for dissolved and water-soluble polymers, as highlighted by Arp and Knutsen (2020). Additionally, scattering methods have been used to characterise the hydrodynamic radius of polymers in solution (Armstrong *et al.* 2004), and techniques such as DLS, MALS, and NTA are applicable to large molecules in solution and thus can be applied to dissolved and water-soluble polymers. However, whilst some analyses of water-soluble polymers in environmental matrices have been carried out (e.g. Antić *et al.* 2011), overall few techniques have been developed for environmental analysis of dissolved and water-soluble polymers (Huppertsberg *et al.* 2020), presenting a key research need for environmental exposure assessment. Information on size and hydrodynamic radius from scattering techniques may need to be balanced with chemical and structural information from chemical identification techniques. It has been noted that characterisation of water-soluble polymers is complicated by their complexity (due to the presence of a range of polymer chains across a molecular weight distribution), with multiple signals and low sensitivity giving rise to difficulties in full characterisation and quantification (Huppertsberg *et al.* 2020). Development of mass spectrometry methods such as that described by Huppertsberg *et al.* (2020) which utilise multiple reaction monitoring to give rise to specific fragments independent of molecular weight, and combination with size exclusion chromatography to gain size and molecular weight information, are likely to be useful in analysis of high molecular weight water-soluble polymers. However, the lack of studies on water-soluble polymers compared with plastics highlights the need for further analysis and method development (Arp and Knutsen 2020; Huppertsberg *et al.* 2020).

Each technique has a workable size range (Figure 2.4) and provides different levels of information, emphasising the importance of addressing the research need in question (Elert *et al.* 2017). It is likely that full characterisation of a polymer and its degradation products for fate and exposure assessment will require a combination of techniques which should be tailored to the nature of the polymer in question. This may include all or a combination of chromatographic, spectroscopic, scattering, and spectrometric

techniques. For example, Mintenig *et al.* (2018) recently combined AF4-MALS with py-GCMS to characterise both particle size and polymer type of nanoplastics in environmental samples within a suggested framework for micro- and nano-plastic analysis.

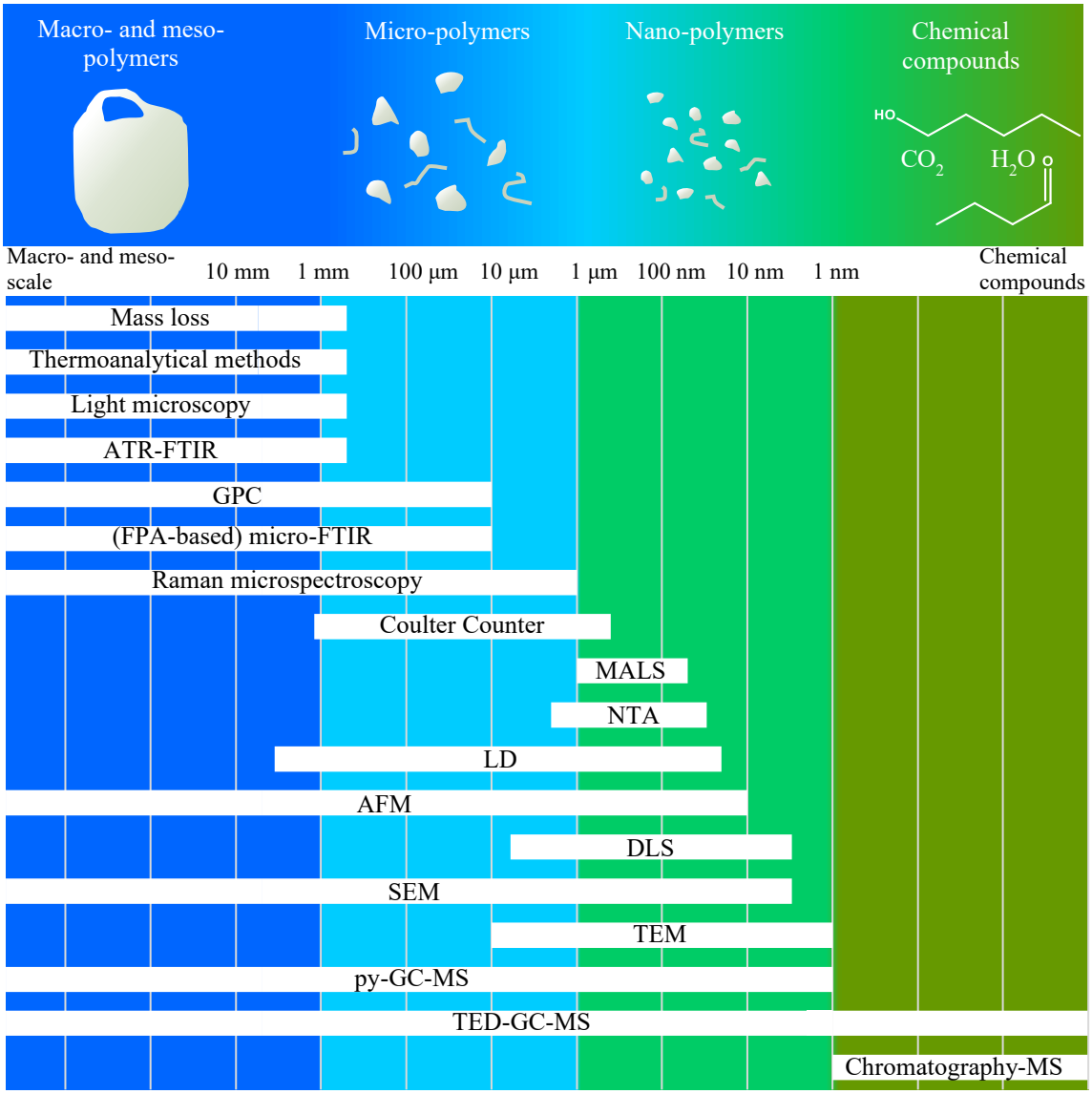


Figure 2.4: Size ranges of key analytical methods for analysis of polymers and polymer degradation, including the corresponding size ranges of solid polymer degradation products that can be characterised.
Abbreviations: see Table 2.3. Note that 'macro-polymer', 'meso-polymer', 'micro-polymer', and 'nano-polymer' refer to polymeric substances with size ranges of ≥10 mm, 1 to <10 mm, 1 to <1000 µm and 1 to <1000 nm, respectively, according to the recommendations given by Hartmann et al. (2019) for plastic debris.

Use of multiple techniques may aid in analysis of diverse polymer degradation products in standard degradation tests when characterising full rate and route (e.g. OECD 2002b, 2008) as well as facilitating development of new standard test methods for polymer-specific properties and fate parameters. For example, DLS and spectrophotometry may be useful in establishing standardised methods for determining α of polymer particles to describe aggregation with suspended particles (Besseling *et al.* 2017) as an alternative to partition coefficients. However, the need for full sample characterisation should be balanced with time and cost-effectiveness, and the level of information needed for adequate risk assessment. As methods and data relating to polymer risk assessment continue to develop, the key properties, polymer types, and degradation products dictating fate and hazard may be elucidated and used to refine and focus risk assessment methodologies and analytical technique development. Analytical techniques developed for nanoparticles and microplastics will be useful in solid polymer risk assessment; however, it has been recognised that a previous lack of standardisation and adequate quality control of techniques for microplastic analysis has hindered progress in assessing their environmental risk (Burns and Boxall 2018). Moving forward in polymer analysis, further development and standardisation of techniques is required for robust risk assessment methodologies, with improvement and adaptation of the techniques discussed in the present review as well as development of novel methods likely being necessary.

2.5.4. Fate and exposure models for polymers

Given the differences in applicability and importance of fate parameters to polymers compared with LMW compounds, development of methods for prediction of fate properties as well as higher tier exposure models for polymers which incorporate both measured and predicted fate parameters is warranted. Whilst some efforts have been made to predict environmental fate of polymers based on their intrinsic properties (Min *et al.* 2020) and QSARs have been developed for algal toxicity of polymer particles (Nolte *et al.* 2017b), further development of robust datasets for model development to establish an array of QSARs for polymer environmental fate is warranted. Adaptation of QSARs for engineered nanoparticles may also be useful for application to polymer particles.

Exposure models for engineered nanoparticles have now been developed, and range in complexity from emission-based mass-balance models (e.g. Gottschalk *et al.* 2009) to multimedia (e.g. Meesters *et al.* 2014) and spatiotemporally resolved (e.g. Quik *et al.* 2015; Domercq *et al.* 2018). Recently, fate models have also been applied to micro- and nano-plastics (e.g. Nizzetto *et al.* 2016; Besseling *et al.* 2017), with the unique combination of low density, wide size range, persistence, and variable shape of plastic particles distinguishing them from other particle types in fate and exposure modelling (Kooi *et al.* 2018). Research on environmental exposure to dissolved polymers remains scarce, and exposure models may again require development of additional input parameters, given the additional properties of polymers which are not applicable to LMW chemical compounds. Some dissolved and water-soluble polymers may also contain polymer molecules in the nano size range, and thus may be influenced by colloidal properties, meaning models for engineered nanoparticles may also be useful for adaptation to water-soluble polymers. Given the potential crossover of polymer components and transformation products between solid and water-soluble polymers, and thus their corresponding key properties (discussed in Section 2.3.4), models which incorporate fate properties for all of solid, dissolved, and low molecular weight polymer components may be necessary for some polymer exposure assessments.

2.6. Conclusions and recommendations

Given the widespread and increasing use of both solid and liquid or water-soluble polymers, and their subsequent release into the environment, development of environmental risk assessment approaches is essential. The unique and complex nature of polymers, including their high and distributed molecular weights, potentially complex matrix properties, and the presence of various additives, means that adaptation of current risk assessment approaches is warranted.

In environmental exposure assessment, use of key fate parameters is essential for fate characterisation and modelling; however, some parameters established for LMW chemical compounds are unlikely to be relevant to polymers. In the present review, an assessment of the relevance of typically used fate parameters to polymers has been performed, revealing that solidity and solubility of polymers are key to the applicability of such parameters and providing a useful basis for development of an environmental exposure assessment framework. Additional parameters, and parameters describing the

unique properties of polymers compared to LMW compounds, have also been suggested, many of which may be useful in higher-tier fate and exposure assessments of polymers.

Incorporation of these parameters into an environmental exposure assessment framework for polymers has been suggested in the present review based around this categorisation, highlighting which parameters may be most important both in polymer identification and grouping, and for exposure assessment and fate modelling. However, it is clear that limitations and knowledge gaps remain; key research needs in order to develop environmental exposure assessment methodologies for polymers are identified and highlighted as follows:

- Standard identification methods for polymers which incorporate their complexity and key properties should be developed. Additionally, the relative significance of key fate parameters, particularly in polymer identification and in impacting fate behaviour, should be assessed in order to establish a base set of parameters for screening-level assessments as well as provide insight on which parameters are most significant for higher tier assessment. This will facilitate prioritisation efforts for polymers and subsequent in-depth exposure assessments.
- Research into characterising and defining polymer solidity and solubility to reduce ambiguity in classification is essential.
- The potential for polymers to further expose the environment to a complex mixture of degradation products with altered fate parameters should be accounted for in exposure assessment. In order to incorporate degradation products into a risk assessment, a deeper understanding of the pathways and products of polymer degradation under environmentally relevant conditions is required, with particular focus on potential changes in key fate parameters and environmental risk.
- There is a clear need to develop, adapt, and standardise validated and reliable analytical methods for characterisation of polymers and their degradation products, in order to measure properties relevant to exposure assessment as well as characterise degradation processes and products for exposure characterisation and modelling. For full characterisation, multiple techniques tailored to the polymer analyte in question may be required in tandem; for example, all of chromatography, scattering or microscopy, and spectroscopy or spectrometry may be required for complete characterisation of a non-homogeneous mixture of polymer particles. However, as knowledge of key polymer

types, properties, and degradation products implicating risk assessment improves, methods can be refined and focussed to provide sufficient levels of information with minimum application of techniques.

- Whilst simple lower tier models may be appropriate for polymer exposure assessment, higher tier exposure models that account for the unique properties and fate characteristics of polymers should be developed. Adaptation of models from analysis of engineered nanoparticles may be useful for application to micro- and nano-polymer particles, such as microplastics, and a combination of modelling approaches from both LMW compounds and nanoparticles may be necessary for characterising the fate of both a parent polymer and its chemical degradation products. This will be further supplemented by development of QSAR approaches and datasets for polymers.
- Further research into the critical fate properties of water-soluble polymers and their breakdown products is warranted in order to better characterise their risk to the environment. This would help to prioritise data generation needs and identify polymers for further investigation.

Approaches to polymer environmental exposure and risk assessment should incorporate and allow for the complexity of polymers. Developing knowledge of how polymer properties influence fate, and therefore which are most important in characterising risk, as well as methods to incorporate complex degradation products in exposure and hazard assessment, is essential to develop adequate and robust risk assessment methodologies for polymers.

Based on this literature review, further research into the environmental fate properties of polymers was conducted for this thesis. Key fate parameters pertaining to sorption and biodegradation, which were highlighted in this chapter, were studied. Based on the identified research needs, particular focus was given to analysis of water-soluble polymers due to the relative lack of research and scarcity of data on these substances in the environment compared to plastic polymers, despite their high usage volumes and likely environmental emission pathways (Arp and Knutsen 2020; Huppertsberg *et al.* 2020). In addition, focus was given to analytical method development, measurement of specific polymer properties and components, and in-depth analysis of polymer degradation and transformation. These studies are presented in *Chapter 4* and *Chapter 5*. However, it was first recognised that there are currently a wide range of water-soluble

polymers in current use, with a scarcity of exposure data and a lack of data on emissions with which to apply lower-tier exposure models.

Therefore in order to inform the choice of water-soluble polymers for use in the subsequent experimental work, a risk-based prioritisation of polymers was performed which is described in the next chapter. The prioritisation work not only identified classes of polymer of most concern but also addressed key knowledge gaps around the identification and grouping of polymers. The results of this research were then used to select polymers for sorption and biodegradation studies that are described in the final two experimental chapters.

Chapter 3

Environmental Risks of Water-Soluble Polymers in Household Products: Identification, Grouping, and Prioritisation

3.1. Introduction

There are a number of potential emission pathways of water-soluble polymers (WSPs) to the environment, given their widespread use in agriculture, wastewater treatment, and chemical products (Arp and Knutsen 2020), with millions of tonnes of WSPs in use in Europe each year (Huppertsberg *et al.* 2020). Household cleaning and personal care products contain WSPs as surfactants (often in the form of ethoxylated compounds; Cowan-Ellsberry *et al.* 2014), polycarboxylates used as builders and anti-redeposition agents (Soap and Detergent Association (SDA) 1996; DeLeo *et al.* 2020), and polyquaterniums used as antistatic or film forming agents (Johnson *et al.* 2016), along with a range of other polymers with various functions. These polymers may be released down-the-drain to wastewater treatment plants (WWTPs) following use, and thus may subsequently be released to surface waters, or sorbed to biosolids and applied to agricultural soil in sludge.

Despite the numerous potential release pathways and high use volumes of WSPs, there is little knowledge of the types of WSPs which may be present in the environment, and environmental exposure concentration data for these substances are currently lacking (Huppertsberg *et al.* 2020; Duis *et al.* 2021). Characterisation of exposure is essential for environmental risk assessment (ERA) and is also useful in prioritising WSPs for further assessment, analytical method development, and design of fate and ecotoxicity experiments. Incorporation of exposure-based indicators into polymer prioritisation approaches has been recommended recently (Groh *et al.* 2023). Exposure data are currently only available for a limited number of WSPs, with predicted environmental concentrations (PECs) being estimated using the European Union System for the Evaluation of Substances (EUSES) for alcohol ethoxylates (AE), alcohol ethoxy sulfates (AES), and polycarboxylates (polyacrylic acid (PAA) homopolymers, polyacrylic/maleic

acid (PAA/MA) copolymers, and their sodium salts) as part of the Human & Environmental Risk Assessment on ingredients of European household cleaning products (HERA) initiative (HERA 2004, 2009, 2014a, 2014b). Whilst monitoring data are also available for AE and AES, there are no monitoring data for the assessed polycarboxylate polymers to provide measured environmental concentrations (MECs) for comparison to the calculated PEC (HERA 2014a, 2014b). A more recent assessment of the environmental risk of PAA and PAA/MA polymers used in U.S. cleaning products has also been performed (DeLeo *et al.* 2020), using the U.S. Environmental Protection Agency (USEPA) Exposure and Fate Assessment Screening Tool (E-FAST) to obtain PEC values, providing a more up-to-date exposure estimate of these two polycarboxylate polymers. For usage quantities for model input, estimates of polymer usage and concentration as well as product usage are required; DeLeo *et al.* (2020) utilised market sales data to determine product usage volumes, survey data to determine the frequency of use of the polymers in the products, and safety data sheets to estimate polymer concentration based on concentrations of other ingredients. However, although PAA and PAA/MA are prominently used, other types of polycarboxylate polymers as well as other WSP classes in current use remain understudied. Available data on the fate and effects of WSPs found in cosmetic products (polyethylene glycols (PEG), anionic homo- and co-polymers of acrylic acid, and polyquaterniums) were recently evaluated in the form of a critical review (Duis *et al.* 2021), however the authors highlighted a lack of exposure data limiting a conclusive risk assessment of these polymers.

Whilst in each of the aforementioned risk assessments, the WSPs studied were found to be unlikely to pose significant risk to the environment, these studies cover only a small fraction of WSPs in current use, and the lack of environmental exposure data for most WSPs inhibits definitive environmental risk assessment. Pecquet *et al.* (2019) assessed data availability for environmental risk assessment of polymers found in US household cleaning products, using databases and an industry survey to identify polymers in current use before evaluating available data from the literature and further databases. The authors found that of 65 polymers identified to be in current use in household cleaning products, 18 had insufficient data available to conduct an ERA (Pecquet *et al.* 2019). Four of these polymers were polycarboxylate polymers which had not been incorporated within the HERA assessments, along with an alcohol ethoxylate polymer, although there is likely to be potential for read-across for these polymers. Exposure concentrations again could not

be obtained (Pecquet *et al.* 2019). In addition, there has been concern over the hazard potential of cationic polymers such as polyquaterniums (e.g. USEPA 1997; Cumming *et al.* 2008; Costa *et al.* 2014); however, there is a paucity of information available for current-use polyquaterniums to characterise risk (Pecquet *et al.* 2019), including data on exposure (Duis *et al.* 2021).

It is likely that the reduced regulatory requirements for polymers (for example polymers are excluded under REACH; European Parliament and Council (EP&C) 2006) have facilitated some of the lack of data, despite recent efforts to incorporate polymers into regulatory and ERA frameworks (e.g. European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) 2019, 2020). Adequate analytical methods for polymer monitoring are lacking, and a scarcity of fate data and publicly available production and import volumes impedes use of exposure models such as EUSES, meaning neither sufficient MEC nor PEC data are easily obtainable (Duis *et al.* 2021). Whilst exposure models are a useful first step to prioritise compounds and focus testing, for many WSP classes a lack of publicly available data on usage volumes has inhibited calculations of PEC, meaning that many WSPs in current use are being overlooked.

There is a clear requirement to further develop knowledge of the types of WSPs that have the potential to be released into the environment, along with their key properties and potential environmental concentrations and effects. Given the diversity and large number of WSPs in current use, conducting high-tier ERAs for all individual polymers is not feasible, and so there is also a need for development and application of grouping approaches for polymers to facilitate data generation, read-across and risk assessment of similar polymers in a single evaluation (ECETOC 2019). It is also essential to develop methods to estimate exposure which are effective in cases where little or no data are available as input parameters for exposure models.

Here we describe and apply a method to identify WSPs in current use, without prior knowledge of polymer types or identities, and predict their environmental concentrations in order to prioritise polymer types for further assessment. Specifically, polymers emitted down-the-drain from common household products (including cleaning and personal care products) were studied, due to the abundance and wide diversity of WSPs used in such products and their high potential for emission to the environment making them useful candidates for prioritisation of WSPs that are likely to be present in the environment. Note that although the majority of polymers in these products are expected to be water-

soluble, all polymers in the studied products were incorporated, allowing both insoluble and soluble polymers to be identified and prioritised.

3.2. Materials and methods

The overall exposure modelling and prioritisation approach is summarised in Figure 3.1, with data collection and model calculations for each stage of the workflow described in detail in sections 3.2.1-3.2.8 below.

3.2.1. Product and brand identification and ingredients inventory

Household cleaning and personal care product types that are expected to be released down-the-drain at point of use were identified by browsing UK-based supermarket websites (Appendix 3.1). The products included in the final dataset were laundry detergents, dishwashing detergents (for machine and washing by hand), toilet cleaners (including bleach and disinfectants), and a variety of personal cleansers for skin (handwash, bodywash, soap bars, and bath liquids (such as bubble bath)), and for hair (shampoo and conditioner). Some product sub-types were analysed together (e.g. laundry detergent liquid and laundry detergent powder, toilet cleaner and bleach/disinfectant, and 3in1 personal cleansers and bodywash) under the assumption that usage patterns and polymer concentrations are likely to be similar.

Major brands for each product type were then identified from the websites of the top four UK supermarkets (Tesco, Sainsbury's, Asda, and Morrisons; Coppola 2021). For shampoo, conditioner, personal cleansers, and toilet cleaners, only brands listed by more than one supermarket website were included in the data collection, due to the large numbers of brands (> 45 in each case) initially identified. Supermarket own-brands were not included, due to limited availability of ingredients data for some product types and based on the assumption that formulations are likely to be similar to other market brands.

The ingredients of all individual products of the relevant product types from each brand were then collated from publicly available information on brand and company websites, between April 2020-May 2021. For some brands initially identified, information on ingredients could not be found, and so these brands were removed from the dataset. The number of brands included in the final study for each product type are shown in Appendix 3.2.

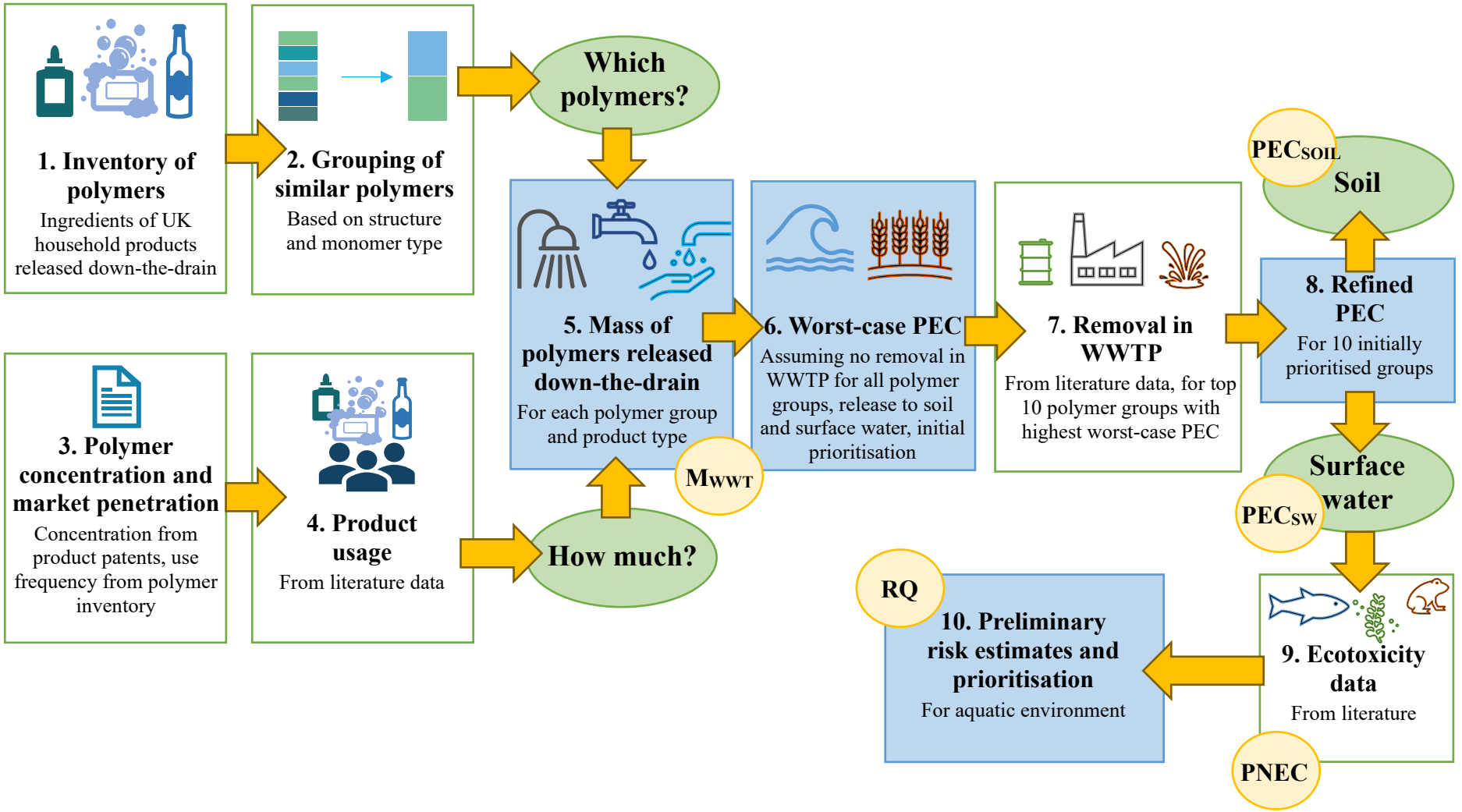


Figure 3.1: Summary of the exposure modelling and prioritisation approach developed and employed in the present study. M_{WWT} = mass of polymer released to wastewater treatment, PEC = predicted environmnental concentration, WWTP = wastewater treatment plant, SW = surface water, PNEC = predicted no-effect concentration, RQ = risk quotient.

3.2.2. Polymer identification and grouping

Polymers in each product were identified following the OECD definition of a polymer (OECD 1991), which is summarised as criteria 1-4 in Table 3.1. Ingredients were classified as polymers in the present study using these criteria, with two additional criteria (in keeping with the OECD polymer definition) being used to narrow the scope of the study (Table 3.1). Whilst enzymes were excluded (Criterion 5), some other identified proteins/polypeptides were included (i.e. gelatin, keratin, wheat gluten, and whey protein) due to the fact that these may consist of multiple proteins of a range of molecular masses (Farrugia *et al.* 1998; Wang and Lucey 2003; Bragulla and Homberger 2009; Vensel *et al.* 2014).

Table 3.1: Criteria for polymer identification in household products based on the OECD definition of a polymer, and further exclusions applied in the present study in keeping with the established criteria.

Classification criteria based on definition of a polymer	
Criterion 1	The substance consists of molecules comprising a sequence of one or more types of monomer units
Criterion 2	The substance comprises a simple weight majority of molecules containing ≥ 3 monomer units covalently bound to at least one other monomer unit or other reactant
Criterion 3	The substance contains molecules distributed over a range of molecular weights with differences in molecular weight being primarily due to differences in the number of monomer units
Criterion 4	The substance consists of less than a simple weight majority of molecules of the same molecular weight
Further exclusions applied in the present study	
Criterion 5	Enzymes were excluded from the final dataset due to the fact that most enzymes will not fit the OECD definition of a polymer (USEPA 1997)
Criterion 6	Silicates were excluded due to the fact that degree of polymerisation is dependent on metal content, concentration, and pH, and upon release to the aquatic environment depolymerisation is expected to occur (OECD 2004c)

Polymers were defined based on the name listed in the product ingredients list, and where necessary, using information on chemicals provided by the European Chemicals Agency (ECHA 2020), and databases such as PubChem, the Environmental Working Group (EWG) Skin Deep® database, SpecialChem, The Good Scents Company (TGSC) Information System, ChemID*plus*, and SAAPedia (EWG 2021; Kim *et al.* 2021; NLM

2021; SAAPedia 2021; SpecialChem 2021; TGSC 2021), as well as other publicly available sources of structure or identity information such as Sigma Aldrich/Merck (Merck 2021). In cases where insufficient information was available to make a definitive assignment (e.g. no information was available on the average number of monomer units (Criterion 2)), most were assigned as polymers in order to give more conservative estimates of exposure. In addition, in most cases it was not possible to ascertain whether substances met Criterion 4, but again these were included in the final dataset to give worst-case estimates. Ingredients which are potentially identifiable as polymers but which have not been included in the final dataset are listed in Appendix 3.3. In addition, whilst most polymers present in the studied products are expected to be water-soluble, solubility was not an applied criterion and thus there is a possibility that some of the identified polymers are likely not water-soluble (e.g. polymers present as beads or emulsions).

Identified polymers were then broadly categorised into groups based on structural similarities, monomer types, and functional groups. Group classifications were also consolidated in uncertain cases if the polymers were used in similar quantities in the products identified (i.e. groupings based on function in products).

3.2.3. Polymer concentration in products and market penetration

Fractional concentrations of polymers (F_{pol}) in each product type were obtained from patents identified using Google Patents. Search terms included the product types in question (e.g. 'laundry detergent composition'), and either the names of individual polymers (e.g. 'styrene/acrylates copolymer') or polymer groups (e.g. 'polycarboxylate'). The broadest and most preferred concentration ranges (most commonly listed as % by weight) for each polymer or polymer group were recorded for a minimum of three patents (where possible), or from the first 3-5 pages of search results. For example, if a patent listed a polymer concentration as "generally 0.5 to 15%, preferably 0.5 to 10%, more preferably 1 to 5 wt. %", values of 0.5 to 15 and 1 to 5% were recorded. Concentrations deemed most representative of the acquired patents for each polymer group, whilst generally accounting for higher concentrations to provide worst-case estimates, were then selected for use in exposure modelling. Fractional concentrations (F_{pol}) selected for each polymer group and product type, with final referenced patents are listed in Appendix 3.5. It was assumed that individual polymers

within a group would perform similar functions in the products and therefore would contribute to a combined total polymer concentration for that group, and thus products containing multiple members of a polymer group were assumed to have the same concentration ranges as products containing only one member of a group. It should be noted that in some cases, polymer concentrations were difficult to estimate; for example, polyvinyl alcohol is likely most commonly used as a film surrounding detergent capsules or tablets, however, estimates of the mass concentration of such films used in the detergents was not possible to obtain. Concentrations which may reflect less common instances in which polyvinyl alcohol is used in a dissolved or dispersed form in the products were instead used, and assumed to reflect polyvinyl concentration when used in a film form.

An estimate of market penetration (F_{prod}) was calculated for each polymer group and product type, as the fraction of products of a particular type that contained one or multiple polymers belonging to each group (Equation 3.1, Appendix 3.4).

$$F_{prod} = \frac{N_{prod}}{T_{prod}} \quad (3.1)$$

Where F_{prod} = estimate of market penetration, N_{prod} = number of individual products of a particular type containing one or multiple members of the polymer group, and T_{prod} = total number of individual products of the selected product type that were included in the dataset. This approach was used due to the limited public availability of data for market penetration, and production and import volumes, instead making use of widely available product ingredients data. It is expected this estimate provides an approximation of market penetration for the relevant polymer and product types due to the wide range of brands included in the study and based on the assumption that the proportion of all products containing a polymer type is analogous to market penetration of the polymer.

3.2.4. Determination of masses of polymers released down-the-drain

Estimates of usage data (U_{prod}) in g capita^{-1} day^{-1} for each product type were obtained from the literature with values used in the final model presented in Table 3.2.

Table 3.2: Values for product usage (U_{prod}) used for each product type, collated from literature data.

Product type	**U_{prod} (g capita^{-1} day^{-1})**	**References**	**Notes**
Laundry detergent	11.3	Eriksson *et al.* 2002; A.I.S.E. 2019	Value range of 10.1-20.5 g pc^{-1} day^{-1} for USA, Sweden, Denmark, Finland and Norway in 2002 (Eriksson *et al.* 2002). Laundry detergent tonnage in Europe decreased by 45% since 1997 in 2017 (A.I.S.E. 2019). Assuming a similar decrease from 2002-2021 and taking upper limit (20.5 g pc^{-1} day^{-1}) gives 65% of 20.5 = 11.3 g capita^{-1} day^{-1} calculated in the present study.
Machine dishwashing detergent	2.4	DeLeo *et al.* 2020	California sales of machine dishwashing detergent in 2015 = 206,180 lb day^{-1}, and population of California (in 2018) = 39,557,045 people (DeLeo *et al.* 2020). Usage therefore calculated in present study as 2.4 g capita^{-1} day^{-1} (1dp).
Hand dishwashing detergent	5.0	Schneider *et al.* 2019	Arithmetic mean of use frequency per individual for frequent users = 0.9 day^{-1}, and amount used per event = 5.5 g (Schneider *et al.* 2019). Therefore usage calculated in present study = 5.0 g capita^{-1} day^{-1}.
Toilet cleaners and bleach	4.3	HERA 2005	Values given for toilet cleaner liquid = 30 ml per task and typically 1 task per week (HERA 2005). Assuming 1 ml = 1 g of toilet cleaner and values correspond to per person, usage calculated in the present study as 4.3 g^{-1} capita^{-1} day^{-1}.
Bodywash	8.3	Garcia-Hidalgo *et al.* 2017	Mean amount used per day by adults (Garcia-Hidalgo *et al.* 2017).
Handwash	10.3	Garcia-Hidalgo *et al.* 2017	Mean amount used per day by adults (Garcia-Hidalgo *et al.* 2017).
Soap bars	3.2	Gomez-Berrada *et al.* 2017	Mean amount used per day by adults (Gomez-Berrada *et al.* 2017).
Bath liquid	0.8	Garcia-Hidalgo *et al.* 2017	Mean amount used per day by adults (Garcia-Hidalgo *et al.* 2017).
Shampoo	2.9	Garcia-Hidalgo *et al.* 2017	Mean amount used per day by adults (Garcia-Hidalgo *et al.* 2017).
Conditioner	2.9	Garcia-Hidalgo *et al.* 2017	Mean amount used per day by adults (Garcia-Hidalgo *et al.* 2017).

For a number of the personal care product categories, multiple data were available (Hall *et al.* 2011; Garcia-Hidalgo *et al.* 2017; Gomez-Berrada *et al.* 2017a; Gomez-Berrada *et al.* 2017b). Where possible, values from data that were most recent, included the largest population sample size, included a greater number of the relevant product types, and were assumed most representative of real-world usage (i.e. surveys rather than imposed usage regimes) were used. Data from the usage survey conducted by Garcia-Hidalgo *et al.* (2017) were therefore key for obtaining values for most personal care products in the present study; these data were obtained from postage questionnaires for over 700 participants in 2015, and included detailed information on participant usage of 12 household products and 22 personal care products. Multiple data sources were also available for laundry detergent usage. In the present study, the value incorporated in the model was extrapolated from estimates of the International Association for Soaps, Detergents and Maintenance Products (A.I.S.E.) for reduction of detergent usage by 45% between 1997 – 2017 (A.I.S.E. 2019) along with a value for usage in Denmark (the highest usage value from the study in question, in order to give a more conservative estimate) from 2002 (Eriksson *et al.* 2002). This was assumed to give values more relevant for Europe (as oppose to using values given for California by DeLeo *et al.* (2020)). Limited data were available for usage of toilet cleaners (HERA 2005), and the obtained value may be higher than actual usage, based on values for other products from the same source (e.g. typical laundry detergent powder usage reported at 107 g day^{-1} (HERA 2005), which is significantly more conservative than the estimate of 11.3 g ($capita^{-1}$) day^{-1} calculated for total usage of liquid and powder laundry detergent in the present study).

Masses of polymer groups emitted down-the-drain (and thus expected to be transported to wastewater treatment) from each product type were estimated using Equation 3.2.

$$M_{WWT(prod)} = F_{prod} \times F_{pol} \times U_{prod} \quad (3.2)$$

Where $M_{WWT(prod)}$ = mass of polymer entering wastewater treatment from a particular product type (g $capita^{-1}$ day^{-1}), F_{prod} = fraction of products containing polymer type (estimate of market penetration), F_{pol} = fractional concentration of polymer in product (from % by weight), and U_{prod} = product usage (g $capita^{-1}$ day^{-1}). Ranges of F_{pol} values for both widest and most preferred concentrations given by patents were used (Appendix 3.5), giving a range of values for $M_{WWT(prod)}$ for each polymer group.

3.2.5. Determination of worst-case surface water exposure (PEC_{SW})

Worst-case estimates of PEC_{SW} (i.e. assuming all polymers released down-the-drain remained in water following wastewater treatment, with an absence of degradation processes) were obtained for each polymer group and product type (Equation 3.3), based on the method given by the European Medicines Agency (EMA) for environmental risk assessment of human medicines (EMA 2018).

$$PEC_{SW(prod)} = \frac{M_{WWT(prod)}}{WW_{INHAB} \times DF} \quad (3.3)$$

Where $PEC_{SW(prod)}$ = worst-case predicted environmental concentration in surface water for a particular polymer group and product type (mg L^{-1}), $M_{WWT(prod)}$ = mass of polymer entering wastewater treatment from a particular product type (mg $capita^{-1}$ day^{-1}), WW_{INHAB} = amount of wastewater per inhabitant per day (L $capita^{-1}$ day^{-1}), and DF = dilution factor for entering surface water. Default values for WW_{INHAB} and DF of 200 L $capita^{-1}$ day^{-1} and 10, respectively, were used (EMA 2018).

Total worst-case PEC_{SW} estimates for each polymer group were then obtained as the sum of estimates for each product type according to Equation 3.4.

$$PEC_{SW} = \sum_{all\ product\ types} PEC_{SW(prod)} \quad (3.4)$$

Where PEC_{SW} = total worst-case predicted environmental concentration in surface water (mg L^{-1}).

3.2.6. Determination of worst-case soil exposure (PEC_{SOIL})

Concentrations of polymers present in sludge following wastewater treatment were again based on $M_{WWT(prod)}$, and were calculated using Equation 3.5. A worst-case scenario was assumed in which all polymers released down-the-drain (M_{WWT}) were partitioned to and present in sludge, with an absence of degradation processes.

$$C_{SLUDGE(prod)} = \frac{M_{WWT(prod)}}{S_{INHAB}} \quad (3.5)$$

Where $C_{SLUDGE(prod)}$ = worst-case concentration of polymer present in sludge from a particular product type (mg kg^{-1}), and S_{INHAB} = mass of sludge per inhabitant per day (kg $capita^{-1}$ day^{-1}). A value for S_{INHAB} of 0.074 kg $capita^{-1}$ day^{-1} was used (Guo *et al.* 2016).

Worst-case estimates of PEC_{SOIL}, assuming no degradation of polymers following emission, for sludge-amended soil after the first year of sludge application were determined for each product type using Equation 3.6.

$$PEC_{SOIL(prod)} = \frac{C_{SLUDGE(prod)} \times A_{SLUDGE} \times 1\ year}{D_{SOIL} \times RHO_{SOIL}} \quad (3.6)$$

Where $PEC_{SOIL(prod)}$ = worst-case predicted environmental concentration in sludge-amended soil from a particular product type (mg kg^{-1}), A_{SLUDGE} = sludge application rate to land (kg m^{-2} yr^{-1}), D_{SOIL} = soil mixing depth (m), and RHO_{SOIL} = bulk density of soil (kg m^{-3}) (European Chemicals Bureau (ECB) 2003; Guo *et al.* 2016). Default values for A_{SLUDGE}, D_{SOIL}, and RHO_{SOIL} of 0.5 kg m^{-2} yr^{-1}, 0.2 m, and 1,700 kg m^{-3}, respectively, were used (ECB 2003; Guo *et al.* 2016).

The total worst-case PEC_{SOIL} was then calculated for each polymer group as the sum of the estimates for each product type according to Equation 3.7.

$$PEC_{SOIL} = \sum_{all\ product\ types} PEC_{SOIL(prod)} \quad (3.7)$$

Where PEC_{SOIL} = total worst-case predicted environmental concentration in soil (mg kg^{-1}).

3.2.7. Polymer prioritisation and refined PEC

Exposure concentrations for the top ten polymer groups with the highest PEC were refined using values from the literature for removal in wastewater treatment. Web of Science and Google Scholar were searched for specific polymers or polymer groups and "wastewater" or "wastewater treatment". Where multiple values were available, both within and between different data sources, the highest and lowest values from the literature for polymer groups or individual polymers within the selected groups were applied to the lowest and highest bounds of the worst-case PEC estimates in order to account for the most and least conservative scenarios. This also allowed incorporation of the fact that many groups contained a broad range of polymers, with differing molecular weights and monomer units, and therefore likely to exhibit different properties and fate in wastewater treatment. It should be noted that overall WWTP removal data obtained for the ten prioritised polymer groups were based on different levels of information for different polymer types, with some WWTP removal data being theoretical, some

measured, some experimental, and for different stages or types of WWT. Removal data were also frequently based on removal in US WWTP, which may differ, to some extent, from removal in the UK.

The obtained data were applied to the worst-case PEC_{SW} estimates for the selected polymers using Equation 3.8.

$$Refined\ PEC_{SW} = PEC_{SW} - (PEC_{SW} \times F_{WWT}) \quad (3.8)$$

Where refined PEC_{SW} = refined predicted environmental concentration in surface water (mg L^{-1}), and F_{WWT} = fraction removed from water in wastewater treatment.

For refined PEC_{SOIL}, the entirety of the fraction removed from water (F_{WWT}) was assumed to partition to sludge (i.e. no degradation was assumed) for eight of the ten groups, and thus refined PEC_{SOIL} was calculated according to Equation 3.9 for these groups.

$$Refined\ PEC_{SOIL} = PEC_{SOIL} \times F_{WWT} \quad (3.9)$$

For two polymer groups (polyethers and copolymers, and polyvinyl alcohol), data were available on the fraction present in sludge (i.e. accounting for degradation). For these two groups, refined PEC_{SOIL} were thus instead calculated using Equation 3.10.

$$Refined\ PEC_{SOIL} = PEC_{SOIL} \times F_{SLUDGE} \quad (3.10)$$

Where F_{SLUDGE} = fraction of polymer present in WWT influent which is released in sludge.

3.2.8. Potential risk of selected polymers

Environmental effects (hazard) data were gathered from the literature for the ten polymer groups with highest worst-case exposure. For three of these groups, applicable data were already compiled in the HERA reports, and thus these data were used in the present study (HERA 2004, 2009, 2014a, 2014b). For the remaining seven groups, searches were conducted using the ECOTOX Knowledgebase (USEPA 2000), a freely available online database compiling aquatic and terrestrial ecotoxicity data for single chemicals from the literature. Search terms included generic group names (e.g. "polyquaternium") and specific polymer names (e.g. "aziridine homopolymer"). For one of the polymer groups (polyvinyl alcohol), relevant data could not be found in the ECOTOX Knowledgebase, but literature hazard data were available.

Effects data were compiled and screened to exclude data of insufficient quality or where insufficient information was available (Appendix 3.7). Predicted no-effect concentrations (PNEC) were then calculated according to the guidelines given by the EU Water Framework Directive (European Commission (EC) 2011), with the lowest concentration endpoints being selected and combined with an appropriate assessment factor (AF) based on the available data (Appendix 3.8) according to Equation 3.11.

$$PNEC = \frac{C_e}{AF} \tag{3.11}$$

Where C_e = lowest effect concentration (e.g. EC50, NOEC, etc.; mg L^{-1}) and AF = assessment factor. Note that C_e could correspond to a specific polymer within, or analogous to a polymer within, an entire polymer group.

The resulting aquatic PNEC values and refined PEC_{SW} estimates were then used to calculate risk quotients (RQs) using Equation 3.12. If a polymer group had an RQ>1, then it was concluded that an unacceptable risk from the group was possible.

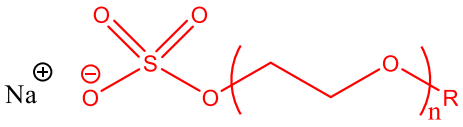
$$RQ = \frac{PEC_{SW}}{PNEC} \tag{3.12}$$

3.3. Results and discussion

3.3.1. Polymers identified in household products, market penetration, and polymer grouping

A total of 339 individual polymers were identified (Table 3.3) across 1,353 products and 10 product types (laundry detergent, machine dishwashing detergent, hand dishwashing detergent, toilet cleaner (including bleach and disinfectant), bodywash, handwash, soap bars, bath liquid, shampoo, and conditioner).

Table 3.3: Polymers identified in UK household products released down-the-drain at point-of-use, along with their assigned groupings based on monomer type, polymer structure, functional groups, and use in products.
Polymer groups are listed in order of highest max. probable worst-case PEC (Section 3.3.2, Appendix 3.6). Individual polymers in each group are listed in order of highest contribution to total worst-case PEC of their group, estimated from application of number of occurrences of this polymer (as a fraction of total occurrences of all polymers in the group for each product type) to total group concentration for each product type, summed across all product types. Example polymer structures are shown for the top polymer (highest contributor to total PEC) in each of the top ten groups, with structural features ubiquitous to all group members (i.e. key chemical functionalities) highlighted in red. Note that in some cases, other members of the polymer groups contain other additional chemical functionalities, which may differ significantly in structure to the examples shown.

Polymer group	Individual polymers	Contribution to group PEC (%)
Alcohol ethoxylate salts e.g. sodium laureth sulfate  R = fatty hydrocarbon chain, C12 for sodium laureth sulfate	Sodium Laureth Sulfate	70.06
	MEA-Laureth Sulfate	15.68
	Sodium C12-15 Pareth Sulfate	4.87
	Sodium C12-14 Pareth-3 Sulfate	2.29
	Ammonium Laureth Sulfate	2.26
	Sodium Coceth-30 Sulfate	1.48
	Sodium C12-13 Pareth Sulfate (A) / Sodium Laureth Sulfate (B)	1.44
	Sodium C12-15 Pareth-3 Sulfate	0.64
	Zinc Coceth Sulfate	0.22
	Alcohols, C12-14, ethoxylated, sulfates, sodium salts	0.21
	Sodium Myreth Sulfate	0.16
	Magnesium Laureth Sulfate	0.10
	Magnesium Laureth-8 Sulfate	0.10
	Magnesium Oleth Sulfate	0.10
	Sodium Laureth-8 Sulfate	0.10
	Sodium Oleth Sulfate	0.10
	MIPA Laureth Sulfate	0.06
	Sodium Trideceth Sulfate	0.06
	MIPA C12-15 Pareth Sulfate	0.05
Alcohol alkoxylates e.g. laureth-4  R = fatty hydrocarbon chain, C12 for laureth-4	Laureth-4	14.20
	PEG/PPG-10/2 Propylheptyl Ether	9.15
	C11-15 Pareth-7	7.15
	C11-15 Pareth-40	7.03
	C12-14 Pareth-7	6.63
	C12-14 Pareth-n	6.12
	Trideceth-n	4.29
	C14-15 Pareth-7	3.87
	C14-15 Pareth-n	3.87
	C12-15 Pareth-7	3.57
	Trideceth-9	3.28

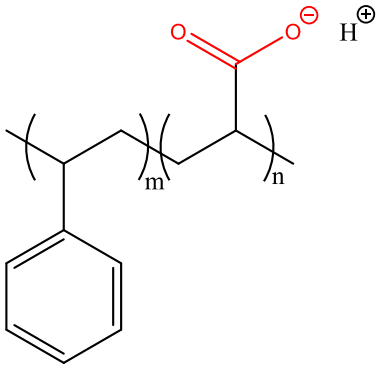
(Table 3.3 continued)

Alcohol alkoxylates *(continued)*	PEG 6 - Methyl Ether	2.55
	C9-11 Pareth-n	2.54
	Steareth-20	1.92
	2-Propylheptanol ethoxylated	1.90
	Trideceth-7	1.59
	Fatty alcohol alkoxylate	1.59
	Laureth-7	1.52
	C15 Pareth-n	1.43
	Laureth-3	1.33
	C12-16 Pareth-n	1.12
	Ceteareth-25	0.94
	PPG-5-Ceteth-20	0.89
	Alcohols, C12-16, ethoxylated, 7-16 EO	0.83
	C9-11 Pareth-6	0.83
	Laureth-10	0.74
	Steareth-4	0.68
	Primary alcohol ethoxylate	0.64
	Deceth-8	0.63
	PEG-8 Propylheptyl Ether	0.63
	Ceteareth-80	0.51
	C9-11 Pareth-8	0.50
	PEG-7 Propylheptyl Ether	0.45
	Trideceth-10	0.45
	PPG-1 Trideceth-6	0.34
	Alkylethoxylate C9-11, 5.5EO	0.33
	Ethoxylated Alcohol	0.33
	Laureth-23	0.31
	Trideceth-6	0.28
	Trideceth-12	0.26
	C12-13 Pareth-n	0.25
	Alcohols C12-14, ethoxylated (7EO)	0.20
	C12-16 pareth-7	0.20
	Pareth-7	0.20
	Alkylethoxylate, C10-16, 10EO	0.17
	C9-11 Pareth-9	0.17
	Undeceth-40	0.17
	PEG-4 Distearyl Ether	0.15
	Steareth-21	0.15
	Ceteareth-20	0.15
	C12-13 Pareth-3	0.11
	C13-15 Pareth-7	0.10
	Ceteareth-15	0.10
	Alcohol alkoxylate	0.10
	Modified Fatty alcohol polyglycolether	0.10
	Polyoxyethylene trimethyldecyl alcohol	0.10
	PPG-5-Laureth-5	0.10

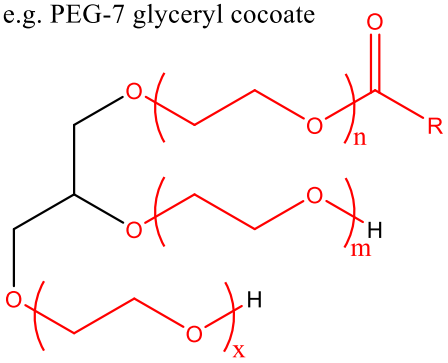
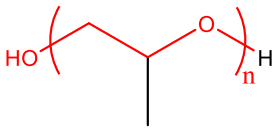
(Table 3.3 continued)

Alcohol alkoxylates *(continued)*	C12-13 Pareth-6	0.05
	Laureth-5	0.04
	C12-13 Pareth-23	0.04
	PPG-3 myristyl ether	0.04
	Laureth-16	0.03
	Laureth-9	0.02
	Coceth-7	0.01
	Macrogol Lauryl Ether (4)	0.01
	Oleth-20	0.01
	PPG-1-PEG-9 Lauryl Glycol Ether	0.01
Polycarboxylates	Styrene/Acrylates Copolymer	38.19
	Sodium Polyacrylate	17.45
	Sodium Acrylic Acid/MA Copolymer	15.97
	Acrylates Copolymer	10.80
	2- propenoic acid, homopolymer, sodium salt, sulfonated	2.97
	Acrylic acid sodium salt polymer, sodium sulfonate terminated	2.01
	Copolymer of acrylic and sulphonic acids	1.76
	Modified Polycarboxylate	1.42
	Maleic- acrylic acid copolymer sodiumsalt	1.32
	Carbomer	1.15
	Acrylic acid maleic acid polymer	0.88
	Polycarboxylate, sodium salt	0.66
	Acrylates/Steareth-20 Methacrylate Copolymer	0.55
	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.53
	Sodium polyaspartate	0.44
	2-Propenoic acid, homopolymer, sodium salt	0.44
	Acrylates/Steareth-20 Methacrylate Crosspolymer	0.43
	Sodium Acrylates Copolymer	0.43
	Ethylene/MA Copolymer	0.35
	Methacrylic acid and acrylic acid ester copolymer	0.35
	No EU INCI name - Acrylic Copolymer	0.35
	Acrylates/Beheneth-25 Methacrylate Copolymer	0.25
	Acrylates/PEG-10 Maleate/Styrene Copolymer	0.24
	Sodium polyitaconate	0.22
	Acrylates Crosspolymer-4	0.17
	Polyacrylate-33	0.14
	2-Propenoic Acid, Telomer with Sodium Hydrogen Sulfite, Sodium Salt	0.11
	Polyacrylic Acid	0.11
	Acrylates/Palmeth-25 Acrylate Copolymer	0.07
	Sodium Styrene/Acrylates Copolymer	0.06

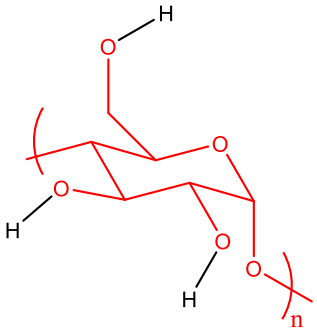
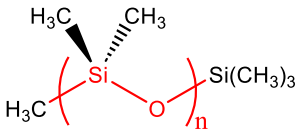
e.g. styrene/acrylates copolymer



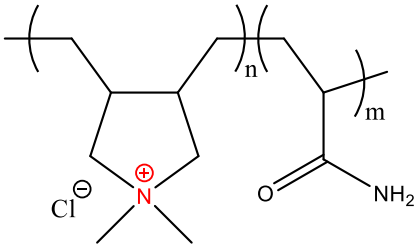
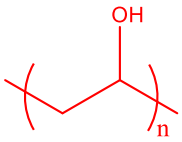
(Table 3.3 continued)

Polycarboxylates *(continued)*	Acrylates/Ammonium Methacrylate Copolymer	0.06
	PVM/MA Copolymer	0.04
	Acrylic Acid/Acrylamidomethyl Propane Sulfonic Acid Copolymer	0.04
	Polyacrylate-1 Crosspolymer	0.04
Polyol ethoxylate esters e.g. PEG-7 glyceryl cocoate  R = fatty hydrocarbon chain, mixture of chain lengths for PEG-7 glyceryl cocoate	PEG-7 Glyceryl Cocoate	29.36
	PEG-200 Hydrogenated Glyceryl Palmate	21.98
	Polysorbate 20	17.23
	PEG-120 Methyl Glucose Dioleate	11.15
	PEG-6 Caprylic/Capric Glycerides	5.15
	PEG-150 Pentaerythrityl Tetrastearate	4.96
	Shea Butter Glycereth-8 Esters	4.35
	PEG-80 Sorbitan Laurate	2.90
	Polysorbate 60	0.99
	PEG-9 Cocoglycerides	0.60
	PEG-90 Glyceryl Isostearate	0.47
	PEG-60 Almond Glycerides	0.27
	PEG-10 Olive Glycerides	0.23
	PEG-200 Hydrogenated Glyceryl Cocoate	0.23
	PEG-120 Methyl Glucose Trioleate	0.14
Polyethers and copolymers e.g. PPG-26 	PPG-26	23.15
	Co-polymer of PEG / Vinyl Acetate	11.50
	Polyethylene Glycol	10.03
	PPG-12	7.63
	PPG-9	7.22
	PPG-34	5.84
	PPG-6	4.77
	Polyethylene Glycol MW >4100	4.00
	Polyethylene Glycol MW <4100	3.58
	PEG Copolymer	2.66
	PEG-45M	2.63
	PEG-75	1.96
	PEG-33	1.89
	PEG-4	1.53
	PEG-80	1.40
	Ethylene/propylene oxide copolymer	1.26
	PEG-130 - PEG-150	1.26
	PEG-135	0.84
	Poloxamer 407	0.80
	PEG-14M	0.74
	Poloxamer 124	0.70
	Peg-30 - Peg-40	0.63
	PEG-23M	0.54
	PEG-10	0.42
	PEG-90	0.42
	Poloxalene	0.42

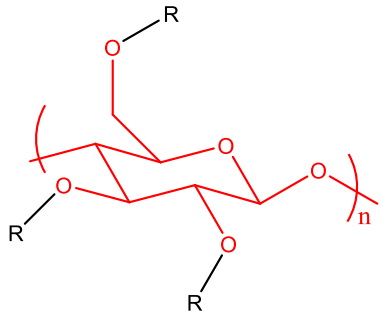
(Table 3.3 continued)

Polyethers and copolymers *(continued)*	PEG-2M	0.35
	PEG-180M	0.27
	PEG-180	0.27
	PEG- 30 - PEG-150	0.21
	PEG-150	0.21
	PEG-32	0.21
	PEG-8	0.21
	PEG-9	0.18
	PPG-n	0.14
	PEG-90M	0.12
Starch and derivatives e.g. dextrin 	Dextrin	51.61
	Oryza sativa (rice) starch	18.70
	Hydrogenated Starch Hydrolysate	8.08
	Corn Starch Modified	7.87
	Sodium Starch Octenylsuccinate	3.73
	Maltodextrin	2.53
	Tapioca Starch	1.71
	Sodium Hydroxypropyl Starch Phosphate	1.12
	Sodium Hydrolyzed Potato Starch Dodecenylsuccinate	1.08
	Carboxymethylinulin	0.98
	Hydroxypropyl starch phosphate	0.72
	Triticum vulgare (wheat) starch	0.58
	Starch	0.49
	Potato Starch Modified	0.24
	Zea mays (corn) starch	0.24
	Saccharide Isomerate	0.22
	Potato Starch	0.10
Silicones e.g. dimethicone 	Dimethicone	49.27
	Dimethiconol	14.37
	Trimethylsiloxysilicate	7.48
	Phenylpropyl Ethyl Methicone	6.71
	Simethicone	6.52
	Silicone Compound	5.75
	Siloxanes and Silicones, di-Me, Me octyl, Me 2-phenylpropyl	4.99
	Phenylpropyl Dimethicone	2.49
	Methicone	0.63
	Phenyl Trimethicone	0.48
	C30-45 Alkyl Dimethicone	0.36
	Divinyldimethicone/dimethicone copolymer	0.34
	Dimethiconol/Silsesquioxane Copolymer	0.30
	Trimethylsiloxysilicate/Dimethicone Crosspolymer	0.19
	Caprylyl Methicone	0.12

(Table 3.3 continued)

Polyquaterniums e.g. polyquaternium-7 	Polyquaternium-7	59.24
	Guar Hydroxypropyltrimonium Chloride	17.46
	Polyquaternium-10	7.99
	Polyethylenimine	4.20
	Hydroxypropyl Guar Hydroxypropyltrimonium Chloride	2.06
	Polyquaternium-37	2.00
	Polyquaternium-2	1.31
	Acrylamidopropyltrimonium Chloride/Acrylamide Copolymer	1.29
	Polyquaternium-6	0.89
	Aziridine, homopolymer	0.53
	Polyquaternium-39	0.41
	Polyquaternium-47	0.39
	Polyquaternium-68	0.39
	Polyquaternium-70	0.28
	Polyquaternium-22	0.27
	Starch Hydroxypropyltrimonium Chloride	0.26
	PEI-2500	0.18
	Polyquaternium-55	0.15
	PG-Hydroxyethylcellulose cocodimonium chloride	0.12
	Polyquaternium-28	0.12
	Polyquaternium-52	0.11
	Polyquaternium-16	0.08
	Polyquaternium-4	0.08
	Polyquaternium-76	0.07
	Modified Guar Hydroxypropyltrimonium Chloride	0.04
	Polyacrylamidopropyltrimonium chloride	0.04
	Polyquaternium-30	0.04
Polyvinyl alcohol polyvinyl alcohol 	Polyvinyl Alcohol	96.11
	Polyvinyl alcohol film	1.95
	Thermal shrinkable PVOH film	1.95

(Table 3.3 continued)

Cellulose and derivatives e.g. hydroxyethylcellulose  R = -H or -CH_2CH_2OH for hydroxyethylcellulose	Hydroxyethylcellulose	39.46
	Cellulose Gum	30.51
	Microcrystalline Cellulose	16.69
	Cellulose	9.14
	Hydroxypropyl Methylcellulose	4.02
	Cetyl Hydroxyethylcellulose	0.18
Fatty acid ethoxylates	PEG-40 Hydrogenated Castor Oil	51.26
	PEG-150 distearate	21.03
	PEG-3 Distearate	8.55
	PEG-20 Stearate	7.98
	PEG-35 Castor Oil	2.90
	PEG-4 Dilaurate	2.44
	PEG-4 Laurate	2.44
	PEG Distearate	1.33
	PEG-55 Propylene Glycol Oleate	0.88
	PEG-40 Castor Oil	0.49
	PEG-60 Hydrogenated Castor Oil	0.37
	PEG-20 Castor Oil	0.34
Polyethylenimine ethoxylates and polyether copolymers	PEI Ethoxylate	47.75
	Aziridine homopolymer ethoxylated	34.82
	PEI/PEG/PPG Copolymer	17.44
Other	Ethoxylated m-toluidine	21.75
	Disodium Laureth Sulfosuccinate	19.58
	Methyl Gluceth-10	14.65
	Polyurethane Crosspolymer-2	8.58
	PEG-4 Rapeseedamide	7.59
	Alginic acid	6.81
	Hydroxypropyl Cyclodextrin	4.78
	Sodium Hyaluronate	3.78
	Polyvinylpyridine-N-Oxide	3.43
	Poly (Linseed Oil)	2.41
	Butyl Acrylate/Ethyltrimonium Chloride Methacrylate/Styrene Copolymer	1.72
	PPG-3 Benzyl Ether Myristate	1.60
	Hemicellulose	1.14
	Lignin	1.14
	Laureth-5 Carboxylic Acid	1.05

(Table 3.3 continued)

Polyesters	Anionic modified polyester	90.60
	Hydrogenated Castor Oil/Sebacic Acid Copolymer	5.20
	Capryloyl Glycerin/Sebacic Acid Copolymer	4.20
Proteins/polypeptides	Whey Protein	98.19
	Gelatin	1.38
	Keratin	0.30
	Triticum Vulgare Gluten	0.14
Hydrolysed protein and derivatives	Hydrolyzed keratin	31.64
	Hydrolysed Milk Protein	7.92
	Silk Amino Acids	7.73
	Hydrolyzed Silk	7.40
	Hydrolyzed Rice Protein	6.73
	Hydrolyzed collagen	6.18
	Hydrolysed Wheat Protein	5.80
	Hydroxypropyltrimonium Hydrolyzed Wheat Protein	4.83
	Hydrolyzed vegetable protein PG-propyl silanetriol	4.64
	Hydrolyzed corn protein	3.58
	Hydrolyzed soy protein	3.58
	AMP-Isostearoyl Hydrolyzed Wheat Protein	3.09
	Cocoyl hydrolyzed keratin	1.55
	Ethyltrimonium Chloride Methacrylate/ Hydrolysed Wheat Protein Copolymer	1.55
	Hydrolyzed pea protein	1.55
	Hydrolyzed Wheat Gluten	1.38
	Laurdimonium Hydroxypropyl Hydrolyzed Keratin	0.87
Cationic silicones	Amodimethicone	44.12
	Bis-Aminopropyl Dimethicone	29.37
	PEG-7 Amodimethicone	10.85
	Bis-Cetearyl Amodimethicone	4.00
	Silicone Quaternium-26	3.34
	Bis-Hydroxy/Methoxy Amodimethicone	2.00
	Quaternium-80	2.00
	Silicone Quaternium-18	1.92
	Silicone quaternium-22	1.72
	Bis(C13-15 Alkoxy)PG-Amodimethicone	0.67
Polyoxyalkylene terephthalate/polyalkylene terephthalates	Polypropylene Terephthalate/ Polyoxyethylene terephthalate	84.21
	Polyethylene Terephthalate	15.79
Plant gums	Xanthan Gum	85.33
	Hydroxypropyl Guar	12.51
	Tamarindus Indica Seed Gum	2.16

(Table 3.3 continued)

Polyolefins	Synthetic Wax	60.00
	Hydrogenated Polydecene	20.00
	Polyethylene	20.00
Polyglyceryl esters and polyglycerin	Argan Oil Polyglyceryl-6 Esters	50.61
	Polyglyceryl-3 laurate	19.12
	Polyglyceryl-10 Stearate	12.74
	Polyglyceryl-3 caprate/caprylate/succinate	7.96
	Polyglycerin-10	4.78
	Polyglyceryl-10 Myristate	4.78
Polymerised aromatic sulfonate salts	Sodium Polynaphthalenesulfonate	89.84
	Calcium Divinylbenzene Styrene Copolymer Sulfonate	10.16
Vinylimidazole/vinylpyrrolidone homo- and co-polymers	PVP	63.38
	Copolymer of 1-vinylimidazole and 1-vinyl-2-pyrrolidone	15.80
	Polyvinylpirrolydone/Vinylimidazole copolymer	15.80
	VP/Methacrylamide/Vinyl Imidazole Copolymer	5.02
Silicone alkoxylates	PEG-12 Dimethicone	51.00
	Lauryl PEG/PPG-18/18 Methicone	21.00
	Dimethicone PEG-8 Meadowfoamate	7.00
	PEG/PPG-14/4 Dimethicone	7.00
	PEG/PPG-17/18 Dimethicone	7.00
	PEG/PPG-18/18 Dimethicone	7.00
Polymeric colourants	Polymeric Blue Colourant	20.89
	Polymeric Pink Colourant	20.89
	Polymeric Red Colourant	20.89
	Polymeric Yellow Colourant	20.89
	Liquitint® Orange 157	8.21
	Liquitint® Violet	8.21
Amine/formaldehyde polymers	Methoxypolyoxymethylene Melamine	61.54
	Polyoxymethylene Melamine	23.08
	Formamide, N-ethenyl-, homopolymer, hydrolyzed, sulfate	7.69
	Polyoxymethylene Melamine Urea	7.69

The polymer identified in the greatest number of products was sodium laureth sulfate, an anionic ethoxylated fatty alcohol commonly used as a surfactant in home and personal care products (Robinson *et al.* 2010), present in almost half of the products studied (Figure 3.2). Note that although the number of monomer units (n) is often < 3 for AES compounds used in household products (which would not classify as a polymer based on the OECD definition; Table 3.1), longer chain lengths are also used (e.g. n = 8, HERA 2004; also observed in the present study (Table 3.3)). Therefore, sodium laureth sulfate

(and other similar compounds for which n is not specified) incorporated in the present study may include both polymeric and non-polymeric material (based strictly on the OECD definition of a polymer). However, it is worth noting that in reality there is no chemical cut-off between polymers with an average of 3 and 4 monomer units, and thus these low molecular weight "non-polymers" will have similar properties to low molecular weight "OECD polymers", and may contribute to similar environmental effects as a mixture.

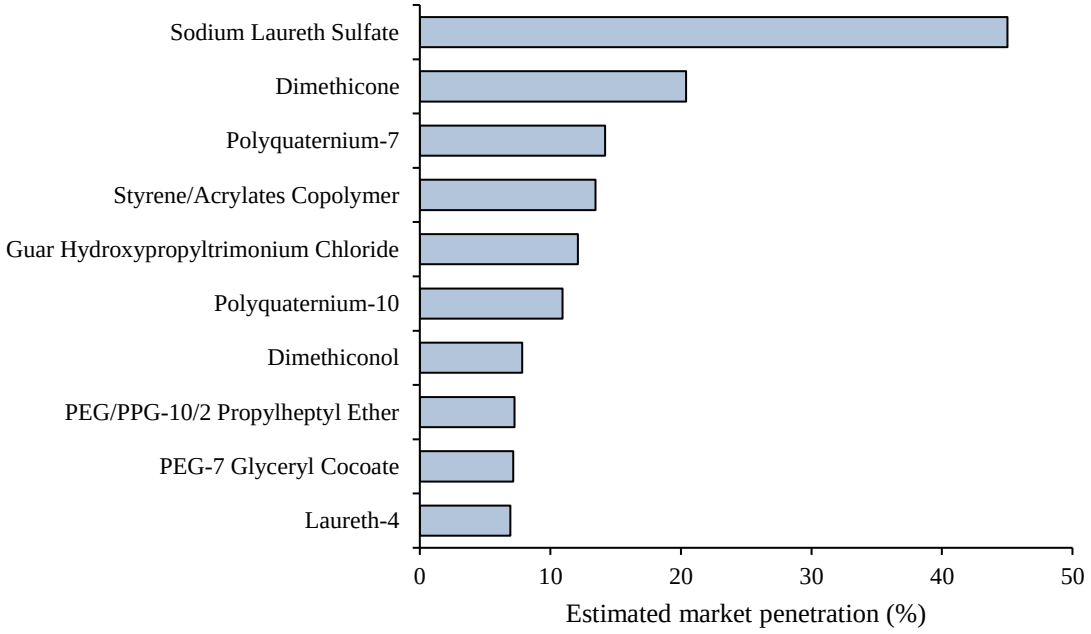


Figure 3.2: Estimated market penetration of the top 10 individual polymers (by market penetration) across all of the studied products, shown as percentage of products containing polymers.

Other commonly occurring polymers (present in > 10 % of products studied) included dimethicone, polyquaternium-7, styrene/acrylates copolymer, guar hydroxypropyltrimonium chloride, and polyquaternium-10 (Figure 3.2). Although most polymers assessed in the present study are water-soluble, some polymers such as styrene/acrylates copolymer which are not expected to be WSPs are also present. It is worth noting that some of the individual polymers identified in the present study were highlighted by Pecquet *et al.* (2019) as having insufficient data available for conducting an ERA in their assessment of data availability for polymers in US household cleaning products, including three of these commonly occurring polymers (polyquaternium-10,

polyquaternium-7, and styrene/acrylates copolymer). In addition, Pecquet *et al.* (2019) excluded polymers identified only by trade names and those lacking in CAS numbers from their dataset due to inadequate characterisation, whereas in the present study polymers were identified based only on names listed in product ingredients. Therefore whilst the data in the present study may incorporate some materials which do not strictly fit the definition of a polymer, there is also potential for inclusion of other polymers which do not have sufficient data for conducting an ERA but which were excluded from analyses by Pecquet *et al.* (2019).

The 339 identified polymers were categorised into 26 individual groups (Table 3.3), based on monomer type, polymer structure and functional groups, and expected functions in the products, with the exception of one group ('other') which contained 15 remaining polymers that were unrelated. These 15 polymers were analysed separately to obtain individual PEC_{SW} estimates before combining them into a group. Grouping of the polymers in this way not only simplifies analysis, providing a useful basis for grouping for polymer ERA, but also allows identification of key polymer types and functional groups that are likely to be present in the products studied and thus have the potential to be released to the environment.

The most common polymer groups by market penetration included alcohol ethoxylate salts and alcohol alkoxylates (commonly used as anionic and nonionic surfactants, respectively; e.g. Cowan-Ellsberry *et al.* 2014), and polyquaterniums (commonly used as anti-static and film-forming agents; e.g. Johnson *et al.* 2016). Other key polymer groups included polycarboxylates, silicones, polyethers and copolymers, and polyol ethoxylate esters (Figure 3.3, Appendix 3.4). Only a few of these groups or their members have been assessed for environmental risk previously, mainly alcohol ethoxy sulphates, alcohol ethoxylates, and polycarboxylates (PAA and PAA/MA), which have been assessed as part of the HERA initiative (HERA 2004, 2009, 2014a, 2014b). It is also worth noting that these HERA assessments only include some members of the polymer groups identified in the present study, with many individual polymers identified in the present study not having been incorporated.

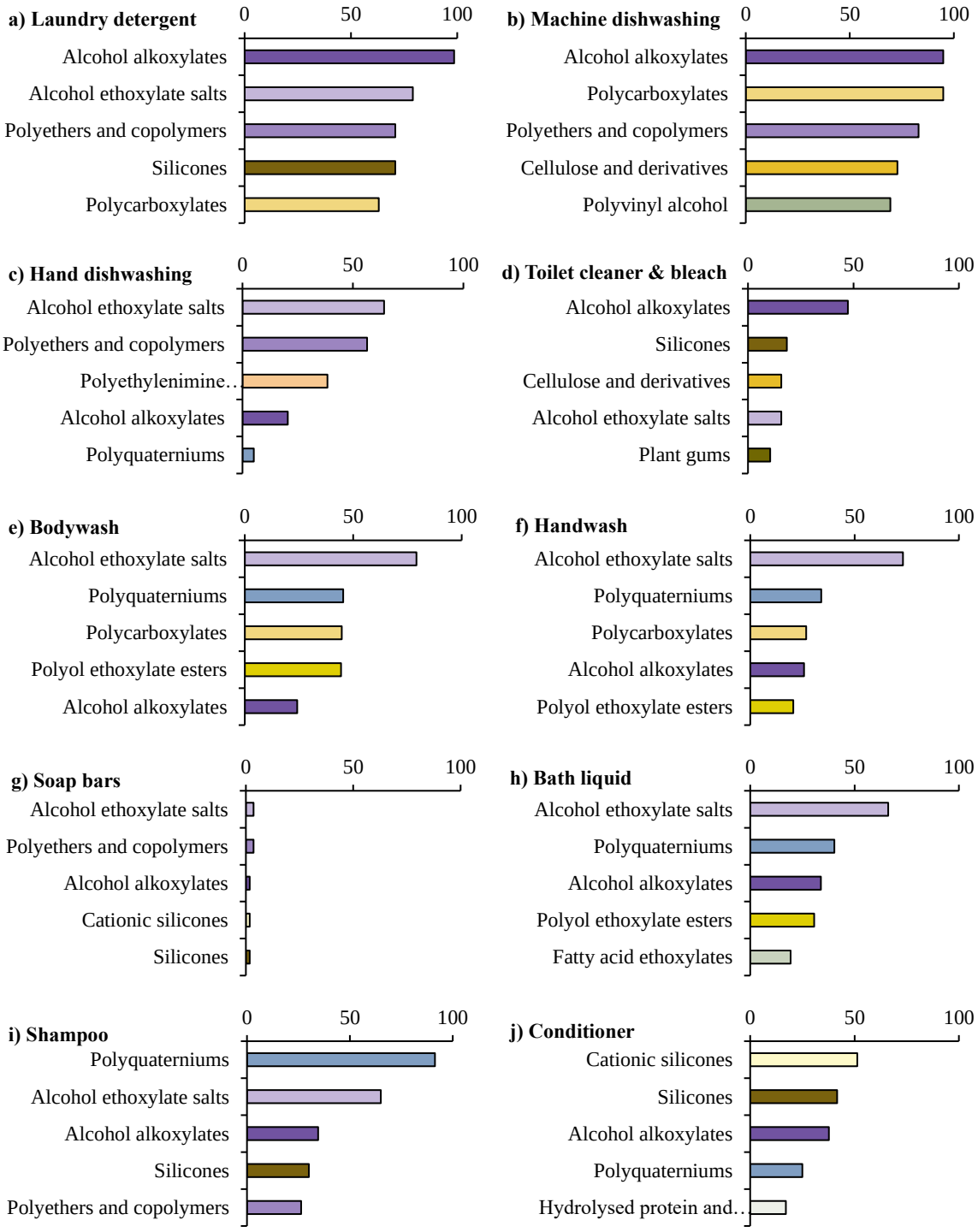


Figure 3.3: Estimated market penetration of the top 5 polymer groups (by market penetration) in each of the studied product types, shown as percentage of products containing polymer groups.
Polymer groups are coloured for ease of comparison between graphs.

As is to be expected, the most prevalent groups by market penetration also differ by product type (Figure 3.3), with additional polymer groups being key for different products. For example, cationic silicones are in the top 5 polymer groups by market

penetration for both conditioner and soap bars, with cellulose polymers being prevalent in machine dishwashing detergents and toilet cleaners. It is also worth noting that some product categories contained certain polymer groups in close to 100% of the products studied (e.g. laundry detergent, machine dishwashing detergent, and shampoo), whilst other product types had no polymer groups present in more than about half of the products (conditioner and toilet cleaner). Soap bars had the lowest market penetration of all polymers, with all polymer groups present in less than 4% of the products studied.

3.3.2. Worst-case exposure (PEC)

Worst-case PEC_{SW} estimates were in the range of 8.2 ng L^{-1} (amine/formaldehyde polymers) to 5.1 mg L^{-1} (alcohol ethoxylate salts), with 'preferred' worst-case PEC_{SW} estimates ranging from 24.7 ng L^{-1} (amine/formaldehyde polymers) to 2.4 mg L^{-1} (alcohol ethoxylate salts) (Figure 3.4, Appendix 3.6.1). Whilst alcohol ethoxylate salts, alcohol alkoxylates, and polycarboxylates PEC_{SW} estimates ranged to above 1 mg L^{-1}, all other polymer groups had worst-case PEC_{SW} ranges below 1 mg L^{-1}.

Worst-case PEC_{SOIL} estimates were in the range of 0.3 µg kg^{-1} (amine/formaldehyde polymers) to 202.6 mg kg^{-1} (alcohol ethoxylate salts), with 'preferred' PEC_{SOIL} estimates ranging from 1.0 µg kg^{-1} (amine/formaldehyde polymers) to 95.9 mg kg^{-1} (alcohol ethoxylate salts) (Appendix 3.6.2). Estimates of PEC_{SOIL} followed an identical pattern to PEC_{SW} estimates, due to the assumption of worst-case (i.e. that all polymers present in WW influent were released in sludge and in effluent for PEC_{SOIL} and PEC_{SW}, respectively) and no degradation during WWT.

Laundry detergents were a significant contributor to total modelled PEC estimates for a large number of polymer groups, including in several of the ten groups with the highest worst-case PEC. For example, laundry detergents contributed 72% to the worst-case PEC_{SW} for cellulose and derivatives, 71% to polycarboxylates, and 59% to each of silicones and polyvinyl alcohol (Figure 3.5). Handwash and bodywash were also shown to significantly contribute, collectively, to several polymer groups, including polyol ethoxylate esters (86%) and polyquaterniums (70%). The high contributions from these three product types reflect the high usage rates of 11.3, 10.3, and 8.3 g $capita^{-1}$ day^{-1} for laundry detergent, handwash, and bodywash, respectively (Eriksson *et al.* 2002; Garcia-Hidalgo *et al.* 2017; A.I.S.E. 2019), which were notably higher than values for each of the other product types (Table 3.2). However, for a small number of polymer groups,

other product types contribute more significantly to worst-case PEC (Figure 3.5), reflective of higher concentrations and greater market penetration. Some polymer groups were also absent from certain product types, with functionalised silicones (cationic silicones and silicone alkoxylates), hydrolysed proteins, polyol ethoxylate esters, polyolefins, and polyglycerins being examples of polymer types which were only present in personal care products.

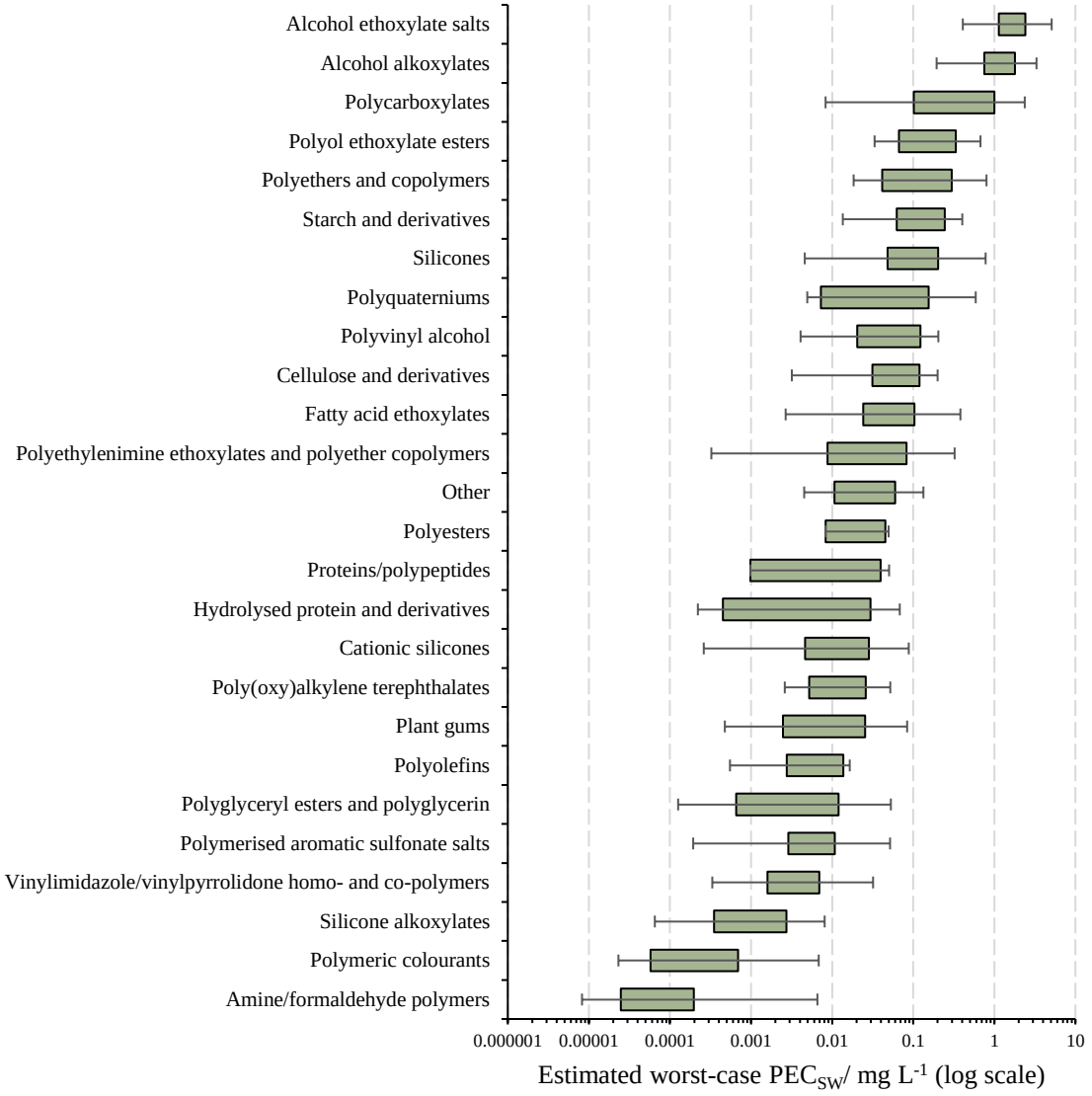


Figure 3.4: Worst-case PEC_{SW} estimates for identified polymer groups in household products emitted down-the-drain. Boxes depict values obtained from 'preferred' concentration ranges given by patents, whilst error bars depict values derived from widest concentration ranges given by patents.

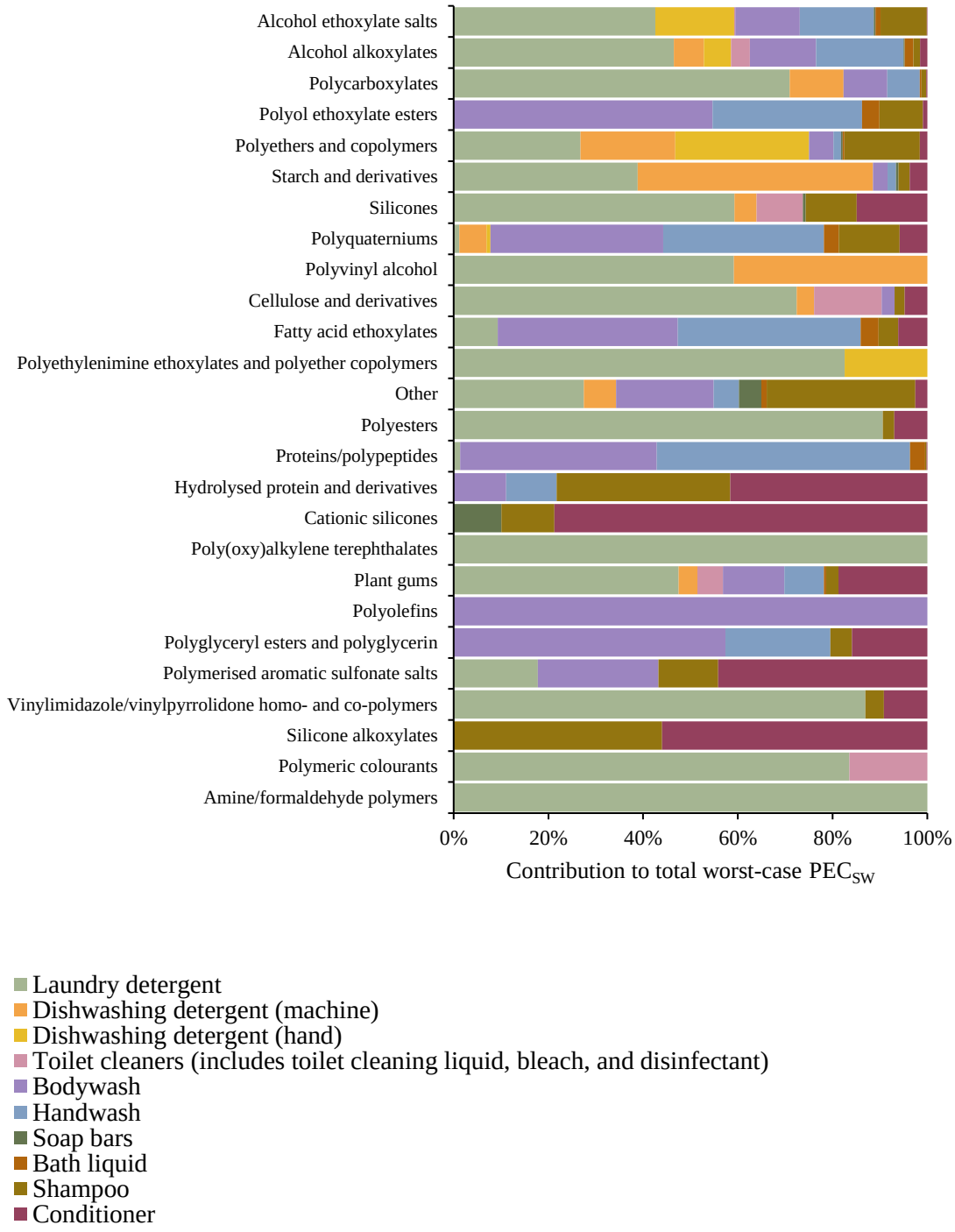


Figure 3.5: Contribution to total preferred maximum worst-case PEC_{SW} for each polymer group from each of the product types included in the study.

3.3.3. Polymer prioritisation and refined PEC

The top ten polymer groups with the highest worst-case PEC (Figure 3.4) were prioritised for calculation of refined PEC estimates (by incorporation of removal in wastewater treatment based on available data).

Table 3.4: Estimates from the literature of removal from wastewater for members of the top 10 prioritised polymer groups identified in the present study, used to refine PEC_{SW} estimates.

Polymer group	Percentage removal in WWTP/ %	Notes	Reference
Alcohol ethoxylate salts	69.7-99.9	Values for alkyl/alcohol ethoxy sulfates. Obtained from monitoring of influent and effluent of US WWTP. Lowest and highest removal estimates used. 69.7 % = trickling filter, 99.9 % = activated sludge.	McAvoy *et al.* 1998; Matthijs *et al.* 1999
Alcohol alkoxylates	79.4-99.9	Values for alcohol ethoxylates. Obtained from monitoring of influent and effluent of US WWTP. Lowest and highest removal estimates used. 79.4 % = trickling filter, 99.9 % = oxidative ditch, trickling filter, activated sludge.	McAvoy *et al.* 1998; Morrall *et al.* 2006
Polycarboxylates	9-98	9 % = homopolymer of acrylic acid, mean MW 1,000 g mol^{-1}, OECD 303 A (Activated sludge simulation test), DOC influent concentration 15 mg L^{-1}. 98 % = copolymer of acrylic/maleic acid, mean MW 70,000 g mol^{-1}, OECD 303 A (Simulation test), DOC removal.	HERA 2014a, 2014b
Polyol ethoxylate esters	-	Literature values for WWTP removal not found.	-
Polyethers and copolymers	70-96	70 % = PEG-8000 (Pluriol® E 8000), OECD 303A (simulation test - aerobic sewage treatment) / ISO 11733 (activated sludge simulation test), DOC reduction (56 d). 96 % = PEG-400 (^{14}C-labelled), OECD confirmatory test: continuous activated sludge model WWTP, 3 days, ^{14}C mass-balance at test end; 4% of polymer in effluent, 41% in sludge. Removal of PEG in German WWTP has also been reported at approximately 95% from monitoring of influent and effluent.	Steber and Wierich 1985; BASF 2018; Duis *et al.* 2021; Pauelsen *et al.* 2023
Starch and derivatives	-	Literature values for WWTP removal not found.	-
Silicones	94-97	94 % = polydimethylsiloxane (PDMS), monitoring of WWTPs in North America. 97 % = PDMS, based on WWTP models and laboratory scale calculations.	Fendinger *et al.* 1997; Graiver *et al.* 2003
Polyquaterniums	8.1-38	8.1 % = Polyquaternium-28 (Gafquat® HS100), 38 % = Polyquaternium-6 (poly(DADMAC)). Equifugacity model used to predict removal of various polyquaternium compounds in WWTP.	Cumming *et al.* 2011a
Cellulose and derivatives	50	Carboxymethyl cellulose (CMC). CAS test developed from OECD Test Guideline 303 A, 14 days.	Van Ginkel and Gayton 1996
Polyvinyl alcohol	84.24	Model based on literature data for PVA degradation in critical processes of WWTPs. Mass balance; estimated that ~61.20% of PVA is emitted via sludge, and ~15.76% is emitted via effluent.	Rolsky and Kelkar 2021

Some data on WWTP removal were available for most of the ten prioritised polymer groups (Table 3.4). However, monitoring data were only available for four polymer groups (alcohol ethoxylate salts, alcohol alkoxylates, polyethers and copolymers, and silicones). For the remaining groups only values from simulation experiments or modelling were available. In addition, for polyol ethoxylate esters, and starch and derivatives, values for WWTP removal were not found and thus no removal was assumed, meaning refined PECs for these two polymer groups remain the same as worst-case PEC estimates.

For five of the prioritised polymer groups (alcohol ethoxylate salts, alcohol alkoxylates, polyethers and copolymers, silicones, and polyvinyl alcohol), removal estimates were relatively high, ranging from ca. 70 % to close to 100 % across these groups (Table 3.4). This suggests that relatively small proportions of the polymers in these groups entering WWTPs are likely to be released in treated effluent. For polycarboxylates, whilst the upper estimate of WWTP removal was also high (98 %), the lower estimate of 9 % indicates high variation in removal depending on polymer structure and molecular weight within the group. For the remaining two polymer groups (polyquaterniums, and cellulose and derivatives), WWTP removal was estimated to be ≤ 50 %, suggesting relatively low removal rates for these polymer groups and high potential for release in WWTP effluent.

Refined PEC_{SW} estimates (Table 3.5, Figure 3.6) were of course reduced compared to worst-case estimates in the cases of the eight polymer groups for which WWTP removal data were available, and these ranged from 0.1 µg L^{-1} (silicones) to 2.2 mg L^{-1} (polycarboxylates). Preferred concentration ranges for the prioritised polymer groups were all reduced to < 1 mg L^{-1}, and ranged from 0.8 µg L^{-1} (alcohol alkoxylates) to 0.9 mg L^{-1} (polycarboxylates). The differing removal estimates between polymer groups also influenced the relative importance of the groups, with refined PEC_{SW} estimates for groups such as polycarboxylates, polyquaterniums, and cellulose increasing relative to the other groups, and refined PEC_{SW} estimates for groups such as polyethers and copolymers, and silicones being reduced relative to concentration estimates for other polymer types.

Table 3.5: Refined PEC_{SW} estimates (mg L^{-1}) for prioritised polymer groups in household products emitted down-the-drain.
Probable values were obtained from 'preferred' concentration ranges given by patents (and are thus expected to be more representative of actual environmental concentration), whilst absolute values were derived from widest concentration ranges given by patents. Note that literature data for WWTP fate could not be obtained for polyol ethoxylate esters and starch and derivatives, thus refined estimates remain the same as worst-case estimates. Polymer groups are listed in order of highest probable max. refined PEC_{SW}.

Polymer groups	Absolute min. refined PEC_{SW}	Absolute max. refined PEC_{SW}	Probable min. refined PEC_{SW}	Probable max. refined PEC_{SW}
Polycarboxylates	0.0002	2.2	0.002	0.9
Alcohol ethoxylate salts	0.0004	1.5	0.001	0.7
Alcohol alkoxylates	0.0002	0.7	0.0008	0.4
Polyol ethoxylate esters	0.03	0.7	0.07	0.3
Starch and derivatives	0.01	0.4	0.06	0.2
Polyquaterniums	0.003	0.5	0.005	0.1
Polyethers and copolymers	0.0007	0.2	0.002	0.09
Cellulose and derivatives	0.002	0.1	0.02	0.06
Polyvinyl alcohol	0.0006	0.03	0.003	0.02
Silicones	0.0001	0.05	0.001	0.01

Preferred ranges of refined PEC_{SW} estimates from the present study were generally in good agreement with both PEC_{SW} and measured environmental concentrations in surface water (MEC_{SW}) values from the literature, where data were available (Figure 3.6, Appendix 3.9). In the case of polycarboxylates, there was particularly good agreement with literature values, with the preferred refined PEC_{SW} of the present study ranging from 0.002-0.915 mg L^{-1}, and PEC_{SW} values from various literature studies ranging from 0.03-0.70 mg L^{-1} (ECETOC 1993; DeLeo *et al.* 2020). MEC_{SW} for polyethers also closely matched the range of estimates determined in the present study, with PEC_{SW} values from the present study ranging from 0.002 to 0.090 mg L^{-1}, and MEC_{SW} from various literature studies ranging from 0.0001 to 0.212 mg L^{-1} (Rychłowska *et al.* 2003; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014). PEC_{SW} and MEC_{SW} values from the literature for other polymer groups also generally fall within or close to preferred PEC_{SW} ranges of the present study, but were often towards the lower ends of the ranges predicted (Figure 3.6).

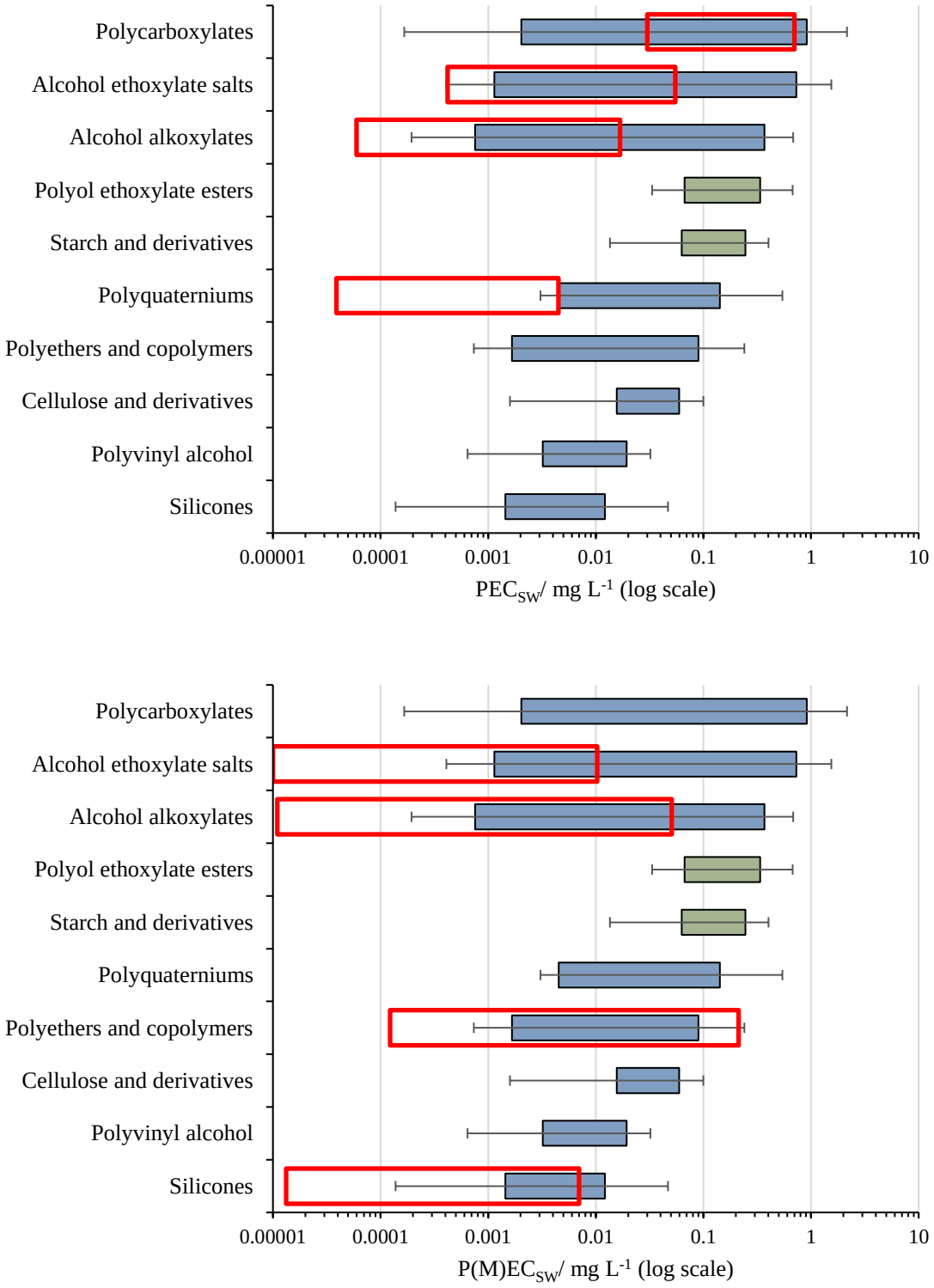


Figure 3.6: Comparison of refined PEC_{SW} estimates determined in the present study (box-and-whisker; boxes depict values obtained from 'preferred' concentration ranges given by patents, whilst error bars depict values derived from widest concentration ranges given by patents), with data for PEC_{SW} (top) and MEC_{SW} (bottom) from the literature for members of each polymer group (red boxes). Note that for polyol ethoxylate esters and starch and derivatives, refined estimates of the present study remain the same as worst-case estimates. Literature values and references are listed in Appendix 3.9.

It is likely that, although the wide ranges of PEC_{SW} estimated in this study reflect the wide concentration ranges for polymers given in product patents, actual product formulations will use minimal amounts of polymer whilst maintaining function in order to minimise cost. This is exemplified by a comparison with concentrations of polycarboxylates in laundry detergents determined by DeLeo *et al.* (2020), where polyacrylic acid sodium salt concentrations in laundry detergents were estimated to be approx. 1 % based on the order listed in ingredients and knowledge of concentrations of other ingredients. Similarly, typical concentrations of polyacrylic acid homopolymers and polyacrylic/maleic acid copolymers in laundry detergents were reported to be approx. 0.5 and 3.0 %, respectively, in the corresponding HERA reports (HERA 2014a, 2014b). In the present study, however, concentrations of polycarboxylates in laundry detergents were instead estimated to be in the range of 0.1-50 %, or more preferably 2-20 %, based on patents (Appendix 3.5.1). Therefore actual polymer concentrations may potentially fall within the lower ends of the ranges predicted in the present study. However, it should also be noted that most literature data focus on only one or a few members of the polymer groups presented in the present study, whereas our PEC_{SW} estimates reflect a combined concentration of a greater number of polymers and are thus expected to be higher.

PEC_{SW} of the present study may also be increased due to the inclusion of potentially non-polymeric materials for some groups (i.e. where insufficient data were available to confirm assignment as polymer/not-polymer) in order to give conservative estimates of exposure. For example, a large number of alcohol ethoxy sulphate (AES) compounds were included as polymers in which the average number of ethoxylate units were not specified yet it has been shown that for AES sold into household use, often n is < 3 (HERA 2004) which would not classify as a polymer based on the OECD definition. However, higher values of n are also likely to be present (HERA 2004), and thus inclusion of these substances is likely to cover both polymeric and non-polymeric compounds, giving a more conservative estimate. In addition, given the similarity in structure of such compounds to confirmed polymers in the same group, the potential for additive effects may further justify their inclusion. The broad application of WWTP removal processes to polymer groups rather than individual polymers in the present study may also affect refined PEC_{SW}, given that different polymers within the groups may have relatively wide ranges of properties and are thus likely to have differing levels of removal in WWT.

Refined PEC_{SOIL} estimates (Table 3.6, Figure 3.7) ranged from 15.9 µg kg^{-1} (polyquaterniums) to 202.4 mg kg^{-1} (alcohol ethoxylate salts), with preferred concentration estimates ranging from 23.5 µg kg^{-1} (polyquaterniums) to 95.8 mg kg^{-1} (alcohol ethoxylate salts). Preferred ranges for PEC_{SOIL} were thus all reduced to < 100 mg kg^{-1}, and the relative concentrations of polymer groups were altered compared to refined PEC_{SW} due to estimations of relative removal into wastewater effluent and sludge.

Table 3.6: Refined PEC_{SOIL} estimates (mg kg^{-1}) for prioritised polymer groups in household products emitted down-the-drain.
Probable values were obtained from 'preferred' concentration ranges given by patents (and are thus expected to be more representative of actual environmental concentration), whilst absolute values were derived from widest concentration ranges given by patents. Note that literature data for WWTP fate could not be obtained for polyol ethoxylate esters and starch and derivatives, thus refined estimates remain the same as worst-case estimates. Polymer groups are listed in order of highest probable max. refined PEC_{SOIL}.

Polymer groups	**Absolute min. refined PEC_{SOIL}**	**Absolute max. refined PEC_{SOIL}**	**Probable min. refined PEC_{SOIL}**	**Probable max. refined PEC_{SOIL}**
Alcohol ethoxylate salts	11.3	202.4	31.5	95.8
Alcohol alkoxylates	6.1	131.5	23.8	71.3
Polycarboxylates	0.03	92.4	0.4	39.1
Polyol ethoxylate esters	1.3	26.8	2.7	13.4
Starch and derivatives	0.5	16.0	2.5	9.8
Silicones	0.2	30.1	1.8	7.8
Polyethers and copolymers	0.3	13.0	0.7	4.9
Polyvinyl alcohol	0.1	5.0	0.5	3.0
Cellulose and derivatives	0.06	4.0	0.6	2.4
Polyquaterniums	0.02	8.9	0.02	2.3

Literature data for PEC_{SOIL} are scarce and even more limited than data for surface waters (Figure 3.7, Appendix 3.10). MEC data were available only for silicones, with concentrations of polydimethylsiloxane measured in sludge-amended agricultural soil ranging from <0.41-10.4 mg kg^{-1} (Fendinger *et al.* 1997). These values are in good agreement with preferred PEC_{SOIL} for the entire silicones group determined in the present study (1.80-7.82 mg kg^{-1}). Values of PEC_{SOIL} determined for PAA and PAA/MA (ECETOC 1993; HERA 2014a, 2014b) are also in close agreement with values for the polycarboxylates group from the present study (Figure 3.7). PEC_{SOIL} for polyquaternium-68 is also within range of the present study (Australian National Industrial Chemicals Notification and Assessment Scheme (NICNAS) 2009), albeit on the lower end of the values predicted here, as is to be expected on comparison of a single polymer with the

entire polymer group. However, literature PEC_{SOIL} for alcohol ethoxylate sulfates and alcohol ethoxylates (HERA 2004, 2009) are estimated to be significantly lower than the PEC_{SOIL} determined for alcohol ethoxylate salts and alcohol alkoxylates, respectively, in the present study. This may be due to the incorporation of polymer degradation in soil following release in these literature values, as well as the smaller number of polymers incorporated. In addition, in the present study it was assumed that removal of these polymers from wastewater in wastewater treatment was a result of partitioning only (due to the nature of the literature monitoring data obtained); however, in reality, degradation during wastewater treatment will occur, and thus the concentrations of these polymers sorbed to sludge is likely a conservative estimate.

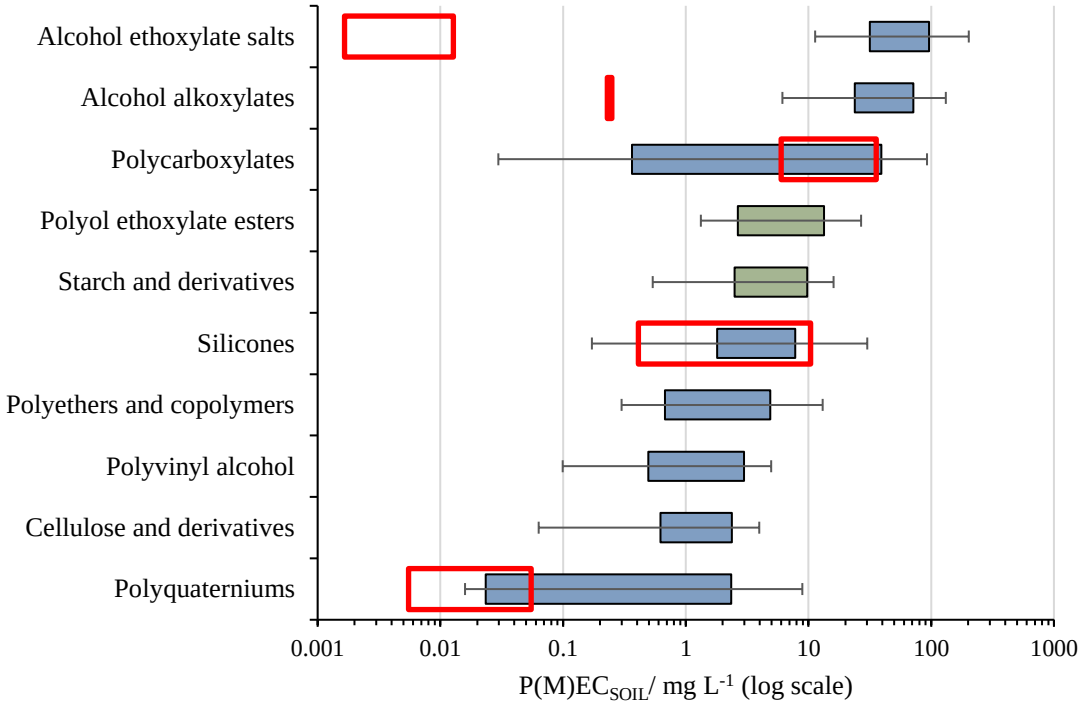


Figure 3.7: Comparison of refined PEC_{SOIL} determined in the present study (blue box-and-whisker; boxes depict values obtained from 'preferred' concentration ranges given by patents, whilst error bars depict values derived from widest concentration ranges given by patents), with data for PEC_{SOIL} and MEC_{SOIL} from the literature for members of each polymer group (red boxes). Literature data for silicones correspond to MEC, the remaining literature data are PEC. Note that for polyol ethoxylate esters and starch and derivatives, refined estimates of the present study remain the same as worst-case estimates. Literature values and references are listed in Appendix 3.10.

The PEC estimates determined in the present study provide a key first step in addressing the lack of data on environmental exposure for many of the identified polymers as well as improving knowledge of the types of polymers which may be released to the environment. However, whilst some MEC data are available for some polymer types (namely alcohol alkoxylates and their salts, polyethers and copolymers, and silicones) it is clear that there are limited data available overall, with no MEC data available for the remaining polymer groups, and the MEC data that are available covering only a small selection of polymers from each group (Appendices 3.9 and 3.10), leaving other members of the groups unstudied. Values for removal from water during WWT are often based on influent and effluent polymer concentrations, and thus levels of degradation and partitioning to sludge during WWT remain uncertain for some polymer groups. In addition, MEC data for soil are available for only one polymer group (silicones; Fendinger *et al.* 1997). The lack of MEC data for the identified polymer groups limits verification of the PEC estimates obtained in the present study, as well as assessment of exposure and therefore environmental risk.

3.3.4. Potential risk of selected polymers

Of the ten polymer groups prioritised from the exposure model, only five had base set experimental ecotoxicity data (the base set consists of acute toxicity data for fish, invertebrates and algae, and is defined as the minimum dataset required for determination of environmental quality standards; EC 2011) (Appendices 3.7 and 3.8). These included alcohol alkoxylates, alcohol ethoxylate salts, and polycarboxylates (for which data were obtained from corresponding HERA reports), and polyquaterniums and cellulose (for which data were obtained from the ECOTOX Knowledgebase). In addition, although relevant data were not found in the ECOTOX Knowledgebase for polyvinyl alcohol (Appendix 3.7), chronic data were available from the literature for fish, invertebrates, and algae, along with acute data for fish and invertebrates, which were equivalent to a full dataset (Arfsten *et al.* 2004; Appendix 3.8). Of the remaining four groups, some environmentally relevant endpoint data were available (Appendices 3.7 and 3.8). It was therefore possible to derive a PNEC for all ten polymer groups, noting that four of these PNECs (for polyol ethoxylate esters, starch and derivatives, polyethers and copolymers, and silicones) were derived without base set experimental data.

Organisation of the polymer groups based on upper estimated RQs indicates that polyethers and copolymers, polyquaterniums, and alcohol alkoxylates are of the highest potential concern in an aquatic environment based on the modelled exposure estimates and available hazard data used in the present study, with cellulose and derivatives, starch and derivatives, and polyvinyl alcohol likely to pose the lowest aquatic environmental risk (Table 3.7). This is supported by the current concerns related to environmental hazard and risk of cationic polymers such as polyquaterniums (e.g. USEPA 1997; Cumming *et al.* 2008; Costa *et al.* 2014), and the assumption that "natural" polymers such as starch and cellulose may be less likely to pose risk than some classes of synthetic polymers due to the fact that they are already ubiquitous in the environment (although natural origin does not necessarily preclude environmental risk of chemicals).

Table 3.7: Estimates of PNEC calculated using literature data, and corresponding risk quotients (RQ) for surface water for each polymer group, using preferred ranges of modelled PEC_{SW}.

Polymer group	**PNEC/ mg L^{-1}**	**Lower estimated RQ**	**Upper estimated RQ**
Polyethers and copolymers	0.0000125-0.00005	33.2	7179
Polyquaterniums	0.00002	226	7115
Alcohol alkoxylates	0.003	0.252	123
Alcohol ethoxylate salts	0.006	0.190	122
Polyol ethoxylate esters	0.02	3.34	16.8
Silicones	0.00316	0.457	3.85
Polycarboxylates	0.375	0.005	2.44
Cellulose and derivatives	0.0873	0.179	0.683
Starch and derivatives	1-3	0.021	0.246
Polyvinyl alcohol	0.218	0.015	0.089

However, it should also be noted that the PNEC values calculated in the present study are based on effects data from only a single polymer, before application to exposure data for the entire group. Here we assume that polymers in each group have similar effects and thus environmental hazard is a result of the mixture of all polymers in the group. In reality, it may be the case that individual polymers within a group have different environmental effects and therefore further sub-categorisation may be necessary to refine risk estimates. Even in the case of polyvinyl alcohol, for which the group was highly homogeneous, molecular weights were not specified and thus hazard data may not be specifically for the polyvinyl alcohol used in the studied products. Calculated RQs are also dependent on exposure estimates of the present study, and thus span a wide range

for many groups; in particular, alcohol alkoxylates, alcohol ethoxylate salts, silicones, and polycarboxylates have RQ values ranging from < 1 to > 1 (0.3 to 123, 0.2 to 122, 0.5 to 4, and 0.005 to 2, respectively). Given that RQ > 1 indicates unacceptable risk, determination of potential concern for these polymer groups remains uncertain based on currently available data, although it can be noted that alcohol ethoxylates, alcohol ethoxysulfates, and polyacrylic acid homo- and co-polymers used in detergents have previously been found to pose minimal risk to the environment (HERA 2004, 2009, 2014a, 2014b). DeLeo *et al.* (2020) also calculated RQ < 1 for homo- and co-polymers of polyacrylic acid used in U.S. cleaning products. However, the present study includes a greater number of polymers within groups, derived from a larger number of product types, which will contribute to larger RQ values compared with those given in the HERA reports and by DeLeo *et al.* (2020).

The entire range of RQ estimates for polyethers and copolymers, polyquaterniums, and polyol ethoxylate esters is > 1, suggesting that these groups may be likely candidates for prioritisation and further study. In addition, RQ ranges for the cellulose, starch, and polyvinyl alcohol groups remain < 1, indicating that polymers from these groups present in household and personal care products are unlikely to pose excessive risk to the environment.

3.3.5. Future applications

In the present study, we have provided a framework for prediction of environmental exposure of polymers from household products based on the limited data currently available, allowing environmental concentrations to be predicted for initially unidentified polymers without the need for substance-specific usage or emissions data. The method applied allows estimation of PECs using only publicly available product ingredients and patent data, and usage data for broad product types (i.e. no polymer-specific production or import volumes are required). In addition, the approach used allows identification of specific polymers without prior knowledge of polymer identities, meaning the full range of polymers used in the incorporated products can be accounted for. Household products which were expected to be released down-the-drain at point of use were included in the model, however, the model could be adapted to include other household products which are likely to be eventually washed down-the-drain (e.g. make-up, hair styling products, surface cleaners, etc.) and which may therefore contribute to the types and quantities of

polymers which may be present in the environment. In addition, some product types which are expected to be released down-the-drain at point of use were not included in order to limit the scope of the study, including fabric conditioner, deep conditioner for hair, and fabric stain removers. These product types could be easily incorporated into the model to estimate their contribution to polymer PEC estimates. Where more accurate and precise estimates of polymer concentration in products become available, these could be used to further refine PEC estimates based on the method presented. Principles of the model could also be adapted for application to other sectors, such as polymers used in agriculture and wastewater treatment, as well as to other non-polymeric substances in household products for which usage, emissions, and environmental concentration data may be limited or unavailable.

The present study also presents a basis for grouping polymers, with broad polymer groups being identified and applied in practise to carry out an exposure assessment. The groupings illustrate common structural features and functionalities of polymers which may be present in the environment and may be useful in environmental risk assessment. Whilst the polymer groups established in the present study are a useful first step, it should be noted that many of these groups contain a broad range of polymers with different molecular weights, monomer units, and structural features; for higher-tier exposure and effects assessment, it may be useful to test the extent to which these differences in polymer properties impact their behaviour and ecotoxicities and subsequent environmental risk. This may also lead to the need for further refinement of groups and sub-groups as more data become available in order to provide more accurate classifications based on actual environmental behaviour.

The model used to estimate PEC in the present study was a simple, lower-tier model which does not account for polymer degradation or transport following release to the environment; as more data become available on environmental fate behaviour of the identified polymers and the identified knowledge gaps are addressed, more complex models could be developed, using the method of the present study to determine emissions along with fate information to refine concentration estimates. Spatially resolved models may also be useful in analysis of polymer concentrations following initial release to the environment.

3.4. Conclusions

Results from the exposure modelling approach developed in the present study suggest that a wide variety of WSPs found in household products are likely to be present in the environment, and that several identified polymer groups have the potential to pose environmental risk. Preliminary RQ estimates indicate that starch, cellulose, and polyvinyl alcohol polymers released from household products are unlikely to pose environmental risk (RQ < 1), but for the remaining groups, RQ values > 1 are possible. In particular, all RQ estimates for polyethers and copolymers, polyquaterniums, and polyol ethoxylate esters were determined to be > 1, suggesting these polymer groups may be likely candidates for prioritisation for environmental risk assessment. Further research providing data on measured concentrations, higher-tier estimates, environmental fate behaviour, and ecotoxicity of the prioritised polymers will be key in further defining and consolidating risk estimates, as well as an analysis of the applicability of read-across and bulk analysis within polymer groups.

Based on the final risk-based prioritisation of water-soluble polymers presented in this chapter, polyether polymers were selected for environmental fate experiments conducted in *Chapter 4* and *Chapter 5*, due to the fact that this polymer group had the highest estimated risk quotient value (based on the upper PEC limit). Despite the fact that many polyethers are expected to be biodegradable and to have low hazard potential, their extremely high usage rates as identified in the present study indicate that they are still likely to be present in the environment at significant concentrations, and thus further assessment of their environmental fate is warranted. Incorporation of production volumes and usage patterns, as exposure indicators, into polymer prioritisation approaches has also been recommended previously (Groh *et al.* 2023). The likely presence of polyethers in the environment is further confirmed by their measurement in literature monitoring studies, with concentrations similar to those predicted in the present work. Given the wide range of individual polyethers identified in the group, two polymers (polyethylene glycol and polypropylene glycol) were selected in order to represent the two key functionalities observed, with average molecular weights of ca. 400 in order to reflect the highest contributors to the group as well as facilitate analytical method development by use of relatively low molecular weight polymers.

Chapter 4

Environmental Fate and Sorption Behaviour of Water-Soluble Polyethers in Soil

4.1. Introduction

In this chapter, an analytical method was developed for detection of the two prioritised water-soluble polymers, to address a key research need identified in *Chapter 2* and enable experimental studies. This method was then used to characterise the environmental fate of water-soluble polymers in soil, providing key data to inform the results of exposure estimates in *Chapter 3* as well as insight into the preliminary grouping approach employed in *Chapter 3*. Focus was given to characterisation and analysis of individual polymer homologues within polymer mixtures in order to address the complexity of polymer properties as well as the implications for polymer exposure assessment methods and QSAR development, as discussed in *Chapter 2.*

Understanding the environmental fate of chemical compounds is essential to environmental exposure assessment, in order to determine emissions and removal from the environment and accurately characterise environmental concentrations (Di Guardo *et al.* 2018). Sorption coefficients such as the soil/water partition coefficient (K_d) and soil organic carbon/water partition coefficient (K_{oc}) describe the distribution of a chemical between the aqueous phase and solid phases (usually soil or sediment) in the environment, and were identified as key parameters for exposure assessment of water-soluble polymers in *Chapter 2*. Sorption to soil is key to biodegradation and transport potential and thus environmental fate of chemical compounds, and is regularly assessed for pesticides (e.g. Wauchope *et al.* 2002). Sorption to soil is also relevant to WSPs used in agriculture, and WSPs released to terrestrial environments through other means, such as those released down-the-drain or used in wastewater treatment and subsequently applied to agricultural land during sludge application (e.g. Arp and Knutsen 2020), as well as in predicting sorption to sediment in the aquatic environment (e.g. European Medicines Agency (EMA) 2018).

There have been a limited number of studies characterising sorption behaviour of WSPs, including for polyethers, polyquaterniums, and polyacrylic acid homo- and co-polymers (reviewed by Duis *et al.* 2021). Polymer sorption may be strongly influenced by chain conformation and multisegment adsorption, with high molecular weight polymers more likely to adsorb irreversibly (Podoll *et al.* 1987), and like other chemical compounds, polymers of differing functionalities may undergo different mechanisms of sorption (Duis *et al.* 2021). However, few studies to date report K_d or K_{oc} values for WSPs, and analyses of the sorption behaviour of individual components of polymer mixtures and mixture interactions are lacking. Given the wide range of polymers in current use and lack of environmental fate data, there is also a need to develop grouping and quantitative structure-activity relationship (QSAR) approaches for polymers (e.g. Nolte *et al.* 2017b; Min *et al.* 2020) in order to predict key fate parameters, such as sorption coefficients, for risk assessment. Whilst QSARs exist for sorption of low molecular weight single compounds (e.g. in the Estimation Program Interface (EPI) Suite; United States Environmental Protection Agency (USEPA) 2012), to date no such QSARs have been developed for polymers. The unique properties of polymers (including high and distributed molecular weights, existence as complex mixtures, and large molecular size) present challenges for characterisation and analysis, and there is a need to approach sorption of polymers in the context of environmental risk assessment (Brunning *et al.* 2022).

The work reported in this chapter was therefore performed to explore the sorption behaviour of polyether polymers in soils. In particular, the chapter focuses on analysing the behaviour of individual polymer homologues, determining mixture interactions (which remain unstudied to date), characterising the influence of polymer properties such as molecular weight and functionality on sorption behaviour for development of polymer QSARs, and supplementing environmental fate data for this relatively understudied class of materials for use in fate modelling and exposure assessment.

Polyethers (including polyethylene glycol (PEG), polypropylene glycol (PPG), and their copolymers), are a class of WSP characterised by repeating ether groups along the polymer backbone. PEG and PPG are widely used in household and cosmetic products, pharmaceuticals, chemical products, agriculture, and in hydraulic fracturing, among other uses (*Chapter 3*; Castanho *et al.* 2009; McLaughlin *et al.* 2016; Rogers *et al.* 2019), with many of these applications likely to contribute to direct or indirect emissions to the

environment. PEG and PPG may also be released as biodegradation products from copolymers and from commonly used nonionic surfactants such as alkyl ethoxylates (Zgoła-Grześkowiak *et al.* 2006; Castanho *et al.* 2009; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014). Although PEG and PPG are generally recognised to be of low hazard and high biodegradability (and thus relatively low concern; Pecquet *et al.* 2019), polyethers were identified as one of a number of groups of WSPs that may be a priority for further study (*Chapter 3*), with the high usage quantities of these polymers indicating significant environmental concentrations at the point of emission, despite an estimated removal of up to 96% during wastewater treatment (Steber and Wierich 1985; Duis *et al.* 2021) (*Chapter 3*). These modelling data are supported by the fact that both PEG and PPG have been measured in the environment (Crescenzi *et al.* 1997; Rychłowska *et al.* 2003; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014; Traverso-Soto *et al.* 2014; Pauelsen *et al.* 2023), so there is a need to further characterise their environmental fate. In addition, approximately 41% of PEG (400 g mol^{-1}) in water has been found to be present in sludge following wastewater treatment (Steber and Wierich 1985; Duis *et al.* 2021; *Chapter 3*), suggesting that soils may be a significant receiving compartment for these polymers.

Sorption of PEG to soils, sludge, and sediments has been previously studied (Podoll *et al.* 1987; Szymanski *et al.* 2003; de Brito Galvão *et al.* 2007; Castanho *et al.* 2009; McLaughlin *et al.* 2016; Traverso-Soto *et al.* 2014); however, data remain relatively limited. In particular, few studies include analysis of individual homologues within a polymer mixture (McLaughlin *et al.* 2016), with the majority of data including only analysis of the bulk mixtures which in reality contain a distribution of polymer chains. Sorption coefficients have also been rarely reported (Podoll *et al.* 1987; Castanho *et al.* 2009; Traverso-Soto *et al.* 2014), and these values are only for bulk polyether mixtures or for individual polymer chains isolated and studied separately. In addition, K_d values have not yet been reported for PPG.

4.2. Materials and methods

4.2.1. Soils

Six standard soils (“2.1” (sand, 0.55 %C), “2.2” (loamy sand, 1.66 %C), “2.3” (silty sand, 0.66 %C), “2.4” (sandy loam, 1.83 %C), “5M” (loamy sand, 0.97 %C), and “6S” (clayey loam, 1.50 %C)) were obtained from Lufa Speyer (Speyer, Germany) and stored

at 4 °C until use. Soils were selected to provide a range in soil properties including organic carbon, nitrogen, pH, cation exchange capacity, and particle size distribution. Soil characteristics and properties are available online (Lufa Speyer 2022) and are summarised in Table 4.1. Soils were used directly, without sieving, as particle sizes were already < 2 mm.

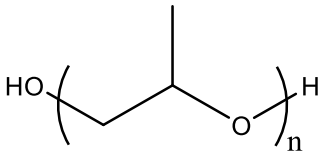
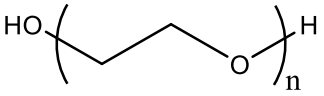
Table 4.1: Summary of chemical and physical characteristics of standard soils (as dry matter) according to Good Laboratory Practice (GLP), provided by LUFA Speyer as mean values from different batch analyses (± standard deviation). Particle size distributions (PSD) and soil types are given according to the German Institute for Standardisation (DIN) classification.

Standard soil number	**2.1**	**2.2**	**2.3**	**2.4**	**5M**	**6S**
Soil type	Sand	Loamy sand	Silty sand	Sandy loam	Loamy sand	Clayey loam
Organic carbon (% C)	0.55 (±0.10)	1.66 (±0.60)	0.66 (±0.05)	1.83 (±0.17)	0.97 (±0.21)	1.50 (±0.13)
Nitrogen (% N)	0.06 (±0.01)	0.19 (±0.06)	0.08 (±0.01)	0.23 (±0.02)	0.12 (±0.03)	0.17 (±0.01)
pH (0.01 M $CaCl_2$)	4.6 (±0.1)	5.5 (±0.1)	6.0 (±0.4)	7.5 (±0.1)	7.5 (±0.1)	7.3 (±0.04)
Cation exchange capacity (meq/100g)	2.9 (±0.2)	8.5 (±1.8)	5.7 (±0.5)	17.4 (±0.8)	8.8 (±0.8)	18.7 (±1.2)
Maximum water holding capacity (g/100g)	29.5 (±4.1)	44.2 (±6.0)	35.2 (±2.7)	47.1 (±1.9)	41.6 (±5.1)	41.7 (±1.8)
Weight per volume (g/1000mL)	1468 (±57)	1205 (±108)	1315 (±65)	1182 (±38)	1226 (±96)	1267 (±31)
Particle size distribution (mm) according to German DIN (%)						
< 0.002	3.5 (±0.7)	10.8 (±1.7)	7.0 (±1.0)	23.5 (±1.0)	12.4 (±1.4)	42.3 (±2.8)
0.002 – 0.006	2.0 (±0.8)	3.4 (±0.8)	4.5 (±0.4)	7.5 (±0.7)	5.1 (±0.6)	9.5 (±1.0)
0.006 – 0.02	2.6 (±0.7)	5.5 (±0.8)	11.2 (±0.8)	14.4 (±1.2)	9.5 (±1.2)	12.7 (±1.5)
0.02 – 0.063	5.0 (±0.9)	8.0 (±1.0)	19.8 (±1.4)	25.9 (±1.7)	21.9 (±0.8)	14.2 (±0.6)
0.063 – 0.2	28.9 (±2.9)	30.6 (±3.1)	25.6 (±1.8)	21.5 (±1.3)	36.3 (±3.5)	9.7 (±1.1)
0.2 – 0.63	55.7 (±2.7)	40.9 (±3.4)	29.5 (±2.4)	5.9 (±1.9)	13.6 (±2.4)	9.3 (±1.3)
0.63 – 2.0	2.5 (±0.3)	0.8 (±0.2)	2.5 (±0.3)	1.3 (±0.4)	1.3 (±0.4)	2.2 (±0.4)

4.2.2. Polymers and chemicals

Polypropylene glycol-7 (PPG-7, MW_N ca. 400, Merck, UK) and polyethylene glycol-9 (PEG-9, MW_N ca. 400, Merck, UK) were selected as the study WSPs based on previous prioritisation of several groups of water-soluble polymers (*Chapter 3*). Key properties of the studied WSPs are shown in Table 4.2. The molecular weight ranges were selected to represent prioritised PPG of similar average molecular weights (*Chapter 3*) whilst keeping within mass ranges of the single quadrupole mass spectrometer detector (Sections 4.2.5 and 4.2.6), and to allow comparisons to be made based on homologue chain length and functional groups. Both polymers were obtained as pure polymer liquids, with polymer stock solutions being made up by dissolution of polymer in 0.01M $CaCl_2$ (made up in deionised water); note that as polymers were obtained as complex mixtures containing a distribution of chain lengths, all stock solutions were made up as the total concentration of all polymer components. Acetonitrile (ACN; LC-MS grade), water (LC-MS grade), and calcium chloride dihydrate (analytical reagent grade) were obtained from Fisher Scientific (UK).

Table 4.2: Summary of key physicochemical properties of the studied polymers as reported on safety data sheets (Merck, UK).

Polymer	**Polypropylene glycol-7**	**Polyethylene glycol-9**
Structure		
	Average n = 7	Average n = 9
Number average molecular weight (MW_N) (g mol^{-1})	446	ca. 400
Water solubility (g L^{-1})	"completely miscible"	256.084 at 25 °C ("completely soluble")
n-octanol/water partition coefficient ($logK_{ow}$)	0.3-0.9 at 23 °C	-0.698 at 30 °C
Melting point (°C)	< -150	< -14.08
Boiling point (°C)	287.6	205.7
Vapour pressure (hPa) at 20 °C	< 0.1	< 0.1
Density (g mL^{-1}) at 20 °C	1.01	1.116

4.2.3. Preliminary experiments

Initial analyses were conducted to check for sorption to test vessels and loss of polymer during filtration, and to determine the optimum soil:solution ratio, equilibration time, and biodegradation, as recommended in OECD Test No. 106: Adsorption – Desorption Using a Batch Equilibrium Method (OECD 2000a). These analyses were initially conducted using Soils 2.1 and 2.4 and PPG-7. Aliquots of 0.01 M $CaCl_2$ solution (made up using deionised water) were added to 1 g (± 5 mg) of soil in 50 mL plastic centrifuge tubes, and left to equilibrate on an orbital shaker overnight (200 rpm). A solution of PPG in 0.01 M $CaCl_2$ was then added (in quantities ≤ 10 % of the final volume of solution, such that the final volume of all solutions was either 1, 5, or 25 mL to give soil:solution ratios of 1:1, 1:5, and 1:25, respectively) to give PPG concentrations of 1 mg L^{-1}. Samples were left on an orbital shaker (200 rpm, room temperature, in the dark) for 24 and 48 hours (for all three soil:solution ratios and both soils), and 24, 48, 72, and 96 hours (for the 1:1 soil:solution ratio and Soil 2.4), before removal and centrifugation at 4000 rpm for 10 minutes. Approximately 1.5 mL of the supernatant of each sample was then filtered through a 0.45 µm hydrophilic PTFE syringe filter before analysis by HPLC-MS. Parallel abiotic experiments containing 5 g (± 5 mg) of autoclaved Soil 2.4 (121 °C, 30 minutes) were prepared at a 1:1 soil solution ratio for 24, 48, 72 and 96 hours, for analysis of biodegradation in the non-autoclaved samples. Parallel control experiments (containing no soil) in plastic centrifuge tubes and 20 mL glass vials were tested to check for loss of polymer via sorption to test vessels, and loss via filtration was tested for polymer solutions. Based on these analyses, preliminary experiments for PEG to determine equilibration time were conducted using autoclaved soil and a 1:1 soil:solution ratio for 24 and 48 hours as described above.

4.2.4. Final adsorption experiment

The adsorption study was adapted from OECD Test No. 106: Adsorption - Desorption Using a Batch Equilibrium Method (OECD 2000a). Based on preliminary tests, a soil:solution ratio of 1:1, equilibration times of 24 hours (PEG) and 48 hours (PPG), and autoclaved soil were used for the sorption experiments (Figure 4.1).

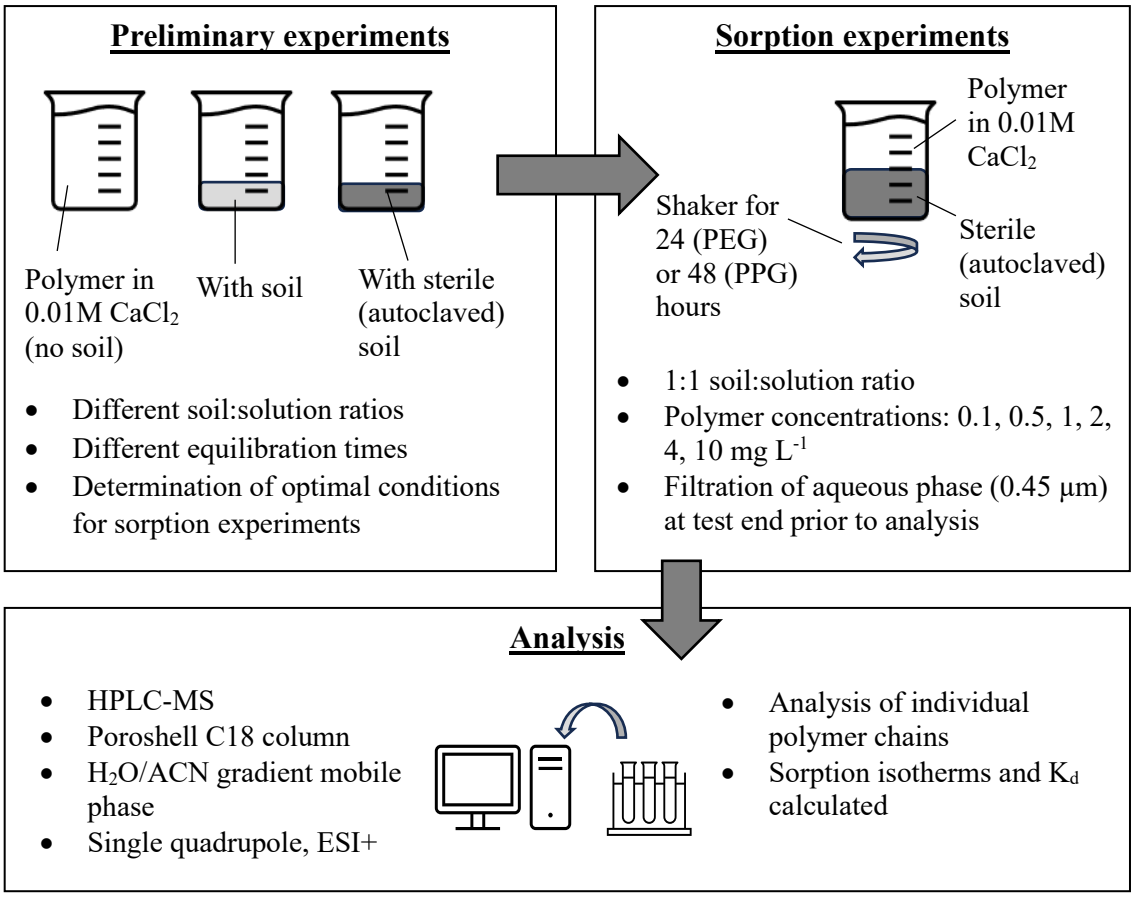


Figure 4.1: Summary of the experimental procedures employed for characterisation of PEG and PPG sorption to soil.

For each isotherm experiment, samples of 5 g of soil (± 5 mg) were weighed directly into a 20 mL glass vial before autoclaving at 121 °C for 30 minutes. Vial lids were sterilised using acetone. Where present, excess moisture from steam during autoclaving was poured out of samples (whilst minimising loss of soil) before use in isotherm experiments. Aliquots of 0.01 M $CaCl_2$ solution (made up using deionised water) were added to the autoclaved soil and left to equilibrate on an orbital shaker overnight (200 rpm). A solution of polymer in 0.01 M $CaCl_2$ was then added (in quantities ≤ 10 % of the final volume of solution) to give concentrations of 0.1, 0.5, 1, 2, 4, and 10 mg L^{-1} of polymer and final solution volumes of 5 mL (discounting soil). Concentrations were chosen to cover a two orders of magnitude concentration range (recommended in test method; OECD 2000a) whilst also covering similar concentration ranges to those estimated to occur in the natural environment (*Chapter 3*). Samples were left on an orbital shaker for 24 hours (PEG) or 48 hours (PPG) (200 rpm) in the dark, at room temperature, before being removed and left to settle for 30-60 minutes. Approximately 1.5 mL of the

supernatant of each sample was then filtered through a 0.45 µm hydrophilic PTFE syringe filter before analysis by HPLC-MS. In cases where the supernatant contained high amounts of suspended particulates causing filter blockage, multiple filters were used. The 10 mg L^{-1} samples were diluted 1 in 10 prior to analysis to ensure they fitted within the linear calibration range. Blank samples (containing no polymer) were included for each soil type, and control samples (containing polymer solution but no soil) were also included. All experimental samples and controls were prepared in triplicate.

4.2.5. HPLC-MS analysis of PPG-7

An HPLC-MS method was developed and optimised based on previously reported methods from the literature (Rissler *et al.* 1993; Rissler 1996; Zgoła-Grześkowiak *et al.* 2006; Davey *et al.* 2017; Thurman *et al.* 2017; Rogers *et al.* 2019). Analyses were conducted using a 1260 Infinity II LC/MSD iQ, equipped with an InfinityLab Poroshell 120 EC-C18 column (4.6 x 150 mm, 2.7 µm) maintained at 30 °C. The mobile phase comprised water and ACN. The initial mobile phase contained 5 % ACN with the ACN concentration then increasing over time (Table 4.3). The post-run time was 10 minutes. The mobile phase flow rate was 0.450 mL min^{-1}.

Table 4.3: Mobile phase gradient applied for HPLC-MS analysis of PPG-7.

Time (min)	Solvent A (H_2O) (%)	Solvent B (ACN) (%)
0	95	5
25	0	100
30	0	100
30.1	95	5

PPG homologues were detected via electrospray ionisation in positive ion mode (ESI+) using selected ion monitoring (SIM) of ions corresponding to $[M+Na]^+$ of homologues with chain lengths of 3 to 12 monomer units (Table 4.4). The single quadrupole mass detector parameters were as follows: gas temperature 325 °C, gas flow 10 L min^{-1}, nebuliser 40 psi, capillary voltage 3500 V, fragmentor 110 V.

Table 4.4: List of homologue chain lengths detected in PPG-7 mixture (MW_N ca. 400 g mol^{-1}), along with their corresponding theoretical molecular masses and detected mass of $[M+Na]^+$ (g mol^{-1}) used for SIM.

Homologue	Molecular mass	$[M+Na]^+$ mass
PPG-3	191	215
PPG-4	249	273
PPG-5	307	331
PPG-6	365	389
PPG-7	424	447
PPG-8	482	505
PPG-9	540	563
PPG-10	598	621
PPG-11	656	679
PPG-12	714	737

As standards were not available for the polymer mixtures or their component homologues, external calibration was used for quantitation, using 0.01, 0.1, 0.5, 1, 2, and 4 mg L^{-1} solutions of the polymer mixture (as the total concentration from all homologues present in the mixture) made up by dissolution of the pure liquid polymers in 0.01 M $CaCl_2$ and subsequent dilution. Individual polymer homologues of 4 to 10 monomer units were quantified by determining the relative proportions of each homologue using their peak areas from analysis of these solutions, assuming equal response in mass detection for each chain length. This allowed calibration curves to be obtained for each polymer chain length, which were weighted (1/amount) for improved fit and detection. Limits of detection (LoD) and quantitation (LoQ) were defined as a signal:noise ratio of 3 and 10, respectively, and were estimated for each homologue from analysis of the lowest concentration (0.01 and 0.1 mg L^{-1}) calibration standards. Linearity of the calibration curve for each homologue was determined from the R^2 value of the calibration line across the total concentration range (0.01 – 4 mg L^{-1}); p-values were determined from a two-tailed t-distribution (Microsoft Excel) for each curve, from t-statistics obtained using Equation 4.1:

$$t = \frac{r\sqrt{(n-2)}}{\sqrt{(1-r^2)}} \tag{4.1}$$

Where t is the t-statistic, r is the correlation coefficient (obtained from the R^2 of the calibration), and n is the sample size.

Repeatability was measured as the relative standard deviation of seven 2 mg L^{-1} calibration standards analysed between experimental samples over a 48 hour run. Note that all experimental replicates were randomised and spread out across the run for all HPLC-MS analyses.

4.2.6. HPLC-MS analysis of PEG-9

An HPLC-MS method was developed and optimised based on previously reported methods from the literature (Rissler *et al.* 1993; Rissler 1996; Zgoła-Grześkowiak *et al.* 2006; Davey *et al.* 2017; Thurman *et al.* 2017; Rogers *et al.* 2019) and from the developed method for PPG (Section 4.2.5). HPLC column, conditions, and MS parameters were the same as for PPG analysis with a differing HPLC mobile phase gradient and SIM of PEG homologues with chain lengths of 4 to 16 monomer units (Tables 4.5 and 4.6, respectively; previously tested gradients for analysis of PEG-9 are shown in Appendix 4.1). Individual homologues of 4 to 14 monomer units were quantified as described in Section 4.2.5; note that for homologues which produced multiple major ions in MS (PEG-13 and PEG-14), concentrations of the individual ions were calculated and summed to give a total concentration for each homologue. Method validation parameters (LoD, LoQ, linearity, and repeatability) were determined as described for PPG.

Table 4.5: Mobile phase gradient applied for HPLC-MS analysis of PEG-9.

Time (min)	Solvent A (H_2O) (%)	Solvent B (ACN) (%)
0	95	5
20	60	40
21	0	100
22	0	100
22.1	95	5

Table 4.6: List of homologue chain lengths detected in PEG-9 mixture (MW_N ca. 400 g mol^{-1}), along with their corresponding theoretical molecular masses and detected masses of $[M+Na]^+$ and $[M+2Na]^{2+}$ (g mol^{-1}) used for SIM.

Homologue	Molecular mass	$[M+Na]^+$ mass	$[M+2Na]^{2+}$ mass
PEG-4	193	217	Not monitored
PEG-5	237	261	Not monitored
PEG-6	281	305	Not monitored
PEG-7	325	349	Not monitored
PEG-8	369	393	Not monitored
PEG-9	413	437	Not monitored
PEG-10	457	481	Not monitored
PEG-11	502	525	Not monitored
PEG-12	546	569	Not monitored
PEG-13	590	613	318
PEG-14	634	657	340
PEG-15	678	701	362
PEG-16	722	745	384

4.2.7. Biodegradation data and half-life

The biodegradation curves for the total PPG-7 mixture and individual homologues were obtained using data from the preliminary experiments with non-sterilised (non-autoclaved) soil (Standard Soil 2.4) by correcting each measured concentration for losses due to sorption (obtained from the abiotic (autoclaved) sorption control experiment after 48 hours), according to Equation 4.2:

$$C_b = C_m \times \frac{C_i}{C_f} \tag{4.2}$$

Where C_b = corrected concentration for biodegradation experiment (i.e. losses only from biodegradation, mg L^{-1}), C_m = measured concentration for biodegradation experiment (mg L^{-1}), C_i = average initial polymer concentration (polymer standard solution; mg L^{-1}), and C_f = average final polymer concentration from abiotic control experiment (after 48 hours with autoclaved soil, mg L^{-1}).

The corrected concentrations were then subsequently used to derive concentration as a percentage of the concentration at time 0 (4 mg L^{-1} standard solution). The biodegradation half-life ($t_{1/2}$) was estimated for the total PPG-7 mixture as the time taken to reach approximately 50 % of the initial concentration.

4.2.8. Sorption isotherms and sorption coefficients

Initial concentrations of each polymer chain length added to test vessels were determined by calculation of theoretical concentrations for each chain length from LC-MS peak areas of calibration standards, in order to calculate concentrations of each chain length adsorbed to soil from measured solution concentrations for each sample.

Values of the distribution coefficient (K_d) and Freundlich adsorption coefficient (K_F), and corresponding confidence intervals, were determined in Microsoft Excel using linear regression analysis according to equations 4.3-4.5.

$$C_S = K_d \times C_W \quad (4.3)$$

$$C_S = K_F {C_W}^{1/n} \quad (4.4)$$

$$lnC_S = lnK_F + (1/n) lnC_W \quad (4.5)$$

Where K_d = distribution coefficient ($cm^3\ g^{-1}$), C_S = concentration of polymer in soil at equilibrium ($\mu g\ g^{-1}$), C_W = concentration of polymer in solution at equilibrium ($\mu g\ cm^{-3}$), K_F = Freundlich adsorption coefficient ($cm^3\ g^{-1}$ or $\mu g^{1-1/n}(cm^3)^{1/n}g^{-1}$), n = regression constant (OECD 2000a). K_d was thus determined as the gradient from linear regression according to Equation 4.3 (for concentrations 0.1-4 mg L^{-1}), and K_F was determined from the intercept from linear regression according to Equation 4.5 (for concentrations 0.1-10 mg L^{-1}), respectively. Associated p-values for the correlation coefficients of each linear regression were determined according to Equation 4.1 (Section 4.2.5). Other common sorption isotherms, including the Langmuir isotherm (Al-Ghouti and Da'ana 2020) were also plotted but were found to be poor fits for the data and thus were not analysed further. Values of K_d and K_F were determined for individual homologues and bulk polymer mixtures. Statistical analyses (Spearman's rank correlation) for analysis of relationships between soil properties and polyether sorption, and polymer properties and sorption, were conducted in Microsoft Excel.

Modelled estimates of K_{oc} (soil organic carbon/water partition coefficient) were determined using KOCWIN from EPI Suite (Estimation Program Interface; USEPA 2012) for individual PPG homologues of chain lengths 1-11, and PEG homologues of chain lengths 1-15, using molecular connectivity index (MCI)- and log(K_{ow})-based QSARs corrected for polar molecules. Over-correction adjustments were not used.

Predicted K_d values were then determined for each soil according to Equation 4.6 (OECD 2000a).

$$K_{oc} = K_d \frac{100}{\%C} \quad (4.6)$$

Where %C = percentage organic carbon content of the soil. Predicted values of K_d were compared to experimental data to assess the accuracy and suitability of the EPI Suite K_{oc} QSARs for the studied PEG and PPG, acting as a case study in determining how existing QSARs for low molecular weight single compounds may be applicable to polymer mixtures of low molecular weights.

4.3. Results and discussion

4.3.1. HPLC-MS analysis

The HPLC-MS methods used for analysis of PEG and PPG allowed separation and quantification of individual homologues in both polymer mixtures. Singly sodiated ions ($[M+Na]^+$) were the dominant species formed on ionisation for both polymers at lower chain lengths (Tables 4.4 and 4.6), with some negligible contribution from $[M+K]^+$ (not quantified); previous studies have also shown that sodiated ions and/or other ions formed by complexation of ethoxylated compounds with a cation can be expected to form as major species during MS analysis (e.g. Crescenzi *et al.* 1997; Cohen *et al.* 2001; Lara-Martin *et al.* 2011). As polymer chain length of PEG increased from 13 monomer units onwards, appearance of $[M+2Na]^{2+}$ ions was observed, increasing in intensity with polymer chain length until these became the dominant species for PEG-16.

Example chromatograms of the studied PEG and PPG mixtures are shown in Figure 4.2, with a typical distribution of polymer homologues being evident in both mixtures. “Shoulders” and peak broadening in PPG chromatograms were observed, arising from structural isomers in the PPG mixture (Davey *et al.* 2017; Rogers *et al.* 2019), the number of which exponentially increases with PPG chain length as the monomers (with varying positioning of the methyl group) increases.

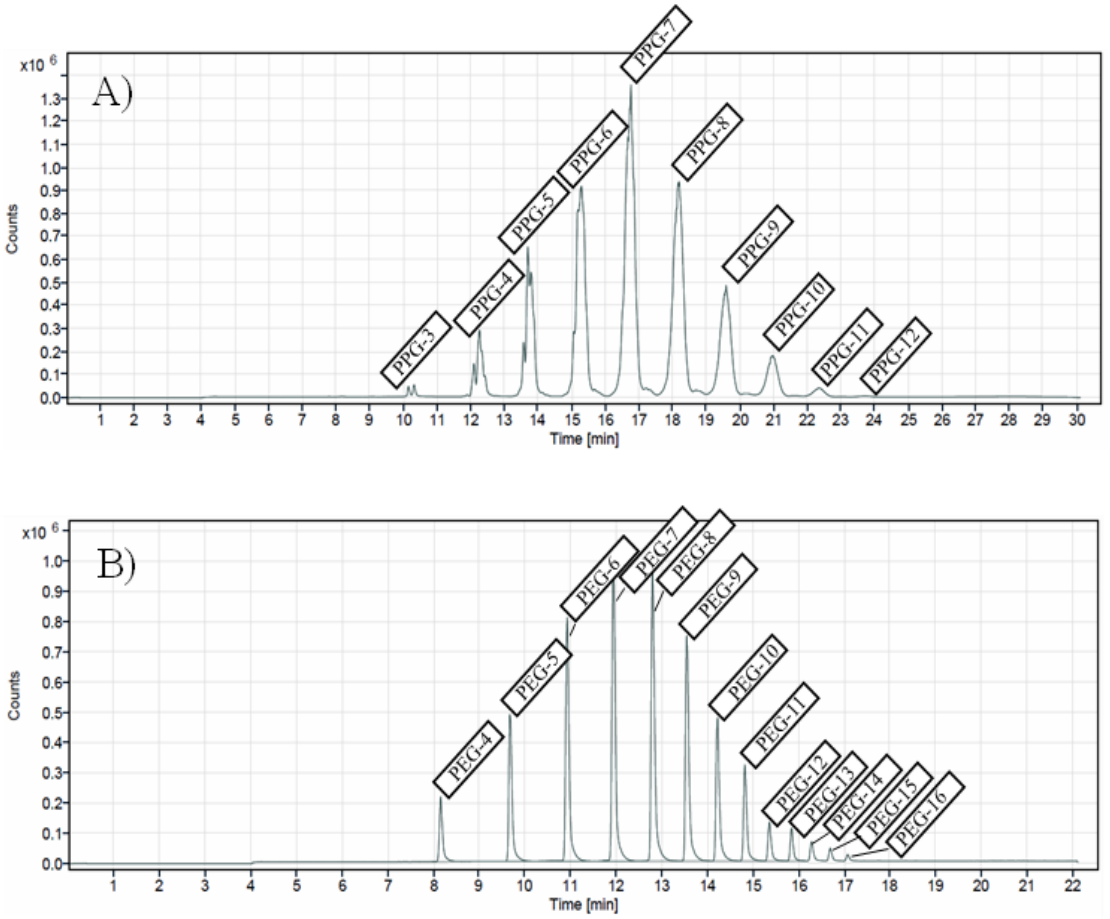


Figure 4.2: Example HPLC-MS chromatograms of A) PPG-7 and B) PEG-9 (both 2 mg L^{-1} calibration standards).

Although polymer chain lengths of 4-16 (PEG) and 3-12 (PPG) could be detected in many samples, homologues at the extremes of the distributions could not be reliably quantified at lower concentrations due to their relatively lower abundance, and thus only chain lengths of 4-14 (PEG) and 4-10 (PPG) were quantified. Limits of detection (LoD) ranged from < 1 to 2 µg L^{-1} for both PEG and PPG homologues, and limits of quantitation (LoQ) ranged from < 1 to 5 µg L^{-1} for PPG homologues and < 1 to < 20 µg L^{-1} for PEG homologues (Tables 4.7 and 4.8). Calibration curves displayed high linearity (> 98 %) across the concentration range (0.01 – 4 mg L^{-1} total polymer concentration) for all polymer homologues (Figure 4.3, Tables 4.7 and 4.8) and repeatability was at an acceptable level (relative standard deviation ≤ 15 %).

Table 4.7: Method validation for LC-MS analysis of PPG.

Homologue	Limit of detection (LoD, mg L^{-1})	Limit of quantitation (LoQ, mg L^{-1})	Linearity (%)	Repeatability (%)
PPG-4	0.002	0.005	98.8	9.5
PPG-5	0.001	0.002	98.7	11.0
PPG-6	<0.001	0.001	98.5	12.3
PPG-7	<0.002	<0.002	98.1	12.9
PPG-8	<0.001	<0.001	98.2	13.0
PPG-9	<0.001	<0.001	98.6	12.1
PPG-10	<0.001	<0.001	98.6	12.2

Table 4.8: Method validation for LC-MS analysis of PEG.

Homologue	Limit of detection (LoD, mg L^{-1})	Limit of quantitation (LoQ, mg L^{-1})	Linearity (%)	Repeatability (%)
PEG-4	<0.001	0.001	98.8	3.2
PEG-5	<0.001	<0.001	98.8	4.8
PEG-6	<0.002	<0.002	98.8	7.1
PEG-7	<0.002	0.002	98.6	6.9
PEG-8	0.002	<0.02	98.5	7.4
PEG-9	0.002	<0.02	98.5	7.5
PEG-10	0.001	<0.02	98.6	8.1
PEG-11	0.001	<0.01	98.6	7.8
PEG-12	0.001	0.006	98.8	8.3
PEG-13 (2Na)	<0.001	0.001	98.8	15.1
PEG-13 (1Na)	<0.001	0.003	98.8	8.6
PEG-14 (2Na)	<0.001	<0.001	98.8	14.5
PEG-14 (1Na)	<0.001	<0.001	98.9	7.6

It is worth noting that the present method assumed equal response of the individual homologues present in the polymer mixtures during electrospray ionisation in order to determine their relative concentrations and thus distributions (as polymer stock solutions could only be made up for the total concentration of all homologues present in the polymer mixtures), however in reality differences in response with polyether chain length are to be expected (Crescenzi *et al.* 1997; Pratesi *et al.* 2006; Lara-Martin *et al.* 2011), with detector response being expected to increase exponentially for PEG with chain lengths from 2-6 and only a slight increase in response with PEG chain length increasing above 6 (Lara-Martin *et al.* 2011). Whilst derivatisation to e.g. ethoxysulphates with analysis in negative ion mode has been developed for alkyl ethoxylate compounds to overcome this issue (with responses thus not being dependent on ion formation in the

mass spectrometer due to the covalently bonded anionic sulphate group being already present) (Pratesi *et al.* 2006), analysis of non-derivatised PEGs has still been successfully employed in environmental monitoring analyses (e.g. Lara-Martin *et al.* 2011) and thus polyethers were analysed in their native form in the present study.

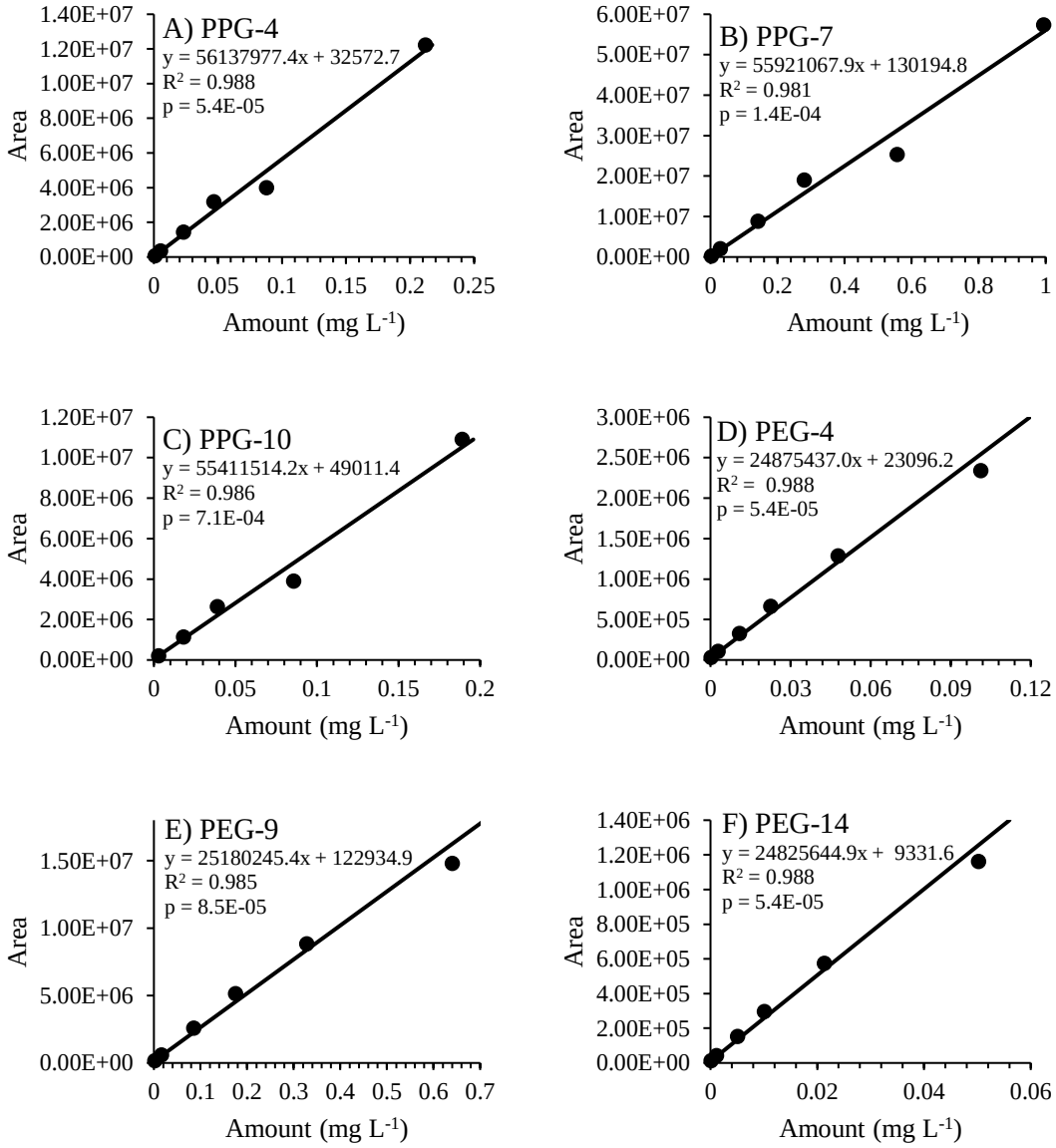


Figure 4.3: Example HPLC-MS calibration curves of A) PPG-4, B) PPG-7, C) PPG-10, D) PEG-4, E) PEG-9, and F) PEG-14 (singly sodiated ion, $[M+Na]^+$) for total polymer mixture concentrations from 0.01 – 4 mg L^{-1}. Calibration curves were weighted 1/x. Note that calibration curves were obtained from the HPLC-MS instrument software and recreated in Microsoft Excel by plotting the obtained calibration curves with their corresponding calibration data.

Whilst polyethers are a relatively well-studied class of water-soluble polymers, and previous studies have characterised some aspects of the environmental fate behaviour of individual polymer chains for several of these polymers (e.g. Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007; Bernhard *et al.* 2008; McLaughlin *et al.* 2016; Rogers *et al.* 2019), characterisation of environmental fate behaviour of individual polymer homologues quickly becomes unattainable for many higher molecular weight polymers using currently available methods, primarily due to low signal intensity and high complexity arising from analysis of polymers as complex mixtures (Huppertsberg *et al.* 2020). The use of relatively low molecular weight polymers in the present study allowed application of the developed methods to inform a case study in directly assessing the behaviour of individual polymer chains, along with the resulting implications for polymer environmental fate and risk assessment.

4.3.2. Preliminary experiments

Preliminary experiments indicated an optimum soil:solution ratio of 1:1 for sorption experiments to give the required levels of sorption (Appendix 4.2), as sorption levels of > 20% are recommended to reduce the error associated with measuring small changes in test substance concentrations (OECD 2000a). Equilibration times were determined to be 24 hours for PEG and 48 hours for PPG (based on stabilisation of concentration in abiotic preliminary experiments). Losses from sorption to test vessels and filtration were determined to be minimal (92 and 107 % recovery, respectively; equal recoveries were obtained using plastic and glass test vessels). Note that some losses were observed in some control experiments for the final sorption experiments, which were confirmed to be due to dilution from steam condensed in test vessels following autoclaving; thus measured concentrations in experimental samples are likely to indicate slightly higher levels of sorption than is actually occurring. However, losses in control experiments were variable and reliant on amounts of steam condensation in individual samples, and corrections often resulted in negative values for levels of sorption, and thus these losses were not corrected for in experimental data. Similarly, signal drift during analytical runs (Sections 4.2.5 and 4.2.6) was monitored, however correction frequently resulted in higher variability in data and negative values for levels of sorption, and thus signal drift was not corrected for and the associated analytical variability was assumed to be represented in the results of experimental repeats (which were spread out over the course of runs for all experiments).

A decrease in the total PPG concentration was observed over the course of 96 hours with non-sterilised Standard Soil 2.4; given that concentrations remained stable after 48 hours in experiments with sterilised (autoclaved) soil, these decreases were attributed to polymer biodegradation by soil microorganisms.

Individual PPG homologues were observed to degrade at different rates (Figure 4.4), with longer chain homologues disappearing faster and a shift to a lower molecular weight distribution being observed as degradation proceeded. Whilst for many polymers, longer polymer chains are expected to be more persistent (Duis *et al.* 2021), this shift to a lower molecular weight distribution with degradation has been observed previously for PPG (Tisler *et al.* 2021), and may result from chain fragmentation or from oxidation followed by cleavage of terminal ether bonds as has been suggested for the biodegradation mechanisms of PEG and PPG (Kawai 2002; Zgoła-Grześkowiak *et al.* 2006; West *et al.* 2007), leading to formation of shorter chain homologues as degradation products of longer polymer chains. In contrast, other studies have observed PPG biodegradation proceeding without shortening of polymer chains, potentially suggesting a different mechanism of degradation (Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007), or a lack of release of intracellular degradation products to the surrounding solution preventing their measurement (West *et al.* 2007). Studies have also observed no change in molecular weight distribution for PEG in artificial seawater (Bernhard *et al.* 2008), and a shift to higher molecular weights in agricultural topsoil (McLaughlin *et al.* 2016), suggesting that this phenomenon may not be limited to PPG. An alternative hypothesis to explain the more rapid degradation of longer polymer chains in PPG is from the influence of conformational effects, as PPG can form tightly coiled disks in aqueous solution which may extend on mixing, with longer flexible PPG chains undergoing a proportionally larger expansion and the extended, fully solvated PPG potentially having greater affinity for microbial enzymes or improved membrane transport (West *et al.* 2007). Faster degradation of longer PPG chains may also be a combination of degradation into shorter chains, and longer chains having greater hydrophobicity and thus potentially higher cellular uptake and higher biodegradation potential (Tisler *et al.* 2021).

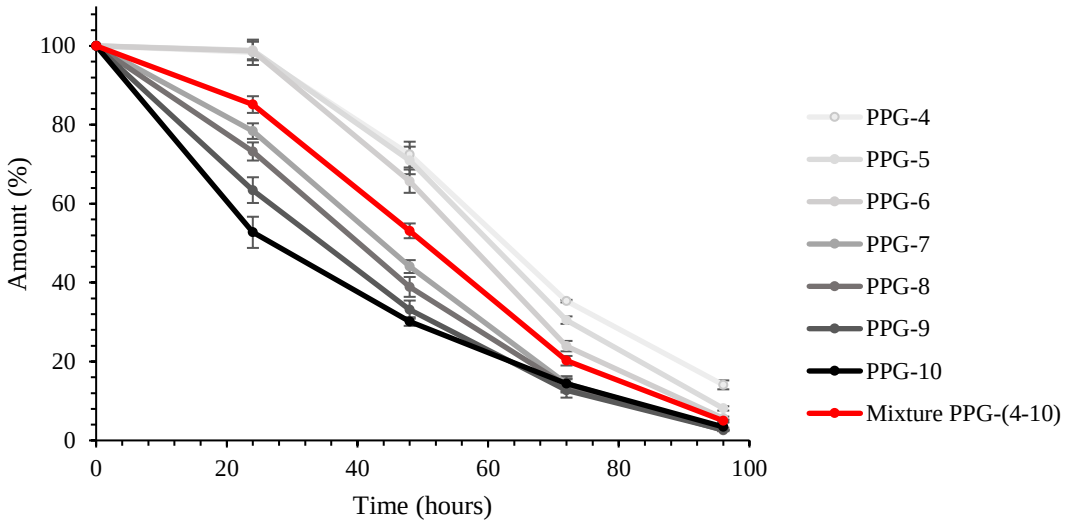


Figure 4.4: Degradation (presented as percentage of original concentration, corrected for losses due to sorption to soil) of individual PPG homologues and the total PPG-7 mixture (added at an initial total concentration of 4 mg L^{-1}) over time during experiment with non-sterilised soil (Soil 2.4).
Note that 0 hour sample is 4 mg L^{-1} calibration standard. Lines are links between datapoints, not fitted trendlines. Error bars show 95% confidence intervals calculated from experimental triplicates.

Due to the potential for formation of shorter polymer chains during biodegradation, values of the biodegradation half-life ($t_{1/2}$) could not be calculated for individual PPG homologues. Estimation of $t_{1/2}$ for the total mixture gives an approximate $t_{1/2}$ value of 48 hours (53% of initial concentration reached, Table 4.9), suggesting relatively rapid biodegradation of the polymer; this is expected given that PPG is expected to be readily biodegradable at low molecular weights (up to 1,000 g mol^{-1}) (Beran *et al.* 2013; Duis *et al.* 2021). Faster degradation was observed here than in some previous studies, with half-lives between 2.5 and 14 days being reported for PPG in microcosms simulating spills of hydraulic fracturing fluids (Rogers *et al.* 2019); however degradation is likely to depend on the experimental conditions and microbial community present.

Table 4.9: Change in concentration (presented as percentage of original concentration, corrected for losses due to sorption to soil) of the total PPG mixture (chain lengths 4-10) over time during experiment with non-sterilised soil (Soil 2.4).
95% confidence intervals calculated from experimental triplicates are shown in brackets. Data are also presented graphically in Figure 4.4.

Time (hours)	Concentration (%)
0	100.0 (± 2.5)
24	85.1 (± 2.1)
48	53.1 (± 1.9)
72	20.2 (± 1.2)
96	5.0 (± 0.3)

It should be noted that application of the bulk mixture $t_{1/2}$ value does not accurately encapsulate removal of individual polymer chains, particularly those at the extremes of the molecular weight distribution (Figure 4.4). Shorter polyether homologues are likely to undergo a slower overall rate of removal in the environment than higher molecular weight polymer chains, from their formation as degradation products and conformational influence on degradation rate (in the case of PPG) either alone or in combination, which is significant given that shorter polymer chains may often be expected to have higher hazard potential (OECD 2009). In the case of PPG, degradation rates can also be influenced by the structural isomers present (West *et al.* 2007; Rogers *et al.* 2019). This illustrates the complexity of polymer degradation analyses, given the potentially vast number of products that may form as well as the formation of some mixture components upon breakdown of others, and the influence of macromolecular conformational effects (Brunning *et al.* 2022). Further research into biodegradation of these polymers under environmentally relevant conditions is therefore warranted, along with research into these effects in other polymer types which may be present in the environment. Biodegradation of the case study polymers is further explored in *Chapter 5*.

4.3.3. Final adsorption experiment

4.3.3.1. Sorption isotherms and sorption coefficients

Adsorption isotherms for the total polymer mixtures plotted according to Equation 4.3 (linear isotherms) showed a mostly linear relationship at lower concentrations, with a deviation from linearity at the highest concentration (10 mg L^{-1}) for most soils (Figures 4.5 and 4.6). In general, it is expected that sorption will either continue to increase as the added concentration of a chemical compound is increased, or will plateau if soil sorption

sites become saturated, depending on the mechanism of sorption taking place (Podoll *et al.* 1987; Khalfaoui *et al.* 2003; Al-Ghouti and Da'ana 2020). The plateaus observed in the present study are therefore likely to be due to saturation of sorption sites at the highest concentration. Due to the shape of the isotherms, only the lower concentration range (0.1– 4 mg L^{-1}) was used for derivation of K_d values via linear regression.

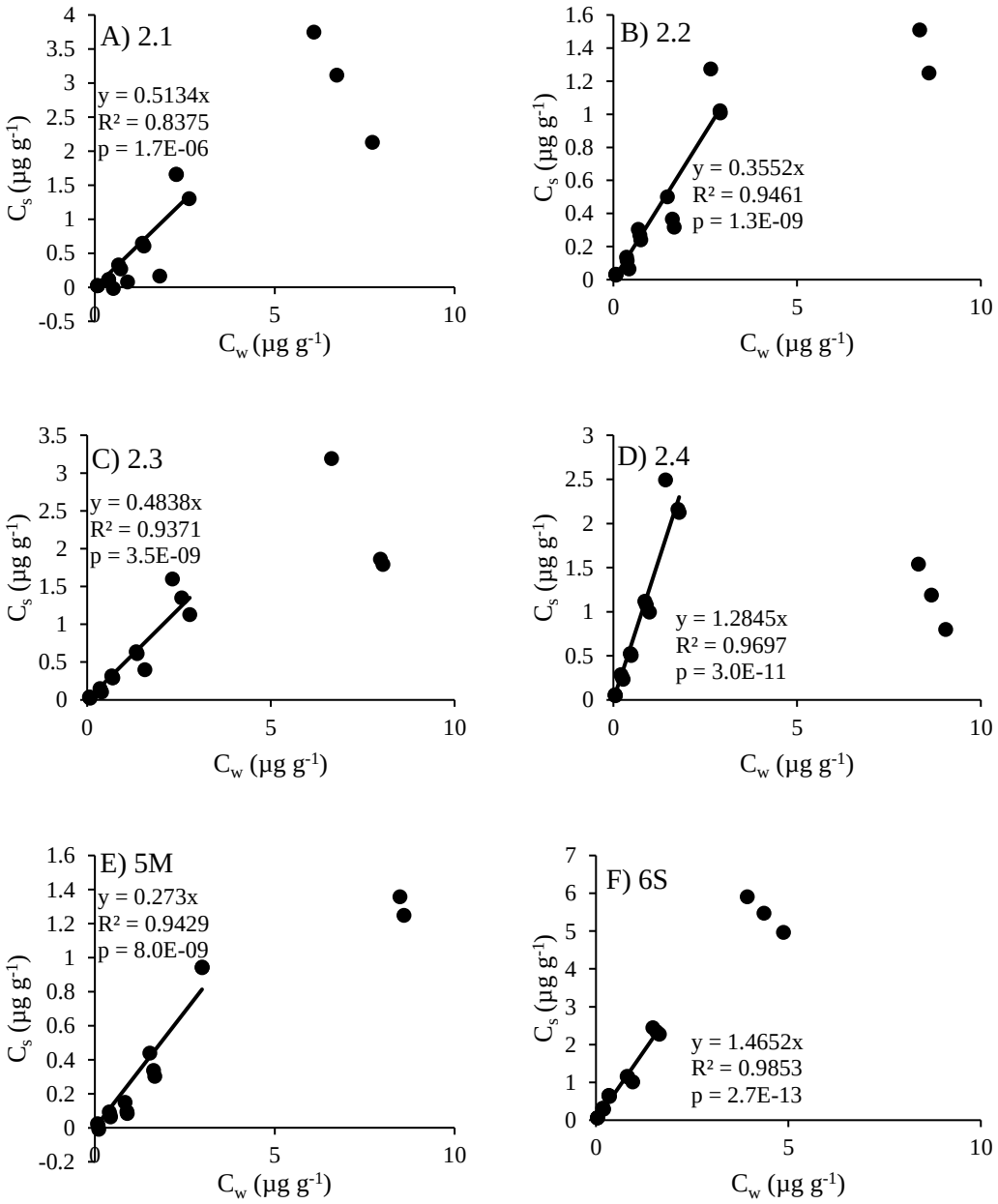


Figure 4.5: Linear isotherms for the total PPG mixture (chain lengths 4-10) used to calculate K_d for Standard Soils A) Soil 2.1; B) Soil 2.2; C) Soil 2.3; D) Soil 2.4; E) Soil 5M; and F) Soil 6S.

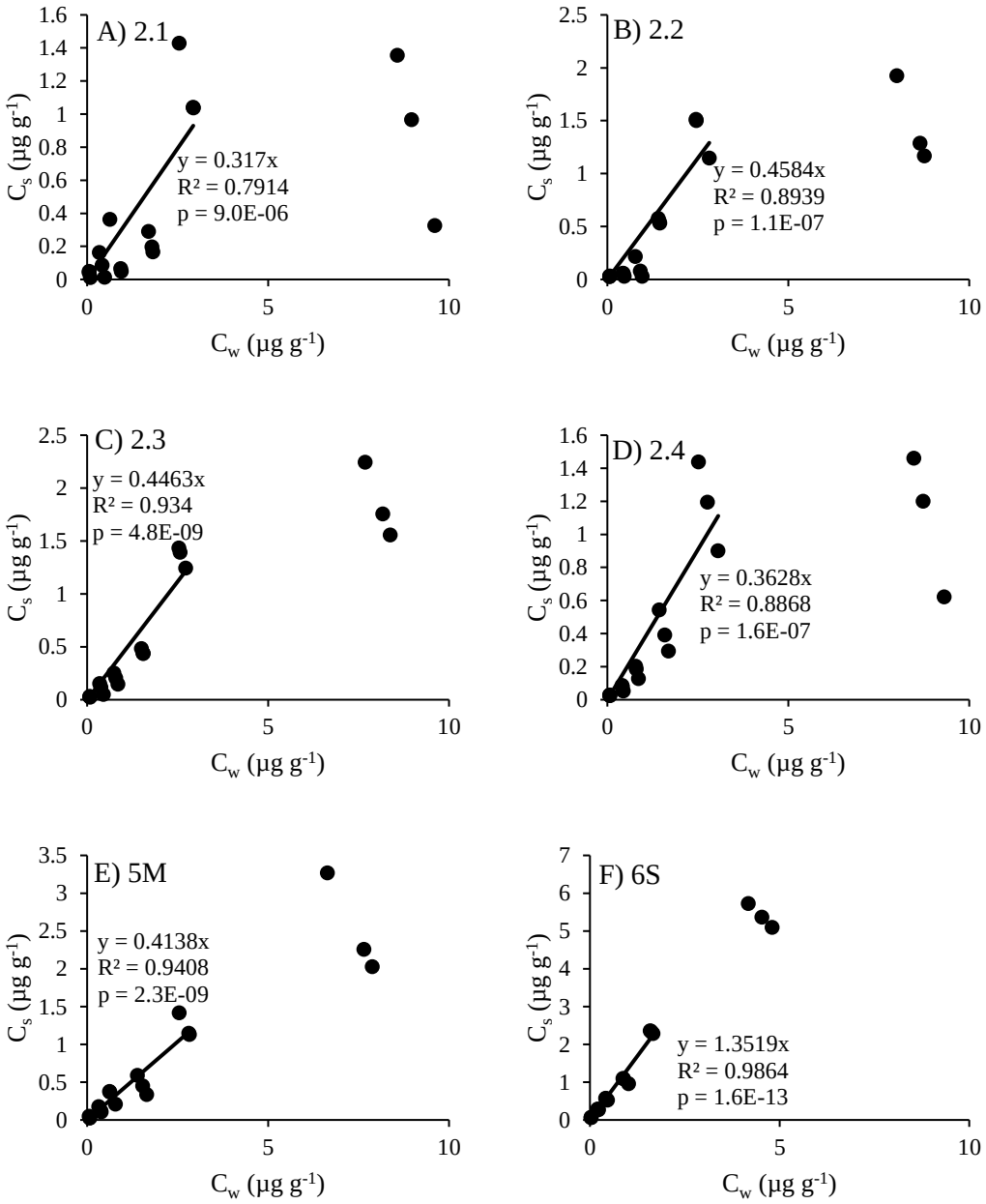


Figure 4.6: Linear isotherms for the total PEG mixture (chain lengths 4-14) used to calculate K_d for Standard Soils A) Soil 2.1; B) Soil 2.2; C) Soil 2.3; D) Soil 2.4; E) Soil 5M; and F) Soil 6S.

Analysis of linear isotherms of individual polymer chains (Appendices 4.3-4.14) shows differences in isotherm shape between longer and shorter polymer chains for both PPG and PEG, indicating changes in sorption behaviour with changing homologue chain length/molecular weight. In particular, atypical isotherms showing a decrease in sorption at higher concentrations were observed in the present study for shorter polymer chain lengths (up to a chain length of 9 in some cases) in some soils. This was not observed for longer polymer chains (chain length of 10 or greater), for which all isotherms either

continued to increase or levelled off at higher polymer concentrations. The observed decrease in sorption at higher concentrations for shorter homologues is likely to result from mixture interactions. Given that longer polymer chains are expected to have higher sorption coefficients than shorter chains (Podoll *et al.* 1987; Brownawell *et al.* 1997; McLaughlin *et al.* 2016; Section 4.3.3.3), competitive sorption may occur between polymer homologues of differing chain length, with longer chain homologues filling sorption sites at higher concentrations and resulting in a smaller proportion of shorter polymer chains being able to sorb to the soil. A similar atypical isotherm shape (with a decrease in apparent sorption at the highest concentration) was also observed for the total PPG mixture for Soil 2.4 (Figure 4.5-D), and again may result from saturation of sorption sites by longer (not quantified) polymer chains (PPG-11 and PPG-12). Despite the fact that these longer chain lengths are of a relatively low concentration compared to many of the shorter PPG chains, they may also occupy more sorption sites due to their larger size and thus have a proportionally larger effect than may be expected based on their concentrations.

Freundlich isotherms (Appendices 4.15-4.26) were plotted for the full concentration range (0.1 – 10 mg L^{-1}) for linear regression derivation of K_F and 1/n values due to the generally lower curvature at higher concentrations in the ln-transformed data. However similar to the linear isotherms, some polymer chain lengths and soils had a generally better fit whilst others were more curved. In general, both linear and Freundlich isotherm fit was improved for longer polymer chain lengths for both PEG and PPG for most soils, potentially due to mixture interactions more strongly impacting the sorption behaviour of the lower chain homologues as described above. Isotherm fit was also generally improved in soils with higher levels of sorption occurring, with e.g. Soil 6S (showing the highest levels of sorption for both PEG and PPG) giving relatively good fit of both linear and Freundlich isotherms for most chain lengths (Appendices 4.8, 4.14, 4.20, and 4.26). Since Freundlich isotherms in general did not have an improved fit (based on R^2 values) compared to linear isotherms for most polymer chain lengths, and calculated K_F values were broadly similar to K_d values but with wider confidence intervals, linear isotherms and corresponding K_d values are focussed on for the remainder of the discussion in the present study.

Overall, both PEG and PPG showed relatively little sorption across most of the studied soils, with K_d values for PEG homologues ranging from 0.28 – 19.68 $cm^3\ g^{-1}$, and values for PPG homologues ranging from 0.18 – 13.72 $cm^3\ g^{-1}$ (Tables 4.10 and 4.11). Several previous studies (Szymanski *et al.* 2003; de Brito Galvão *et al.* 2007; Castanho *et al.* 2009; Traverso-Soto *et al.* 2014; McLaughlin *et al.* 2016) have also reported low levels of sorption for PEG, to various solids (sludge, soil, and sediment). Traverso-Soto *et al.* (2014) report K_d values in the range of 100 and K_F values of 30-60 $cm^3\ g^{-1}$ for PEG of selected chain lengths (4, 6, and 8) sorbing to marine sediment at initial concentrations of 0.005 to 0.5 mg L^{-1}. These values, whilst relatively low, are still significantly higher than the values calculated for the soils and polymer mixtures in the present study, although it is worth noting that homologues were not analysed as a mixture, but instead as separate compounds (Traverso-Soto *et al.* 2014). Podoll *et al.* (1987) reported values of the sorption coefficient for PEG (600 and 1000 Da) sorbed to sediment ranging from 47 to 336 $cm^3\ g^{-1}$, with higher initial PEG concentrations (from a few mg L^{-1} to several thousand mg L^{-1}).

Most of the values calculated in the present study are closer to the values of K_d reported by Castanho *et al.* (2009) at < 0.31 $cm^3\ g^{-1}$, for sorption of PEG 4000 to agricultural soil. However, significantly increased sorption was observed in clay soil (Standard Soil 6S) for both polymers in the present study, particularly for longer chain homologues, with this soil also showing the strongest molecular weight dependence of sorption (Section 4.3.3.3). The results of the present study also show that like PEG, levels of PPG sorption to soil are low, with K_d values for PPG being similar to those for PEG.

Table 4.10: Values of the linear sorption coefficient (K_d), Freundlich sorption coefficient (K_F), and Freundlich regression constant (reported as 1/n) determined for PPG homologues and the PPG mixture, for each of the six studied soils.

PPG chain length	***PPG molecular weight (g mol^{-1})***	**Soil 2.1**	**Soil 2.2**	**Soil 2.3**	**Soil 2.4**	**Soil 5M**	**Soil 6S**
				K_d/ cm^3 g^{-1} (95% CI)			
4	249.327	0.37 (0.26-0.49)	0.33 (0.26-0.40)	0.40 (0.31-0.49)	1.19 (1.09-1.28)	0.21 (0.10-0.31)	0.48 (0.41-0.56)
5	307.407	0.44 (0.31-0.57)	0.35 (0.28-0.42)	0.45 (0.36-0.53)	1.21 (1.11-1.32)	0.21 (0.12-0.29)	0.67 (0.59-0.75)
6	365.487	0.49 (0.36-0.62)	0.35 (0.29-0.41)	0.46 (0.39-0.54)	1.26 (1.15-1.37)	0.23 (0.17-0.28)	1.01 (0.93-1.09)
7	423.567	0.51 (0.38-0.63)	0.33 (0.30-0.37)	0.46 (0.39-0.52)	1.05 (0.93-1.16)	0.18 (0.15-0.22)	1.21 (1.10-1.33)
8	481.647	0.55 (0.42-0.68)	0.35 (0.31-0.39)	0.49 (0.41-0.57)	1.31 (1.16-1.46)	0.29 (0.24-0.33)	2.57 (2.29-2.85)
9	539.727	0.61 (0.46-0.76)	0.41 (0.35-0.47)	0.58 (0.48-0.68)	1.77 (1.52-2.01)	0.48 (0.38-0.58)	5.45 (4.67-6.23)
10	597.807	0.69 (0.52-0.85)	0.45 (0.38-0.52)	0.69 (0.56-0.82)	2.61 (2.25-2.96)	1.07 (0.82-1.32)	13.72 (10.88-16.56)
4-10 (mixture)	Mixture	0.51 (0.38-0.64)	0.36 (0.31-0.40)	0.48 (0.41-0.56)	1.28 (1.15-1.41)	0.27 (0.23-0.31)	1.47 (1.36-1.57)
				K_F/ µg$^{1-1/n}$ (cm^3)$^{1/n}$ g^{-1} (95% CI)			
4	249.327	0.28 (0.15-0.54)	0.10 (0.05-0.23)	0.16 (0.08-0.32)	0.18 (0.07-0.50)	0.11 (0.02-0.61)	0.42 (0.30-0.58)
5	307.407	0.24 (0.05-1.08)	0.17 (0.11-0.27)	0.23 (0.15-0.35)	0.27 (0.14-0.54)	0.04 (0.01-0.14)	0.50 (0.41-0.60)
6	365.487	0.33 (0.19-0.58)	0.21 (0.15-0.29)	0.30 (0.23-0.40)	0.38 (0.22-0.65)	0.06 (0.02-0.15)	0.81 (0.72-0.92)
7	423.567	0.34 (0.15-0.79)	0.24 (0.19-0.30)	0.35 (0.28-0.44)	0.29 (0.17-0.51)	0.12 (0.08-0.18)	1.06 (0.92-1.22)
8	481.647	0.44 (0.20-0.94)	0.27 (0.21-0.34)	0.42 (0.32-0.55)	0.40 (0.23-0.70)	0.19 (0.08-0.46)	2.09 (1.71-2.54)
9	539.727	0.84 (0.50-1.42)	0.25 (0.13-0.47)	0.65 (0.40-1.05)	0.57 (0.28-1.18)	0.39 (0.20-0.75)	4.86 (3.27-7.23)
10	597.807	1.25 (0.56-2.81)	0.25 (0.16-0.39)	0.59 (0.37-0.94)	1.50 (0.67-3.34)	2.60 (1.06-6.39)	10.26 (2.68-39.37)
4-10 (mixture)	Mixture	0.36 (0.26-0.50)	0.30 (0.25-0.36)	0.40 (0.34-0.47)	0.69 (0.49-0.98)	0.17 (0.11-0.24)	1.47 (1.36-1.58)

(Table 4.10 continued)

PPG chain length	***PPG molecular weight (g mol^{-1})***	**Soil 2.1**	**Soil 2.2**	**Soil 2.3**	**Soil 2.4**	**Soil 5M**	**Soil 6S**
				1/n (95% CI)			
4	249.327	1.04 (0.85-1.22)	0.71 (0.49-0.93)	0.85 (0.64-1.06)	0.62 (0.34-0.90)	1.00 (0.49-1.52)	1.07 (0.98-1.17)
5	307.407	1.02 (0.46-1.58)	0.78 (0.61-0.95)	0.86 (0.70-1.02)	0.61 (0.38-0.84)	0.68 (0.21-1.16)	0.93 (0.87-1.00)
6	365.487	0.98 (0.72-1.24)	0.78 (0.64-0.92)	0.88 (0.76-1.00)	0.63 (0.42-0.84)	0.67 (0.19-1.15)	0.88 (0.83-0.92)
7	423.567	1.06 (0.64-1.48)	0.81 (0.69-0.92)	0.91 (0.80-1.02)	0.51 (0.28-0.75)	0.93 (0.70-1.16)	0.84 (0.78-0.89)
8	481.647	1.15 (0.81-1.49)	0.91 (0.80-1.03)	0.99 (0.87-1.11)	0.63 (0.42-0.84)	1.02 (0.62-1.42)	0.84 (0.78-0.90)
9	539.727	1.35 (1.16-1.54)	1.00 (0.77-1.22)	1.16 (1.00-1.33)	0.79 (0.57-1.00)	1.03 (0.79-1.27)	0.91 (0.82-1.00)
10	597.807	1.32 (1.08-1.57)	0.90 (0.79-1.02)	0.97 (0.85-1.09)	1.01 (0.83-1.19)	1.36 (1.14-1.59)	0.88 (0.64-1.11)
4-10 (mixture)	Mixture	1.05 (0.84-1.27)	0.85 (0.73-0.97)	0.94 (0.83-1.05)	0.65 (0.45-0.86)	0.83 (0.57-1.09)	0.90 (0.86-0.95)

Table 4.11: Values of the linear sorption coefficient (K_d), Freundlich sorption coefficient (K_F), and Freundlich regression constant (reported as 1/n) determined for PEG homologues and the PEG mixture, for each of the six studied soils.

PEG chain length	***PEG molecular weight (g mol^{-1})***	**Soil 2.1**	**Soil 2.2**	**Soil 2.3**	**Soil 2.4**	**Soil 5M**	**Soil 6S**
				K_d/ cm^3 g^{-1} (95% CI)			
4	193.195	0.28 (0.19-0.38)	0.81 (0.69-0.92)	0.44 (0.35-0.54)	0.38 (0.29-0.48)	0.35 (0.29-0.41)	0.40 (0.35-0.46)
5	237.242	0.29 (0.19-0.39)	0.63 (0.53-0.73)	0.42 (0.36-0.48)	0.41 (0.32-0.51)	0.36 (0.30-0.42)	0.53 (0.49-0.58)
6	281.289	0.29 (0.21-0.37)	0.57 (0.48-0.66)	0.44 (0.39-0.50)	0.35 (0.27-0.43)	0.37 (0.31-0.43)	0.63 (0.57-0.69)
7	325.336	0.29 (0.19-0.39)	0.43 (0.35-0.52)	0.40 (0.34-0.47)	0.30 (0.22-0.38)	0.31 (0.26-0.36)	0.66 (0.62-0.71)
8	369.383	0.32 (0.21-0.42)	0.40 (0.31-0.49)	0.39 (0.33-0.46)	0.28 (0.21-0.35)	0.33 (0.28-0.39)	0.86 (0.80-0.92)
9	413.43	0.32 (0.22-0.41)	0.39 (0.31-0.47)	0.42 (0.36-0.49)	0.29 (0.23-0.35)	0.35 (0.30-0.41)	1.27 (1.18-1.36)
10	457.477	0.35 (0.23-0.46)	0.40 (0.32-0.49)	0.45 (0.38-0.52)	0.37 (0.31-0.44)	0.41 (0.35-0.47)	1.96 (1.79-2.12)
11	501.524	0.39 (0.29-0.48)	0.45 (0.35-0.55)	0.51 (0.43-0.58)	0.43 (0.36-0.50)	0.51 (0.44-0.57)	3.43 (3.14-3.71)
12	545.571	0.37 (0.27-0.46)	0.49 (0.38-0.61)	0.56 (0.47-0.64)	0.61 (0.53-0.68)	0.63 (0.56-0.70)	5.93 (5.34-6.51)
13	589.618	0.48 (0.40-0.57)	0.55 (0.43-0.67)	0.62 (0.53-0.70)	0.83 (0.74-0.91)	0.85 (0.76-0.94)	10.84 (9.78-11.91)
14	633.665	0.47 (0.37-0.57)	0.61 (0.49-0.73)	0.70 (0.61-0.80)	1.15 (1.05-1.24)	1.21 (1.10-1.32)	19.68 (17.60-21.75)
4-14 (mixture)	Mixture	0.32 (0.22-0.41)	0.46 (0.37-0.55)	0.45 (0.38-0.51)	0.36 (0.29-0.44)	0.41 (0.35-0.47)	1.35 (1.26-1.44)
				K_F/ µg$^{1-1/n}$ (cm^3)$^{1/n}$ g^{-1} (95% CI)			
4	193.195	0.22 (0.04-1.39)	0.19 (0.08-0.48)	0.16 (0.07-0.37)	0.45 (0.03-5.77)	0.17 (0.09-0.33)	0.19 (0.10-0.38)
5	237.242	0.10 (0.03-0.27)	0.23 (0.11-0.49)	0.19 (0.09-0.39)	0.09 (0.04-0.21)	0.18 (0.11-0.30)	0.25 (0.19-0.35)
6	281.289	0.11 (0.06-0.19)	0.20 (0.10-0.42)	0.20 (0.12-0.33)	0.10 (0.05-0.19)	0.21 (0.13-0.33)	0.33 (0.24-0.46)
7	325.336	0.10 (0.03-0.29)	0.20 (0.10-0.38)	0.24 (0.17-0.36)	0.05 (0.02-0.15)	0.24 (0.15-0.36)	0.51 (0.43-0.61)
8	369.383	0.11 (0.05-0.24)	0.21 (0.11-0.38)	0.26 (0.18-0.37)	0.13 (0.08-0.21)	0.28 (0.19-0.40)	0.75 (0.66-0.87)
9	413.43	0.17 (0.08-0.38)	0.22 (0.11-0.41)	0.32 (0.23-0.43)	0.12 (0.07-0.20)	0.33 (0.23-0.47)	1.13 (0.98-1.30)
10	457.477	0.15 (0.07-0.32)	0.21 (0.10-0.41)	0.29 (0.21-0.41)	0.22 (0.16-0.31)	0.35 (0.25-0.48)	1.63 (1.33-1.99)
11	501.524	0.17 (0.06-0.48)	0.22 (0.09-0.55)	0.35 (0.24-0.51)	0.28 (0.20-0.40)	0.42 (0.31-0.57)	2.24 (1.63-3.07)

(Table 4.11 continued)

PEG chain length	***PEG molecular weight (g mol^{-1})***	**Soil 2.1**	**Soil 2.2**	**Soil 2.3**	**Soil 2.4**	**Soil 5M**	**Soil 6S**
				K_F/ μg$^{1-1/n}$ (cm^3)$^{1/n}$ g^{-1} (95% CI) ***(continued)***			
12	545.571	0.18 (0.05-0.65)	0.23 (0.06-0.83)	0.31 (0.19-0.51)	0.48 (0.33-0.69)	0.53 (0.39-0.70)	5.32 (3.41-8.29)
13	589.618	1.09 (0.03-36.41)	0.20 (0.06-0.72)	0.39 (0.25-0.60)	0.48 (0.33-0.70)	0.46 (0.31-0.68)	9.36 (4.46-19.68)
14	633.665	0.27 (0.07-1.03)	0.21 (0.06-0.69)	0.35 (0.20-0.63)	1.17 (0.56-2.45)	0.94 (0.63-1.40)	19.24 (9.76-37.93)
4-14 (mixture)	Mixture	0.18 (0.11-0.30)	0.23 (0.15-0.35)	0.31 (0.25-0.39)	0.23 (0.18-0.30)	0.39 (0.33-0.47)	1.29 (1.18-1.41)
				1/n (95% CI)			
4	193.195	1.29 (0.65-1.92)	0.75 (0.52-0.97)	0.85 (0.62-1.08)	1.30 (0.55-2.06)	0.82 (0.67-0.97)	0.85 (0.68-1.01)
5	237.242	0.79 (0.43-1.14)	0.82 (0.60-1.04)	0.87 (0.65-1.08)	0.70 (0.43-0.96)	0.79 (0.63-0.95)	0.77 (0.69-0.86)
6	281.289	0.65 (0.41-0.88)	0.79 (0.54-1.04)	0.81 (0.64-0.98)	0.67 (0.44-0.91)	0.80 (0.65-0.96)	0.78 (0.68-0.88)
7	325.336	0.82 (0.34-1.29)	0.92 (0.64-1.20)	0.93 (0.77-1.09)	0.57 (0.07-1.07)	0.89 (0.73-1.06)	0.89 (0.82-0.95)
8	369.383	0.68 (0.33-1.03)	0.98 (0.71-1.24)	0.99 (0.84-1.14)	0.86 (0.66-1.07)	0.96 (0.80-1.11)	0.93 (0.88-0.98)
9	413.43	0.84 (0.53-1.14)	1.06 (0.78-1.34)	1.04 (0.91-1.16)	0.80 (0.57-1.04)	0.99 (0.84-1.14)	0.92 (0.88-0.97)
10	457.477	0.73 (0.45-1.01)	1.03 (0.76-1.30)	0.98 (0.85-1.11)	0.90 (0.77-1.03)	0.96 (0.83-1.09)	0.92 (0.86-0.98)
11	501.524	0.84 (0.53-1.15)	1.06 (0.74-1.38)	1.01 (0.88-1.13)	0.93 (0.82-1.05)	0.93 (0.83-1.04)	0.86 (0.78-0.94)
12	545.571	0.90 (0.59-1.21)	1.10 (0.71-1.48)	0.93 (0.79-1.08)	0.98 (0.88-1.08)	0.95 (0.87-1.04)	0.98 (0.87-1.09)
13	589.618	1.40 (0.48-2.32)	0.96 (0.63-1.30)	0.96 (0.85-1.08)	0.87 (0.78-0.95)	0.81 (0.72-0.90)	0.96 (0.82-1.11)
14	633.665	0.94 (0.62-1.27)	0.91 (0.64-1.18)	0.91 (0.78-1.04)	1.03 (0.87-1.20)	0.94 (0.86-1.03)	1.01 (0.89-1.13)
4-14 (mixture)	Mixture	0.73 (0.41-1.04)	0.95 (0.65-1.24)	0.94 (0.80-1.09)	0.86 (0.69-1.02)	0.91 (0.78-1.03)	0.90 (0.85-0.95)

4.3.3.2. Influence of soil properties on polyether sorption

Statistical analyses (Spearman's rank correlation) were performed to assess the impact of soil properties on sorption of the studied polyethers. Spearman's rank was used due to the fact that a linear relationship between the variables was not apparent, and thus testing for a monotonic (but not linear) relationship was most applicable. Correlation of percentage adsorption (which is directly related to K_d) with soil properties was analysed for total homologue mixtures for each initial polymer concentration, to give more data pairs for statistical analyses (as only a single K_d value was available for each soil from isotherm graphs (giving six data pairs), whereas percentage adsorption could be calculated for each experimental triplicate and analysed for correlation with soil properties (giving 18 data pairs for each concentration)). However, it should be noted that soil properties as reported from Lufa Speyer (Table 4.1) are for non-autoclaved soil, and autoclaving may significantly affect soil properties (Lees *et al.* 2018); if these changes in soil properties are not uniform across the studied soil types, the results of statistical analyses may be impacted. Therefore, the correlation analyses performed in the present study are preliminary, and testing of soil properties after autoclaving is required to verify the results.

Adsorption did not show a significant correlation with soil pH for either of the two polymers (p-value > 0.05 for all polymer concentrations, Appendices 4.27 and 4.28). Similarly, sorption of PEG was not correlated with soil carbon or nitrogen content (note that values of the Spearman's rank coefficient R_s and p-values are the same for these two soil properties for each polymer, due to the soils having the same ranking of these properties). Sorption of PPG also did not significantly correlate with soil carbon or nitrogen content (p-values > 0.05 for all polymer concentrations except 0.1 and 0.5 mg L^{-1}, Appendix 4.27). The potentially significant positive correlation at the two lowest concentrations could be due to minor hydrophobic interactions due to the slightly increased hydrophobicity of PPG compared to PEG; however, the correlation was not strong ($R_s < 0.60$), and visual analysis of the relationship between soil carbon/nitrogen content and percentage sorption was also not indicative of correlation (Appendices 4.29 and 4.30), and thus the present data do not suggest that sorption is strongly correlated with soil organic carbon or nitrogen for PPG. Previous studies have also shown that PEG sorption is independent of soil organic carbon content (Podoll *et al.* 1987; Castanho *et al.* 2009). In the present study, the soil which resulted in the highest levels of polymer

sorption was Soil 6S (clayey loam, 1.50 %C) which had the highest clay mineral content. Sorption of polyethers to clay minerals was therefore concluded to be the likely main mechanism of sorption. Values of K_{oc} were therefore not relevant and thus not calculated or used in the present study.

Sorption of PEG to clay minerals is also supported by previous studies, with hydrogen bonding being suggested as the key sorption mechanism (Podoll *et al.* 1987); this may also explain the overall low levels of polyether sorption observed in the present and some previous studies (e.g. Szymanski *et al.* 2003; de Brito Galvão *et al.* 2007; Castanho *et al.* 2009; Traverso-Soto *et al.* 2014; McLaughlin *et al.* 2016), as hydrogen bonding with water can also occur (Castanho *et al.* 2009). As has been suggested previously for alkyl-PEG compounds, hydrogen bonding may occur between minerals and ether groups along the polymer chain or terminal hydroxy groups (Brownawell *et al.* 1997).

In the present study, a moderate positive correlation between polyether sorption and soil cation exchange capacity and percentage of particles < 0.002 mm was observed, with PPG at initial concentrations of 0.1 – 2 mg L^{-1} and PEG at initial concentrations of 1, 2, and 10 mg L^{-1} showing statistically significant correlation for these two properties (R_s values between 0.5 and 0.7, p-values < 0.05, Appendices 4.27 and 4.28). Although it is not possible to separate these two properties in terms of their potential effects on polyether sorption due to both properties having the same rankings across soils (and thus the same values of R_s and p-values), since cation exchange capacity describes the ability of the soil to exchange cations, this property is unlikely to significantly affect sorption of polyethers. In contrast, soils with a greater percentage of particles of the smallest size range (< 0.002 mm) will have a greater surface area available for hydrogen bonding with PEG or PPG and thus it can be expected that sorption will increase in this case. Visual analysis of these relationships confirms that some correlation is likely to be present between polyether sorption and percentage of particles < 0.002 mm at these polymer concentrations (Appendices 4.31 and 4.32).

4.3.3.3. Impact of polymer properties

Values of K_d appear to increase with polymer chain length for many of the studied soils (Figures 4.7 and 4.8). Spearman's rank correlation confirmed a statistically significant positive correlation between percentage adsorption and chain length for most polymer concentrations in soils 2.3, 2.4, 5M, and 6S (Appendices 4.33 and 4.34), with

the strongest correlation being seen for Soil 6S (clayey loam, 1.50 %C) for both PEG and PPG (R_s > 0.7, p-value < 0.05 for all polymer concentrations). In contrast, fewer significant positive correlations were observed for soils 2.1 and 2.2, with significant negative correlations being observed at some polymer concentrations (R_s < -0.4, p-value < 0.05, Appendices 4.33 and 4.34). Given that K_d values for soils 2.1 and 2.2 were low in general, competitive hydrogen bonding of the polyether chains with water in solution (Castanho *et al.* 2009) rather than soil minerals may have contributed to these effects. For the other soils, however (2.3, 2.4, 5M, and 6S), it can be concluded that the observed increases in K_d with polymer chain length (Figures 4.7 and 4.8) are statistically significant. A QSAR between chain length (or molecular weight) and polyether sorption to these soils can thus be developed for this range of homologues. Increase in polyether sorption with chain length may be due to a range of factors, including: more ether groups in longer chains allowing a greater number of sorption interactions to occur, as well as greater possibility of ether groups to interact; reduced chances of desorption and partially irreversible desorption; and longer polymer chains having higher degrees of freedom (i.e. more possible conformations) and thus greater potential to rearrange and favourably interact with soil minerals (Podoll *et al.* 1987; Brownawell *et al.* 1997).

In soils with significant increases in K_d values with polymer chain length, K_d values of the individual homologues deviate more strongly from the K_d values calculated for the bulk polymer mixture (Figures 4.7 and 4.8). It is already expected that application of bulk K_d values to a polymer mixture may not encapsulate parameters of individual homologues, preventing accurate characterisation of the changes in molecular weight distribution that may occur in reality (e.g. Podoll *et al.* 1987), with the anticipated shift to lower molecular weights in solution having been observed previously for PEG 400 sorbed to soil (McLaughlin *et al.* 2016) and in the present study upon sorption of both PPG and PEG to Soil 6S (Appendix 4.35). For Soil 6S, only one K_d value for an individual polymer homologue is within the 95% confidence interval of the mixture K_d value across both polymers (Figures 4.7-F and 4.8-F). This is important to note in environmental exposure assessment, since application of a bulk mixture K_d value may significantly over- or under-estimate sorption of polymer homologues at the extremes of the distribution; reporting of K_d as a range (rather than a single value) may be necessary for many polymer types (ECETOC 2020).

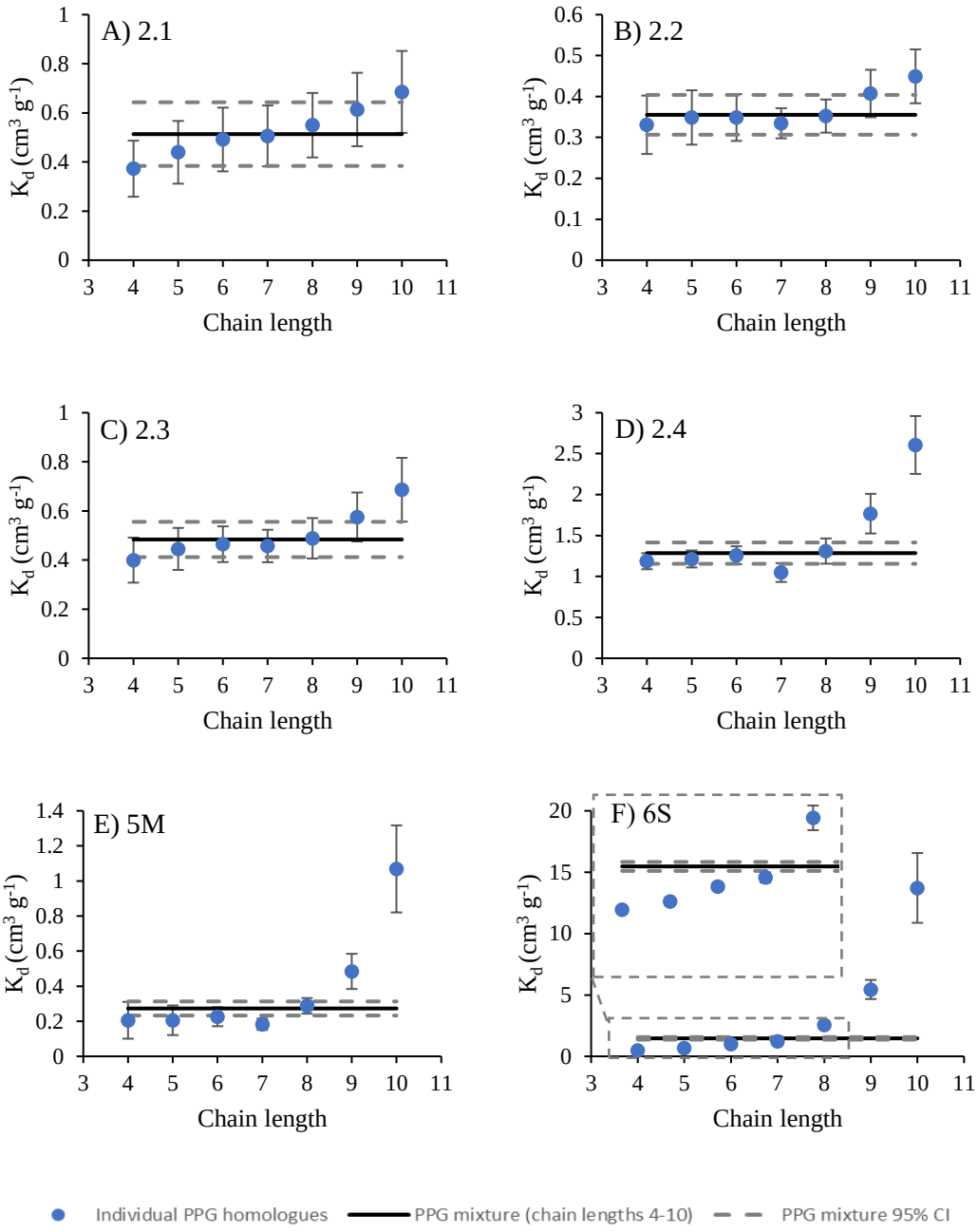


Figure 4.7: Comparison of calculated values of linear sorption coefficient (K_d) for individual PPG homologues with values calculated for the total PPG mixture, for A) Soil 2.1, B) Soil 2.2, C) Soil 2.3, D) Soil 2.4, E) Soil 5M, and F) Soil 6S. Error bars show 95% confidence intervals for K_d calculated from regression analysis. Expanded axis is shown for K_d = 0 – 3, and chain length = 4-8, for Soil 6S.

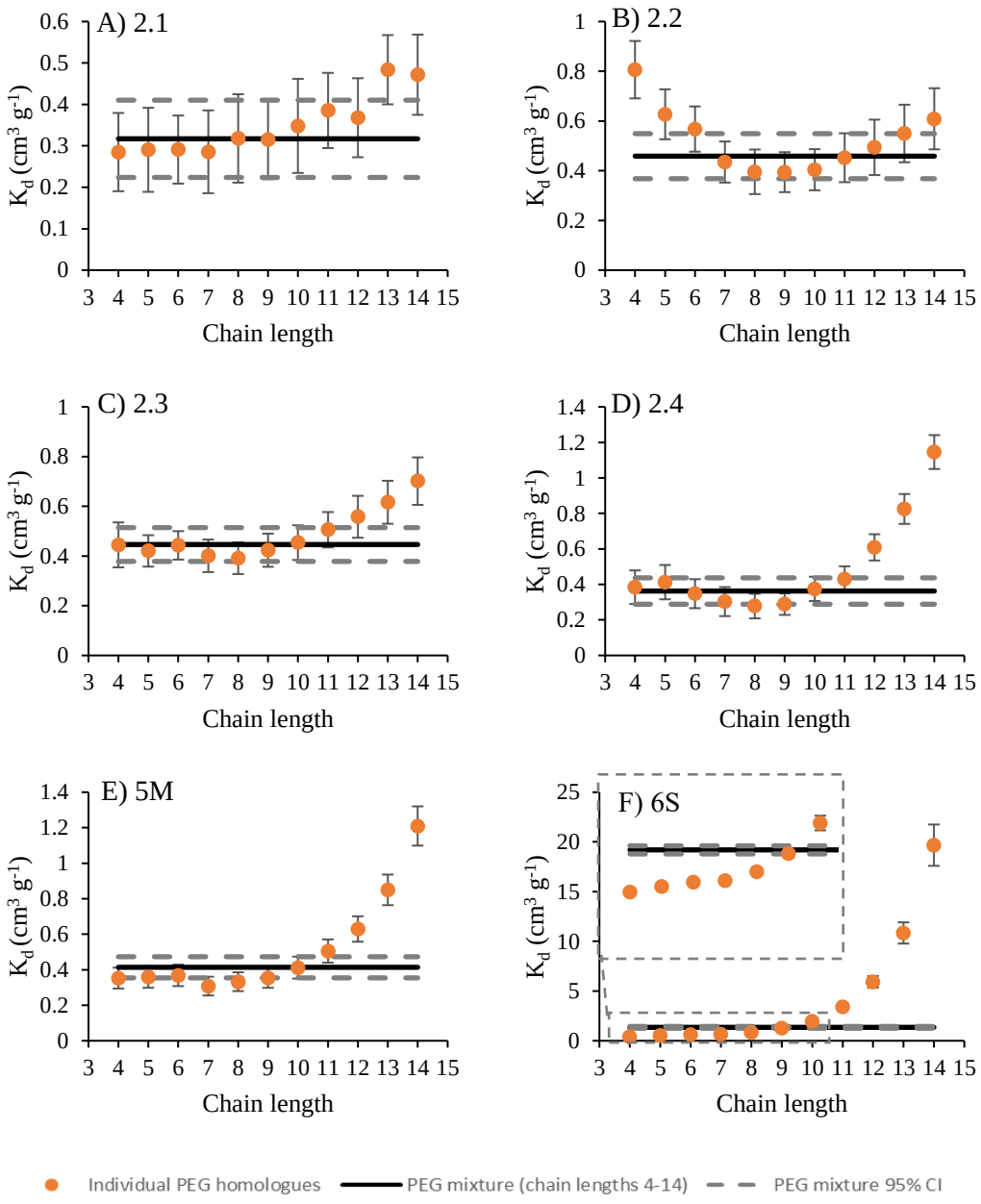


Figure 4.8: Comparison of calculated values of linear sorption coefficient (K_d) for individual PEG homologues with values calculated for the total PEG mixture, for A) Soil 2.1, B) Soil 2.2, C) Soil 2.3, D) Soil 2.4, E) Soil 5M, and F) Soil 6S. Error bars show 95% confidence intervals for K_d calculated from regression analysis. Expanded axis is shown for K_d = 0 – 3, and chain length = 4-10, for Soil 6S.

For a given polyether chain length, PPG showed stronger sorption to Soil 6S than PEG, however this difference was diminished between PPG and PEG of a similar molecular weight (Figure 4.9). Given that the primary mechanism of sorption of these polymers is hydrogen bonding (Section 4.3.3.2), the reverse trend may be expected, since PEG and PPG homologues of the same chain length will contain the same number of ether groups which can hydrogen bond to clay minerals (Podoll *et al.* 1987). The increased sorption of PPG to Soil 6S for a given chain length may thus result from additional secondary effects, such as the slightly lower aqueous solubility of PPG compared to PEG, additional minor hydrophobic interactions involving the PPG methyl groups, or conformation of the polymer chain. The similarity in sorption of PEG and PPG of a similar molecular weight may thus result from the greater number of ether bonds in PEG counteracting functional and conformational effects in PPG of the same molecular weight (since for a given molecular weight, a PEG homologue will have a greater number of ether bonds than a PPG homologue).

A similar pattern of increased similarity between PPG and PEG K_d values for the same molecular weight, and greater differences in sorption for the same chain length, could also be observed in the other studied soils, but to a lesser degree (Appendix 4.36, Tables 4.10 and 4.11). In cases where significant sorption occurs, the chemical functionality (i.e. presence of methyl groups) of the studied polyethers may therefore be a strong predictor of sorption for a given PEG or PPG chain length, however not for a given molecular weight; similarly, polyether molecular weight may be a useful sorption predictor for grouped PEG and PPG. Both of these observations are useful in development of grouping approaches and QSARs for environmental fate behaviour and risk assessment of polyethers (as well as for other groups of highly similar polymers). Given the similarity in sorption coefficients for a given polyether molecular weight, grouping of PEG and PPG of similar molecular weight ranges is likely to be a valid and useful approach for this aspect of environmental fate and risk assessment (*Chapter 3*).

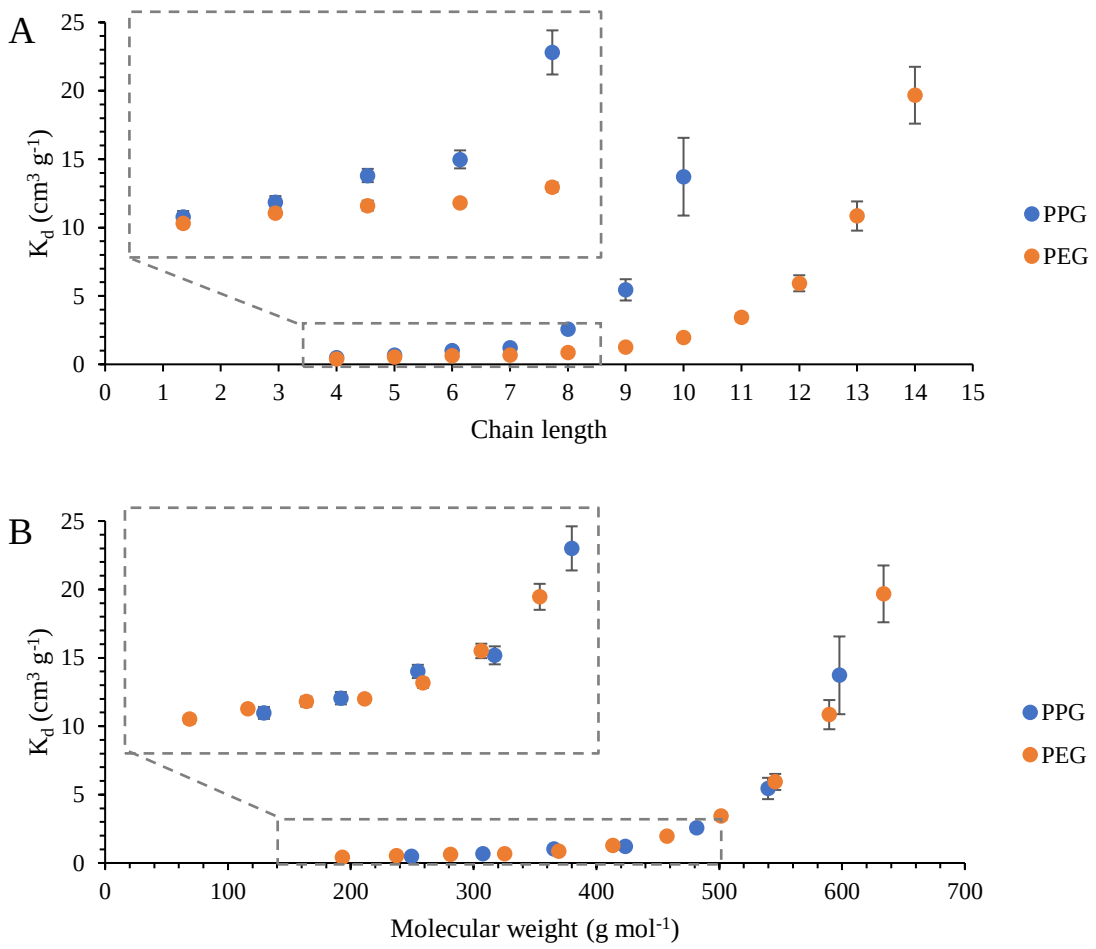


Figure 4.9: Relationship between linear sorption coefficient (K_d) and A) chain length and B) molecular weight for PEG and PPG with Soil 6S, 1.50 %C, clayey loam. Error bars show 95% confidence intervals for K_d calculated from regression analysis. Expanded axes are shown for K_d = 0-3, and A) chain length = 4-8, B) molecular weight = 150-500 g mol^{-1}.

4.3.3.4. Comparison of experimental K_d with predictions obtained from EPI Suite

EPI Suite predictions of K_{oc} (and corresponding K_d) are calculated using QSAR models derived from correlation of either molecular connectivity index (MCI) or log(K_{ow}) with experimental K_{oc} values for various low molecular weight compounds (USEPA 2012). Most existing QSARs have not considered polymers (ECHA 2016) and there is thus a lack of methods available for prediction of polymer fate parameters (*Chapter 2*). A maximum molecular weight of 665.02 g mol^{-1} included in the experimental dataset of EPI Suite limits the accuracy of predictions above this range (USEPA 2012). Applying these QSARs to the relatively low molecular weight polymers used in the present study and comparison to calculated experimental K_d values provides

a useful assessment of whether the EPI Suite QSARs are applicable to these (and potentially other) low molecular weight polymers for environmental fate assessment.

Predictions of K_d calculated using EPI Suite were not found to closely match with experimental K_d values calculated in the present study (Figures 4.10 and 4.11). Predicted K_d values fall approximately two orders of magnitude below experimental K_d values determined in the present study for most chain lengths (note that PEG-15 is the only homologue which falls slightly outside the molecular weight range included in the experimental dataset of the EPI Suite model). In addition, K_d predictions derived from the MCI significantly over-estimate molecular weight dependence above a chain length of eight monomer units for both PEG and PPG, whilst K_d values derived from the $\log(K_{ow})$ QSAR under-estimate molecular weight dependence for PPG for some soils and show a negative correlation for PEG.

Although it is interesting to note that MCI predictions for PEG encapsulate the decrease (up to PEG-8) and subsequent increase in K_d with polymer chain length observed in the experimental values of the present study in some soils (Figure 4.11), which is due to a maximum of 7 ether bonds being corrected for in the QSAR model, overall the K_d values predicted from EPI Suite are not accurate for the polymers studied. It is worth noting that the maximum number of aliphatic ether bonds per structure in the experimental dataset used to develop EPI Suite QSARs is 2, and thus the higher numbers of ether bonds in all homologues included in the present study may contribute to the limited accuracy of the EPI Suite modelled estimates (USEPA 2012). This is likely to be a significant factor for many water-soluble polymers with repeating functional groups. In addition, experimentally measured K_d values for polymer homologues may depend on other polymer components in the mixture (Section 4.3.3.3) which will not be accounted for in EPI Suite and other QSAR models developed for single compounds rather than complex mixtures.

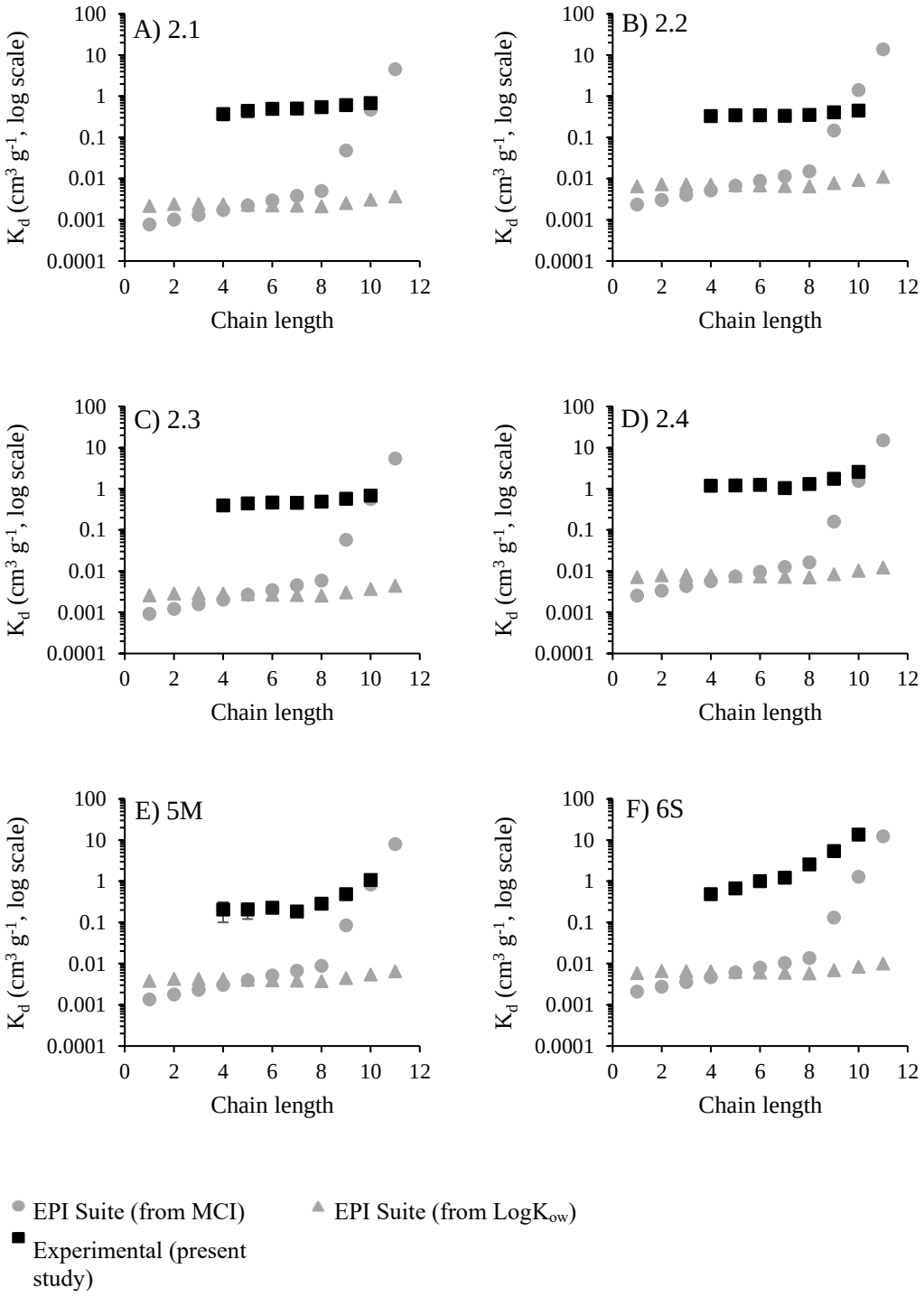


Figure 4.10: Comparison of values of K_d predicted by KOCWIN (EPI Suite) using molecular connectivity index (MCI, without overcorrection adjustment) and $LogK_{ow}$, for PPG homologues 1-11, and values of K_d determined experimentally in the present study, for PPG homologues 4-10 and Lufa Speyer Standard Soils A) 2.1, B) 2.2, C) 2.3, D) 2.4, E) 5M, and F) 6S.

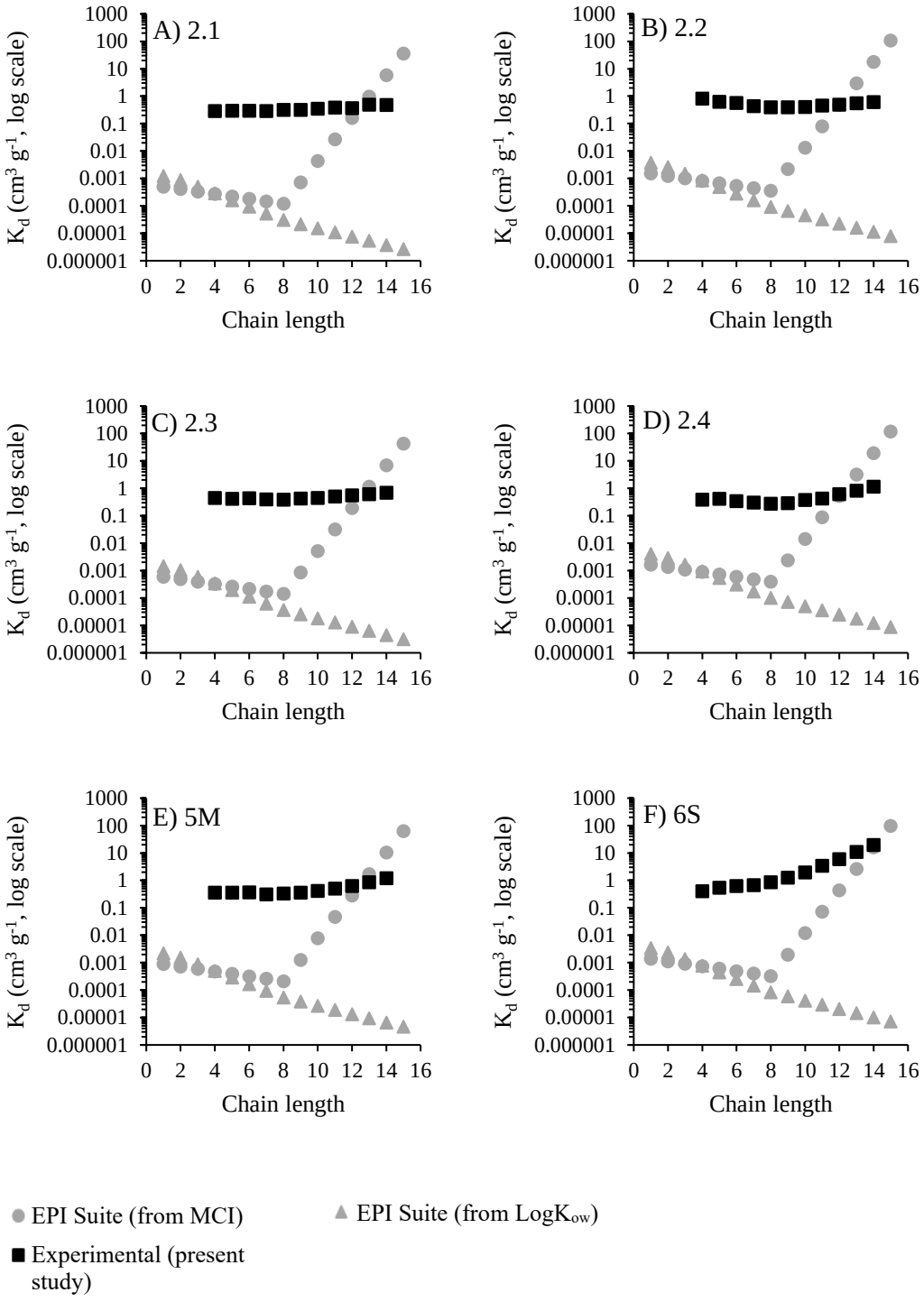


Figure 4.11: Comparison of values of K_d predicted by KOCWIN (EPI Suite) using molecular connectivity index (MCI, without overcorrection adjustment) and $LogK_{ow}$, for PEG homologues 1-15, and values of K_d determined experimentally in the present study, for PEG homologues 4-14 and Lufa Speyer Standard Soils A) 2.1, B) 2.2, C) 2.3, D) 2.4, E) 5M, and F) 6S.

4.3.4. Implications for environmental exposure assessment

Environmental fate parameters such as K_d are relevant in exposure assessment of water-soluble polymers, however there remain key knowledge gaps on the influence of polymer properties (such as high and distributed molecular weights, existence as complex mixtures, and the interplay of chemical and physical properties due to macromolecular size) and how these can be measured (Brunning *et al.* 2022). It has already been recognised that limitations may exist in standard test methods when applied to polymers, and applicability of methods may need to be assessed on a case-by-case basis (ECETOC 2020).

Whilst it has already been established that longer polymer chains will exhibit higher levels of sorption for polyethers (Podoll *et al.* 1987; Brownawell *et al.* 1997; McLaughlin *et al.* 2016), the data in the present study confirm that this will significantly impact risk assessment given that K_d values determined for the total polymer mixtures do not encapsulate actual sorption processes occurring for many soils (even more so in cases of higher sorption). Many shorter-chain homologues, which may be expected to have higher hazard potential (OECD 2009), are likely to be more mobile and less liable to sorption than would be predicted from application of K values to the bulk mixture. Where possible, reporting of K_d and other environmental fate parameters as a range rather than single values is likely to be more appropriate (ECETOC 2020). However for many polymers, including polyethers of very high average molecular weights, analytical methods which characterise and quantify all individual polymer homologues in environmental matrices are not currently feasible (e.g. Huppertsberg *et al.* 2020). Measurement of fate parameters for the bulk polymer mixture is therefore likely to be necessary in many cases, and thus the potential impact on interpretation of results and risk assessment should always be noted.

It is also important to note the role that mixture interactions may play, in both environmental scenarios and in laboratory analyses, for which few data exist. In the present study, competition between sorption sites at the highest initial concentration of PEG and PPG (10 mg L^{-1}) could be observed directly, with shorter chain homologues undergoing less sorption than expected due to the presence of the larger polymer chains in the mixtures. Whilst in the environment, concentrations of PEG and PPG are expected to be much lower than the 10 mg L^{-1} highest concentration used in the present study (e.g. total concentrations of polyethers from down-the-drain household products have been

modelled and are expected to fall below 0.09 mg L^{-1} in surface waters; *Chapter 3*; and PEG in surface waters has been typically measured in the µg L^{-1} range; Crescenzi *et al.* 1997; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014; Traverso-Soto *et al.* 2014), and therefore saturation of sorption sites from polyethers alone in e.g. soils and sediments is unlikely, experimental studies utilising high concentrations of polymer may underestimate sorption of shorter polymer chains. Measurements of other key properties and environmental fate parameters may also be impacted by mixture interactions. Parameters measured for a single polymer homologue may be unique to the specific polymer mixture utilised, and thus could vary between e.g. different molecular weight distributions of the same polymer type. Again, bulk analysis of all of the PEG and PPG polymer chains in the mixture (rather than detection and quantification of individual polymer homologues as has been undertaken in the present study) may cause these phenomena to be overlooked.

Although polyethers such as PEG and PPG are expected to be readily or inherently biodegradable at many molecular weights, they have still been measured in environmental waters (Crescenzi *et al.* 1997; Rychłowska *et al.* 2003; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014; Traverso-Soto *et al.* 2014; Pauelsen *et al.* 2023), emphasising a need for further characterisation of their environmental fate. The K_d values determined in the present study are thus useful for further exposure assessment of these polymers; overall, the low values of K_d suggest that sorption to sediment is unlikely to be a significant removal mechanism for these polymers from the aqueous environment (*Chapter 3*). Sorption to sludge in wastewater treatment is likely to be limited and thus application of polyethers to soil from sludge may be low. In addition, it is also key to note that many shorter-chain homologues, which may be expected to have higher hazard potential (OECD 2009), are likely to be more mobile and less liable to sorption than longer polymer chains, and thus may have higher aqueous availability in the environment.

4.4. Conclusions and recommendations

Sorption behaviour of polyethylene glycol and polypropylene glycol to soils has been characterised, with quantitation of individual homologues within polymer mixtures. The present data support previous literature studies, with the main sorption mechanism likely being hydrogen bonding to clay minerals, and sorption increasing with polymer

molecular weight. However, further observations which impact data interpretation for polyethers and which have wider implications for polymer risk assessment include:

1. For the first time, effects of other homologues in the polyether mixture on sorption of individual chain lengths are reported, with longer chain homologues reducing sorption of shorter chains at an observable level at high concentrations. Where possible, measurement of polymers in their native complex mixture and the influence of other mixture components should be accounted for in measurement of parameters for environmental risk assessment.
2. Sorption of PPG to soil is higher than that of PEG for a given chain length, but this difference is diminished for a given molecular weight for the polymer homologue ranges studied (i.e. there is a clear difference between PPG and PEG when sorption is plotted as a function of chain length, but not when sorption is plotted as a function of molecular weight). Grouping of PEG and PPG based on molecular weight is therefore likely to be a valid approach, as the two polymers show similar levels of sorption at similar molecular weights. In addition, molecular weight may be a useful predictor of sorption for PEG and PPG grouped in this way; conversely, for PEG and PPG of a similar chain length, their chemical structures (i.e. presence of methyl groups in PPG) may be useful in predicting differences in sorption. QSARs can be developed for PEG and PPG homologues relating molecular weight to K_d for some soils.
3. In cases where significant levels of sorption occur (e.g. to soil with high clay mineral content), sorption coefficients calculated for the bulk polymer mixture are unlikely to encapsulate sorption coefficients for any individual polymer homologues, even with relatively homogeneous/low molecular weight polymers as analysed in the present study. Other key fate parameters may also be impacted, and thus application of parameters determined for a whole polymer mixture should be used with caution.

Whilst in the present study, use of low molecular weight polymers allowed characterisation of individual homologues within polymer mixtures and in-depth analysis of the effect of chain length and functional group on sorption for PEG and PPG, for many high molecular weight polymers such analyses are not feasible using current analytical methods (due to the fact that large polymers will contain a very wide range of individual chain lengths which are likely to give rise to complex spectra and low signal intensities; Huppertsberg *et al.* 2020). More research into the impact of polymer properties and

mixture effects on measurement of environmentally relevant parameters should be carried out in order to account for uncertainty in characterisation of large or complex polymers, and subsequent consequences for environmental risk assessment.

Chapter 5

Biodegradation and Transformation of Water-Soluble Polyethers in Freshwater

5.1. Introduction

In the previous chapter, the sorption behaviour of water-soluble polyethers in soil was studied, giving fate data relevant to one of the environmental compartments modelled in *Chapter 3* as well as an assessment of mixture components and implications for testing. In this chapter, biodegradation and transformation of these polymers in surface waters was studied, providing key environmental fate data to inform polymer grouping and surface water exposure estimates modelled in *Chapter 3*, as well as an in-depth analysis of complex polymer degradation processes and products as discussed in *Chapter 2*. This study also provides further environmental fate data for water-soluble polymers, which are currently lacking (*Chapter 2*), and a continuation of analyses of behaviour of individual homologues within polymer mixtures as established in *Chapter 4*.

Measurements of environmental fate properties pertaining to biodegradation (including rate of removal, half-life, and formation of degradation products) are necessary to characterise the persistence and removal of contaminants from environmental matrices. Biodegradation of a substance is dependent on a range of factors, including chemical and physical properties of the substance and environmental conditions. Screening tests for assessing ready and inherent biodegradability and thus potential persistence of substances, typically employing non-specific methods (such as CO_2 production or reduction in DOC) to characterise mineralisation, have been established (OECD 1992b, 1992a), however these were developed predominantly for distinct low molecular weight chemical compounds. Nevertheless, recent studies have successfully applied and evaluated standard OECD ready and inherent biodegradation tests for water-soluble polymers (polyethylene glycol, polyvinyl alcohol, and carboxymethyl cellulose), with modifications including test extension being recommended for polymers which take longer to mineralise (McDonough *et al.* 2023; Menzies *et al.* 2023).

However, whilst non-specific biodegradation tests are useful for screening substances and bulk mixture WSPs for their degradation potential and likelihood of persistence, these methods do not provide information on transformation products and mechanisms, or biodegradation of individual homologues and components of polymer mixtures. For many polymers, a lack of analytical methods hinders such analyses (Huppertsberg *et al.* 2020; Groh *et al.* 2023). Data interpretation also presents a significant challenge, given that for many types of WSPs, shorter chained homologues are likely to be both formed (from transformation of longer chains) and degraded, impeding determination of homologue half-lives and relative formation and loss processes. It is also imperative to gain an understanding of how parallel degradation processes within a polymer mixture may impact results from non-specific analyses of the bulk material, and to what extent the level of polymer biodegradation can be accurately characterised in such studies. In addition, given the general scarcity of studies assessing biodegradation of WSPs in the environment, more research is warranted, particularly for surface waters which are a likely receiving compartment for large amounts of WSPs (*Chapter 3*).

Polyether compounds such as polyethylene glycol (PEG) and polypropylene glycol (PPG) are one such class of WSPs which are likely to be released to surface waters in high volumes (*Chapter 3*). PEG compounds typically show ready or inherent biodegradability (Beran *et al.* 2013), and lower molecular weight PEGs (< 1 kDa) have been previously shown to degrade rapidly in river water (99% biodegradation in 14 days; Zgoła-Grześkowiak *et al.* 2006) and groundwater (half-lives of up to 1.1 days; Rogers *et al.* 2019). Higher molecular weight PEGs (up to 500 kDa) have also been reported to be fully mineralised in OECD 301B and 302B studies, although extension of standard test durations was required to allow for complete degradation of higher molecular weight polymers (26.6-50 kDa or more; Bernhard *et al.* 2008; Menzies *et al.* 2023). In contrast, PEGs ≥ 26.6 kDa were not degraded in seawater after 135 days (Bernhard *et al.* 2008). However, despite their relatively high biodegradability, polyethers may still be of concern due to the sheer quantities that are used and released to the environment. Concern has already been raised given that PEG compounds have still been detected in environmental waters (Pauelsen *et al.* 2023) despite their expected rapid biodegradation. Simulation studies in surface water (e.g. Zgoła-Grześkowiak *et al.* 2006; West *et al.* 2007; Bernhard *et al.* 2008; Rogers *et al.* 2019; Menzies *et al.* 2023) for these and other WSP types remain few, but are essential for characterising degradation under environmentally relevant

conditions and in likely receiving compartments of WSPs. Whilst a limited number of studies have assessed biodegradation of individual PEG and PPG chains in their native polymer mixtures using liquid chromatography and/or mass spectrometry techniques (Zgoła-Grześkowiak *et al.* 2006; Bernhard *et al.* 2008; Rogers *et al.* 2019), the majority of studies of WSP biodegradation remain focussed on non-specific screening tests. Full characterisation of environmental biodegradation kinetics for individual polymer homologues within polymer mixtures, including relative degradation rates and half-lives of individual polymer chains and modelling of their formation and loss processes, has not yet been carried out for WSPs, including polyethers.

The aims of the present study were therefore to characterise the biodegradation of polyethylene glycol (PEG) and polypropylene glycol (PPG) in a range of environmental waters (river and lake water), as well as to utilise specific analytical methods to detect the individual constituent homologues present in the polymer mixtures and subsequently develop a kinetic model to characterise both formation and loss processes of each polymer chain length for the first time. The kinetic modelling approach was also used to derive biodegradation half-lives for individual polyether homologues within the polymer mixtures whilst accounting for their simultaneous formation and degradation, which has to our knowledge not yet been carried out, allowing an in-depth analysis of degradation mechanisms and parallel kinetic processes. The results also provide key data on environmental fate of PEG and PPG, which are likely to be present in surface waters (*Chapter 3*; Pauelsen *et al.* 2023), and include assessment of the effects of polymer and system properties on degradation as well as an analysis of previously contested biodegradation mechanisms of PEG and PPG (Zgoła-Grześkowiak *et al.* 2006; West *et al.* 2007; Zgoła-Grześkowiak *et al.* 2007; Tisler *et al.* 2021). The kinetic modelling also provides a key starting point for characterisation of biodegradation of other WSP types in their native complex mixtures, where analytical methods become available.

5.2. Materials and methods

5.2.1. River and lake water

Seven samples of river and lake water were collected in a plastic bucket from various locations in North Yorkshire in June 2023. Sampling sites were chosen to obtain water samples from a range of water types, including a large, medium, and small river both upstream and downstream of wastewater treatment plants or weirs, and a lake. Key water

quality parameters (pH, conductivity, dissolved organic carbon (DOC), and element and ion content) were measured in triplicate.

The pH and conductivity were measured using Orion Star A111 pH and Orion Star A212 conductivity benchtop meters. For DOC analyses, inorganic carbon was purged from 10 mL of each sample with 0.2 mL of 10% HCl prior to triplicate analysis using an Elementar Vario cube TOC/TNb analyser with the following parameters: injection volume 0.25 mL; combustion temperature 850 °C; detector = infrared. Produced CO_2 was calibrated using standards composed of 0, 5, 10, 20, 50, and 100 mg L^{-1} DOC. Elemental composition was measured in triplicate using a Thermo Scientific iCAP Pro 7000 inductively coupled plasma optical-emission spectrometer (ICP-OES) with the following parameters: injection volume 3 mL; RF power 1150 W; auxiliary gas flow 0.5 L min^{-1}; nebuliser gas flow 0.55 L min^{-1}, pump speed 50 rpm; exposure times 15 seconds (UV) and 5 seconds (visible). Elemental concentrations were calibrated using standards of concentrations 0, 0.25, 0.5, 1, 5, and 10 mg L^{-1}. Anion content was measured in triplicate using a Dionex ICS 2000 ion chromatograph with an AS40 autosampler, ECG III KOH eluent generator cartridge, ASRS 600 2 mm suppressor and DS6 heated conductivity detector, and with a Dionex IonPac AS18 (2 mm id x 250 mm L) analytical column. The eluent was aqueous hydroxide with a gradient from 2 to 41 mM hydroxide. Method parameters were as follows: injection volume 15 µL; suppressor current 26 mA; column oven 30 °C; detector temperature 35 °C. Anion measurements were calibrated using 6 standards containing mixtures of anions with ranges: 0.04-2 mg L^{-1} F^-; 0.03-60 mg L^{-1} Cl^-; 0.05-1 mg L^{-1} NO_2^-; 0.8-70 mg L^{-1} NO_3^-; 0.8-140 mg L^{-1} SO_4^{2-}; and 0.05-5 mg L^{-1} PO_4^{3-}.

Four of the seven collected waters were selected for biodegradation experiments to give a range of water properties that was representative of the range of all collected water samples. The four selected waters also originated from a large river (River Ouse), medium river (River Foss), small river (Bishop Wilton Beck), and a lake (Yearsley Lake), giving a range of location types. Details of sampling locations and measured properties of the selected water samples are shown in Tables 5.1 and 5.2, respectively, with map references given in Figure 5.1 (details of other water samples which were not used in experiments are given in Appendices 5.1-5.3). Background polymer concentrations were also measured (Section 5.2.4.), and water samples were stored at 4 °C for 9 days prior to use in biodegradation experiments.

Table 5.1: Details of sampling locations for the four environmental water samples used in biodegradation experiments.

Location (coordinates)	Water body	Site description
53.894000, -1.097663	River Ouse	River Ouse (large river which runs through the city of York), sampled at Naburn Lock downstream from the city of York and Naburn wastewater treatment plant, upstream of a weir.
54.040841, -1.035345	River Foss	River Foss (medium river which runs through the city of York), sampled in the village of Strensall upstream from the city of York. Total input from three small-scale wastewater treatment plants between Foss source and sampling location.
53.984795, -0.787360	Bishop Wilton Beck	Small beck running through the village of Bishop Wilton, sampled upstream from the associated wastewater treatment plant.
54.175635, -1.089541	Lake at Yearsley Woods	Small lake in Yearsley Woods, a woodland in North Yorkshire accessible via public footpaths.

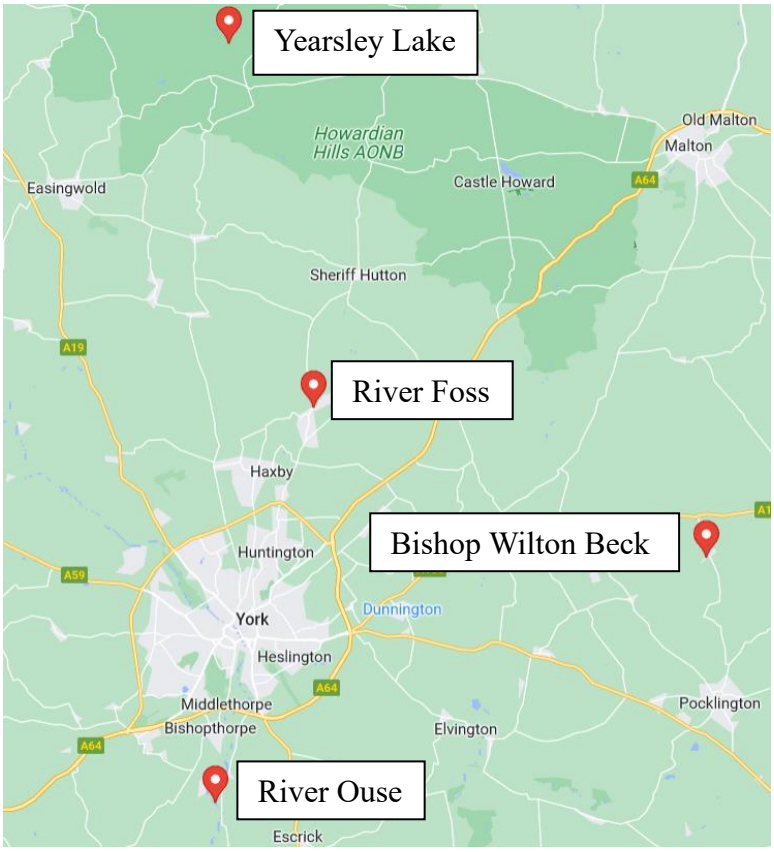


Figure 5.1: Sampling locations of the four water types selected for use in biodegradation experiments.

Table 5.2: Average measured values of water parameters of environmental water samples used for the biodegradation study.
Note that anion concentrations were measured during day 1 of the biodegradation experiment. 95% confidence intervals calculated from analytical replicates are shown in brackets. Elemental composition measurements were measured and averaged in triplicate by the instrument and thus confidence intervals are not given for these measurements.

Parameter	Unit	River Ouse	River Foss	Bishop Wilton Beck	Yearsley Lake
pH	n/a	7.44 (±0.02)	8.35 (±0.06)	7.79 (±0.06)	8.31 (±0.06)
Conductivity	$\mu S\ cm^{-1}$	651.0 (±1.4)	891.3 (±1.3)	495.9 (±1.6)	359.9 (±0.5)
DOC	$mg\ L^{-1}$	5.204 (±0.163)	8.902 (±0.057)	4.160 (±0.059)	7.758 (±0.089)
Magnesium	$mg\ L^{-1}$	16.086	15.738	5.084	3.693
Calcium	$mg\ L^{-1}$	81.399	109.543	84.158	57.474
Sodium	$mg\ L^{-1}$	26.773	43.257	9.302	12.427
Potassium	$mg\ L^{-1}$	5.880	12.757	3.969	2.185
Phosphorous	$mg\ L^{-1}$	0.577	0.430	0.096	0.010
Copper	$mg\ L^{-1}$	0.010	0.011	0.009	0.008
Zinc	$mg\ L^{-1}$	0.006	0.004	0.001	0.001
Iron	$mg\ L^{-1}$	0.010	0.017	0.015	0.072
Manganese	$mg\ L^{-1}$	0.001	0.001	0.000	0.001
Chromium	$mg\ L^{-1}$	0.002	0.002	0.002	0.003
Nickel	$mg\ L^{-1}$	0.000	0.000	0.000	0.000
Fluoride	$mg\ L^{-1}$	0.214 (±0.002)	0.174 (±0.000)	0.057 (±0.001)	0.061 (±0.001)
Chloride	$mg\ L^{-1}$	39.685 (±0.180)	61.200 (±0.055)	16.376 (±0.042)	21.466 (±0.042)
Nitrite	$mg\ L^{-1}$	0.070 (±0.004)	0.829 (±0.004)	0.032 (±0.004)	0.035 (±0.002)
Nitrate	$mg\ L^{-1}$	16.451 (±0.084)	61.759 (±0.045)	30.935 (±0.156)	2.407 (±0.021)
Sulphate	$mg\ L^{-1}$	80.244 (±0.202)	128.782 (±0.170)	39.695 (±0.081)	33.181 (±0.051)
Phosphate	$mg\ L^{-1}$	1.384 (±0.033)	0.857 (±0.019)	0.121 (±0.022)	0.000
Hardness (calculated)	$mg\ L^{-1}$	269.5	338.3	231.1	158.7

5.2.2. Polymers and chemicals

Reagents and chemicals were sourced and used as described in *Chapter 4*. PEG (MW_N ca. 400 g mol^{-1}) and PPG (MW_N 446 g mol^{-1}) were again studied.

5.2.3. Biodegradation experiment

Three millilitres of 100 mg L^{-1} polymer solution (either PEG-9 or PPG-7, made up in deionised water) was added to 72 mL of test surface water in 120 mL clear glass jars, in triplicate (with three vessels being prepared for each polymer and water type), such that the final polymer concentration in each jar was 4 mg L^{-1}. Vessels were then agitated to ensure mixing. Jars were covered with Parafilm-M to minimise evaporative loss of water whilst allowing exchange of O_2 and CO_2. The resulting microcosms were then left in the dark at 20 °C, with 1-1.5 mL of solution being removed at selected timepoints (0 days (immediately after experimental set-up), and 1, 2, 5, 8, 13, 19, and 28 days) and filtered through a 0.45 μm hydrophilic PTFE syringe filter, before storing at -20 °C prior to LC-MS analysis. Sample jars were manually agitated twice per week and on sampling days, to ensure adequate mixing and distribution of O_2 and CO_2 in the water. Abiotic control experiments were prepared in triplicate as described above with sterilised river or lake water (autoclaved at 121 °C for 30 minutes) and sampled at 0, 2, 8, and 28 days. Blank control experiments (containing no polymer) were prepared in triplicate as described above and sampled during day 1 of the experiment.

5.2.4. Analysis of PPG-7 and PEG-9

Polymers were detected using HPLC-MS, with individual polymer homologues being separated and quantified, using the method as described previously in *Chapter 4*. Polymer homologues were again quantified by external calibration, using standard polymer solutions in distilled water for 0.01 – 4 mg L^{-1} of total polymer mixtures to plot calibration curves (*Chapter 4*).

5.2.5. Biodegradation rate constant and half-life

5.2.5.1. Characterisation of degradation kinetics and half-life for polymer mixtures

Degradation of the total polymer mixtures (PPG of chain lengths 4-10, and PEG of chain lengths 4-14) at each time point (represented as the concentration as a percentage of the time 0 concentration averaged across experimental triplicates), was modelled using

the logistic model, a lag phase model characterised by increase of the rate constant up to a maximum value and no clear break point (FOCUS 2014). Microsoft Excel was used to determine the parameters of the equation for the logistic model as shown in Equation 5.1 (FOCUS 2014):

$$M = M_0 \left(\frac{a_{max}}{a_{max} - a_0 + a_0 e^{rt}} \right)^{\frac{a_{max}}{r}} \quad (5.1)$$

Where M = amount of polymer present at time *t* (mg L^{-1} or %); M_0 = amount of polymer present at time *t* = 0 (mg L^{-1} or %); a_{max} = maximum value of degradation rate constant (reflecting microbial activity; day^{-1}); a_0 = initial value of degradation rate constant (day^{-1}); and *r* = microbial growth rate (day^{-1}). Theoretical values of M (starting from M_0 = 100%) were calculated for a time period of up to 80 days in increments of 0.1 days, before manual alteration of values for a_0, a_{max}, and *r* to give a close visual match between theoretical values and experimental data for each water and polymer. The Microsoft Excel solver add-in was then used to minimise the residual sum of squares between the theoretical and measured data by variation of a_0, a_{max}, and *r*, to give final solved values of these parameters for each polymer and water that were most representative of observed degradation.

The degradation half-life ($t_{1/2}$) for each polymer mixture and water was then determined according to Equation 5.2 (FOCUS 2014):

$$t_{1/2} = \frac{1}{r} \ln \left[1 - \frac{a_{max}}{a_0} \left(1 - 2^{(r/a_{max})} \right) \right] \quad (5.2)$$

Where $t_{1/2}$ = the biodegradation half-life in days.

5.2.5.2. Modelling of degradation kinetics for individual polymer homologues

Degradation kinetics of individual homologues within polymer mixtures were modelled for each water type. It was assumed that both PEG and PPG degraded by oxidation followed by sequential shortening of polymer chains by one monomer unit (Kawai 2002; West *et al.* 2007; Bernhard *et al.* 2008; Beran *et al.* 2013; Rogers *et al.* 2019; Figure 5.2).

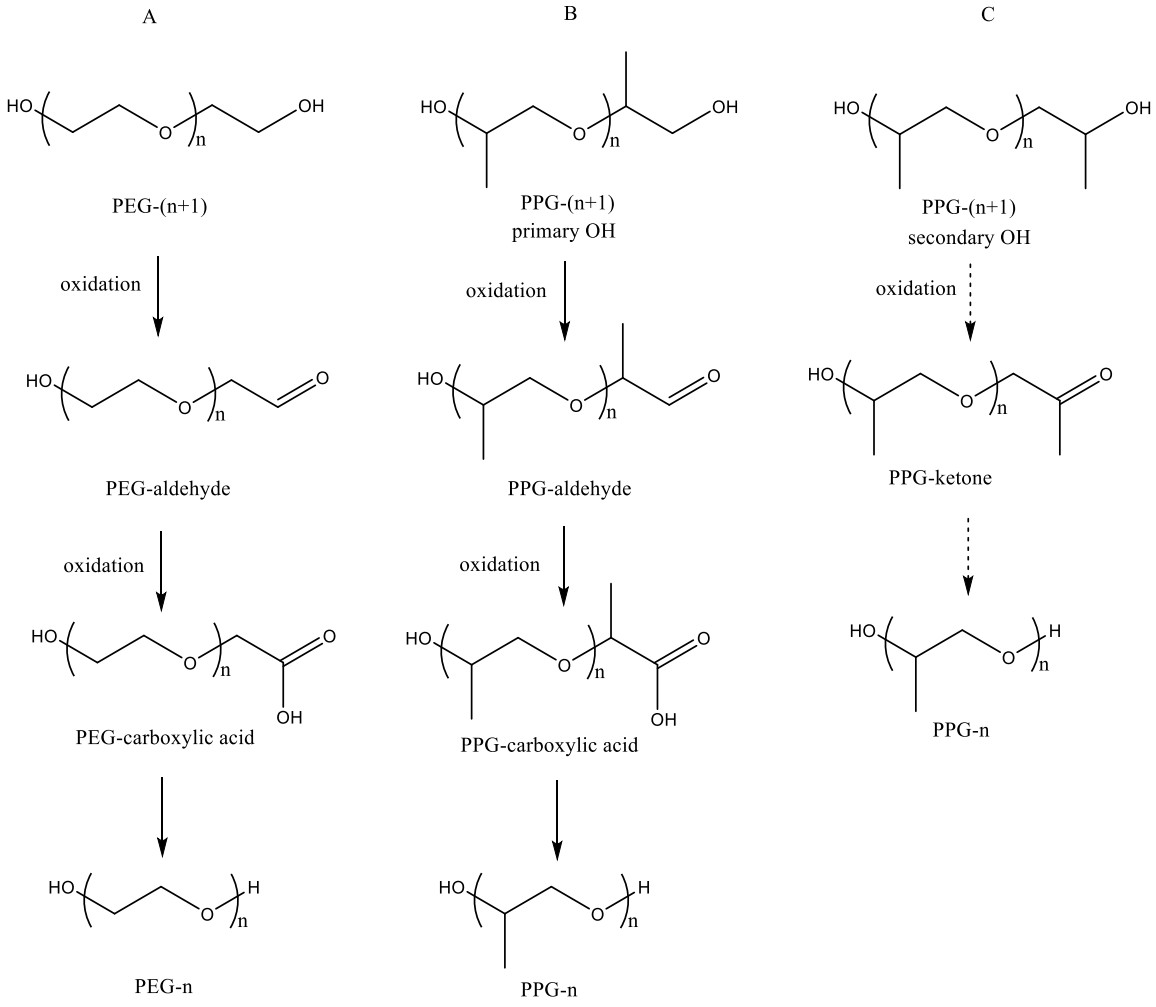


Figure 5.2: Biodegradation reaction schemes of A) PEG; B) PPG with a terminal primary alcohol group; and C) PPG with a terminal secondary alcohol group, proceeding via oxidation and sequential shortening of polymer chains catalysed by dehydrogenase enzymes, where *n* = polymer chain length/ number of monomer units.
See also: Kawai 2002; West *et al.* 2007; Bernhard *et al.* 2008; Beran *et al.* 2013; Rogers *et al.* 2019.

It was also assumed that the longest quantified polymer chains (PPG-10 and PEG-14) were not formed in significant amounts by longer homologues, due to the fact that longer homologues were too low in concentration to be reliably detected and quantified (detailed in *Chapter 4*). The rate of change of each polymer homologue was therefore assumed to proceed according to differential Equations 5.3-5.5 for PPG and Equations 5.6-5.8 for PEG.

$$\frac{d[PPG_{10}]}{dt} = -a_{10}[PPG_{10}]; \quad (5.3)$$

$$\frac{d[PPG_9]}{dt} = -a_9[PPG_9] + a_{10}[PPG_{10}] \dots; \quad (5.4)$$

$$\dots\frac{d[PPG_4]}{dt} = -a_4[PPG_4] + a_5[PPG_5]\,. \quad (5.5)$$

$$\frac{d[PEG_{14}]}{dt} = -b_{14}[PEG_{14}]; \quad (5.6)$$

$$\frac{d[PEG_{13}]}{dt} = -b_{13}[PEG_{13}] + b_{14}[PEG_{14}] \dots; \quad (5.7)$$

$$\dots\frac{d[PEG_4]}{dt} = -b_4[PEG_4] + b_5[PEG_5]\,. \quad (5.8)$$

Where $[PPG_x]$ = concentration of (quantified) PPG homologue with chain length *x* (mg L^{-1}); $[PEG_x]$ = concentration of (quantified) PEG homologue with chain length *x* (mg L^{-1}); t = time (days); and a_x and b_x are biodegradation rate constants for PPG and PEG homologues with chain length *x*, respectively (day^{-1}). Incremental changes in the concentration of each polymer homologue were then modelled from measured concentrations at time 0 based on the above differential equations, modified from differentials to incremental time differences (Δ), according to Equations 5.9-5.14, in increments of 10 minutes for a time period of up to 30 days (for the three river water samples) or a time period of up to 70 days (for water from Yearsley Lake):

$$[PPG_{10}]_{t2} = [PPG_{10}]_{t1} - a_{10(t1)}[PPG_{10}]_{t1}(t2 - t1); \quad (5.9)$$

$$[PPG_9]_{t2} = [PPG_9]_{t1} - a_{9(t1)}[PPG_9]_{t1}(t2 - t1) + a_{10(t1)}[PPG_{10}]_{t1}(t2 - t1) \dots; \quad (5.10)$$

$$\dots[PPG_4]_{t2} = [PPG_4]_{t1} - a_{4(t1)}[PPG_4]_{t1}(t2 - t1) + a_{5(t1)}[PPG_5]_{t1}(t2 - t1)\,. \quad (5.11)$$

$$[PEG_{14}]_{t2} = [PEG_{14}]_{t1} - b_{14(t1)}[PEG_{14}]_{t1}(t2 - t1); \quad (5.12)$$

$$[PEG_{13}]_{t2} = [PEG_{13}]_{t1} - b_{13(t1)}[PEG_{13}]_{t1}(t2 - t1) + b_{14(t1)}[PEG_{14}]_{t1}(t2 - t1) \dots; \quad (5.13)$$

$$\dots[PEG_4]_{t2} = [PEG_4]_{t1} - b_{4(t1)}[PEG_4]_{t1}(t2 - t1) + b_{5(t1)}[PEG_5]_{t1}(t2 - t1)\,. \quad (5.14)$$

Where $[PPG_x]_{t2}$ and $[PEG_x]_{t2}$ = concentration (mg L^{-1}) of (quantified) PPG or PEG homologue with chain length *x* at incremental time = t2 in days; $[PPG_x]_{t1}$ and $[PEG_x]_{t1}$ = concentration (mg L^{-1}) of (quantified) PPG or PEG homologue with chain length *x* at incremental time = t1 in days (10 minutes prior to t2 as described above); and $a_{x(t1)}$ and $b_{x(t1)}$ are biodegradation rate constants (day^{-1}) for PPG and PEG homologues with chain length *x* at time = t1, respectively. Values of the biodegradation rate constant (a_x and b_x) are time-dependent for logistic model kinetics, and were calculated using the differential Equation 5.15 given for parameter estimation for the logistic model (FOCUS 2014):

$$a = \frac{a_0 a_{max}}{a_0 + (a_{max} - a_0)e^{-rt}} \quad (5.15)$$

Where a = the biodegradation rate constant (day^{-1}) at time = *t* days. For the longest quantified polymer homologues (PEG-14 and PPG-10), values of a_0, a_{max}, and *r* were determined using the Microsoft Excel solver add-in as described in Section 5.2.5.1. Values of these parameters were then manually and sequentially modified (without use of Excel solver; discussed in Section 5.3.2) for the other polymer homologues (from longest to shortest polymer chains) to give a close visual match of the modelled data (Equations 5.9-5.14) after conversion to concentration as a percentage of time 0 concentration for each polymer homologue (M_0 = 100%), thus giving estimates of parameter values and degradation/formation curves. These values were then used to estimate biodegradation half-lives for individual polymer homologues according to Equation 5.2.

5.3. Results and discussion

5.3.1. Biodegradation and half-life of polymer mixtures

Losses in abiotic control experiments were not observed for PPG (Figure 5.3) (except for water from the River Ouse, for which total polymer concentrations remained generally constant (Figure 5.3) but a slight shift towards a lower molecular weight distribution was observed). However, for PEG, decreases in total polymer concentration were observed in some abiotic controls (Figure 5.3). Whilst these were relatively small decreases for water from the Rivers Ouse and Foss and from Yearsley Lake, losses in abiotic controls for water from Bishop Wilton Beck were more significant, with PEG concentrations falling to below the limit of detection after 28 days. However, losses in abiotic controls were still significantly slower than the rate of removal observed in experimental samples (discussed below). Other potential loss mechanisms of PEG aside from biodegradation include photolysis, hydrolysis, and sorption to suspended organic matter. Since experiments were conducted in the dark, and sorption of PEG to organic carbon is expected to be minimal (*Chapter 4*), removal via hydrolysis is the only likely mechanism in the absence of biodegradation. While it is possible that minor losses due to hydrolysis occurred in some control samples, given that losses were variable between different water types and control replicates, it is more likely that removal was due to some microorganisms having survived the autoclaving process. This has been observed previously, and may be reduced by use of multiple autoclaving cycles (Otte *et al.* 2018). Therefore given the low overall levels of polymer loss in controls, the variability between control replicates, and the likelihood that losses were still as a result of biodegradation, these were not corrected for in experimental samples.

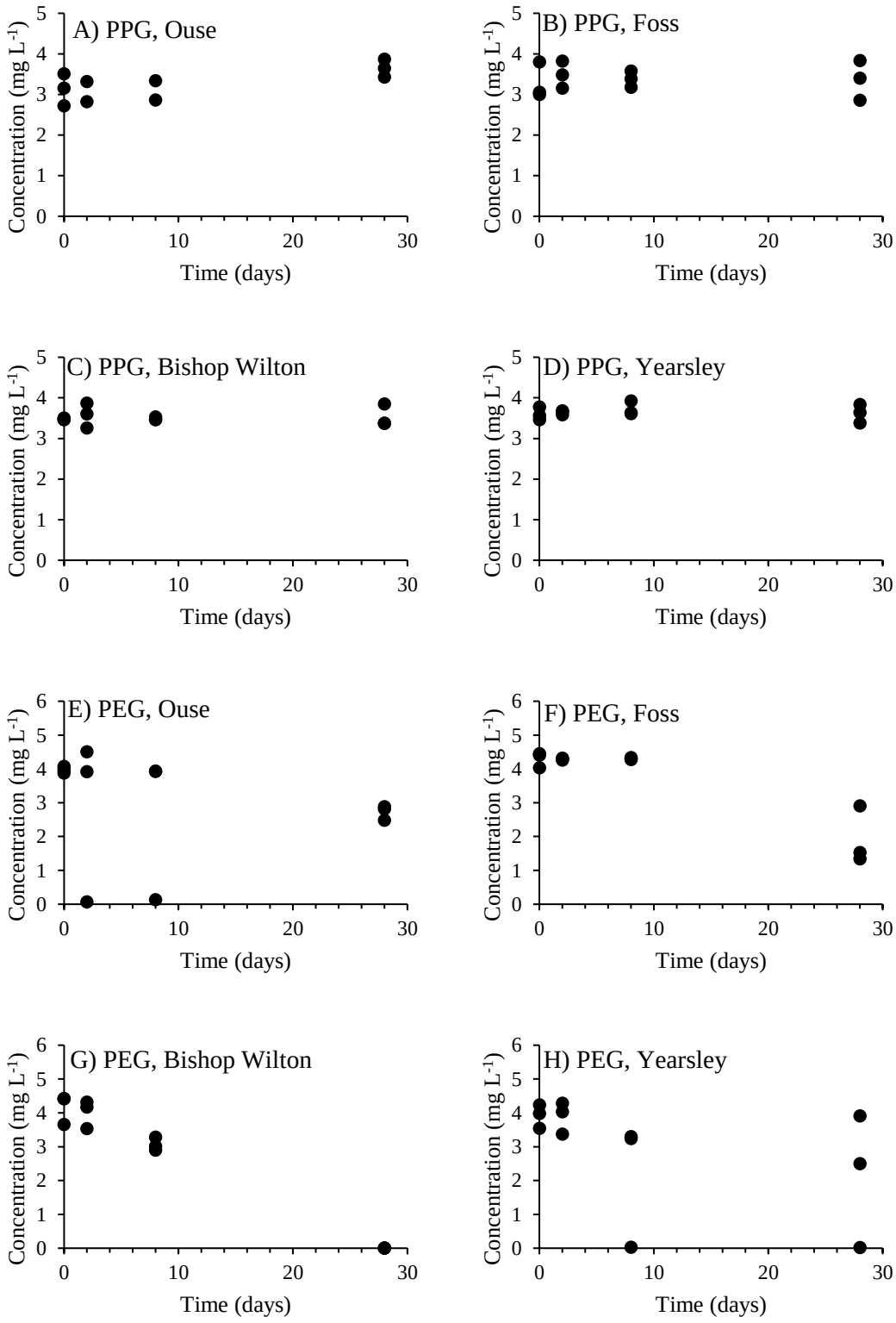


Figure 5.3: Concentration of polymer mixtures in abiotic control experiments for A) PPG in River Ouse water; B) PPG in River Foss water; C) PPG in Bishop Wilton Beck water; D) PPG in Yearsley Lake water; E) PEG in River Ouse water; F) PEG in River Foss water; G) PEG in Bishop Wilton Beck water; and H) PEG in Yearsley Lake water.

Both of the studied polymers showed similar patterns of biodegradation in each river water type, characterised in most cases by a lag phase with no clear breakpoint and an increase in the degradation rate constant up to a maximum value. Degradation could therefore be most closely modelled using the logistic model described in FOCUS (2014) for pesticide degradation (Figures 5.4 and 5.5). Corresponding values of optimised parameters are shown in Table 5.3. Plots of residuals between measured and modelled data are shown in Appendix 5.4.

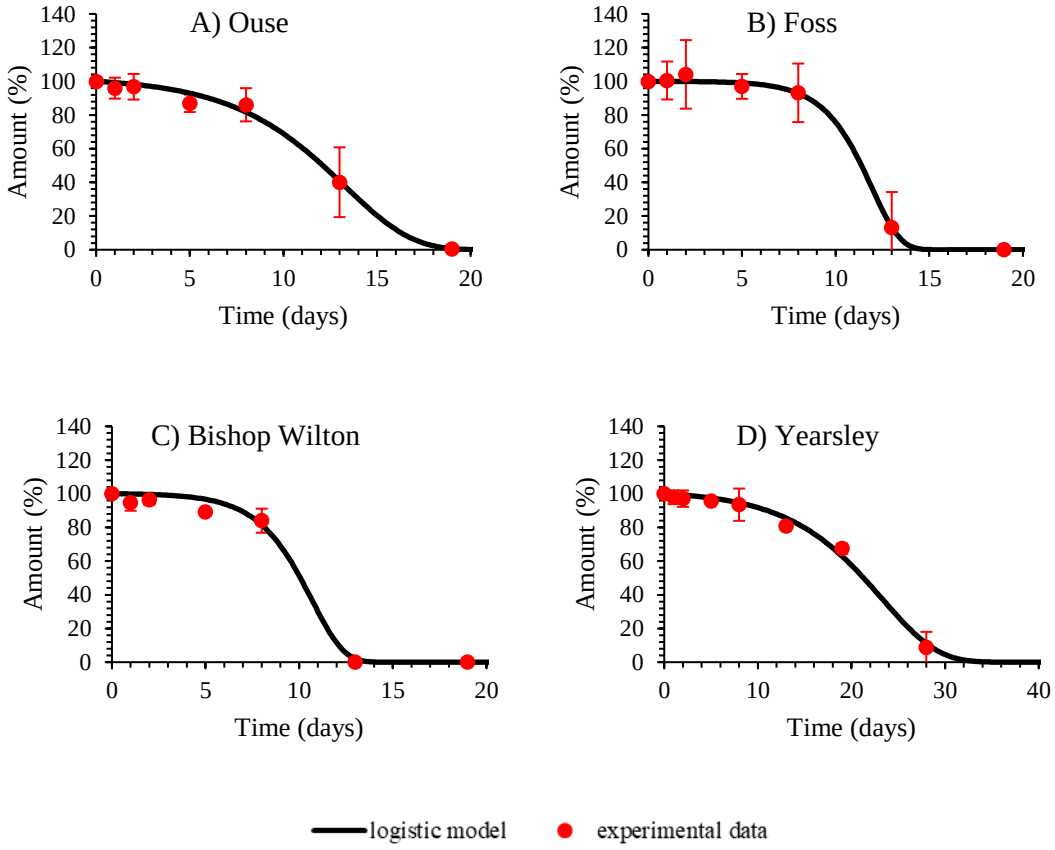


Figure 5.4: Degradation curves obtained for PPG in water from A) the River Ouse; B) the River Foss; C) Bishop Wilton Beck; and D) Yearsley Lake, from solving of the logistic model by optimisation of parameters to minimise the residual sum of squares between modelled and experimental data. Note extended x-axis for Yearsley Lake. Experimental data are averaged across the (three) experimental replicates for each timepoint; error bars show 95% confidence intervals for experimental data, calculated from replicates.

The presence of a lag phase indicates that time is required for microbial growth and/or adaptation to the substrates in question, as has been observed previously for PPG and other polyalkylene glycol compounds (Beran *et al.* 2013). However overall, both PEG-9 (MW_N ca. 400 g mol^{-1}) and PPG-7 (MW_N 446 g mol^{-1}) mixtures showed rapid

biodegradation in all three river waters in the present study. The studied PEG was completely removed (up to the detection limits of the applied HPLC-MS method) from river water after 13 days, and PPG was removed from river water after 19 days for water from the Rivers Ouse and Foss, and after 13 days for water from Bishop Wilton Beck (Figures 5.4 and 5.5). In addition, PEG reached >99% biodegradation after 8 days in water from the River Foss and Bishop Wilton Beck, with only lower molecular weight homologues being present at low concentrations. A previous study has reported similar results for biodegradation of similar polyethers in river water, with PEG (MW_N 300) and PPG (MW_N 425) being observed to reach biodegradation of approximately 99% after 14 and 17 days, respectively (Zgoła-Grześkowiak *et al.* 2006).

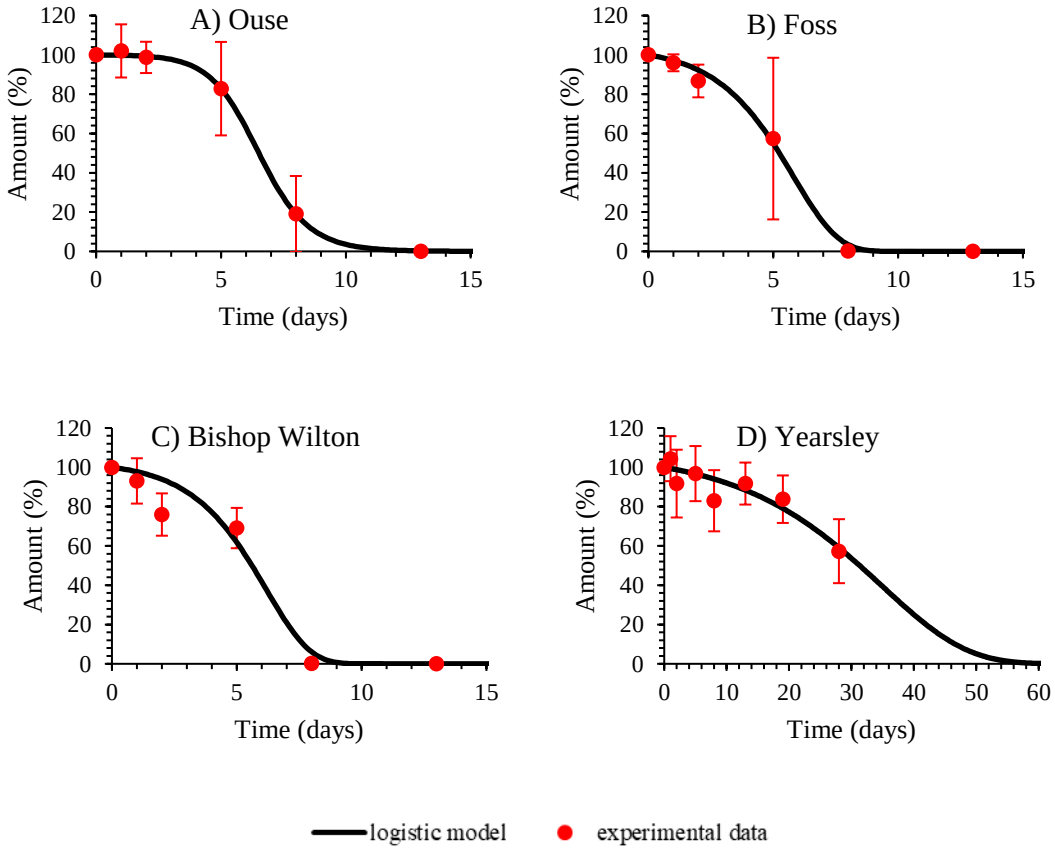


Figure 5.5: Degradation curves obtained for PEG in water from A) the River Ouse; B) the River Foss; C) Bishop Wilton Beck; and D) Yearsley Lake, from solving of the logistic model by optimisation of parameters to minimise the residual sum of squares between modelled and experimental data. Note extended x-axis for Yearsley Lake. Experimental data are averaged across the (three) experimental replicates for each timepoint; error bars show 95% confidence intervals for experimental data, calculated from replicates.

Values of the biodegradation half-life ($t_{1/2}$) determined for the polymer mixtures using Equation 5.2 are dependent on optimised parameters: the initial and maximum values of the biodegradation rate constant (a_0 and a_{max}, respectively), and the microbial growth rate (r). Values of $t_{1/2}$ again indicate similar patterns between different types of river water, with values ranging from 5.2 – 6.5 days for PEG and 10.1 – 12.1 days for PPG (Table 5.3). Despite the fact that environmental biodegradation of PEG has been relatively well-studied, values for the biodegradation half-life in surface waters have been rarely reported. First-order half-lives of PEG (3-14 monomer units) and PPG (2-10 monomer units) in microcosms simulating fracking fluid spills to groundwater have been reported as ranging from <0.4 – 1.1 days, and 2.5 – 14 days, respectively (Rogers *et al.* 2019) showing good agreement with values for PPG in river water obtained in the present study but faster degradation of PEG. Values of $t_{1/2}$ (calculated after subtraction of lag phase) for various propylene glycol substances (propylene glycol up to PPG 2700) in seawater have been reported and are significantly longer than values obtained for freshwater, ranging from 13.6 – 410 days (West *et al.* 2007).

Table 5.3: Values of optimised logistic model parameters (initial biodegradation rate constant, a_0; maximum biodegradation rate constant, a_{max}; and microbial growth rate, r), and subsequent values of the biodegradation half-life ($t_{1/2}$) for bulk PEG and PPG mixtures degraded in each of the studied water types.

Water type	**a_0 (day^{-1})**	**a_{max} (day^{-1})**	**r (day^{-1})**	**$t_{1/2}$ (days)**
Polypropylene glycol (PPG)				
River Ouse	6.69E-03	4.75E+03	0.28	12.1
River Foss	2.53E-04	9.56E+02	0.66	11.4
Bishop Wilton Beck	1.11E-03	2.13E+04	0.59	10.1
Yearsley Lake	3.28E-03	1.42E+04	0.17	21.3
Polyethylene glycol (PEG)				
River Ouse	1.05E-03	8.85E-01	1.08	6.5
River Foss	2.20E-02	3.85E+04	0.56	5.2
Bishop Wilton Beck	1.69E-02	8.57E+04	0.57	5.6
Yearsley Lake	5.65E-03	7.45E+02	0.07	31.3

It should be noted that for some samples, variability was observed across experimental repeats in the present study, as indicated by the wide confidence intervals observed for some experimental datapoints (Figures 5.4 and 5.5). This is most notable for PEG in water from the River Foss, for which one of the three experimental replicates was significantly faster to degrade. High variability and poor repeatability has been observed

previously for biodegradation tests of both typical low molecular weight compounds (Davenport *et al.* 2022) and water-soluble polymers using respirometric methods (Menzies *et al.* 2023). Menzies *et al.* (2023) attributed observed variability to: low abundance of microbial communities in river water which may not always be represented in small-scale sampling; the high test substance concentrations needed for non-specific respirometric methods (such as CO_2 evolution) which are orders of magnitude higher than expected environmental concentrations and which thus require more time for sufficient growth of these sparse microbial communities to reach observed levels of biodegradation; and pH of the river water causing delayed evolution and measurement of CO_2. Theoretical CO_2 and O_2 demand may also be difficult to determine accurately for polymers since they are complex mixtures (ECETOC 2020). In the present study, a specific HPLC-MS method was employed and thus lower concentrations could be used (4 mg L^{-1} as oppose to 100 mg L^{-1} total polymer concentrations; Menzies *et al.* 2023), although this is still 1-3 orders of magnitude higher than measured environmental concentrations of PEG and PPG (Crescenzi *et al.* 1997; Rychłowska *et al.* 2003; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014; Traverso-Soto *et al.* 2014; Pauelsen *et al.* 2023) to ensure polymer homologues remained above the detection limits of the analytical method (*Chapter 4*) for a long enough duration to study their biodegradation kinetics. The low abundance of microbial communities in river water and lack of representativeness of small water samples is thus the likely explanation for the variability observed in the present study. It has been recognised that more research and standardisation of methods is required to overcome this variability (Menzies *et al.* 2023; Davenport *et al.* 2022), with utilisation of higher microbial cell counts and screening of microbial diversity having the potential to improve laboratory biodegradation study accuracy and provide information on relationships between biodegradation and microbial diversity and abundance (Martin *et al.* 2018; Ott *et al.* 2019; Davenport *et al.* 2022).

Whilst biodegradation of both polymers in river water was rapid, biodegradation in lake water was much slower (Table 5.3), with none of the experimental replicates being fully degraded by the end of the test (28 days), and $t_{1/2}$ values of 31.3 days for PEG, and 21.3 days for PPG (however note that on average the PEG mixture had not reached 50% of its initial concentration by the end of the test, and thus the calculated $t_{1/2}$ for PEG in the lake water should be used with caution as the model was extrapolated beyond the range of the experimental data). To our knowledge, biodegradation of water-soluble

polymers in lake water has not been previously reported. Although release of PEG and PPG to river and seawater is likely to be significant, due to release of these compounds in wastewater effluent, there are not likely to be significant sources of these compounds in lake water; however, contamination of lakes is possible from agricultural run-off for both PEG and PPG as well as more isolated sources such as spills from hydraulic fracturing (e.g. Castanho *et al.* 2009; McLaughlin *et al.* 2016; Rogers *et al.* 2019). The lake water studied in the present study may also be more generally representative of freshwater with little to no previous input from wastewater effluent.

It is interesting to note that whilst PEG degraded more quickly than PPG in all river water samples, as has been reported previously (Zgoła-Grześkowiak *et al.* 2006), PEG was much slower to be removed from lake water in the present study, with PEG concentration reaching an average value of only 57% at day 28, compared to 9% for PPG. The range of concentrations remaining in the lake water at day 28 across the three experimental replicates was 39.3 – 74.5% for PEG, compared to 0.5 – 19.8% for PPG. It has been noted previously that organisms which degrade PEG are unable to metabolise PPG (Kawai 2002; Eubeler *et al.* 2010; Beran *et al.* 2013), and that hydrophobicity may be relevant in biodegradation of these compounds. Higher molecular weight PPG has also been observed to degrade more quickly than lower molecular weight PPG across some molecular weight ranges (West *et al.* 2007; Zgoła-Grześkowiak *et al.* 2007). This has been suggested to be, at least in part, due to the increased hydrophobicity of longer chain PPG (Tisler *et al.* 2021), which may increase its uptake by microorganisms.

If hydrophobicity does increase the biodegradation rate of polyethers, this would explain the more rapid degradation of PPG in lake water compared with PEG, but not the faster PEG degradation in river water. It is possible that the faster degradation of the less hydrophobic PEG in river water is primarily due to pre-adaptation of micro-organisms in river water to PEG, which may be present at higher concentrations than PPG, thus counteracting the effects of the reduced hydrophobicity of PEG. There are not likely to be any significant direct sources of PEG or PPG contamination in the lake water sampled in the present study and thus pre-adaptation of microbial communities is unlikely. However, wastewater was not released upstream of the sampling point for river water from Bishop Wilton Beck (Table 5.1), and thus pre-adaptation of microbial communities as a result of release of PEG and PPG in wastewater effluent is also unlikely for this water type. In addition, poor correlation between hydrophobicity (measured as log K_{ow})

and degradation of PPG in seawater and the ready biodegradability test has been reported (West *et al.* 2007), suggesting that hydrophobicity may in fact not be a driving factor for biodegradation of these polymers. West *et al*. (2007) have suggested that molecular conformation or chemical structure of PPG has a more significant influence on its biodegradability (discussed further in Section 5.3.2). Analysis of degradation rates and kinetics of individual polymer chain lengths (Section 5.3.2) provides more insight into the relative rates of degradation of PEG and PPG in lake water.

5.3.2. Modelled degradation kinetics of individual polymer homologues

In the present study, the concentration of individual PEG and PPG homologues present within the polymer mixtures was tracked over the course of the biodegradation experiments. Formation (i.e. an increase in concentration) of shorter PEG and PPG chains was directly observed in water from the River Ouse, and from Yearsley Lake for PEG, but not for the other studied water types (Tables 5.4 and 5.5). This may be partially explained by the fact that degradation in water from the River Foss and Bishop Wilton Beck was most rapid for both polymers (Table 5.3), with degradation of shortened polymer chains proceeding too quickly for an increase in concentrations of shorter chain lengths to be observed; however, degradation of PPG in Yearsley Lake water was slow, but formation (increase in concentration) of shorter-chained PPG was not observed. Formation of shorter-chained PPG was also observed in one of the three experimental replicates for the River Foss. This variability in observable formation of shorter polymer chains in the present study in different media under identical conditions may also arise from low microbial abundance and lack of representation of microbial diversity in small samples (Menzies *et al.* 2023; Davenport *et al.* 2022), but may also be influenced by specific microbial communities, water properties, and nutrient content of each sample, highlighting the importance of measuring biodegradation in a range of environmental water types. An increase in the number of sampling times in future studies may help to confirm whether formation of shorter chains can be more consistently detected, however the relative rates of formation and loss processes are most likely key to these observations (discussed further below).

Table 5.4: Change in concentration of individual polypropylene glycol (PPG) homologues and the total PPG mixture (presented as percentage (%) of concentration measured on day 0) over the course of biodegradation experiments in each of the studied water types.
95% confidence intervals (calculated from the three experimental replicates) are shown in brackets.

Polymer homologue	0 days	1 day	2 days	5 days	8 days	13 days	19 days	28 days
River Ouse								
PPG-4	100.0	99.2 (±2.6)	93.7 (±6.3)	86.0 (±4.1)	87.4 (±8.9)	140.3 (±76.8)	1.6 (±2.5)	0.0 (±0.0)
PPG-5	100.0	98.4 (±3.4)	95.0 (±5.7)	86.1 (±4.3)	83.0 (±6.8)	65.4 (±40.3)	1.0 (±1.6)	0.0 (±0.0)
PPG-6	100.0	96.3 (±5.4)	96.4 (±7.3)	85.6 (±5.0)	85.3 (±8.3)	56.1 (±28.4)	0.9 (±1.4)	0.0 (±0.0)
PPG-7	100.0	94.5 (±7.7)	96.2 (±8.2)	86.5 (±7.4)	85.9 (±11.2)	44.2 (±19.9)	0.4 (±0.7)	0.0 (±0.0)
PPG-8	100.0	94.9 (±7.2)	95.5 (±8.4)	87.5 (±6.2)	84.8 (±13.0)	23.1 (±12.8)	0.1 (±0.1)	0.0 (±0.0)
PPG-9	100.0	97.9 (±4.6)	97.9 (±7.5)	88.4 (±4.5)	87.8 (±10.4)	9.1 (±4.7)	0.0 (±0.0)	0.0 (±0.0)
PPG-10	100.0	95.4 (±9.5)	104.5 (±9.1)	88.5 (±1.9)	92.9 (±5.2)	2.1 (±0.8)	0.0 (±0.0)	0.0 (±0.0)
Mixture (PPG-(4-10))	100.0	96.0 (±6.2)	96.8 (±7.6)	86.9 (±5.2)	86.1 (±9.9)	40.1 (±20.7)	0.4 (±0.7)	0.0 (±0.0)
River Foss								
PPG-4	100.0	99.8 (±10.5)	99.4 (±16.6)	90.6 (±7.1)	82.2 (±13.6)	42.6 (±65.6)	1.7 (±2.4)	0.1 (±0.2)
PPG-5	100.0	101.0 (±11.5)	101.9 (±18.6)	94.5 (±6.3)	87.5 (±14.7)	16.5 (±25.5)	0.3 (±0.5)	0.1 (±0.1)
PPG-6	100.0	101.6 (±10.9)	103.9 (±19.8)	96.7 (±5.7)	91.7 (±15.6)	14.2 (±22.7)	0.0 (±0.1)	0.0 (±0.0)
PPG-7	100.0	101.0 (±11.1)	104.9 (±22.0)	98.5 (±5.9)	95.4 (±18.7)	12.1 (±19.4)	0.0 (±0.0)	0.0 (±0.0)
PPG-8	100.0	100.7 (±11.1)	105.5 (±21.3)	99.0 (±8.0)	97.4 (±19.2)	5.8 (±9.3)	0.0 (±0.0)	0.0 (±0.0)
PPG-9	100.0	97.9 (±12.0)	105.7 (±22.5)	99.3 (±13.4)	99.7 (±21.7)	1.9 (±3.1)	0.0 (±0.0)	0.0 (±0.0)
PPG-10	100.0	93.2 (±16.5)	110.5 (±24.0)	97.7 (±18.9)	101.7 (±25.6)	0.4 (±0.7)	0.0 (±0.0)	0.0 (±0.0)
Mixture (PPG-(4-10))	100.0	100.5 (±11.3)	104.1 (±20.4)	97.0 (±7.4)	93.2 (±17.4)	13.3 (±20.9)	0.2 (±0.3)	0.0 (±0.0)

(Table 5.4 continued)

Polymer homologue	**0 days**	**1 day**	**2 days**	**5 days**	**8 days**	**13 days**	**19 days**	**28 days**
				Bishop Wilton Beck				
PPG-4	100.0	94.7 (±5.2)	93.1 (±3.0)	81.1 (±1.5)	90.7 (±2.0)	0.5 (±0.2)	0.0 (±0.0)	0.5 (±0.2)
PPG-5	100.0	94.9 (±5.3)	95.0 (±3.4)	86.5 (±1.6)	81.5 (±6.5)	0.0 (±0.0)	0.0 (±0.0)	0.1 (±0.1)
PPG-6	100.0	94.9 (±5.2)	95.9 (±2.6)	89.5 (±0.7)	82.6 (±6.6)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PPG-7	100.0	94.6 (±4.5)	96.8 (±2.7)	91.0 (±0.6)	84.8 (±8.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PPG-8	100.0	95.6 (±4.2)	96.7 (±3.5)	91.3 (±1.5)	84.5 (±9.4)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PPG-9	100.0	93.2 (±4.2)	99.5 (±3.2)	91.0 (±1.3)	83.1 (±10.5)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PPG-10	100.0	89.2 (±4.1)	103.8 (±2.2)	90.1 (±2.0)	83.7 (±12.3)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
Mixture (PPG-(4-10))	100.0	94.7 (±4.8)	96.4 (±3.0)	89.2 (±0.6)	84.0 (±7.2)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
				Yearsley Lake				
Polymer homologue	**0 days**	**1 day**	**2 days**	**5 days**	**8 days**	**13 days**	**19 days**	**28 days**
PPG-4	100.0	108.9 (±17.8)	104.7 (±14.6)	85.9 (±1.5)	81.4 (±16.7)	68.0 (±11.5)	47.8 (±7.5)	9.5 (±10.2)
PPG-5	100.0	108.7 (±15.4)	105.3 (±12.8)	90.6 (±0.3)	88.0 (±16.2)	78.9 (±10.6)	59.3 (±7.7)	8.7 (±10.1)
PPG-6	100.0	104.1 (±4.9)	102.4 (±3.8)	96.7 (±0.2)	94.1 (±4.8)	86.0 (±4.2)	70.5 (±3.8)	9.7 (±10.7)
PPG-7	100.0	98.9 (±4.6)	97.4 (±6.0)	97.5 (±0.2)	95.8 (±10.1)	84.8 (±2.9)	72.7 (±3.6)	7.3 (±9.2)
PPG-8	100.0	93.9 (±12.3)	93.6 (±12.8)	98.0 (±0.6)	98.5 (±25.0)	82.9 (±9.4)	72.9 (±8.7)	9.7 (±8.8)
PPG-9	100.0	85.7 (±20.1)	89.0 (±21.3)	97.4 (±2.4)	105.0 (±46.2)	77.9 (±16.6)	70.0 (±15.5)	9.7 (±7.4)
PPG-10	100.0	77.8 (±23.2)	88.7 (±26.5)	95.0 (±5.4)	114.6 (±66.6)	76.4 (±21.1)	68.5 (±19.7)	9.8 (±6.2)
Mixture (PPG-(4-10))	100.0	97.9 (±4.0)	97.1 (±4.9)	95.5 (±0.7)	93.5 (±9.6)	80.8 (±2.5)	67.4 (±3.0)	8.8 (±9.2)

Table 5.5: Change in concentration of individual polyethylene glycol (PEG) homologues and the total PEG mixture (presented as percentage (%) of concentration measured on day 0) over the course of biodegradation experiments in each of the studied water types.
95% confidence intervals (calculated from the three experimental replicates) are shown in brackets.
Note that samples for day 28 in water from the River Foss were not analysed due to the fact that all homologues had fully degraded by day 19.

Polymer homologue	**0 days**	**1 day**	**2 days**	**5 days**	**8 days**	**13 days**	**19 days**	**28 days**
				River Ouse				
PEG-4	100.0	99.9 (±9.0)	93.9 (±5.5)	134.3 (±78.9)	137.8 (±114.6)	0.7 (±1.2)	0.0 (±0.0)	0.0 (±0.0)
PEG-5	100.0	101.0 (±11.2)	97.0 (±5.5)	120.4 (±46.9)	64.7 (±51.7)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-6	100.0	101.6 (±10.9)	97.1 (±7.5)	111.6 (±28.7)	31.5 (±35.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-7	100.0	101.2 (±12.1)	98.0 (±9.4)	87.5 (±15.5)	20.3 (±32.4)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-8	100.0	101.6 (±10.5)	98.7 (±7.7)	79.4 (±29.1)	14.4 (±23.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-9	100.0	100.9 (±11.6)	98.1 (±7.1)	72.3 (±42.2)	9.0 (±14.4)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-10	100.0	101.0 (±15.4)	98.9 (±7.7)	70.0 (±49.4)	6.0 (±9.5)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-11	100.0	102.8 (±17.0)	99.0 (±6.8)	68.9 (±50.1)	4.7 (±7.5)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-12	100.0	104.3 (±17.8)	101.0 (±9.3)	68.5 (±50.4)	3.1 (±4.9)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-13	100.0	106.9 (±20.3)	103.4 (±11.0)	69.5 (±51.1)	2.5 (±4.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-14	100.0	107.5 (±21.2)	104.1 (±16.2)	69.3 (±51.9)	1.6 (±2.6)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
Mixture (PEG-(4-14))	100.0	102.0 (±13.5)	98.7 (±8.0)	82.8 (±23.8)	19.0 (±19.3)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
				River Foss				
Polymer homologue	**0 days**	**1 day**	**2 days**	**5 days**	**8 days**	**13 days**	**19 days**	**28 days**
PEG-4	100.0	93.8 (±5.7)	84.3 (±8.4)	56.2 (±43.8)	5.3 (±5.2)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-5	100.0	96.0 (±6.6)	87.8 (±10.1)	55.8 (±41.9)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-6	100.0	95.1 (±6.6)	87.4 (±13.1)	55.5 (±40.8)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-7	100.0	96.8 (±6.1)	89.0 (±7.5)	58.1 (±41.3)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-8	100.0	96.0 (±4.8)	90.8 (±6.8)	58.9 (±41.2)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-9	100.0	96.3 (±4.0)	89.5 (±5.9)	58.0 (±40.7)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-10	100.0	97.3 (±3.0)	91.2 (±5.1)	58.9 (±41.6)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-11	100.0	95.3 (±2.3)	89.9 (±3.7)	56.9 (±40.7)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-

(Table 5.5 continued)

Polymer homologue	0 days	1 day	2 days	5 days	8 days	13 days	19 days	28 days
River Foss *(continued)*								
PEG-12	100.0	95.2 (±1.7)	90.9 (±3.8)	56.7 (±41.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-13	100.0	96.2 (±2.6)	91.4 (±2.2)	55.2 (±40.5)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
PEG-14	100.0	94.9 (±4.0)	91.7 (±5.1)	55.6 (±40.3)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	-
Mixture (PEG-(4-14))	100.0	96.0 (±4.3)	86.7 (±8.3)	57.4 (±41.1)	0.2 (±0.2)	0.0 (±0.0)	0.0 (±0.0)	-
Bishop Wilton Beck								
PEG-4	100.0	91.6 (±9.3)	65.4 (±12.6)	55.4 (±6.1)	3.6 (±2.9)	0.0 (±0.0)	0.0 (±0.0)	0.2 (±0.3)
PEG-5	100.0	91.0 (±10.4)	68.6 (±12.3)	57.3 (±7.9)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-6	100.0	92.4 (±11.5)	71.8 (±11.3)	63.5 (±8.9)	0.1 (±0.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-7	100.0	93.7 (±11.5)	76.2 (±9.4)	69.2 (±10.6)	0.1 (±0.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-8	100.0	92.4 (±10.6)	78.0 (±10.1)	71.7 (±9.9)	0.0 (±0.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-9	100.0	93.8 (±11.1)	78.7 (±9.8)	73.2 (±11.2)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-10	100.0	93.7 (±11.9)	78.8 (±11.0)	73.8 (±11.3)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-11	100.0	94.8 (±12.7)	79.5 (±12.2)	74.1 (±11.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-12	100.0	93.7 (±12.4)	78.6 (±12.2)	72.3 (±11.8)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-13	100.0	93.4 (±15.3)	78.2 (±12.6)	71.8 (±12.9)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
PEG-14	100.0	91.7 (±19.1)	76.1 (±14.1)	70.1 (±17.7)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
Mixture (PEG-(4-14))	100.0	93.1 (±11.5)	76.0 (±10.8)	69.1 (±10.3)	0.2 (±0.1)	0.0 (±0.0)	0.0 (±0.0)	0.0 (±0.0)
Yearsley Lake								
Polymer homologue	**0 days**	**1 day**	**2 days**	**5 days**	**8 days**	**13 days**	**19 days**	**28 days**
PEG-4	100.0	103.0 (±6.9)	93.1 (±9.6)	86.9 (±8.1)	69.8 (±12.9)	107.4 (±5.9)	119.7 (±22.0)	102.2 (±1.7)
PEG-5	100.0	102.6 (±7.3)	92.3 (±12.7)	91.1 (±9.4)	75.3 (±15.5)	110.7 (±9.4)	103.6 (±15.1)	89.7 (±17.0)
PEG-6	100.0	102.6 (±9.0)	91.5 (±14.3)	93.2 (±11.2)	79.6 (±14.7)	110.8 (±10.8)	105.5 (±10.4)	85.6 (±16.4)
PEG-7	100.0	104.9 (±12.3)	91.4 (±16.8)	97.0 (±15.4)	83.5 (±14.8)	110.8 (±13.2)	104.4 (±12.9)	79.1 (±21.7)
PEG-8	100.0	104.1 (±11.5)	91.5 (±18.9)	97.4 (±16.1)	84.4 (±15.5)	102.8 (±13.2)	95.5 (±14.1)	67.7 (±22.7)
PEG-9	100.0	105.4 (±12.8)	91.3 (±18.5)	98.7 (±14.9)	85.0 (±15.1)	94.7 (±12.1)	86.0 (±15.6)	54.7 (±20.8)
PEG-10	100.0	105.0 (±12.3)	90.9 (±17.9)	99.0 (±14.8)	85.3 (±16.2)	83.3 (±10.3)	75.1 (±15.3)	42.7 (±18.8)

(Table 5.5 continued)

Polymer homologue	0 days	1 day	2 days	5 days	8 days	13 days	19 days	28 days
Yearsley Lake *(continued)*								
PEG-11	100.0	105.3 (±11.8)	92.7 (±17.8)	98.5 (±14.5)	84.7 (±16.4)	74.1 (±9.1)	66.2 (±14.4)	36.0 (±16.6)
PEG-12	100.0	104.4 (±11.9)	93.1 (±19.4)	97.5 (±13.7)	84.4 (±16.3)	60.5 (±7.3)	53.2 (±11.5)	27.7 (±14.9)
PEG-13	100.0	103.6 (±11.9)	91.8 (±18.2)	97.5 (±14.0)	82.7 (±17.5)	55.1 (±8.1)	48.5 (±11.4)	24.7 (±13.5)
PEG-14	100.0	105.8 (±16.4)	91.6 (±19.8)	99.0 (±15.9)	84.5 (±17.4)	60.7 (±9.2)	51.3 (±12.6)	24.4 (±14.3)
Mixture (PEG-(4-14))	100.0	104.4 (±11.5)	91.7 (±17.3)	96.8 (±14.0)	83.0 (±15.6)	91.7 (±10.7)	83.8 (±12.1)	57.3 (±16.3)

A method was applied in the present study to test whether degradation and formation kinetics of individual PEG and PPG homologues could be modelled for these water types, and thus whether values of $t_{1/2}$ could be derived for each homologue. Estimation of biodegradation $t_{1/2}$ values for individual polymer homologues is only possible by modelling both formation and loss processes of polymer chains as has been undertaken in the present study and cannot be derived only from observed losses in experimental samples. Application of the logistic model and differential equations (Section 5.2.5.2) to estimate parameters for each polymer homologue yielded degradation curves which were a close match to experimental data for most chain lengths (Figures 5.6 and 5.7), with greater deviation from modelled curves generally only being observed for shorter polymer chains in the River Ouse and Bishop Wilton Beck (for PPG) and Yearsley Lake and Bishop Wilton Beck (for PEG).

Despite the good fit that could be achieved visually for the experimental and modelled data, models broke down at longer times in some water types (Appendix 5.5). This effect can be reduced by increasing the number of time increments at later timepoints to e.g. Δt = 1 minute instead of 10 minutes (Appendix 5.6), however use of 10 minute increments did not affect the fit of the model to experimental data in this case since experimental concentrations had already reduced to 0 (in all three experimental replicates) before model breakdown (Figures 5.6 and 5.7).

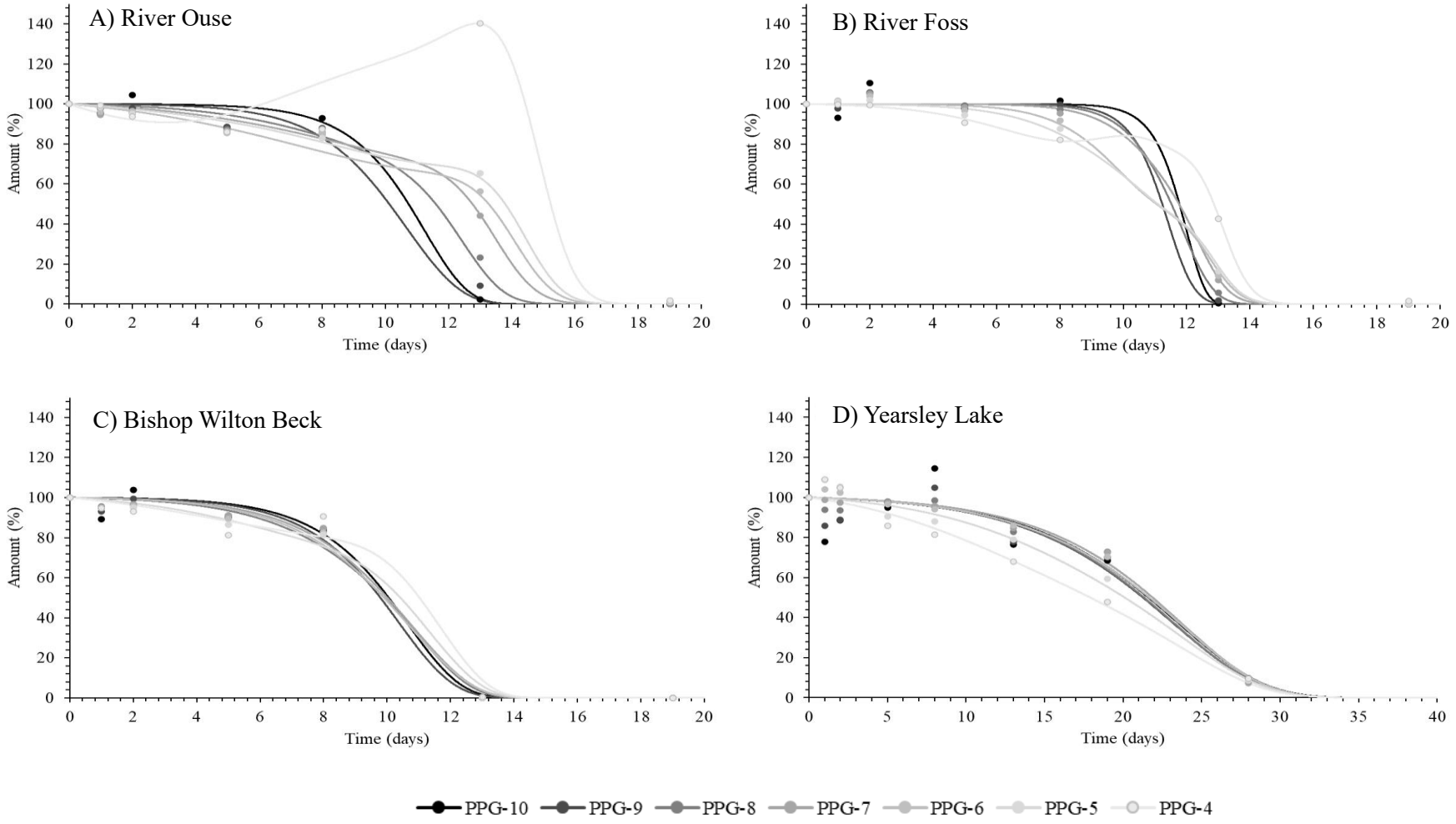


Figure 5.6: Degradation kinetics for individual PPG homologues in water from A) the River Ouse; B) the River Foss; C) Bishop Wilton Beck; and D) Yearsley Lake, shown as visually derived logistic model curves (lines) and averaged experimentally measured concentrations at each time point (circles). Error (confidence intervals) associated with experimental measurements is presented in Table 5.4.

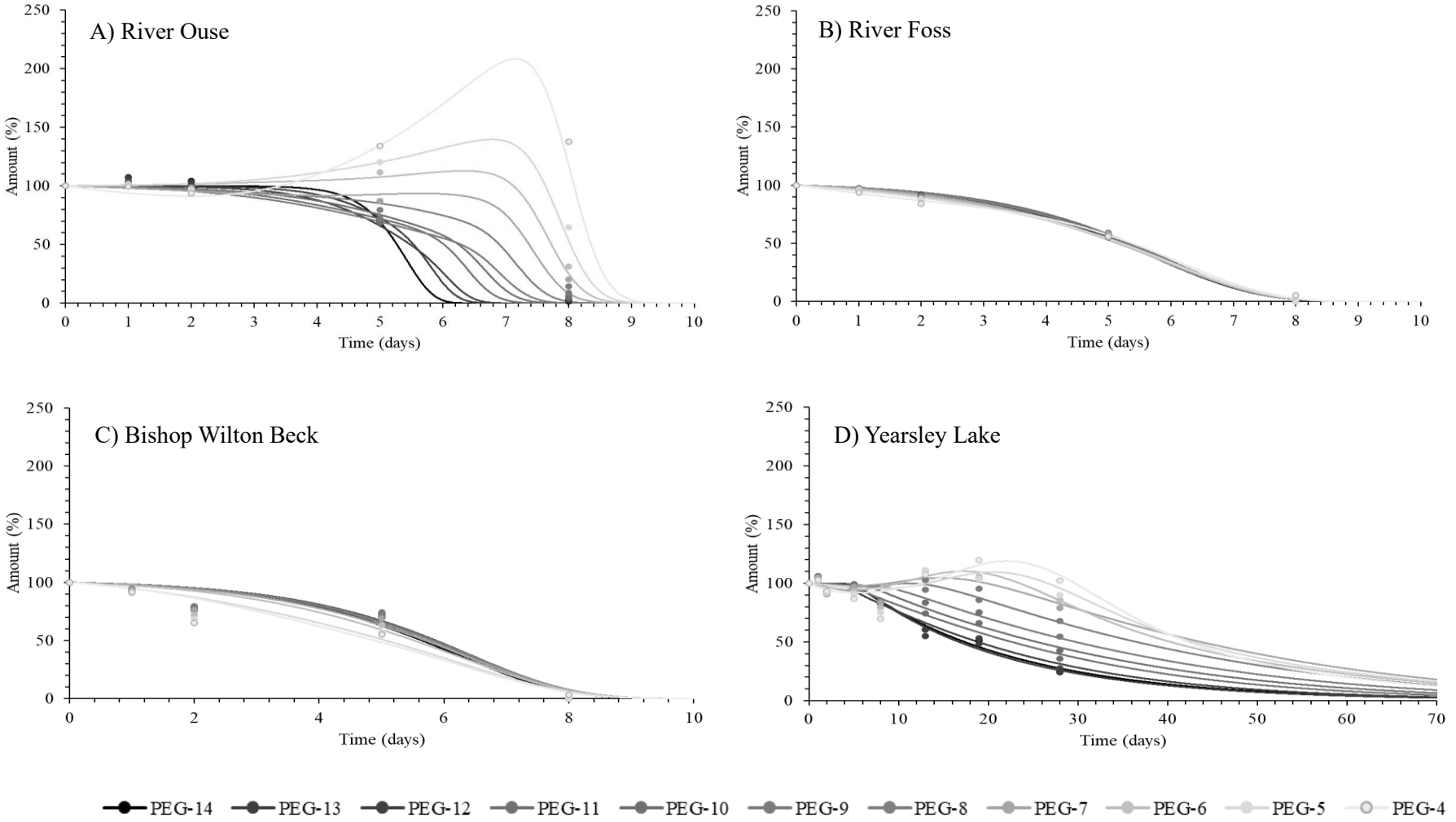


Figure 5.7: Degradation kinetics for individual PEG homologues in water from A) the River Ouse; B) the River Foss; C) Bishop Wilton Beck; and D) Yearsley Lake, shown as visually derived logistic model curves (lines) and averaged experimentally measured concentrations at each time point (circles). Error (confidence intervals) associated with experimental measurements is presented in Table 5.5.

The large number of time increments required in general made using the Excel solver add-in computationally slow; use of the solver add-in to minimise residual sum of squares also resulted in a poor fit to experimental data from later timepoints (Appendix 5.7), with solved model degradation curves being predictive of complete loss of PEG homologues from River Ouse water before 7 days, whereas from experimentally measured data, average concentrations of all PEG chain lengths were > 0% at 8 days, and PEG-4 was still present at 137% of its initial concentration at 8 days. This effect may result from propagation of error from sequential solving of equations for each polymer chain. Therefore, visual estimates of the parameters a_0, a_{max}, and r were used for final derivation of $t_{1/2}$ values for the individual polyether homologues. These were derived by manually changing parameters to provide a close fit of modelled curves to the experimental data (described in Section 5.2.5.2). The derived curves and estimates of $t_{1/2}$ for individual polymer chains are therefore preliminary estimates only; nevertheless, $t_{1/2}$ values strongly depend on the period of rapid biodegradation following the lag phase and are thus similar between curves with small variations in parameters. Preliminary implications for biodegradation kinetics of polyether homologues can also be assessed from the model curves. Final estimated values of a_{max}, a_0 and r, and subsequent calculated values of $t_{1/2}$ (corresponding to the models presented in Figures 5.6 and 5.7), are given in Table 5.6.

As can be observed in Figures 5.6 and 5.7, longer polymer chains followed similar degradation patterns to the bulk mixtures in all water types (Section 5.3.1), due to fewer polymer chains of higher mass being present to break down into these homologues. In some water types, however (most significantly the River Ouse for PPG and PEG, and Yearsley Lake for PEG), as polymer chain length decreases, observed biodegradation appears slower, until for the shortest chain lengths (approximately PEG-7 and below, and PPG-4) measured concentrations increase significantly before decreasing at later times. This observation can be directly attributed to formation of shorter PEG and PPG chains upon degradation of higher molecular weight homologues, and for water from the River Ouse, decreases in concentration of the shortest chain lengths can only be observed after the longest are almost entirely degraded (Figures 5.6 and 5.7). In contrast, for some water types minimal differences between degradation of different homologues are observed (e.g. PEG in the River Foss, Figure 5.7), and in some waters, the reverse trend is seen, with shorter polymer chains disappearing faster than longer chains in water from Bishop Wilton Beck for PEG and water from Yearsley Lake for PPG.

Table 5.6: Final determined logistic model parameters for individual PPG and PEG homologues, and associated biodegradation half-life estimates. Parameters for PPG-10 and PEG-14 were determined using the Microsoft Excel solver add-in; parameters for all other homologues were optimised visually by comparison to experimental data.

Polypropylene glycol (PPG)					Polyethylene glycol (PEG)				
Polymer homologue	**a_0 (day^{-1})**	**a_{max} (day^{-1})**	**r (day^{-1})**	**$t_{1/2}$ (days)**	**Polymer homologue**	**a_0 (day^{-1})**	**a_{max} (day^{-1})**	**r (day^{-1})**	**$t_{1/2}$ (days)**
River Ouse									
PPG-10	2.07E-04	3.33E+04	0.73	10.7	PEG-14	5.07E-06	3.85E+01	2.42	5.3
PPG-9	8.00E-04	3.33E+04	0.65	9.7	PEG-13	1.82E-04	3.85E+01	1.70	5.2
PPG-8	4.00E-03	3.33E+04	0.45	9.7	PEG-12	1.00E-03	3.85E+01	1.40	4.9
PPG-7	1.10E-02	3.33E+04	0.35	9.0	PEG-11	6.00E-03	3.85E+01	1.00	4.8
PPG-6	3.00E-02	3.33E+04	0.30	6.9	PEG-10	1.00E-02	3.85E+01	0.90	4.6
PPG-5	6.50E-02	3.33E+04	0.28	4.9	PEG-9	2.00E-02	3.85E+01	0.80	4.2
PPG-4	2.00E-01	3.33E+04	0.20	2.6	PEG-8	3.00E-02	3.85E+01	0.70	4.1
					PEG-7	5.00E-02	3.85E+01	0.60	3.7
					PEG-6	6.00E-02	3.85E+01	0.58	3.5
					PEG-5	9.00E-02	3.85E+01	0.55	3.0
					PEG-4	2.50E-01	3.85E+01	0.45	1.8
River Foss									
PPG-10	4.22E-09	7.02E+01	1.65	11.8	PEG-14	1.82E-02	3.18E+04	0.61	5.2
PPG-9	5.89E-08	3.00E+01	1.50	11.1	PEG-13	2.80E-02	3.18E+04	0.61	4.5
PPG-8	5.89E-07	4.00E+00	1.30	11.0	PEG-12	3.50E-02	3.18E+04	0.61	4.2
PPG-7	5.89E-06	3.50E+00	1.10	10.8	PEG-11	4.00E-02	3.18E+04	0.61	4.0
PPG-6	1.00E-04	5.00E+00	0.90	9.8	PEG-10	4.80E-02	3.18E+04	0.61	3.7
PPG-5	6.50E-04	1.00E+01	0.77	8.8	PEG-9	6.00E-02	3.18E+04	0.61	3.4
PPG-4	4.60E-03	1.00E+01	0.63	7.3	PEG-8	7.80E-02	3.18E+04	0.61	3.0
					PEG-7	1.10E-01	3.18E+04	0.61	2.6
					PEG-6	1.80E-01	3.18E+04	0.60	2.0
					PEG-5	2.80E-01	3.18E+04	0.58	1.5
					PEG-4	6.00E-01	3.18E+04	0.55	0.9

(Table 5.6 continued)

Polypropylene glycol (PPG)					Polyethylene glycol (PEG)				
Polymer homologue	**a_0 (day^{-1})**	**a_{max} (day^{-1})**	**r (day^{-1})**	**$t_{1/2}$ (days)**	**Polymer homologue**	**a_0 (day^{-1})**	**a_{max} (day^{-1})**	**r (day^{-1})**	**$t_{1/2}$ (days)**
Bishop Wilton Beck									
PPG-10	1.02E-03	1.38E+04	0.60	10.0	PEG-14	1.54E-02	5.26E+03	0.59	5.6
PPG-9	1.50E-03	1.38E+04	0.60	9.4	PEG-13	2.20E-02	5.26E+03	0.59	5.1
PPG-8	4.00E-03	1.38E+04	0.50	8.9	PEG-12	2.80E-02	5.26E+03	0.59	4.7
PPG-7	5.00E-03	1.38E+04	0.50	8.5	PEG-11	3.00E-02	5.26E+03	0.59	4.6
PPG-6	8.00E-03	1.38E+04	0.50	7.6	PEG-10	3.50E-02	5.26E+03	0.59	4.3
PPG-5	2.20E-02	1.38E+04	0.44	6.1	PEG-9	4.20E-02	5.26E+03	0.59	4.0
PPG-4	6.00E-02	1.38E+04	0.40	4.3	PEG-8	5.30E-02	5.26E+03	0.59	3.7
					PEG-7	7.20E-02	5.26E+03	0.59	3.2
					PEG-6	1.10E-01	5.26E+03	0.59	2.6
					PEG-5	2.00E-01	5.26E+03	0.59	1.9
					PEG-4	4.50E-01	5.26E+03	0.59	1.1
Yearsley Lake									
PPG-10	2.50E-03	1.07E+03	0.18	21.6	PEG-14	5.11E-06	5.62E-02	1.85	17.4
PPG-9	3.50E-03	1.07E+03	0.18	19.8	PEG-13	9.00E-06	9.00E-02	1.80	12.8
PPG-8	4.40E-03	1.07E+03	0.18	18.6	PEG-12	5.00E-05	1.00E-01	1.75	11.3
PPG-7	5.50E-03	1.07E+03	0.18	17.4	PEG-11	9.00E-05	1.00E-01	1.70	11.1
PPG-6	9.00E-03	1.07E+03	0.18	14.9	PEG-10	1.00E-03	1.10E-01	1.00	11.0
PPG-5	1.90E-02	1.07E+03	0.18	11.2	PEG-9	5.00E-03	1.20E-01	0.60	11.0
PPG-4	5.00E-02	1.07E+03	0.18	6.9	PEG-8	2.00E-02	1.30E-01	0.30	10.9
					PEG-7	3.00E-02	1.50E-01	0.22	10.4
					PEG-6	6.00E-02	2.80E-01	0.10	8.4
					PEG-5	1.00E-01	4.50E-01	0.09	5.7
					PEG-4	2.50E-01	1.40E+00	0.06	2.6

Previously, there have been both observations of shifts to a lower molecular weight distribution upon biodegradation of PEG and PPG (Zgoła-Grześkowiak *et al.* 2006; Bernhard *et al.* 2008; Tisler *et al.* 2021), and studies which have not observed this trend for PEG > 1900 Da in seawater (Bernhard *et al.* 2008) and PPG in freshwater (Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007). A shift to higher molecular weights upon degradation of PEG in soil has also been reported (McLaughlin *et al.* 2016). The results of the present study across the different water and polymer types thus reflect all of these contrasting previous observations. Although the generally accepted mechanism of PEG biodegradation is oxidation followed by sequential shortening of polymer chains via cleavage of terminal ether bonds, as has been assumed here (Figure 5.2; Kawai 2002; West *et al.* 2007; Bernhard *et al.* 2008; Beran *et al.* 2013; Rogers *et al.* 2019), differing degradation mechanisms have been suggested previously for both PEG and PPG (Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007), with the degradation mechanism for PPG in particular being somewhat more contested (Tisler et al. 2021). However, it has also been suggested that the lack of a shift in molecular weight distribution observed for PPG in some studies (Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007) is due to rapid and complete intracellular degradation of PPG such that intermediates are not released to extracellular space (West *et al.* 2007), rather than a differing mechanism of biodegradation. This may also be attributable to PEG in some studies (Bernhard *et al.* 2008; McLaughlin *et al.* 2016). Given the close fit of experimental data with modelled estimates which assume sequential shortening of polymer chains, the data of the present study also add weight to the theory that PEG and PPG are both biodegraded by loss of single monomer units from chain termini. In addition, we have here shown that faster disappearance of shorter polymer chains is possible even with incorporation of sequential chain shortening in kinetic models (Figures 5.6-D and 5.7-C), and so a lack of measurement of formation of shorter chains does not mean that formation processes are absent. Thus sequential chain shortening can still occur as the primary biodegradation mechanism in cases where formation of shorter chains or shifts to a lower molecular weight distribution are not observed experimentally (Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007; Bernhard *et al.* 2008; McLaughlin *et al.* 2016), and a lack of release of intracellular degradation products or highly rapid degradation of shorter chains are not required to explain this phenomenon, but rather relative rates of formation and loss processes of each homologue within the polymer mixtures. Although environmental PEG biodegradation has been relatively well-

studied (e.g. Zgoła-Grześkowiak *et al.* 2006; West *et al.* 2007; Bernhard *et al.* 2008; Rogers *et al.* 2019; Menzies *et al.* 2023), to our knowledge degradation kinetics of individual homologues have not been previously characterised to this extent, and thus the present study provides novel data on degradation behaviour of both PEG and PPG homologues, which is also significant for polymer environmental exposure and risk assessment (Section 5.3.3).

Estimates of $t_{1/2}$ were thus obtainable for individual PEG and PPG homologues by utilising optimised parameters to calculate $t_{1/2}$ according to the logistic model (FOCUS 2014; Table 5.6). Values of $t_{1/2}$ can be seen to increase with increasing polymer chain length for both PEG and PPG in all water types (Figure 5.8).

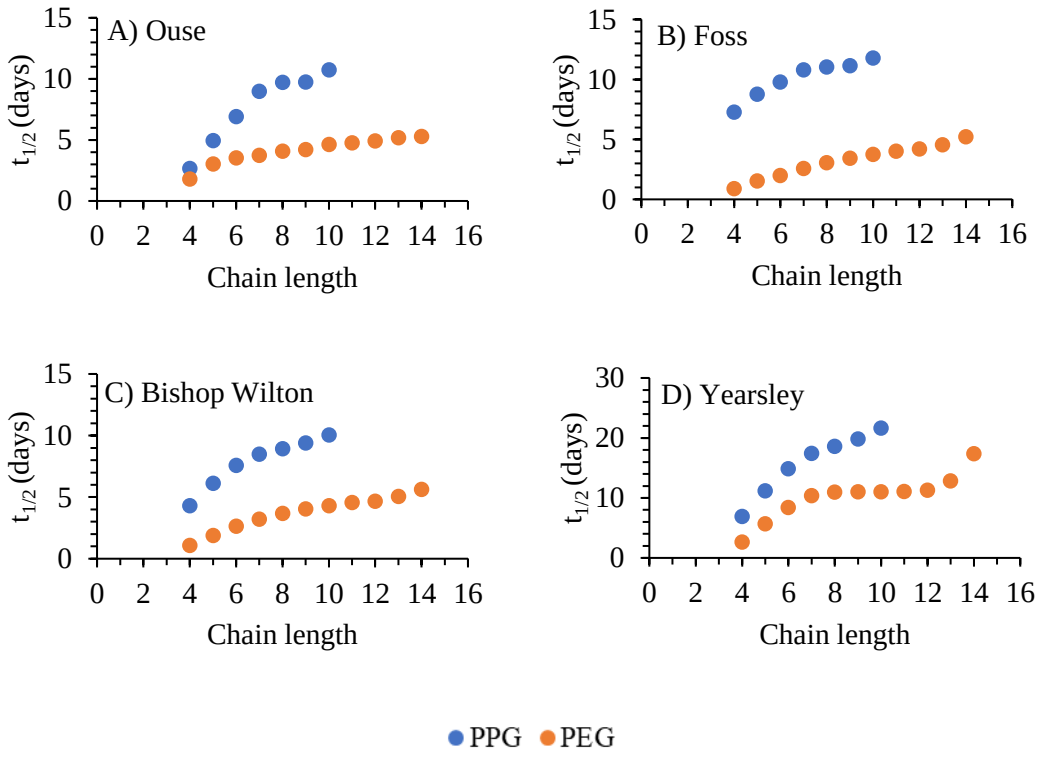


Figure 5.8: Change in estimated biodegradation half-life ($t_{1/2}$) with polymer chain length in water from A) the River Ouse; B) the River Foss; C) Bishop Wilton Beck; and D) Yearsley Lake.

This is consistent with the observed faster rate of degradation of shorter chains in the experimental data during the early lag phase, before significant formation processes occur (Figures 5.6 and 5.7). This may be expected given that biodegradation of water-soluble polymers in general is expected to be faster for polymers of lower molecular weight (Duis *et al.* 2021), and previously PEG and PEG/PPG copolymer biodegradation has been found to decrease with increasing average molecular weight (Watson and Jones

1977; Christopher *et al.* 1992; Corti *et al.* 1998; Bernhard *et al.* 2008; Beran *et al.* 2013; Menzies *et al.* 2023). A similar pattern has been observed previously for propylene glycol oligomers of n = 1-4, and PPG-34 mixtures compared to PPG-46 mixtures; however, this trend was reversed for PPG polymers of intermediate molecular weight, with increased biodegradation observed with increasing average n for PPG-7, PPG-17, and PPG-34 (West *et al.* 2007). PPG of MW_N 725 has also been found to biodegrade more rapidly than PPG of MW_N 425 (Zgoła-Grześkowiak *et al.* 2007). To our knowledge, $t_{1/2}$ values for individual PEG and PPG homologues in polymer mixtures have been reported only once, and formation processes for shorter chains were not accounted for (Rogers *et al.* 2019).

In general, polyether chains of higher molecular weight may be expected to be less bioavailable due to reduced uptake into cells of microorganisms (although this is not necessarily always the case; Groh *et al.* 2023), and terminal hydroxy groups which must be present for oxidation and biodegradation to occur (Corti *et al.* 1998; Figure 5.2) may be less available to enzymes at longer polymer chain lengths, both of which may explain the trends observed in the present study. As in the case of the bulk polymer mixtures (Section 5.3.1), PPG was observed to be slower to degrade than PEG in all river water samples, with greater $t_{1/2}$ for all homologue chain lengths (Figure 5.8). This observation may be attributable to the presence of different PPG isomers (West *et al.* 2007; Rogers *et al.* 2019), with secondary hydroxyl groups not being oxidisable to a carboxylic acid (Figure 5.2); a ketone intermediate has however been observed in some studies (Zgoła-Grześkowiak *et al.* 2007) but not others (Rogers *et al.* 2019). Thus rapid degradation of PEG from both ends of the polymer chain (which are identical) via formation of carboxylic acid and di-carboxylic acid intermediates is possible, whereas it may be that degradation of PPG from only the ends of a polymer chain with a primary hydroxyl group can occur, with formation of di-carboxylated PEG but not PPG intermediates having been observed previously (Rogers *et al.* 2019). Further research and characterisation of oxidised PEG and PPG intermediates is required to confirm whether this is truly the case.

Interestingly, despite the observed faster degradation of PPG mixtures in lake water compared to PEG (Section 5.3.1), estimated half-lives of individual PPG homologues remained longer than those of corresponding PEG homologues of the same chain length (Figure 5.8). Given that the formation of shorter polymer chains was observed for PEG but not PPG in lake water, it is likely that individual PEG polymer chains were faster to

degrade than PPG of the same chain length, but measurement of shorter PEG chains formed upon degradation resulted in observed slower degradation of the bulk mixture. It is worth noting that formation of shorter PPG chains is likely to still occur as discussed above; their lack of measurement can be explained by e.g. a lack of extracellular release of degradation products (West *et al.* 2007), but as discussed above, multiple formation and degradation processes occurring in parallel in the polymer mixture and their relative rates can result in observed decreases of all polyether chain lengths.

5.3.3. Implications for environmental exposure and exposure assessment

The results of the present study have implications for biodegradation testing of polymers and data interpretation, as well as environmental fate and exposure modelling for polymers. Values of the biodegradation half-life determined for bulk polymer mixtures (Table 5.3) were longer than those obtained for individual polymer homologues for the vast majority of chain lengths (Table 5.6), reflecting the overall slower rate of removal of the bulk mixture due to shorter chain degradation products being formed. In addition, the apparent slower degradation of bulk PEG mixtures compared with PPG in lake water was not reflected in actual degradation rates of individual polymer chains, due to shorter PEG chains formed from biodegradation being measured in this water type (in contrast to PPG). This exemplifies the complexity of environmental biodegradation of polymers (reviewed in *Chapter 2*), with formation of a wide array of products from biodegradation which may need to be incorporated in environmental risk assessment, and which may have complex formation and removal processes dependent on other constituents of the polymer mixture. The present findings are also particularly significant for persistence assessment, as for polymers such as PEG and PPG which fragment to shorter homologues of the same polymer during biodegradation, polymer mixtures may be rated as persistent but not their constituent individual homologues. Conversely, polymer biodegradability is also key for polymer prioritisation, with 'substantial' biodegradation indicating potential concern (ECETOC 2019) given that lower molecular weight polymers are often assumed to have higher hazard potential (OECD 2009).

Increases in $t_{1/2}$ with polymer chain length are useful for development of QSARs relating polyether chain length or molecular weight to rate of biodegradation. It is also important to note that the observed increase in estimated $t_{1/2}$ with polymer chain length is not always reflected in measured experimental concentrations due to the formation of

shorter polymer chains with biodegradation, leading to shorter chains remaining for longer periods than larger chains in experimental systems for some water types. This is significant given that despite the estimated shorter half-lives of shorter polymer chains, which may also be expected for many water-soluble polymer types (Duis *et al.* 2021), they may be present in the environment for significantly longer time periods compared with longer polymer chains (Section 5.3.2) when formed during biodegradation. Characterising degradation of only the bulk polymer mixture may therefore underestimate environmental exposure to shorter polymer chains. In addition, derivation of $t_{1/2}$ for individual polymer homologues without accounting for formation processes, whilst giving an estimate of observed removal, will be dependent on the specific polymer mixture in question. Even reporting of $t_{1/2}$ values as a range as has been recommended previously (ECETOC 2020) may not encapsulate actual removal processes if polymer chains are being both biodegraded and formed. It has also been noted that determination of $t_{1/2}$ values for polymers that are not highly homogeneous may not be accurate due to the differences in degradation rates between different constituents (ECETOC 2020), and here we demonstrate that even for the highly homogeneous PEG and PPG polymers studied here, complex differences in removal processes exist between homologues and in different water types. In the present study, a method for estimating biodegradation kinetics of individual polymer homologues whilst accounting for their formation from biodegradation of longer polymer chains has been applied, which will be useful for in-depth biodegradation testing of other water-soluble polymers to elucidate transformation mechanisms and characterise environmental behaviour. However, for most water-soluble polymer types, analytical techniques for characterisation of all components of the polymer mixture are currently lacking (Huppertsberg *et al.* 2020).

Variability in observed formation of shorter PEG and PPG chains was also observed, reflecting different reported results from the literature (e.g. Zgoła-Grześkowiak *et al.* 2006; Zgoła-Grześkowiak *et al.* 2007; Bernhard *et al.* 2008; McLaughlin *et al.* 2016; Tisler *et al.* 2021), with formation (increase in concentration) of shorter chains only being directly observed for the River Ouse (for both polymers) and Yearsley Lake (for PEG only). Improvements in variation in biodegradability tests observed previously (Davenport *et al.* 2022; Menzies *et al.* 2023) may therefore also need to account for potentially different observed degradation mechanisms when characterising complex polymer degradation processes and products. There is also a clear need to incorporate

water from a range of sources and of different types in biodegradation tests, given the significant differences that can be observed in water with different properties and characteristics.

5.4. Conclusions and recommendations

Biodegradation half-lives of the water-soluble polymers PEG (MW_N ca. 400 g mol^{-1}) and PPG (MW_N 446 g mol^{-1}) in river water from three locations (incorporating a large, medium, and small river) were determined by application of the logistic model and found to range from 5.2-6.5 days (PEG) and 10.1-12.1 days (PPG). Biodegradation of water-soluble polymers in lake water was also characterised for the first time, with degradation of both polymers proceeding much more slowly; both PEG and PPG were still present in lake water after 28 days. Individual polymer homologues were also measured at each timepoint and biodegradation kinetics of each polymer chain were characterised, and found to match closely with a model predicting terminal cleavage of single monomer units leading to sequential shortening of polymer chains. Biodegradation half-lives could therefore be determined for each chain length whilst accounting for loss processes (by biodegradation) and formation processes (from biodegradation of longer polymer chains), and were found to generally increase with polymer chain length (PEG-4 to PEG-14, and PPG-4 to PPG-10). Despite the shorter half-lives of shorter polymer chains, in some water types these lower molecular weight homologues persisted after complete loss of longer polymer chains due to their formation during biodegradation. The longer observed half-lives for bulk polymer mixtures compared to individual polymer chains have implications for polymer biodegradation studies and persistence assessment as well as exposure and fate characterisation. Future studies assessing PEG and PPG of different average molecular weights will be useful in further refining and characterising modelled homologue degradation kinetics, as well as application of methods to improve repeatability between biodegradation studies, including concentration and characterisation of micro-organisms. Where analytical methods become available, application of this or similar kinetic models to other types of water-soluble polymers will be useful in characterising their environmental fate behaviour for exposure and risk assessment.

Chapter 6

Final Discussion and Conclusions

Polymers are a diverse class of materials which have fundamental uses across a range of sectors, including in packaging, electronic equipment, construction, household and personal care products, agriculture, and wastewater treatment, amongst numerous other uses (Lambert *et al.* 2014; Danso *et al.* 2019; Huppertsberg *et al.* 2020). Plastic polymers are pervasive and persistent across many environmental compartments (Derraik 2002; Thompson *et al.* 2009; Li *et al.* 2021), and an increasing number of studies are measuring water-soluble polymers (WSPs) in the environment as well (e.g. Huppertsberg *et al.* 2020; Tisler *et al.* 2021; Pauelsen *et al.* 2023). However, polymers in general have often been exempt from regulatory schemes in the past (USEPA 1997; EP&C 2006), and there is now a need to assess their environmental risks but a lack of established methods available to do so. Environmental risk assessment of polymers will require data and methods on both ecological hazard and exposure. In the present work, methods for the environmental fate and exposure assessment of polymers were investigated, developed, and applied in order to provide recommendations on how environmental exposure of water-soluble polymers could be better assessed in practice. In particular, current methods for environmental exposure assessment of chemicals were reviewed in the context of their applicability to polymers; WSPs in current use were identified and prioritised in terms of their potential environmental exposure and risks; and a selection of the prioritised polymers were studied in order to obtain relevant environmental fate data and test application of methods and key considerations for characterisation of fate behaviour and risk assessment.

6.1. Main findings

Investigation of methods for environmental exposure assessment of polymers was initially conducted through a critical review of the literature (*Chapter 2*). Characterisation of fate and behaviour for assessment of exposure requires testing of key parameters including basic physicochemical properties such as solubility and melting point, partition coefficients (such as the soil-water partition coefficient K_d) describing the distribution between solid and aqueous phases, and parameters describing biodegradation such as

half-life ($t_{1/2}$). Standard test methods for these and other key properties have already been established for low molecular weight chemical compounds (e.g. OECD 1995b, 1995a, 2000a, 2002b, 2002a, 2004a). However, polymers are unique compared to most typical low molecular weight chemicals, due to their generally high molecular weights and large molecular size, and the presence of multiple polymer chain lengths, residual monomers, and additives present as a complex mixture (ECETOC 2019). Many existing methods used in environmental risk assessment may not be applicable to polymers (ECETOC 2019, 2020) and methods to assess polymers are lacking. The literature review of the present work determined that several key fate parameters, including bioconcentration and bioaccumulation factors, are not likely to be relevant to polymers. Partition coefficients are also not applicable to solid polymers such as microplastics. Additional parameters, including number and weight average molecular weight, size measured by hydrodynamic radius or particle size distribution, and deposition rate constants, are likely to also be necessary to characterise environmental fate of some polymer types, among other key properties. A broad classification of polymers as solid or dissolved was suggested in the present work as being useful in determining key fate parameters for specific polymers, and underpinning a framework for polymer exposure assessment. Key research needs were also identified, including the need for development and validation of analytical methods for characterisation of both solid and water-soluble polymers (Burns and Boxall 2018; Huppertsberg *et al.* 2020), the need to further identify the most important parameters for polymer fate analysis (ECETOC 2019), characterisation of complex polymer degradation processes and byproducts, development of quantitative structure-activity relationship (QSAR) approaches for polymers (e.g. Nolte *et al.* 2017b; Min *et al.* 2020) and exposure modelling approaches, and further research into the fate of WSPs as a relatively under-studied class of materials (Arp and Knutsen 2020; Huppertsberg *et al.* 2020).

Higher tier exposure models are expected to require the most adaptation and development for polymers, whilst most lower-tier models will be generally applicable (*Chapter 2*). However, the lack of publicly available polymer usage and emissions data for input into models hinders even a basic approach (Duis *et al.* 2021), and given the wide range of polymers in current use, prioritisation is needed to focus the research efforts identified above. Therefore in *Chapter 3*, a lower-tier exposure model was developed to both identify and prioritise polymers in household products. Household

products released down-the-drain at point of use were the focus of the study, as they are potentially a direct source of emissions of primarily water-soluble polymers to the environment. Over three hundred individual polymers were identified from product ingredients and broadly categorised into groups based on chemical structure and monomer types, for which conservative, worst-case exposure estimates (predicted environmental concentrations; PEC) were obtained for soil and surface water. Polymers were identified without prior knowledge of their identities, allowing the full range of polymers in the studied products to be accounted for, although a lack of consistent data on key properties identified in *Chapter 2* such as average molecular weight meant that groupings were broad and are likely to benefit from further refinement as data become available.

Refined estimates of exposure in soil and surface waters were also determined for ten initially prioritised polymer groups. Although conservative, these data are useful preliminary estimates of environmental concentrations, which are severely lacking for most WSPs (Pecquet *et al.* 2019; Huppertsberg *et al.* 2020; Duis *et al.* 2021); the estimates were also in good agreement with the limited predicted and measured data available from the literature. These exposure estimates were used to calculate preliminary estimates of risk in an aquatic environment. Seven polymer groups were identified as having the potential to pose risk: polyethers and copolymers, polyquaterniums, alcohol alkoxylates, alcohol ethoxylate salts, polyol ethoxylate esters, silicones, and polycarboxylates. In particular, polyethers and copolymers, polyquaterniums, and polyol ethoxylate esters are of the highest potential concern based on preliminary risk estimates, with polyethers and copolymers having the highest calculated risk. This is despite the relatively low ecotoxicity and high biodegradability of polyethers, and likely results from their extremely high usage volumes resulting in high concentrations in the environment, which is supported by monitoring data (Crescenzi *et al.* 1997; Rychłowska *et al.* 2003; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014; Traverso-Soto *et al.* 2014; Pauelsen *et al.* 2023). It has also been recognised that prioritisation schemes for polymers should incorporate production volumes and usage as exposure indicators (Groh *et al.* 2023), emphasising the need for further study of high use-volume WSPs such as polyethers.

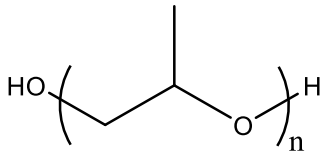
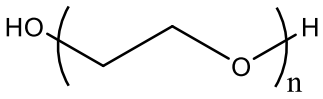
However, whilst the exposure model in *Chapter 3* provides a useful step towards a full environmental risk assessment of many polymer types, it was identified that ecotoxicity data are needed for many polymer groups, as well as higher-tier estimates

which require data on environmental fate and removal processes for the prioritised polymers. Analysis of the suitability of the identified polymer groups is also needed.

Therefore in *Chapter 4*, the sorption behaviour of two polyethers from the prioritised polyether group in *Chapter 3* was studied. This chapter also provided a case study in application of a standard OECD test method (OECD 2000a) to polymers and measurement of a fate parameter identified as key to WSPs in *Chapter 2*. Key results from the exposure model (*Chapter 3*) and experimental data (*Chapter 4* and *Chapter 5*) are summarised for the two case study polymers in Table 6.1.

An analytical method utilising high-performance liquid chromatography – mass spectrometry (HPLC-MS) was developed and validated for both polymers (polyethylene glycol (PEG)-9 and polypropylene glycol (PPG)-7) based on literature studies (Rissler *et al.* 1993; Rissler 1996; Zgoła-Grześkowiak *et al.* 2006; Davey *et al.* 2017; Thurman *et al.* 2017; Rogers *et al.* 2019), allowing separation and quantitation of individual chain lengths in the polymer mixtures. Values of K_d were calculated for the bulk polymer mixtures and for individual homologues across six soil types, which are useful in higher-tier fate and exposure assessment. Whilst some limited data were previously available providing K_d values for PEG (Podoll *et al.* 1987; Castanho *et al.* 2009; Traverso-Soto *et al.* 2014), this study provided the first reported data on K_d values of PPG, as well as the first reported K_d values for individual PEG (and PPG) homologues studied in their native polymer mixtures. Values of K_d indicated low levels of sorption for both polymers, with a positive correlation between K_d values and polymer molecular weight for most soils, providing a useful basis for development of sorption QSARs for these polymers. Existing sorption QSARs for low molecular weight chemicals (USEPA 2012) were also compared to the measured data and found to be poor predictors of K_d values for these polymers, despite the fact that the polymers were within the molecular weight range of the QSAR dataset.

Table 6.1: Summary of modelled and experimental data for the two case study polymers, polypropylene glycol (PPG) and polyethylene glycol (PEG).

	PPG-7	**PEG-9**
Structure	 Average n = 7	 Average n = 9
Number average molecular weight (MW_N) (g mol^{-1})	446	ca. 400
Range of polymer homologues studied	Chain lengths (n) 4-10	Chain lengths (n) 4-14
Polymer group PEC_{SW} (µg L^{-1}) (polyethers and copolymers)		2-90
Polymer group PEC_{SOIL} (µg kg^{-1}) (polyethers and copolymers)		700-4900
Contribution of relevant polyether group members to PEC (%)	PPG-12 = 7.63 PPG-9 = 7.22 PPG-6 = 4.77 PPG-n = 0.14	PEG (MW unspecified) = 10.03 PEG MW < 4100 = 3.58 PEG-4 = 1.53 PEG-10 = 0.42 PEG-8 = 0.21 PEG-9 = 0.18
K_d of polymer mixture across studied soils (cm^3 g^{-1})	0.27-1.47	0.32-1.35
Range of K_d of individual homologues across studied soils (cm^3 g^{-1})	0.18-13.72	0.28-19.68
Trends in K_d	K_d values increase with increasing soil clay content and increasing percentage of soil particles in the smallest size range. K_d values generally increase with polymer chain length/ molecular weight, particularly in soil with high clay content. K_d values of individual homologues are higher for PPG than PEG of a given chain length, but this difference is diminished for PEG and PPG homologues of similar molecular weight.	
Biodegradation $t_{1/2}$ of polymer mixture in river water (days)	10.1-12.1	5.2-6.5
Biodegradation $t_{1/2}$ of polymer mixture in lake water (days)	21.3	31.3
Range of biodegradation $t_{1/2}$ of individual polymer homologues in river water (days)	2.6-11.8	0.9-5.6
Range of biodegradation $t_{1/2}$ of individual polymer homologues in lake water (days)	6.9-21.6	2.6-17.4
Trends in $t_{1/2}$	Biodegradation of PPG and PEG polymer mixtures follow a logistic model. Values of $t_{1/2}$ are shorter in river water compared to lake water. PEG mixtures degrade faster than PPG mixtures in river water, and PPG homologues have greater $t_{1/2}$ values than PEG homologues in all water types. Values of $t_{1/2}$ increase with increasing polymer chain length/molecular weight for both polymers. Shorter polymer chains are both formed and lost during degradation.	

The K_d values determined for the bulk polymer mixtures in *Chapter 4* were also compared to K_d values determined for individual polymer homologues and were found to be poorly representative of homologues at the upper extremes of the characterised molecular weight distribution in cases of higher sorption. This provides a proof of concept that key fate parameters for many polymers may need to be reported as a range (ECETOC 2020), even for these case study polymers which were relatively homogeneous and of relatively low molecular weight compared to many other polymers identified in current use. In addition, mixture interactions were observed, with sorption of shorter polymer chains being impeded by the presence of longer chains in the mixtures at high concentrations of polymer. This provides useful data on the influence of complex polymer properties on measurement of fate parameters (*Chapter 2*). The results of this study also provide values of fate parameters for higher tier modelling and inform the polymer grouping approach of *Chapter 3*, with PEG and PPG showing comparable K_d values at similar molecular weights, suggesting that grouping of these two polymers together at similar molecular weights is likely to be a valid and useful approach for this aspect of fate assessment.

A preliminary degradation study of PPG in soil in *Chapter 4* suggested changes in polymer molecular weight distribution with biodegradation. Characterisation of complex polymer degradation processes and transformation products was also identified as a key research need in *Chapter 2*, and information on fate processes such as biodegradation is key for refining exposure models such as that developed in *Chapter 3*. Therefore in *Chapter 5*, biodegradation of the prioritised polyethers in four types of freshwater was studied. These data also provide accompanying information on the fate of PEG and PPG in freshwater to data on fate in the soil environment from *Chapter 4*, both of which are useful in providing data for aquatic and terrestrial exposure estimates such as those in *Chapter 3*. Both polymer mixtures were found to degrade rapidly in river water, as has been observed previously (Zgoła-Grześkowiak *et al.* 2006). However, biodegradation of PEG and PPG was much slower in lake water, with neither polymer having been completely degraded at the end of the tests (28 days). This study is to our knowledge the first to characterise water-soluble polymer biodegradation in lake water. Whilst bulk PEG mixtures were found to degrade more rapidly than PPG mixtures in river water, PPG degraded more rapidly in lake water, showing a complex dependence on environmental

conditions, microbial activity, and molecular weight, as well as parallel degradation kinetics of individual polymer constituents.

Values of the biodegradation half-life ($t_{1/2}$) were determined for polymer mixtures, providing useful data on a key environmental fate parameter (*Chapter 2*). In addition, biodegradation kinetics of individual polymer homologues were modelled, incorporating both removal and formation processes from shortening of polymer chains during degradation (Kawai 2002; West *et al.* 2007; Bernhard *et al.* 2008; Beran *et al.* 2013; Rogers *et al.* 2019; Tisler *et al.* 2021). This allowed biodegradation half-lives for individual PEG and PPG homologues within their native mixtures, with incorporation of both formation and loss processes, to be determined for the first time. Values of $t_{1/2}$ were found to increase with increasing molecular weight for both PEG and PPG, which is supported by some literature studies (Watson and Jones 1977; Corti *et al.* 1998; Bernhard *et al.* 2008; Beran *et al.* 2013; Menzies *et al.* 2023) but not others (West *et al.* 2007; Zgoła-Grześkowiak *et al.* 2007). Notably, biodegradation half-lives of individual polymer chains were shorter than $t_{1/2}$ values obtained for polymer mixtures in the vast majority of cases. The faster-degrading shorter PEG and PPG were also found to persist for longer than more recalcitrant longer chains in some waters, due to their formation with polymer biodegradation. However, observable formation of shorter polymer chains was variable. In cases where shorter polymer chains disappeared faster than longer chains, kinetics could still be described with modelling of formation processes, showing that understanding of simultaneous formation and biodegradation processes and their relative rates is key to understanding polymer degradation mechanisms. This study also provides the basis of a method to characterise biodegradation kinetics of individual WSP homologues, with implications for exposure and risk assessment.

6.2. Wider implications of research findings

The key findings of the present work have implications for both development of environmental risk assessment methods for polymers, and for the current state of environmental exposure to polymers and corresponding risk. These are summarised in Table 6.2 and discussed in more detail below.

Whilst environmental plastic pollution has long been established (e.g. Derraik 2002; Thompson *et al.* 2009; Li *et al.* 2021), a growing body of work is suggesting that WSPs may be just as ubiquitous in the environment (e.g. Arp and Knutsen 2020; Huppertsberg

et al. 2020; Pauelsen *et al.* 2023), including data from the present study. Predicted environmental concentrations were determined in *Chapter 3* for the largest set of individual WSPs studied thus far. Measured environmental concentrations from the literature for alcohol ethoxylate salts, alcohol alkoxylates, polyethers, and silicones (e.g. Popenoe *et al.* 1994; Fendinger *et al.* 1997; McAvoy *et al.* 1998; Sanderson *et al.* 2013; Cowan-Ellsberry *et al.* 2014; Pauelsen *et al.* 2023; among others) generally corroborate predicted environmental concentrations determined in the present work, with measurements of individual members of the polymer groups often falling on the lower bounds of predicted concentrations for the total group mixture. However, the data of this study suggest that a much wider range of polymer types (both within these groups, and of other basic types and functionalities) are present in the environment, than have been studied previously.

Whilst polymer groupings assigned in the present work are broad, they also highlight the fact that the vast majority of previous studies focus on only one specific polymer, whereas additive concentrations from similar polymers may combine to cause ecological effects as a mixture. Only a very limited number of the WSPs that are likely present in the environment have been previously studied, and whilst some have been found to be unlikely to pose an environmental risk (e.g. alcohol ethoxylates, alcohol ethoxysulfates, and polyacrylic acid homo- and co-polymers; HERA 2004, 2009, 2014a, 2014b), most groups remain understudied; however, the need to adapt and develop methods for polymer environmental risk assessment presents challenges for adequately characterising these polymers (Groh *et al.* 2023). A lack of analytical techniques for most polymers also hinders measurement of actual environmental concentrations. In particular, many available techniques are not specific or sensitive enough for environmental analyses, particularly for high molecular weight polymers consisting of a wide range of individual components as a complex mixture (Huppertsberg *et al.* 2020). It is also imperative that, as analytical methods for polymers are developed, they are sufficiently validated to facilitate collection of robust datasets for polymer exposure assessment.

Table 6.2: Summary of key implications and considerations of main research findings for current environmental exposure and risk of polymers, and exposure and risk assessment approaches.

	Implications for current environmental exposure and risk	**Implications for exposure and risk assessment**
Chapter 2	• Environmental concentrations and risk estimates lacking for many polymer types • Further research and development of methods needed to assess exposure and risk	• Polymer exposure and risk assessment should account for unique polymer properties • Additional methods and parameters needed for characterising fate and behaviour of polymers • Developed methods for polymers should be validated
Chapter 3	• Wide range of WSP types likely to be present in the environment • Several groups have potential to pose risk • Polyethers and copolymers, polyquaterniums, and polyol ethoxylate esters are of highest potential concern based on preliminary risk estimates	• Development of analytical and risk assessment methods should focus on polymer types of highest potential concern • More data required to refine polymer groupings • Measured environmental concentrations and higher tier exposure models needed
Chapter 4	• Sorption of PEG and PPG to solids (such as soil, sludge, sediment, and suspended solids) in the environment likely to be minimal • Higher sorption of longer polymer chains indicates probable shift towards lower molecular weight distribution in the environment	• Bulk polymer mixture K_d unlikely to be representative of individual homologues when high sorption occurring • Mixture interactions may occur in fate studies, impacting results and data interpretation • Individual polymer homologues in native mixtures at environmentally relevant concentrations in a range of environmental media should be analysed where possible • Potential influence on results and risk assessment should be recorded when analysing bulk mixture only
Chapter 5	• PEG and PPG mixtures biodegrade rapidly in river water ($t_{1/2}$ < 2 weeks) and to a lesser extent lake water ($t_{1/2}$ > 3 weeks) • Biodegradation of shorter polymer chains is faster than longer chains • Formation of shorter polymer chains during degradation means they may persist for longer in some environments	• Polymer mixtures have the potential to be classified as persistent even if individual components are not • Polymer degradation mechanisms and transformation products should be incorporated into exposure and risk assessment where possible • Individual polymer homologues in native mixtures at environmentally relevant concentrations in a range of environmental media should be analysed where possible • Potential influence on results and risk assessment should be recorded when analysing bulk mixture only

Polymers present in the environment may pose ecological hazard via a range of potential mechanisms. Ecological hazards of plastics have been extensively studied; plastic debris may cause harm to organisms through entanglement or ingestion (Li *et al.* 2021), and organisms may ingest plastic particles such as microplastics, although actual risks of microplastics are still uncertain (Burns and Boxall 2018). It has been suggested that plastics and microplastics may act as vectors for transport of other chemicals into organisms, but evidence for this effect is again inconclusive (Burns and Boxall 2018; Li *et al.* 2021). Although ecotoxicity of WSPs has been more rarely studied, there is evidence for adverse effects of several types of WSPs. Surfactant polymers such as alcohol ethoxylates may cause adverse effects by disruption of biological membranes (Boeije *et al.* 2006). Sublethal effects have been observed in invertebrates as a result of chronic exposure to polyethylene glycol, polyvinyl alcohol, polyacrylic acid, and polyvinylpyrrolidone (Mondellini *et al.* 2022), all of which were identified as being released down-the-drain in the present work. However, note that adverse effects were observed at or above 5 mg L^{-1}, and actual environmental concentrations are expected to be lower, although mixture effects from multiple polymers may be significant. Concern has also been raised over the potential ecological hazards of cationic polymers, which may cause adverse effects via electrostatic interaction with biological membranes such as algae membranes and fish gills (Duis *et al.* 2021). The preliminary risk data of the present study suggest a potential risk from many polymer types present in the environment based on available ecotoxicity data, although these data remain limited for most polymer types, resulting in conservative risk estimates. Given the large number of identified polymers, focussing initial risk assessment methods and method development on polymer types of highest potential concern is warranted, as well as concentrating efforts on data gaps to refine risk estimates. Whilst polymers have previously been assumed to be of low concern due to their high molecular weights, due to the presence of polymers in the environment and their high usage volumes, potential ecotoxicological effects are of increasing importance. The assumption that polymers with molecular weights > 1,000 Da will have negligible uptake into organisms has also been called into question (Groh *et al.* 2023).

Data from the sorption study for PEG and PPG show that these polymers undergo relatively little sorption to solids from the aqueous phase, suggesting that sorption is unlikely to be a significant removal mechanism from the aqueous environment for these

polymers, and thus is not likely to contribute to significant reductions in modelled surface water concentrations of polyethers. Conversely, concentrations of polyethers in soil from sludge application may be expected to be low, as was shown in literature data incorporated into the emissions model in *Chapter 3* (Steber and Wierich 1985; Duis *et al.* 2021). The low K_d values measured for PEG are in agreement with previous studies (Podoll *et al.* 1987; Castanho *et al.* 2009; Traverso-Soto *et al.* 2014). Whilst biodegradation data (*Chapter 5*) suggest rapid removal of PEG and PPG from river water, which will reduce predicted environmental concentrations after the point of release, it is important to note that shorter-chained homologues may be present in the environment for longer due to their formation during biodegradation of longer chains. The molecular weight dependence of K_d (*Chapter 4*) also suggests that shorter polymer chains may be more mobile and less liable to sorption in the environment. This is significant for many types of WSPs, given that lower molecular weight polymers may in many cases be expected to have higher hazard potential (OECD 2009). Polymers which are rapid to degrade have been previously indicated to be of potential concern (ECETOC 2019). PEG and PPG were also slower to degrade in lake water in the present study, showing that even readily biodegradable polymers may persist for several weeks in some receiving environments. Given that both PEG and PPG have been measured in the environment despite their ready biodegradability (Crescenzi *et al.* 1997; Rychłowska *et al.* 2003; Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014; Traverso-Soto *et al.* 2014; Pauelsen *et al.* 2023), which is likely a result of their high usage and emissions (*Chapter 3*), other WSP types which are more recalcitrant may have significant environmental concentrations (Pauelsen *et al.* 2023), but as mentioned above, analytical techniques for monitoring are lacking (Huppertsberg *et al.* 2020).

Measurement of K_d and $t_{1/2}$ values for individual polymer homologues was made possible by use of relatively low molecular weight PEG and PPG, and allowed comparison to values determined for the bulk polymer mixtures. For many soils, and particularly in cases of high sorption, bulk mixture K_d did not adequately reflect the range of values for individual polymer chains. Observed mixture interactions may also affect measurement of parameters, particularly at higher concentrations of polymer, and thus experimental fate studies should utilise environmentally relevant concentrations wherever possible. The measured mixture effects also suggest that values of K_d (and potentially other fate parameters) determined for individual polymer homologues may be

unique to the polymer mixture in question. This is also significant for development of QSARs for polymers, given that relationships between fate properties and polymer molecular weight may also depend on all components of the polymer mixture, so properties such as molecular weight distribution and polydispersity may impact measurements and thus may need to be defined during testing and risk assessment. These and other additional parameters accounting for the unique properties of polymers defined in *Chapter 2* are therefore likely to be useful in risk assessment. The convergence of K_d values of PEG and PPG of similar molecular weights (compared to chain length) also highlights that the method of grouping and subsequent read-across in risk assessment is important.

Similarly, bulk $t_{1/2}$ values are in most cases longer compared with values for individual homologues due to formation of shorter polymer chains during biodegradation, suggesting that some polymer mixtures could be classified as persistent even when individual polymer chains are not. The wide array of degradation products formed upon polymer degradation in the environment, which may include both polymeric and non-polymeric substances with varying fate properties, should also be accounted for in exposure and risk assessment where possible. Apparent biodegradation mechanisms of PEG and PPG also vary between different water types based on empirically observed data, highlighting the need to study a range of environmental media in fate experiments. The potential for polymer components to be both formed and biodegraded in parallel, with removal processes dependent on other components of the polymer mixture, will also impact results and should be noted in data interpretation. Values of $t_{1/2}$ for both individual polymer homologues and bulk mixtures are likely to be dependent on the specific polymer mixture in question, and even reporting $t_{1/2}$ values as a range may not adequately encapsulate actual removal and transformation processes occurring. Measurement of parameters for bulk polymer mixtures is therefore unlikely to be totally sufficient for most polymers, and may cause phenomena related to mixture interactions as well as the differences in properties that may be observed across a polymer mixture to be overlooked. Parameters measured for individual homologues may need to be measured for different molecular weight distributions and average molecular weights in which these homologues may appear. Where possible, individual polymer homologues should be analysed in their native mixtures in fate experiments, with a combination of measured experimental data and modelling being useful for assessment. However, measurement of

individual homologues is not feasible for many polymers with currently available analytical methods, particularly higher molecular weight polymers (Huppertsberg *et al.* 2020). Therefore, the results of the present study provide a useful insight into the potential limitations of data that may be obtained for other polymers, as well as the potential impact on interpretation of results and ultimate risk assessment, which should be noted in future reporting of data when only the bulk polymer mixture can be analysed.

The methods employed in this thesis have been summarised in Figure 6.1 below, highlighting the processes and test methods needed to better understand the environmental exposure and risks of WSPs. These analyses can be transferred to other polymer types and use sectors, including other WSP groups identified in the present study. Useful next steps to further characterise exposure and thus subsequent risk of these substances, incorporating key tests and results of this research, have also been highlighted (Figure 6.1).

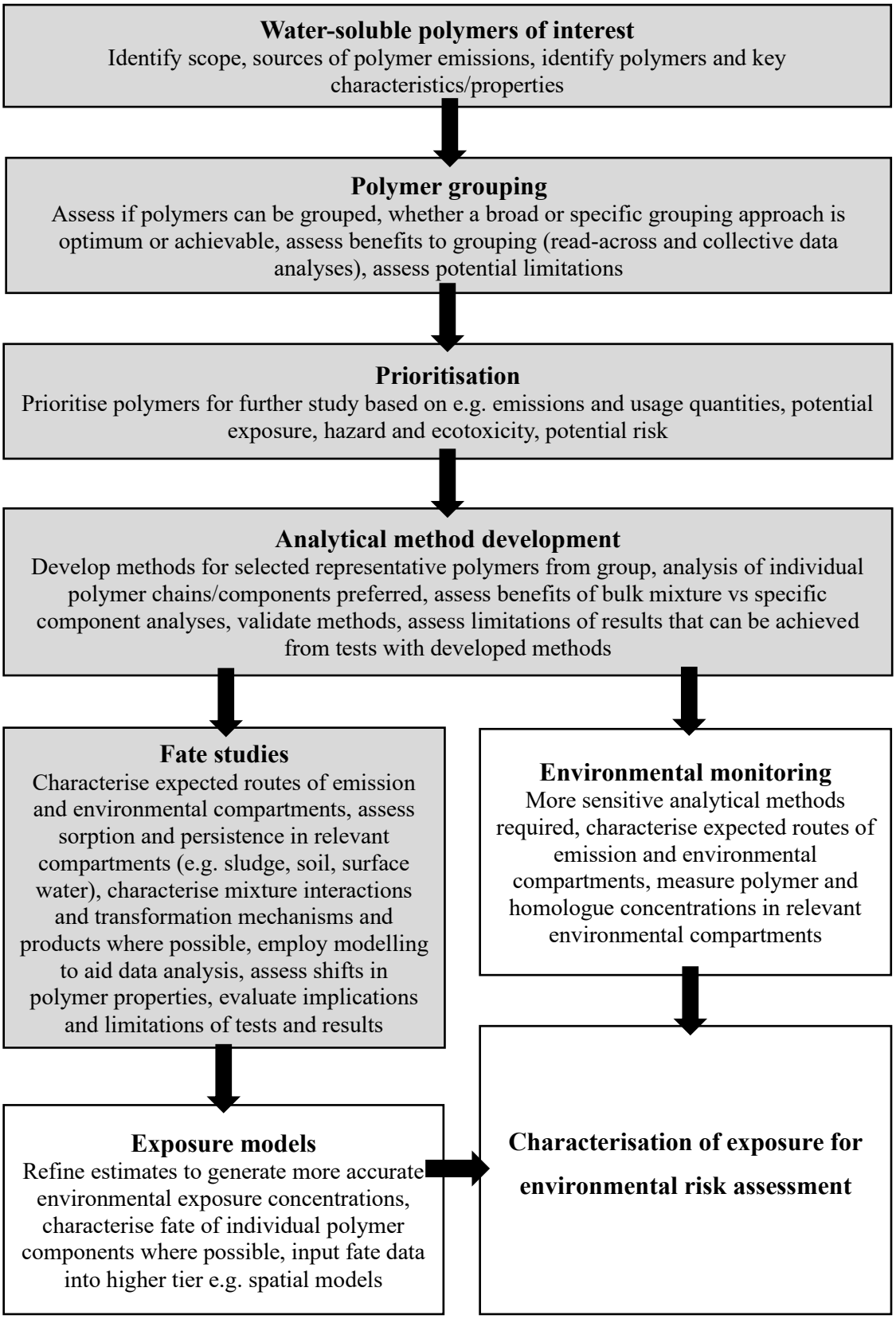


Figure 6.1: Flow chart describing general process for environmental exposure assessment of water-soluble polymers based on the methods developed and employed in this thesis. Aspects tackled in the current research are shaded in grey, and useful next steps for future studies are also shown (white).

6.3. Conclusions

In this thesis, methods for the environmental fate and exposure assessment of water-soluble polymers were investigated, developed, and applied, and used to provide recommendations for future environmental exposure assessment of water-soluble polymers. Environmental risk assessment methods are likely to require significant development and adaptation for application to polymers, and different polymer types are likely to require different treatment in testing. There remains a lack of data on both the presence and potential effects of polymers in the environment, particularly water-soluble polymers, however the results of this thesis show that there is a potential for ecological risk based on current usage. Testing of environmental fate properties and parameters for risk assessment is challenging for polymers given their nature as complex mixtures and unique properties compared to low molecular weight compounds. Case studies on low-molecular weight water-soluble polyethers have provided key fate data as well as useful insight into future assessment of polymers, with mixture interactions, individual components of polymer mixtures, complex degradation processes, and macromolecular properties all being aspects which should be taken into account in further testing.

6.4. Recommendations

6.4.1. Recommendations specific to the present work

Key recommendations to directly expand on and develop the work presented in this thesis include:

1. Fate data (K_d and $t_{1/2}$) obtained for the two polyethers in the present study (PPG-7 and PEG-9) can be combined with experimental data for fate in wastewater treatment and used as input for higher-tier modelled estimates (incorporating formation, removal, and dissipation processes as well as spatial and temporal resolution) of predicted environmental concentrations for these polymers and their constituent homologues based on the worst-case estimates modelled in the present work. Obtaining fate data (K_d and $t_{1/2}$) for homologues of PEG and PPG of additional average molecular weights to those studied here is also warranted, in order to test differences in parameters in different polymer mixtures and expand the ranges of molecular weight for QSAR development for polyethers.

2. Analytical methods for characterisation of other types of water-soluble polymers identified and prioritised in the present work are warranted, particularly polyquaterniums and polyol ethoxylate esters, as such methods are essential to obtaining further data for risk assessment. Methods for analysing higher molecular weight polymers in particular are warranted, given the current scarcity of methods and the lack of suitability of techniques such as LC-MS for many of these compounds. Techniques which utilise methods from polymer science such as size-exclusion chromatography may be useful, and for many studies a balance between non-specific measurement of a bulk polymer and incorporation of individual mixture components may need to be struck.

3. Fate data should be obtained for polymers from other groups prioritised in the present work, in order to test the applicability of methods for different polymer functionalities and further assess the suitability of the grouping approach applied, as well as the need for sub-groups. Particular focus on polyquaterniums and polyol ethoxylate esters is warranted. In particular, analyses of polymer transformation mechanisms and products are warranted, as well as analyses of all components of polymer mixtures when possible. Fate data are also imperative for further risk assessment of polymers in general, in order to: refine worst-case predicted environmental concentrations; develop higher-tier exposure models for polymers; develop a wider range of QSARs for polymers incorporating molecular weight and functional group as well as other key polymer properties; and accurately determine environmental exposure. More data are also required to further assess the key considerations for polymer testing and risk assessment, as well as the impact of different polymer properties and available methods.

4. Ecotoxicity data for polymers and polymer groups identified in the present work should be obtained, with particular focus on groups which do not currently have a complete dataset for determination of predicted no-effect concentrations (polyol ethoxylate esters, polyethers and copolymers, silicones, and starch and derivatives). Study of similar polymer types present in mixtures may also be warranted, given the multitude of similar polymers which may be present in the environment and which may have similar and thus additive ecological effects.

5. Where individual polymer components cannot be characterised, the potential impacts on results, data interpretation and ultimate risk assessment should be

noted. Therefore, data on a wider range of polymer types and potential for analytical method development as described above should be used to further assess the impact of individual polymer chains and mixture interactions on parameter testing and risk classification. Measurement and reporting of basic polymer properties such as molecular weight distribution should also be carried out to adequately assess potential limitations of employed tests and account for processes which cannot be directly characterised, particularly for large and complex polymers.

6. Where data on usage concentrations and emissions of polymers become available, predicted environmental concentrations and the associated exposure model of the present work should be updated in order to make use of more precise input data.

7. As key properties and fate parameters of a wider range of polymers become available, assessment of the key fate parameters for exposure and risk assessment identified in the present study should be refined to streamline data collection and prioritise environmentally relevant parameters to expediate risk assessment of polymers in current use.

6.4.2. General recommendations for further research

1. Exposure estimates should be developed for water-soluble polymers from a wider range of product types and from other emission sources, such as agriculture and wastewater treatment, in order to supplement the data obtained here for down-the-drain household products and provide data on prominent polymers present in the environment due to other sources.

2. Development of higher-tier exposure modelling approaches for both solid and water-soluble polymers is warranted, which may require adaptation of methods from both chemical exposure models and models for nanoparticles.

3. Methods for analytical characterisation of both solid and water-soluble polymers should be developed. In particular, efforts should be made to adequately validate and standardise methods to increase reliability of results and prevent influxes of data that are not adequate for thorough environmental risk assessment. Methods

for characterisation of polymer degradation products are also needed to assess their environmental risks.

4. As analytical methods become available, monitoring of both aquatic and terrestrial environments for measurement of actual environmental concentrations of polymers is warranted, in order to validate predicted environmental concentrations and accurately assess the presence and potential risk of polymers in the environment.
5. Development of standard methods for polymer identification and classification is warranted, given the ambiguity which arises from current naming conventions for polymers and the necessity of detailed information on polymer characteristics (including molecular weight distribution and mixture components) for exposure and risk assessment.
6. Methods to characterise and define polymer solidity and solubility are also necessary for further development of exposure and risk assessment methods and application of fate and ecotoxicity parameters.

Appendices

List of Appendices

Chapter 2 Appendices

Appendix 2.1: Extended summary of degradation data for several types of water-soluble polymers (alcohol ethoxylates, alcohol ethoxysulfates, polycarboxylates, polyethylene glycol, and polyquaterniums) obtained from a meta-review of previously collated data from the literature, with full details of polymers analysed, methods, additional notes, and limitations.

Polymer class	Polymers covered	Methods	Results	Notes	Limitations	References
Ready biodegradability						
Alcohol ethoxylates	C: 8-18 EO[a]: 2-30	OECD 301D (Closed Bottle); Closed bottle test; OECD 301F (Manometric respirometer); BOD; Sapromat	60-92 % ThOD	Test durations 28 days, 30 days, or not specified. Includes data for single homologues and commercial mixtures.	For some data reliability not assignable as secondary reference.	(HERA 2009)
	C: 10-18 EO: 3 to >20	OECD 301B; CO_2 evolution test; Modified Sturm	60-95.4 % CO_2 formation/ThCO_2	Test durations 28 days or not specified. Includes data for single homologues and commercial mixtures. Includes data for branched alcohols and isomeric mixtures.	For some data reliability not assignable as secondary reference.	
	C: 11-15 EO: 3-20	Die away screening test; modified OECD screening test	65-100 % DOC	Test durations 28 days. Includes data for oxo-C_x alcohols with 10 % branching. Data from two studies total[b].	For some data reliability not assignable.	
	C: 13 EO: 9	OECD 301E	80 % primary biodegradation	C13 alcohol = mixture of different isomers. Single study.		

Alcohol ethoxysulfates	C: 14-15 EO: 2.25	Modified Sturm with minor modifications, 22 ± 3 °C	0.18 day^{-1} (mineralisation rate, CO_2 evolution) 3.9 days ($t_{1/2}$, CO_2 evolution)	Value from single study Sturm test, for single homologue.	Values listed obtained from personal communication.	(Federle *et al.* 1997; HERA 2004)
Polycarboxylates	P-AA, mean MW 4 kDa or not specified; P-MAA/EA, MW approx. 500 kDa; P-AM/AA, MW 10,000 kDa (25% sodium acrylate (w/w))	Modified MITI tests, closed bottle tests	<20 % biodegradation or not indicated. All polymers found to be not readily biodegradable.	Some test results were not indicated, however qualitative data for each test indicates that all polymers in question were found to be not readily biodegradable.	Reliability not assignable due to insufficient information on experimental details.	(Duis *et al.* 2021)
Polyethylene glycol	Mean MW 0.2-57.8 kDa	OECD 301B (CO2 evolution test); OECD 310 (CO_2 headspace test); Combined CO_2/DOC test	-5 to 95 % CO_2 evolution	Study durations 10 and 28 days.	For all studies reliability could not be assigned due to lack of experimental details or non-public availability of data.	(Duis *et al.* 2021)
	Mean MW 0.2-57.8 kDa (MW_W 0.251-57.8 kDa or not specified, MW_N 0.120-25.1 kDa or not specified)	OECD 301A (DOC die-away test); Combined CO_2/DOC test	>70 to >90 % DOC reduction/ removal	Study durations 20, 45 and 65 days. In some cases adsorption processes may have contributed to observed removal.	For some studies reliability could not be assigned due to lack of experimental details.	
	Mean MW 350 Da	ISO 14593 (CO_2 headspace test)	77 % CO_2 production (measured as total inorganic carbon)	Study duration 28 days. One study total.		

	Mean MW 0.2-4,000 kDa	OECD 301F or equivalent; OECD 301E: CO_2 evolution test; modified OECD screening test; OECD 301F (manometric respirometry test); DIN 38412 (not further specified); OECD 301B (CO_2 evolution test)	4.1 to >95 % (endpoints not specified)	Study durations 10, 21, 23 and 28 days.	Endpoints not specified. In some cases methods were not specified. For all studies reliability could not be assigned due to lack of experimental details.	
Polyquaterniums	PQ-10 (UCARE® JR-30M), MW approx. 30,000 kDa, 1.0 meq g^{-1}	Not specified	1 % BOD (not readily biodegradable)	Test duration 20 days. Single study and datapoint.	Reliability not assignable due to lack of information on experimental details.	(Duis *et al.* 2021)
	PQ-16 (Luviquat® FC 370), MW approx. 100 kDa, 2.0 meq g^{-1} (pH 7); PQ-16 (Luviquat® HM 552), MW approx. 400 kDa, 3.0 meq g^{-1} (pH 7)	OECD 301F (manometric respirometry test) with municipal activated sludge	< 10 % ThOD (mineralisation rate)	Test durations 28 days. Two studies and datapoints total.	Reliability not assignable due to lack of information on experimental details.	

	PG-6, MW_N > 10 kDa; PQ-10 (UCARE® polymer JR-400), MW_N approx. 240 kDa, MW approx. 400 kDa, 1.2 meq g^{-1}; PQ-7 (Dehyquart® CC7 BZ), MW 4,300-5,200 kDa, 1.6 meq g^{-1}	Not specified	General and ready biodegradability, qualitative data only: "not readily biodegradable", "poorly biodegradable"	One of the tests corresponds to general information on biodegradability rather than specifically ready biodegradability.	Reliability could not be assigned due to lack of information on experimental details.	
Removal in wastewater treatment (including data for inherent biodegradability, batch, and simulation tests)						
Alcohol ethoxylates	C: 12-16 EO: 1-9	Activated sludge die away test, 20 °C, radiolabelled alkyl chains	0.28-2.32 minutes ($t_{1/2}$) 18-146 $hour^{-1}$ (k_1)	Data for single homologues, from two studies total (multiple datapoints).		(HERA 2009)
Alcohol ethoxysulfates	C: 12-18 EO: 2-12	SCAS and OECD CAS confirmatory test	95.4-100 % removal	Primary degradation from simulation/ higher tier test.		(Federle *et al.* 1997; HERA 2004)
	C: 14-15 EO: 2.25	$^{14}CO_2$ evolution from test system with activated sludge, 22 ± 3 °C	1.79 day^{-1} (mineralisation rate) 0.39 days ($t_{1/2}$)	Value from single study, for single homologue in activated sludge.	Values listed obtained from personal communication.	

Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	CO_2 evolution test, water (domestic activated sludge), ^{14}C tagged; CO_2 production test coupled with SCAS or batch activated sludge test (inocula from WWTP, adapted to homopolymers of acrylic acid)	8-43 % CO_2 evolution	Test durations 28, 31, 45 and 90 days. Includes data for both inherent biodegradability and simulation tests.	Reliability not assignable for some tests due to insufficient experimental detail/study not publicly available/secondary reference.	(HERA 2014a, 2014b; Duis *et al.* 2021)
	P-AA (and sodium salts), mean MW 1-15 kDa or not specified; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa; P-MAA/EA, mean MW approx. 500 kDa	OECD 302A (SCAS Test); OECD 302B; OECD 302B with industrial activated sludge; ISO 18749; ISO 9888, 88/302/EEC, part C; OECD 303A (Activated sludge simulation test)	9-100 % DOC reduction	Test durations 7-28 days or unspecified. One study and datapoint only for methacrylic acid-ethyl acrylate copolymer. Adsorption processes may have contributed to observed removal for some tests. Includes data for both inherent biodegradability and simulation tests.	For one study reliability unassignable due to insufficient information on experimental detail.	
	P-AA, mean MW 1 and 2 kDa	OECD 303 A (Activated sludge simulation test)	9-24 % DOC or ^{14}C removal (no clear information on test endpoint)	No clear information on test endpoint. Data for range of DOC influent concentrations.		

	P-AA (and sodium salts), mean MW 4.5 kDa	Waste water treatment simulation test, domestic; OECD 303A (Activated sludge simulation test)	55 and 76 % (removal of radiolabelled material)	Data for sewage treatment plant. Two datapoints from two studies total.		
	P-AA, MW 4.5-215 kDa or not specified	OECD 303A (Activated sludge simulation test); various activated sludge tests, including SCAS and CAS; waste water treatment simulation test (domestic); model sewage treatment plant and CAS tests with addition of $FeCl_3$; Continuous activated sludge test	16-98 % overall removal	Test durations 7 and 28 days or not specified. Some studies used radiolabelled polymer. Adsorption processes may have contributed to observed removal. Removal dependent on effluent solids for one test. Includes data for inherent biodegradability, simulation tests, and tertiary treatment simulation tests.	For some studies reliability not assignable due to insufficient experimental detail/secondary reference/lack of clarity on product tested.	

	P-AA, mean MW 4.5 kDa	Series of batch experiments in hard tap water, autoclaved sewage sludge suspended in distilled or hard (with ^{14}C-labelled polymer) water, and mixture of sewage sludge and hard water; Model dynamic settling tank simulating primary treatment	13-98 % removal	Two studies total, multiple datapoints. Tests include data for a range of polymer concentrations and media. Removal by precipitation, adsorption, or a combination. Includes data for both batch and simulation tests.	Reliability could not be assigned due to insufficient information on experimental details or lack of clarity on product tested.	
Polyethylene glycol	Mean MW 0.2-20 kDa	OECD 302A (modified SCAS test); batch system (modified 2-L Erlenmeyer flasks) with water inoculated with adapted or non-adapted sludge, 23 ± 3 °C; OECD 303A (simulation test - aerobic sewage treatment) / ISO 11733 (activated sludge simulation test)	41-102 % DOC removal	Test durations 30 days (aerobic batch tests) or not specified. For most data, adsorption processes may have contributed to observed removal. Includes data for inherent biodegradability, batch, and simulation tests.	In some cases reliability could not be assigned due to study not being publicly available/lack of information on experimental details.	(Duis *et al.* 2021)
	Mean MW 350 Da	ISO 9888 (Zahn-Wellens test (modified))	>80 % COD reduction	Single datapoint from single study only. Test duration 28 days. Data for inherent biodegradability.		

	Mean MW 1-20 kDa	CO_2 production test with activated sludge from SCAS test with the same PEG as inoculum; batch experiment in electrolytic respirometer using adapted activated sludge as inoculum, 20 °C; batch system (modified 2-L Erlenmeyer flasks) with water inoculated with adapted or non-adapted sludge; OECD confirmatory test: continuous-flow model WWTP (^{14}C-labelled PEG-400)	40 to >90 % CO_2 evolution/ mineralisation	Test durations 3, 21, 30, and 50 days. Includes data for inherent biodegradability, batch, and simulation tests, and for both adapted and non-adapted sludge. OECD confirmatory test: ^{14}C-mass balance at test end - 52% CO_2, 4% in effluent (supernatant), 41% in sludge.	Reliability could not be assigned due to lack of experimental details.	
	Mean MW 0.3-6 kDa	OECD 302B (Zahn-Wellens test); DIN 38412 L 24	<20 to >95 % (endpoint not specified)	Test durations 10 days, 26 days or not specified. Includes data for both inherent biodegradability and simulation tests.	Endpoints not specified. Reliabilities could not be assigned due to lack of information on experimental details.	
	Mean MW 4.6 kDa.	Sealed vessel test	79-86 % mineralisation (based on inorganic carbon production) at test end	One/two studies total. Data for inherent biodegradability.	Reliability could not be assigned due to lack of public availability of study.	

	Mean MW 0.6-20 kDa	Batch experiment (shake flask test) using microorganisms from a terylene plant, 30 °C	77-88 % primary degradation based on chemical analysis	Single study, three datapoints. Test durations 4 and 5 days. Terylene plant wastewater generally contains organic acids, ethylene glycol and polymers.	Determined to be not reliable due to limited information on methods and/or results.	
Polyquaterniums	PQ-7 (Conditioner P7NA) (MW not specified).	OECD 302B (Zahn-Wellens test)	30-50 % DOC or COD elimination	Single study only. Data for inherent biodegradability.	Reliability not assignable due to lack of information on experimental details.	(Duis *et al.* 2021)
	PQ-16 (Luviquat® Excellence), MW approx. 40 kDa, 6.1 meq g^{-1} (pH 7); PQ-16 (Luviquat® FC 550), MW approx. 80 kDa, 3.3 meq g^{-1} (pH 7); PQ-16 (Luviquat® FC 370), MW approx. 100 kDa; 2.0 meq g^{-1} (pH 7)	OECD 302B (Zahn-Wellens test)	20-70 % DOC elimination	Test durations 28 days or not specified. Adsorption processes may have contributed to observed removal. Data for inherent biodegradability.	Reliability not assignable due to lack of information on experimental details.	

	PQ-6, MW_N > 10 kDa; PQ-16 (Luviquat® Excellence), MW approx. 40 kDa, 6.1 meq g^{-1} (pH 7); PQ-16 (Luviquat® FC 550), MW approx. 80 kDa, 3.3 meq g^{-1} (pH 7); PQ-16 (Luviquat® FC 370), MW approx. 100 kDa, 2.0 meq g^{-1} (pH 7); PQ-16 (Luviquat® HM 552), MW approx. 400 kDa, 3.0 meq g^{-1} (pH 7); PQ-16 (Luviquat® FC 550)	OECD 302 (further information not provided); not specified	Qualitative data only: "not inherently biodegradable"; "Moderately/ partly eliminated from water; virtually eliminated from water by e.g. sorption to activated sludge"; "Removed from waste water by e.g. strong sorption on activated sludge"	Data for inherent biodegradability and unspecified methods/tests.	Reliability not assignable due to lack of information on experimental details.	
Fate in wastewater treatment (anaerobic)						
Alcohol ethoxylates	C: 9-11 EO: 8	Measurement of gas production, digested sludge, 35° C	60-83 % $ThCH_4$	Test durations 40-50 days. Data from a single study. Data for ultimate anaerobic biodegradability in digested sludge.	Reliability not assignable.	(HERA 2009)
	C: 9-11 EO: 8	Measurement of gas production, digested sludge, 35° C	79 % ThGP	Test duration 56 days. Data from a single study. Data for ultimate anaerobic biodegradability in digested sludge.	Reliability not assignable.	

	C: 18 EO: 7	$^{14}CH_4$ and $^{14}CO_2$ evolution, digested sludge, 35 °C	84 % $ThCH_4$ + $ThCO_2$	Test duration 28 days. Data from a single study. Data for ultimate anaerobic biodegradability in digested sludge.	Reliability not assignable.	
Polycarboxylates	P-AA/MA (and sodium salts), 70 kDa	Incubation in mixture of digester sludge and nutrient solution, radiolabelled polymer, 35 °C	Biodegradability extent between 11 and 16 %	Test duration 258 days. Single study only.		(HERA 2014b)
Polyethylene glycol	Mean MW 0.4-10 kDa (included tests on mixtures of 0.4/0.6/1 kDa, and 0f 1.5/3/10 kDa)	Batch experiment using digested activated sludge; batch experiments in stirred 1 L reactors using digested activated sludge (previously adapted to PEG-10,000 for > 2 years), 35°C	Approx. 85-92 % TOC removal	Test duration 10 days/HRT 18-30 days/HRT 20-40 days (corresponding to each of the 3 results from the 2 studies). Sludge from one study previously adapted.	One of the two studies was determined to be not reliable due to limited information on methods and/or results.	(Duis *et al.* 2021)
	Mean MW 0.6-20 kDa	Batch experiment (sealed flasks on rotary shaker) using micro-organisms adapted for 46 days to PEG-containing wastewater, 37°C	40-70 % primary degradation (based on chemical analysis)	Single study, three datapoints. Adapted sludge used. Test durations 6, 9, and 10 days.	Determined to be not reliable due to limited information on methods and/or results.	

Degradation in river water						
Alcohol ethoxylates	C: 8-18 EO: 1-20	Experimental determination of rate of disappearance of AE homologues C12, 13 & 14 and EO 2-20 (electrospray LCMS). Extrapolation of experimental values to other chain lengths. Approx. 12 °C.	4-24 hours ($t_{1/2}$)	Data for single homologues. Expected to be conservative estimates.		(HERA 2009)
Alcohol ethoxysulfates	C: 14-15 or not specified EO: 2.25 or not specified	$^{14}CO_2$ evolution from test system with river water and settled sludge supernatant, 22 ± 3 °C; unspecified methods	0.48 day^{-1} and 0.7 $hour^{-1}$ (mineralisation/ degradation rate). 1.4 days and approx. 1 hour ($t_{1/2}$). Approx. 16.6 day^{-1} (rate constant).	Two studies total.	Values from one study obtained from personal communication. Could not obtain information on methods from other study.	(Federle *et al.* 1997; HERA 2004)
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	CO_2 evolution tests in river water or mixture of water and sediment, ^{14}C tagged polymers. One test used pre-adapted river water.	6-63 % CO_2 evolution	Test durations 100, 106, 133 and 135 days.	For one test reliability could not be assigned due to insufficient experimental detail and non-publicly available study.	(HERA 2014a, 2014b; Duis *et al.* 2021)
Polyethylene glycol	Mean MW 0.3 kDa	River water die-away test	99 % primary biodegradation	Test duration 14 days. Single study and datapoint only.		(Duis *et al.* 2021)

Degradation in seawater						
Polyethylene glycol	MW_W 0.251-57.8 kDa, MW_N 0.120-25.1 kDa	Combined CO_2/DOC test with artificial seawater and marine micro-organisms	No biodegradation to >90 % (DOC removal)	Data from a single study (multiple datapoints). Test durations 37-180 days. Lag phases 6 and 20 days.		(Duis *et al.* 2021)
	Mean MW 0.6 kDa	OECD 306 (biodegradability in seawater)	55 % (endpoint not specified)	Single datapoint from a single study. Test duration 28 days.	Endpoint not specified. Reliability could not be assigned due to lack of availability of experimental details.	
Degradation in sediment						
Polycarboxylates	P-AA (and sodium salts), mean MW 1-10 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa	CO_2 evolution test, sediment (river water and sediment), ^{14}C tagged	6-58 % CO_2 evolution	Test durations 100, 106, and 135 days.		(HERA 2014a, 2014b)
Degradation in sediment (anaerobic)						
Alcohol ethoxylates	C: 9-11 EO: 8	Gas production in freshwater swamp material and marine sediment, 35 °C	66-77 % ThGP	Test durations 56 days. Two results total, taken from the same study.	Reliability not assignable as secondary reference.	(HERA 2009)
	C: 10-12 EO: 7.5-23	CH_4 production in polluted creek mud, 28 °C	70-80 % $ThCH_4$	Test durations 37 days. Two results total, taken from the same study.	Reliability not assignable as secondary reference.	
	C: 12 EO: 8-9	$^{14}CH_4$ and $^{14}CO_2$ evolution in pond sediment and wastewater pond sediment, 22 °C	13-40 % $ThCH_4$ + $ThCO_2$	Test durations 87 days. Two results total, taken from the same study.	Reliability not assignable as secondary reference.	

Polyethylene glycol	Mean MW 0.4 kDa	Anaerobic water-sediment test with marine sediments and seawater, incubated at 30°C	92 % (primary degradation, based on chemical analysis). 18 days ($t_{1/2}$, based on primary degradation).	Single datapoint from a single study. Test duration 169 days; primary degradation mainly within first 64 days. Half-life estimated based on first order kinetics.		(Duis *et al.* 2021)
Degradation in soil						
Alcohol ethoxysulfates	C: 14-15 EO: 2.25	Measurement of $^{14}CO_2$ evolution from test system with sludge-amended soil, 22 ± 3 °C	0.29 day^{-1} (mineralisation rate) 2.4 days ($t_{1/2}$)	Value from single study, for single homologue in soil.	Values listed obtained from personal communication.	(Federle *et al.* 1997; HERA 2004)
Polycarboxylates	P-AA (and sodium salts), mean MW 1-530.4 kDa; P-AA/MA (and sodium salts), mean MW 12 and 70 kDa; P-AM/AA	CO_2 evolution test, sludge treated soil, ^{14}C tagged polymer; biodegradation in agricultural soil, incubated at 25°C, ^{13}C tagged polymer; biodegradation studied in flask or tube reactors containing agricultural soil and ground wheat straw and white rot or brown rot fungi, ^{14}C labelled polymer	0.91-35 % mineralisation/ CO_2 evolution	Test durations 81, 149, 154, and 165 days. Data for both sludge-treated and non-sludge-treated soil.	One of the studies may not be reliable due to lack of information on MW and clear information on polymer concentration in reactors.	(HERA 2014a, 2014b; Duis *et al.* 2021)

	P-AM/AA (Superfloc 836A) consisting of approx. 80% acrylamide and approx. 20% acrylic acid, mean MW 12,000-15,000 kDa (18% negative charge density)	Field study (8 years) on an agricultural site, degradation rates of applied polymer investigated based on stable isotope (^{13}C) ratios	13-74 % degradation relative to total amount of polymer added over 3 or 6 years. 9.8% per year (mean degradation rate).	Test duration 12 years. Data from a single study, for multiple sampling periods. Applied polymer amounts are much higher than application rates typically used to control irrigation-induced erosion		
Polyethylene glycol	Mean MW 4 kDa (^{14}C labelled).	Biodegradation in three tropical soils (sandy clay loam, sandy clay, sandy loam), 25±2°C	approx. 5-10 % mineralisation/ $^{14}CO_2$ production (read from graph)	Single study only. Test duration 70 days.	Results read from graph. Assigned not reliable due to limited information on methods and/or results.	(Duis *et al.* 2021)

[a] Data for EO=0 (i.e. for corresponding fatty alcohols) has not been included in the present summary due to the absence of monomer units.

[b] For entries which summarise data from less than three studies, the number of studies has been noted.

C = number of carbons in alcohol, EO = average number of ethoxy monomer units, ThOD = theoretical oxygen demand, $ThCO_2$ = theoretical carbon dioxide, DOC = dissolved organic carbon, $t_{1/2}$ = half-life, P-AA = homopolymer of acrylic acid, MW = molecular weight, P-MAA/EA = copolymer of methacrylic acid and ethyl acrylate, P-AM/AA = copolymer of acrylamide and acrylic acid, MW_W = weight average molecular weight, MW_N = number average molecular weight, BOD = biochemical oxygen demand, PQ = polyquaternium, k_1 = first order rate constant, P-AA/MA = copolymer of acrylic acid and maleic acid, WWTP = wastewater treatment plant, COD = chemical oxygen demand, PEG = polyethylene glycol, $ThCH_4$ = theoretical methane, ThGP = theoretical gas production, TOC = total organic carbon, HRT = hydraulic retention time, AE = alcohol ethoxylate, LCMS = liquid chromatography mass spectrometry.

Chapter 3 Appendices

Appendix 3.1: Supermarket websites used for identification of household product types released down-the-drain at point-of-use, and major brands for each product type, for the UK.

Supermarket	Link	Dates accessed
Tesco	https://www.tesco.com/	April 2020-January 2021
Sainsbury's	https://www.sainsburys.co.uk/	April 2020-January 2021
Asda	https://www.asda.com/	April 2020-January 2021
Morrisons	https://groceries.morrisons.com/	April 2020-January 2021

Appendix 3.2: Total numbers of brands included in the final dataset for each product type.

Product type	Number of brands included in the final study
Laundry detergent	9
Dishwashing detergent (machine)	4
Dishwashing detergent (hand)	3
Toilet cleaners (including toilet cleaning liquid, bleach, and disinfectant)	9
Shampoo	21
Conditioner	19
Bodywash	22
Handwash	15
Soap bars	14
Bath liquid	13

Appendix 3.3: Potential polymers identified from product ingredients that have been excluded from the dataset due to insufficient information.

Name	**Reason for exclusion**
1,4-Benzenedicarboxylic acid, 1,4-dimethyl ester, polymer:1,	Insufficient information /incomplete name does not allow polymer identification for gathering of information from patents
Peptides, salts, sugars from fermentation (process)	Mixture of polymer (peptides) and non-polymers, with insufficient information to determine composition
Poly(oxy-1,2-ethanediyl), alpha-(1-oxohexadecyl)-omega-hydroxy-	Insufficient information /incomplete name does not allow polymer identification for gathering of information from patents
Polymers	Insufficient information from name does not allow polymer identification for gathering of information from patents
Sulfonated polymer	Insufficient information from name does not allow polymer identification for gathering of information from patents

Appendix 3.4: Estimated market penetration (F_{prod}) of polymer groups for each of the studied product types.

Appendix 3.4.1: Estimated market penetration (F_{prod}) of polymer groups for laundry detergent.
Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	**No. products containing group/polymer**	**Total no. products**	**F_{prod}**
Alcohol alkoxylates	203	206	0.99
Alcohol ethoxylate salts	163	206	0.79
Polyethers and copolymers	146	206	0.71
Silicones	146	206	0.71
Polycarboxylates	130	206	0.63
Cellulose and derivatives	105	206	0.51
Polyethylenimine ethoxylates and polyether copolymers	83	206	0.40
Starch and derivatives	58	206	0.28
Polyvinyl alcohol	44	206	0.21
Polyquaterniums	33	206	0.16
Plant gums	22	206	0.11
Poly(oxy)alkylene terephthalates	19	206	0.092
Ethoxylated m-toluidine*	19	206	0.092
Polyesters	15	206	0.073
Polymeric colourants	14	206	0.068
Amine/formaldehyde polymers	12	206	0.058
Vinylimidazole/vinylpyrrolidone homo- and co-polymers	11	206	0.053
Fatty acid ethoxylates	7	206	0.034
Polymerised aromatic sulfonate salts	7	206	0.034
Polyvinylpyridine-N-oxide*	3	206	0.015
Proteins/polypeptides	1	206	0.0049
Hemicelluose*	1	206	0.0049
Lignin*	1	206	0.0049

*Individual polymer, group 'Other'

Appendix 3.4.2: Estimated market penetration (F_{prod}) of polymer groups for machine dishwashing detergent. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	No. products containing group/polymer	Total no. products	F_{prod}
Alcohol alkoxylates	56	59	0.95
Polycarboxylates	56	59	0.95
Polyethers and copolymers	49	59	0.83
Cellulose and derivatives	43	59	0.73
Polyvinyl alcohol	41	59	0.69
Starch and derivatives	30	59	0.51
Silicones	26	59	0.44
Polyquaterniums	11	59	0.19
Plant gums	2	59	0.034
Alginic acid*	2	59	0.034

*Individual polymer, group 'Other'

Appendix 3.4.3: Estimated market penetration (F_{prod}) of polymer groups for hand dishwashing detergent. Groups are listed in order of highest market penetration for this product type.

Group	No. products containing polymer/group	Total no. products	F_{prod}
Alcohol ethoxylate salts	25	39	0.64
Polyethers and copolymers	22	39	0.56
Polyethylenimine ethoxylates and polyether copolymers	15	39	0.38
Alcohol alkoxylates	8	39	0.21
Polyquaterniums	2	39	0.051

Appendix 3.4.4: Estimated market penetration (F_{prod}) of polymer groups for toilet cleaner and bleach. Groups are listed in order of highest market penetration for this product type.

Group/polymer	No. products containing polymer/group	Total no. products	F_{prod}
Alcohol alkoxylates	18	38	0.47
Silicones	7	38	0.18
Cellulose and derivatives	6	38	0.16
Alcohol ethoxylate salts	6	38	0.16
Plant gums	4	38	0.11
Polymeric colourants	2	38	0.053

Appendix 3.4.5: Estimated market penetration (F_{prod}) of polymer groups for bodywash. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	No. products containing polymer/group	Total no. products	F_{prod}
Alcohol ethoxylate salts	239	302	0.79
Polyquaterniums	137	302	0.45
Polycarboxylates	135	302	0.45
Polyol ethoxylate esters	134	302	0.44
Alcohol alkoxylates	73	302	0.24
Fatty acid ethoxylates	57	302	0.19
Polyethers and copolymers	37	302	0.12
Starch and derivatives	14	302	0.046
Plant gums	12	302	0.040
Polyglyceryl esters and polyglycerin	10	302	0.033
Hydrolysed proteins and derivatives	8	302	0.026
Proteins/polypeptides	6	302	0.020
Disodium Laureth Sulfosuccinate*	5	302	0.017
Polyurethane Crosspolymer-2*	5	302	0.017
Cellulose and derivatives	4	302	0.013
Polyolefins	4	302	0.013
Polymerised aromatic sulfonate salts	1	302	0.0033
Butyl Acrylate/Ethyltrimonium Chloride Methacrylate/Styrene Copolymer*	1	302	0.0033
PEG-4 Rapeseedamide*	1	302	0.0033

*Individual polymer, group 'Other'

Appendix 3.4.6: Estimated market penetration (F_{prod}) of polymer groups for handwash. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	No. products containing polymer/group	Total no. products	F_{prod}
Alcohol ethoxylate salts	71	97	0.73
Polyquaterniums	33	97	0.34
Polycarboxylates	26	97	0.27
Alcohol alkoxylates	25	97	0.26
Polyol ethoxylate esters	20	97	0.21
Fatty acid ethoxylates	15	97	0.15
Polyethers and copolymers	3	97	0.031
Hydrolysed proteins and derivatives	2	97	0.021
Plant gums	2	97	0.021
Proteins/polypeptides	2	97	0.021
Starch and derivatives	2	97	0.021
PEG-4 Rapeseedamide*	2	97	0.021
Polyglyceryl esters and polyglycerin	1	97	0.010

*Individual polymer, group 'Other'

Appendix 3.4.7: Estimated market penetration (F_{prod}) of polymer groups for soap bars. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	No. products containing polymer/group	Total no. products	F_{prod}
Alcohol ethoxylate salts	2	56	0.036
Polyethers and copolymers	2	56	0.036
Alcohol alkoxylates	1	56	0.018
Cationic silicones	1	56	0.018
Silicones	1	56	0.018
Starch and derivatives	1	56	0.018
Hydroxypropyl Cyclodextrin*	1	56	0.018

*Individual polymer, group 'Other'

Appendix 3.4.8: Estimated market penetration (F_{prod}) of polymer groups for bath liquid. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	No. products containing polymer/group	Total no. products	F_{prod}
Alcohol ethoxylate salts	41	62	0.66
Polyquaterniums	25	62	0.40
Alcohol alkoxylates	21	62	0.34
Polyol ethoxylate esters	19	62	0.31
Fatty acid ethoxylates	12	62	0.19
Polycarboxylates	12	62	0.19
Polyethers and copolymers	3	62	0.048
Plant gums	1	62	0.016
Proteins/polypeptides	1	62	0.016
Disodium Laureth Sulfosuccinate*	1	62	0.016
PEG-4 Rapeseedamide*	1	62	0.016

*Individual polymer, group 'Other'

Appendix 3.4.9: Estimated market penetration (F_{prod}) of polymer groups for shampoo. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	**No. products containing polymer/group**	**Total no. products**	**F_{prod}**
Polyquaterniums	243	266	0.91
Alcohol ethoxylate salts	173	266	0.65
Alcohol alkoxylates	92	266	0.35
Silicones	80	266	0.30
Polyethers and copolymers	70	266	0.26
Polyol ethoxylate esters	57	266	0.21
Fatty acid ethoxylates	52	266	0.20
Polycarboxylates	46	266	0.17
Hydrolysed protein and derivatives	40	266	0.15
Cationic silicones	29	266	0.11
Cellulose and derivatives	23	266	0.086
Starch and derivatives	21	266	0.079
Methyl Gluceth-10*	14	266	0.053
Plant gums	12	266	0.045
Silicone alkoxylates	11	266	0.041
Disodium Laureth Sulfosuccinate*	10	266	0.038
Polyesters	4	266	0.015
Sodium Hyaluronate*	3	266	0.011
Polyglyceryl esters and polyglycerin	2	266	0.0075
Proteins/polypeptides	2	266	0.0075
Poly(Linseed Oil)*	2	266	0.0075
Polymerised aromatic sulfonate salts	1	266	0.0038
Vinylimidazole/vinylpyrrolidone homo- and co-polymers	1	266	0.0038
Laureth-5 Carboxylic Acid*	1	266	0.0038

*Individual polymer, group 'Other'

Appendix 3.4.10: Estimated market penetration (F_{prod}) of polymer groups for conditioner. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest market penetration for this product type.

Group/polymer	**No. products containing polymer/group**	**Total no. products**	**F_{prod}**
Cationic silicones	117	228	0.51
Silicones	95	228	0.42
Alcohol alkoxylates	86	228	0.38
Polyquaterniums	57	228	0.25
Hydrolysed protein and derivatives	39	228	0.17
Polyol ethoxylate esters	24	228	0.11
Starch and derivatives	24	228	0.11
Fatty acid ethoxylates	20	228	0.088
Cellulose and derivatives	15	228	0.066
Plant gums	15	228	0.066
Polyethers and copolymers	15	228	0.066
Polyesters	10	228	0.044
Polycarboxylates	9	228	0.039
Silicone alkoxylates	8	228	0.035
PPG-3 Benzyl Ether Myristate*	5	228	0.022
Polymerised aromatic sulfonate salts	3	228	0.013
Alcohol ethoxylate salts	2	228	0.0088
Polyglyceryl esters and polyglycerin	2	228	0.0088
Vinylimidazole/vinylpyrrolidone homo- and co-polymers	2	228	0.0088
Sodium Hyaluronate*	2	228	0.0088
Proteins/polypeptides	1	228	0.0044
Poly(Linseed Oil)*	1	228	0.0044

*Individual polymer, group 'Other'

Appendix 3.5: Estimated fractional concentration of polymers (F_{pol}) in each of the studied product types, and referenced patents.

Appendix 3.5.1: Estimated polymer concentration in product (F_{pol}) of polymer groups for laundry detergent, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min. F_{pol}	Max. F_{pol}	Preferred min. F_{pol}	Preferred max. F_{pol}	References (patents)
Alcohol ethoxylate salts	0.03	0.35	0.14	0.23	Hsu *et al.* 2006b; Della Noce 2016
Polycarboxylates	0.001	0.5	0.02	0.2	Machin and van de Pas 1992; Reyes 2011; Gori and Baltsen 2016
Alcohol alkoxylates	0.01	0.3	0.09	0.15	Arisandy *et al.* 2014
Lignin*	0.001	0.3	0.004	0.11	Batchelor and Bird 2015
Polyesters	0.02	0.1	0.02	0.1	Bennett *et al.* 2012
Hemicelluose*	0.001	0.4	0.005	0.1	Hüffer *et al.* 2016
Polyvinyl alcohol	0.002	0.1	0.01	0.06	Antwerpen *et al.* 1994
Starch and derivatives	0.005	0.1	0.03	0.06	Desforges 1972; Temple *et al.* 1978; Casteel *et al.* 2001
Fatty acid ethoxylates	0.001	0.1	0.01	0.05	Hsu *et al.* 2006a
Poly(oxy)alkylene terephthalates	0.005	0.1	0.01	0.05	Beagle *et al.* 1999
Cellulose and derivatives	0.001	0.05	0.01	0.03	Leupin and Gosselink 2002; Wang *et al.* 2003
Ethoxylated polyethyleneimines	0.0001	0.1	0.003	0.03	Souter *et al.* 2006; Borne 2012
Silicones	0.001	0.1	0.01	0.03	Zhen and Strickland 1998; Depoot *et al.* 2003; Zhu and Hsu 2004
Polyvinylpyridine-N-oxide*	0.0005	0.05	0.002	0.025	Meine and Bessler 2015
Plant gums	0.0001	0.05	0.001	0.02	Corominas *et al.* 2013
Polyethers and copolymers	0.001	0.1	0.003	0.02	Jones 1984; Kud *et al.* 1987
Proteins/polypeptides	0.0001	0.1	0.0001	0.02	Gorlin *et al.* 2008
Vinylimidazole/ vinylpyrrolidone homo- and co-polymers	0.001	0.1	0.005	0.02	Detering *et al.* 1997; Gopalkrishnan and Guiney 1999
Ethoxylated m-toluidine*	0.000033	0.0165	0.000033	0.0165	Fernandes *et al.* 2013
Polymerised aromatic sulfonate salts	0.00001	0.2	0.005	0.01	McDonald 1966; Garcia *et al.* 1998; Moeller *et al.* 2002
Polyquaterniums	0.0001	0.1	0.0005	0.002	Boutique *et al.* 2008
Polymeric colourants	0.00006	0.0175	0.00015	0.0015	Schramm *et al.* 2005
Amine/formaldehyde polymers	0.000025	0.02	0.000075	0.0006	Fossum *et al.* 2007; Ohtani and Azuma 2016

*Individual polymer, group 'Other'

Appendix 3.5.2: Estimated polymer concentration in product (F_{pol}) of polymer groups for machine dishwashing detergent, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Starch and derivatives	0.0001	0.3	0.001	0.2	Saito and Takada 2016
Alcohol alkoxylates	0.001	0.2	0.01	0.1	Fischer *et al.* 2012
Polycarboxylates	0.001	0.2	0.01	0.1	Sabatelli and Brungs 1971; Weber *et al.* 2012
Alginic acid*	0.005	0.1	0.005	0.1	Chun *et al.* 1992
Polyethers and copolymers	0.005	0.1	0.0075	0.06	Manske 2004
Polyvinyl alcohol	0.002	0.1	0.01	0.06	Antwerpen *et al.* 1994
Polyquaterniums	0.0001	0.1	0.0025	0.04	Parran 1970; Eiting *et al.* 2016
Plant gums	0.005	0.05	0.0125	0.025	Fox *et al.* 1981
Silicones	0.0001	0.03	0.01	0.018	Charles 2014
Cellulose and derivatives	0.0001	0.02	0.001	0.005	Gomez Ruiz *et al.* 2013

*Individual polymer, group 'Other'

Appendix 3.5.3: Estimated polymer concentration in product (F_{pol}) of polymer groups for hand dishwashing detergent, with selection of patents (corresponding to final concentration estimates) referenced. Groups are listed in order of highest preferred maximum F_{pol} for this product type.

Groups	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Alcohol ethoxylate salts	0.05	0.42	0.15	0.25	Moffatt 1995
Alcohol alkoxylates	0.02	0.4	0.03	0.2	Evers and Maddox 2014
Polyethers and copolymers	0.005	0.1	0.0075	0.06	Manske 2004
Polyethylenimine ethoxylates and polyether copolymers	0.0001	0.1	0.002	0.015	Borne 2012
Polyquaterniums	0.00001	0.1	0.0005	0.01	Perez-Prat Vinuesa *et al.* 2014

Appendix 3.5.4: Estimated polymer concentration in product (F_{pol}) of polymer groups for toilet cleaner and bleach, with selection of patents (corresponding to final concentration estimates) referenced. Groups are listed in order of highest preferred maximum F_{pol} for this product type.

Groups	**Min F_{pol}**	**Max F_{pol}**	**Preferred min F_{pol}**	**Preferred max F_{pol}**	**References (patents)**
Alcohol alkoxylates	0.001	0.3	0.01	0.07	Klinkhammer *et al.* 2004
Cellulose and derivatives	0.00001	0.05	0.00001	0.05	Cheung and Costa 2003
Silicones	0.0001	0.5	0.0001	0.05	Cermenati and Tomarchio 2006
Alcohol ethoxylate salts	0.001	0.1	0.005	0.02	Baixas Veiga *et al.* 1994
Plant gums	0.0001	0.05	0.002	0.006	Miskiel and Solanki 1999
Polymeric colourants	0.000001	0.001	0.000001	0.001	Marin and Bergstrom 2013

Appendix 3.5.5: Estimated polymer concentration in product (F_{pol}) of polymer groups for bodywash, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Alcohol alkoxylates	0.05	0.3	0.08	0.25	Rosser 1990
Polyolefins	0.01	0.3	0.05	0.25	Dixon *et al.* 2000; Glenn *et al.* 2000; Gittleman *et al.* 2015
Polymerised aromatic sulfonate salts	0.005	0.35	0.05	0.2	Taylor *et al.* 2002; Seitz *et al.* 2005
Proteins/polypeptides	0.005	0.2	0.005	0.2	Staples 1982; Giddey *et al.* 1991
Alcohol ethoxylate salts	0.02	0.3	0.03	0.1	Malik *et al.* 1987
Polyol ethoxylate esters	0.01	0.2	0.02	0.1	Sebillotte-Arnaud and Guillou 2002
Polyurethane Crosspolymer-2*	0.001	0.3	0.005	0.1	Noor and Lemma 2007; Yu *et al.* 2009; Hourigan *et al.* 2015
Disodium Laureth Sulfosuccinate*	0.01	0.2	0.015	0.07	Fan *et al.* 2008
Cellulose and derivatives	0.001	0.1	0.01	0.06	Conklin 1991
Fatty acid ethoxylates	0.001	0.2	0.01	0.05	Zofchak *et al.* 2006
Polycarboxylates	0.001	0.1	0.005	0.05	Margosiak *et al.* 2009
Polyglyceryl esters and polyglycerin	0.0005	0.25	0.0025	0.05	Fevola 2012
Starch and derivatives	0.0001	0.1	0.02	0.04	Yang and Tsaur 2012
Hydrolysed proteins and derivatives	0.001	0.1	0.001	0.03	Giddey *et al.* 1991; Fan *et al.* 2014
Polyethers and copolymers	0.0001	0.1	0.001	0.03	Oldenhove *et al.* 2011; Fan *et al.* 2014
Polyquaterniums	0.001	0.1	0.001	0.03	Tsaur 2012; Fan *et al.* 2014
PEG-4 Rapeseedamide*	0.0001	0.1	0.005	0.03	Librizzi 2002
Plant gums	0.0001	0.1	0.001	0.02	Tsaur and Aronson 2003; Merces 2013
Butyl Acrylate/Ethyltrimonium Chloride Methacrylate/Styrene Copolymer*	0.0005	0.05	0.001	0.015	Mabille and Leroy 2010

*Individual polymer, group 'Other'

Appendix 3.5.6: Estimated polymer concentration in product (F_{pol}) of polymer groups for handwash, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Alcohol alkoxylates	0.05	0.3	0.08	0.25	Rosser 1990
Proteins/polypeptides	0.005	0.2	0.005	0.2	Staples 1982; Giddey *et al.* 1991
Alcohol ethoxylate salts	0.02	0.3	0.03	0.1	Malik *et al.* 1987
Polyol ethoxylate esters	0.01	0.2	0.02	0.1	Sebillotte-Arnaud and Guillou 2002
Fatty acid ethoxylates	0.001	0.2	0.01	0.05	Zofchak *et al.* 2006
Polycarboxylates	0.001	0.1	0.005	0.05	Margosiak *et al.* 2009
Polyglyceryl esters and polyglycerin	0.0005	0.25	0.0025	0.05	Fevola 2012
Starch and derivatives	0.0001	0.1	0.02	0.04	Yang and Tsaur 2012
Hydrolysed proteins and derivatives	0.001	0.1	0.001	0.03	Giddey *et al.* 1991; Fan *et al.* 2014
Polyethers and copolymers	0.0001	0.1	0.001	0.03	Oldenhove *et al.* 2011; Fan *et al.* 2014
Polyquaterniums	0.001	0.1	0.001	0.03	Tsaur 2012; Fan *et al.* 2014
PEG-4 Rapeseedamide*	0.0001	0.1	0.005	0.03	Librizzi 2002
Plant gums	0.0001	0.1	0.001	0.02	Tsaur and Aronson 2003; Merces 2013

*Individual polymer, group 'Other'

Appendix 3.5.7: Estimated polymer concentration in product (F_{pol}) of polymer groups for soap bars, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Alcohol alkoxylates	0.001	0.25	0.05	0.15	Wis-Surel and Moaddel 2013; Pan *et al.* 2014
Alcohol ethoxylate salts	0.01	0.25	0.05	0.15	Potgeiter *et al.* 1999; Pan *et al.* 2014
Cationic silicones	0.001	0.2	0.005	0.1	Schmucker-Castner *et al.* 2005; Seidling and Cunningham 2014
Hydroxypropyl Cyclodextrin*	0.001	0.2	0.01	0.1	Salvador *et al.* 2011
Starch and derivatives	0.001	0.25	0.02	0.05	Thiessies *et al.* 2013; Astolfi *et al.* 2017
Silicones	0.0001	0.08	0.001	0.045	Payne and Chupa 1999
Polyethers and copolymers	0.005	0.05	0.01	0.02	Demson and Dalton 2004

*Individual polymer, group 'Other'

Appendix 3.5.8: Estimated polymer concentration in product (F_{pol}) of polymer groups for bath liquid, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Alcohol alkoxylates	0.05	0.3	0.08	0.25	Rosser 1990
Proteins/polypeptides	0.005	0.2	0.005	0.2	Staples 1982; Giddey *et al.* 1991
Alcohol ethoxylate salts	0.02	0.3	0.03	0.1	Malik *et al.* 1987
Polyol ethoxylate esters	0.01	0.2	0.02	0.1	Sebillotte-Arnaud and Guillou 2002
Disodium Laureth Sulfosuccinate*	0.01	0.2	0.015	0.07	Fan *et al.* 2008
Fatty acid ethoxylates	0.001	0.2	0.01	0.05	Zofchak *et al.* 2006
Polyethers and copolymers	0.0001	0.2	0.01	0.05	Ribery and Penverne 2003; Oldenhove *et al.* 2011
Polycarboxylates	0.001	0.1	0.005	0.05	Margosiak *et al.* 2009
Polyquaterniums	0.001	0.1	0.001	0.03	Tsaur 2012; Fan *et al.* 2014
PEG-4 Rapeseedamide*	0.0001	0.1	0.005	0.03	Librizzi 2002
Plant gums	0.0001	0.1	0.001	0.02	Tsaur and Aronson 2003; Merces 2013

*Individual polymer, group 'Other'

Appendix 3.5.9: Estimated polymer concentration in product (F_{pol}) of polymer groups for shampoo, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Alcohol ethoxylate salts	0.05	0.65	0.05	0.25	Janchitraponvej and Brown 1995
Polymerised aromatic sulfonate salts	0.005	0.35	0.05	0.25	Seitz *et al.* 2005
Laureth-5 Carboxylic Acid*	0.05	0.65	0.05	0.25	Janchitraponvej and Brown 1995
Disodium Laureth Sulfosuccinate*	0.05	0.5	0.12	0.2	Hilvert and Winstel 2014
Polyethers and copolymers	0.005	0.2	0.025	0.125	Takebayashi and Ishiwatari 1999
Polyol ethoxylate esters	0.01	0.2	0.02	0.1	Sebillotte-Arnaud and Guillou 2002
Methyl Gluceth-10*	0.002	0.1	0.005	0.08	Bergmann 1994
Alcohol alkoxylates	0.0001	0.15	0.025	0.05	Preston 1986
Hydrolysed protein and derivatives	0.00001	0.1	0.0005	0.05	Hippe *et al.* 2012; Gerardi *et al.* 2014; Patron and Ditschun 2017
Polyesters	0.0005	0.1	0.001	0.05	Barrios *et al.* 2008
Polyglyceryl esters and polyglycerin	0.0005	0.2	0.005	0.05	Zhou *et al.* 2017
Silicones	0.001	0.1	0.005	0.05	Bolich and Williams 1988
Starch and derivatives	0.001	0.1	0.003	0.05	Coffindaffer and Schrader 1998
Vinylimidazole/vinyl pyrrolidone homo- and co-polymers	0.001	0.1	0.003	0.05	Coffindaffer and Schrader 1998
Polycarboxylates	0.001	0.1	0.009	0.04	Holt and Shaw 2006
Silicone alkoxylates	0.001	0.05	0.005	0.02	Mabille and Leroy 2010
Cationic silicones	0.001	0.05	0.005	0.02	Mabille and Leroy 2010
Cellulose and derivatives	0.0005	0.05	0.001	0.02	Hirota and Takaya 1986
Poly(Linseed Oil)*	0.001	0.1	0.005	0.02	Thiel *et al.* 1994
Fatty acid ethoxylates	0.002	0.02	0.015	0.015	Yu 2015
Polyquaterniums	0.0005	0.05	0.001	0.015	Mabille and Leroy 2010
Plant gums	0.001	0.05	0.0025	0.01	Janchitraponvej and Brown 1995
Proteins/polypeptides	0.00001	0.5	0.00001	0.01	Kelly and Roddick-Lanzilotta 2004
Sodium Hyaluronate*	0.0009	0.01	0.0009	0.01	Dos Santos 2017

*Individual polymer, group 'Other'

Appendix 3.5.10: Estimated polymer concentration in product (F_{pol}) of polymer groups for conditioner, with selection of patents (corresponding to final concentration estimates) referenced. Note that polymers grouped as 'Other' are treated separately, as individual polymers. Groups/polymers are listed in order of highest preferred maximum F_{pol} for this product type.

Groups/polymers	Min F_{pol}	Max F_{pol}	Preferred min F_{pol}	Preferred max F_{pol}	References (patents)
Polymerised aromatic sulfonate salts	0.005	0.35	0.05	0.25	Seitz *et al.* 2005
Alcohol ethoxylate salts	0.01	0.25	0.07	0.15	Jordan 2013
Polyglyceryl esters and polyglycerin	0.002	0.25	0.01	0.15	Carew *et al.* 2003
Cellulose and derivatives	0.001	0.1	0.01	0.06	Conklin 1991
Starch and derivatives	0.035	0.08	0.05	0.06	Gevgilili and Liang 2017
Alcohol alkoxylates	0.005	0.15	0.01	0.05	Grit *et al.* 2006
Fatty acid ethoxylates	0.002	0.2	0.011	0.05	Hindley 2016
Hydrolysed protein and derivatives	0.00001	0.1	0.0005	0.05	Hippe *et al.* 2012; Gerardi *et al.* 2014; Patron and Ditschun 2017
Plant gums	0.001	0.1	0.005	0.05	Zofchak and Carson 2005
Polyethers and copolymers	0.001	0.1	0.005	0.05	Deryon *et al.* 2013
Polyesters	0.0005	0.1	0.001	0.05	Barrios *et al.* 2008
Silicones	0.0001	0.2	0.001	0.05	Sturla *et al.* 2013
Vinylimidazole/vinyl pyrrolidone homo- and co-polymers	0.002	0.1	0.005	0.05	Shih *et al.* 1992
Poly(Linseed Oil)*	0.0001	0.2	0.005	0.05	Meralli *et al.* 2014
Polycarboxylates	0.0005	0.1	0.001	0.04	Quenzer 2000
Silicone alkoxylates	0.0001	0.1	0.001	0.03	Molenda and Tietjen 2017
Cationic silicones	0.0001	0.1	0.005	0.03	Read and Southey 2015
PPG-3 Benzyl Ether Myristate*	0.005	0.04	0.01	0.03	Demitz *et al.* 2009
Polyquaterniums	0.001	0.05	0.003	0.025	Hoffmann and Ning 2016
Polyol ethoxylate esters	0.0001	0.05	0.0005	0.02	Uehara and Yang 2004
Sodium Hyaluronate*	0.00001	0.05	0.0005	0.02	Hammond *et al.* 2006
Proteins/polypeptides	0.00001	0.5	0.00001	0.01	Kelly and Roddick-Lanzilotta 2004

*Individual polymer, group 'Other'

Appendix 3.6: Worst-case predicted environmental concentrations for polymer groups from household products in surface water and soil.

Appendix 3.6.1: Worst-case PEC_{SW} estimates (mg L^{-1}) for polymer groups in household products emitted down-the-drain. Probable values were obtained from 'preferred' concentration ranges given by patents (and are thus expected to be more representative of actual environmental concentration), whilst absolute values were derived from widest concentration ranges given by patents. Polymer groups are listed in order of highest probable max. worst-case PEC.

Polymer groups	Absolute min. worst-case PEC_{SW}	Absolute max. worst-case PEC_{SW}	Probable min. worst-case PEC_{SW}	Probable max. worst-case PEC_{SW}
Alcohol ethoxylate salts	0.4	5.1	1.1	2.4
Alcohol alkoxylates	0.2	3.3	0.8	1.8
Polycarboxylates	0.008	2.4	0.1	1.0
Polyol ethoxylate esters	0.03	0.7	0.07	0.3
Polyethers and copolymers	0.02	0.8	0.04	0.3
Starch and derivatives	0.01	0.4	0.06	0.2
Silicones	0.005	0.8	0.05	0.2
Polyquaterniums	0.005	0.6	0.007	0.2
Polyvinyl alcohol	0.004	0.2	0.02	0.1
Cellulose and derivatives	0.003	0.2	0.03	0.1
Fatty acid ethoxylates	0.003	0.4	0.02	0.1
Polyethylenimine ethoxylates and polyether copolymers	0.0003	0.3	0.009	0.08
Other	0.005	0.1	0.01	0.06
Polyesters	0.008	0.05	0.008	0.05
Proteins/polypeptides	0.0010	0.05	0.001	0.04
Hydrolysed protein and derivatives	0.0002	0.07	0.0004	0.03
Cationic silicones	0.0003	0.09	0.005	0.03
Poly(oxy)alkylene terephthalates	0.003	0.05	0.005	0.03
Plant gums	0.0005	0.08	0.002	0.03
Polyolefins	0.0006	0.02	0.003	0.01
Polyglyceryl esters and polyglycerin	0.0001	0.05	0.0007	0.01
Polymerised aromatic sulfonate salts	0.0002	0.05	0.003	0.01
Vinylimidazole/vinylpyrrolidone homo- and co-polymers	0.0003	0.03	0.002	0.007
Silicone alkoxylates	0.00007	0.008	0.0004	0.003
Polymeric colourants	0.00002	0.007	0.00006	0.0007
Amine/formaldehyde polymers	0.000008	0.007	0.00002	0.0002

Appendix 3.6.2: Worst-case PEC_{SOIL} estimates (mg kg^{-1}) for polymer groups in household products emitted down-the-drain. Probable values were obtained from 'preferred' concentration ranges given by patents (and are thus expected to be more representative of actual environmental concentration), whilst absolute values were derived from widest concentration ranges given by patents. Polymer groups are listed in order of highest probable max. worst-case PEC.

Polymer groups	**Absolute min. worst-case PEC_{SOIL}**	**Absolute max. worst-case PEC_{SOIL}**	**Probable min. worst-case PEC_{SOIL}**	**Probable max. worst-case PEC_{SOIL}**
Alcohol ethoxylate salts	16.2	202.6	45.2	95.9
Alcohol alkoxylates	7.7	131.7	30.0	71.4
Polycarboxylates	0.3	94.3	4.0	39.9
Polyol ethoxylate esters	1.3	26.8	2.7	13.4
Polyethers and copolymers	0.7	31.8	1.6	11.9
Starch and derivatives	0.5	16.0	2.5	9.8
Silicones	0.2	31.0	1.9	8.1
Polyquaterniums	0.2	23.4	0.3	6.2
Polyvinyl alcohol	0.2	8.1	0.8	4.9
Cellulose and derivatives	0.1	7.9	1.2	4.7
Fatty acid ethoxylates	0.1	15.2	1.0	4.1
Polyethylenimine ethoxylates and polyether copolymers	0.01	12.9	0.3	3.3
Other	0.2	5.3	0.4	2.4
Polyesters	0.3	2.0	0.3	1.8
Proteins/polypeptides	0.04	2.0	0.04	1.6
Hydrolysed protein and derivatives	0.009	2.7	0.02	1.2
Cationic silicones	0.01	3.5	0.2	1.1
Poly(oxy)alkylene terephthalates	0.1	2.1	0.2	1.0
Plant gums	0.02	3.3	0.1	1.0
Polyolefins	0.02	0.7	0.1	0.5
Polyglyceryl esters and polyglycerin	0.005	2.1	0.03	0.5
Polymerised aromatic sulfonate salts	0.008	2.1	0.1	0.4
Vinylimidazole/vinylpyrrolidone homo- and co-polymers	0.01	1.3	0.06	0.3
Silicone alkoxylates	0.003	0.3	0.01	0.1
Polymeric colourants	0.0009	0.3	0.002	0.03
Amine/formaldehyde polymers	0.0003	0.3	0.001	0.008

Appendix 3.7: Summary of ecotoxicity data obtained from the ECOTOX Knowledgebase for polyol ethoxylate esters, starch and derivatives, polyquaterniums, polyethers and copolymers, cellulose and derivatives, polyvinyl alcohol, and silicones.

Ecotoxicity data obtained from the ECOTOX Knowledgebase (USEPA 2000) for polyol ethoxylate esters, starch and derivatives, polyquaterniums, polyethers and copolymers, cellulose and derivatives, polyvinyl alcohol, and silicones are summarised below. All available data were for an aquatic environment. Alternative endpoints that do not directly correspond to standard endpoints (e.g. NR-LETH) were excluded from the dataset except in cases where they could be used to supplement incomplete data for EC50, LC50, and NOEC (or comparable endpoints). Where endpoints were not reported but had lower values than reported data (thus potentially indicating a lower value of PNEC), original papers were sought where possible and the information assessed to determine whether a comparable endpoint could be derived, and therefore whether the datapoint in question should be included in the dataset. In these cases, where original papers could not be accessed, or a comparable endpoint could not be derived, datapoints were excluded from the dataset. Reasons for exclusions of datapoints are summarised below and specified for relevant datapoints in each table;

1. Insufficient information available to derive endpoint
2. No effect at concentration tested
3. Effect of polymer not reported
4. No ecotoxicological effect at concentration tested
5. Data not investigated further because inclusion would not influence derived PNEC
6. Alternative/non-standard endpoint not directly comparable to EC50/LC50/NOEC
7. Experimental conditions not relevant to environmental exposure
8. Units not comparable to exposure estimates of the present study
9. Study duration not reported, unclear if comparable to long-term NOEC data.

Appendix 3.7.1: Summary of ecotoxicity data from the ECOTOX Knowledgebase for polyol ethoxylate esters.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Guppy	Fish	350	AI mg/L	Mortality	LC50	1	Yarzhombek *et al.* 1991	Y
Monooctadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	> 1000	AI mg/L	Mortality	LC50	1	Tsuji *et al.* 1986	Y
Monooctadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	260	AI mg/L	Mortality	LC50	1	Tsuji *et al.* 1986	Y
Monooctadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	240	AI mg/L	Mortality	LC50	2	Tsuji *et al.* 1986	Y
Monooctadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	520	AI mg/L	Mortality	LC50	2	Tsuji *et al.* 1986	Y
Monooctadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	> 1000	AI mg/L	Mortality	LC50	2	Tsuji *et al.* 1986	Y
Monohexadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	> 1000	AI mg/L	Mortality	LC50	1	Tsuji *et al.* 1986	Y
Monohexadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Japanese Medaka	Fish	> 1000	AI mg/L	Mortality	LC50	2	Tsuji *et al.* 1986	Y
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Yellow Fever Mosquito	Insects/ Spiders	8	% v/v	Mortality	LC50	0.1667	Kramer *et al.* 1983	Y
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Brine Shrimp	Crustaceans	1089.6	AI mg/L	Mortality	LD50	2	Castritsi-Catharios *et al.* 1982	Y
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Ciliate	Invertebrates	~1820.115	AI mg/L	Behavior	NOEC	0.0417	Matsubara *et al.* 2006	Y
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Ragworm	Worms	2	AI mg/L	Genetics	NOEC	3	Chen *et al.* 2012	Y
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Ragworm	Worms	2	AI mg/L	Genetics	NOEC	7	Chen *et al.* 2012	Y

Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Ragworm	Worms	2	AI mg/L	Genetics	NOEC	14	Chen *et al.* 2012	Y
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Turbellarian Flatworm	Worms	500	AI mg/L	Mortality	NR-LETH	0.1392	Saski *et al.* 1971	N[6]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Turbellarian Flatworm	Worms	500	AI mg/L	Mortality	NR-LETH	0.4104	Saski *et al.* 1971	N[6]
Monooctadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Turbellarian Flatworm	Worms	500	AI mg/L	Mortality	NR-LETH	1.1533	Saski *et al.* 1971	N[6]
Monohexadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Turbellarian Flatworm	Worms	1000	AI mg/L	Mortality	NR-LETH	0.3733	Saski *et al.* 1971	N[6]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Green Algae	Algae	100	AI mg/L	Population	NR	21	Nyberg 1988	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Green Algae	Algae	500	AI mg/L	Population	NR	21	Nyberg 1988	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Blue-Green Algae	Algae	(20-500)	AI mg/L	Population	NR	NR	Tözüm-Calgan and Atay-Güneyman 1994	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Blue-Green Algae	Algae	(20-500)	AI mg/L	Physiology	NR	NR	Tözüm-Calgan and Atay-Güneyman 1994	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Sand Shrimp	Crustaceans	1	AI mg/L	Feeding behavior	NR	1	Evans *et al.* 1977	N[1]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Water Flea	Crustaceans	10	AI mg/L	Intoxication	NR	2	Brown *et al.* 1998	N[2]
Monohexadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Copepod	Crustaceans	(1820.115-18201.15)	AI mg/L	Mortality	NR	1	Stom and Zubareva 1994	N/A[5]
Monohexadecanoate sorbitan, Poly(oxy-1,2-ethanediyl) derivs	Water Flea	Crustaceans	(1820.115-18201.15)	AI mg/L	Mortality	NR	1	Stom and Zubareva 1994	N/A[5]

Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Water Flea	Crustaceans	10	AI mg/L	Mortality	NR	21	Brown *et al.* 1998	Y
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Water Flea	Crustaceans	(1-100)	AI mg/L	Mortality	NR	21	Brown *et al.* 1998	Y
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Water Flea	Crustaceans	10	AI mg/L	Reproduction	NR	21	Brown *et al.* 1998	N[2]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Water Flea	Crustaceans	32	AI mg/L	Reproduction	NR	21	Brown *et al.* 1998	Y
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Agohaze, Goby	Fish	2	AI mg/L	Physiology	NR	0.0104	Umezu 1991	N[1]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Red Sea Bream	Fish	10	AI mg/L	Physiology	NR	0.0104	Umezu 1991	N[1]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Japanese Medaka	Fish	20	AI mg/L	Physiology	NR	0.0104	Umezu 1991	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Japanese Medaka	Fish	1	%	Development (Delayed)	NR	NR	Shugart *et al.* 1990	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Japanese Medaka	Fish	1	%	Genetics	NR	16	Shugart *et al.* 1990	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Japanese Medaka	Fish	1	%	Morphology	NR	NR	Shugart *et al.* 1990	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Japanese Medaka	Fish	1	%	Mortality	NR	NR	Shugart *et al.* 1990	N[1]
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Japanese Medaka	Fish	1	%	Reproduction	NR	NR	Shugart *et al.* 1990	N[1]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Atlantic Salmon	Fish	2	%	Cell(s)	NR	1	Johnsen 2012	N[3]
Sorbitan, Monododecanoate, Poly(oxy-1,2-ethanediyl)derivs.	Echinoderm	Invertebrates	(0.002-0.01)	%	Development	NR	2.9167	Bresch and Ockenfels 1977	Y
Sorbitan, Mono-9-octadecenoate, (Z)-Poly(oxy-1,2-ethanediyl) derivs.	Ciliate	Invertebrates	0.25	%	Population	NR	NR	Wiger 1985	N[4]

Appendix 3.7.2: Summary of ecotoxicity data from the ECOTOX Knowledgebase for starch and derivatives.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
Starch	American Or Virginia Oyster	Molluscs	3000	AI mg/L	Mortality	NR-LETH	4	Daugherty 1951	Y
Starch	American Or Virginia Oyster	Molluscs	1000	AI mg/L	Mortality	NR-ZERO	4	Daugherty 1951	Y
Starch	Pigfish	Fish	5000	AI mg/L	Mortality	NR-ZERO	4	Daugherty 1951	Y
Starch	Pinfish	Fish	5000	AI mg/L	Mortality	NR-ZERO	4	Daugherty 1951	Y
Starch	Silver Perch	Fish	5000	AI mg/L	Mortality	NR-ZERO	4	Daugherty 1951	Y

Appendix 3.7.3: Summary of ecotoxicity data from the ECOTOX Knowledgebase for polyquaterniums.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Green Algae	Algae	0.0088 (0.0077-0.01)	AI mg/L	Population	EC50	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Diatom	Algae	0.083 (0.078-0.089)	AI mg/L	Population	EC50	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Diatom	Algae	0.09 (0.076-0.106)	AI mg/L	Population	EC50	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Blue-Green Algae	Algae	0.11 (0.1-0.12)	AI mg/L	Population	EC50	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	0.266 (0.228-0.316)	AI mg/L	Intoxication	EC50	2	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Inflated Duckweed	Flowers, Trees, Shrubs, Ferns	> 0.65	AI mg/L	Population	EC50	14	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Northern Quahog Or Hard Clam	Molluscs	0.35 (0-0.71)	AI mg/L	Intoxication	EC50	2	EPA 1992	Y

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Harlequinfish, Red Rasbora	Fish	0.32	AI mg/L	Mortality	LC10	2	Tooby *et al.* 1975	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Harlequinfish, Red Rasbora	Fish	0.47	AI mg/L	Mortality	LC10	1	Tooby *et al.* 1975	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Opossum Shrimp	Crustaceans	13 (9.1-16)	AI mg/L	Mortality	LC50	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	0.218	AI mg/L	Mortality	LC50	2	Giltner and Baumann 1991	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	(>2 to <3)	AI mg/L	Mortality	LC50	2	Cowgill and Milazzo 1991	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Harlequinfish, Red Rasbora	Fish	0.17	AI mg/L	Mortality	LC50	4	Tooby *et al.* 1975	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Harlequinfish, Red Rasbora	Fish	0.39	AI mg/L	Mortality	LC50	2	Tooby *et al.* 1975	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Harlequinfish, Red Rasbora	Fish	0.66	AI mg/L	Mortality	LC50	1	Tooby *et al.* 1975	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Bluegill	Fish	0.206 (0.13-0.36)	AI mg/L	Mortality	LC50	4	EPA 1992	Y

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Bluegill	Fish	0.45	AI mg/L	Mortality	LC50	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Bluegill	Fish	1.21 (0.8-1.76)	AI mg/L	Mortality	LC50	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Sheepshead Minnow	Fish	> 600	AI mg/L	Mortality	LC50	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Channel Catfish	Fish	3.35 (2.82-3.96)	AI mg/L	Mortality	LC50	2	Waller *et al.* 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Fathead Minnow	Fish	0.353	AI mg/L	Mortality	LC50	2	Giltner and Baumann 1991	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Rainbow Trout	Fish	0.047 (0.037-0.06)	AI mg/L	Mortality	LC50	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Rainbow Trout	Fish	0.43 (0.4-0.47)	AI mg/L	Mortality	LC50	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Rainbow Trout	Fish	0.044 (0.041-0.048)	AI mg/L	Mortality	LC50	2	Waller *et al.* 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Three-Horned Wartyback	Molluscs	> 60	AI mg/L	Mortality	LC50	2	Waller *et al.* 1993	Y

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	> 60	AI mg/L	Mortality	LC50	2	Waller *et al.* 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Diatom	Algae	0.02	ml/L	Cell(s)	LOEC	0.0417	Jellyman *et al.* 2010	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	0.02	AI mg/L	Mortality	LOEC	21	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	(12.5-25)	AI mg/L	Population	LOEC	1	Srikanth and Berk 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	0.7	AI mg/L	Population	LOEC	1	Srikanth and Berk 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	(12-25)	AI mg/L	Population	LOEC	1	Srikanth and Berk 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	6	AI mg/L	Population	LOEC	1	Srikanth and Berk 1993	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	1	AI mg/L	Behavior	LT50	7.2917	Martin *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	2	AI mg/L	Behavior	LT50	6.9167	Martin *et al.* 1993	N[6]

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	4	AI mg/L	Behavior	LT50	5.125	Martin *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	8	AI mg/L	Behavior	LT50	4.4583	Martin *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	4.8	AI mg/L	Mortality	LT50	1.8667	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	2.4	AI mg/L	Mortality	LT50	2.0625	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	1.2	AI mg/L	Mortality	LT50	2.2625	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Mollusc	4.8	AI mg/L	Mortality	LT50	4.2083	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	4.8	AI mg/L	Mortality	LT50	5.1792	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	2.4	AI mg/L	Mortality	LT50	7.2375	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	0.6	AI mg/L	Mortality	LT50	8.6917	McMahon *et al.* 1993	N[6]

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	1.2	AI mg/L	Mortality	LT50	8.9875	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	0.3	AI mg/L	Mortality	LT50	10.6542	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	0.6	AI mg/L	Mortality	LT50	20.7792	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	0.15	AI mg/L	Mortality	LT50	23.1708	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	0.3	AI mg/L	Mortality	LT50	29.175	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	0.012	AI mg/L	Mortality	NOEC	21	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Green Algae	Algae	< 0.001	AI mg/L	Population	NOEL	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Diatom	Algae	< 0.024	AI mg/L	Population	NOEL	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Diatom	Algae	0.044	AI mg/L	Population	NOEL	5	EPA 1992	Y

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Blue-Green Algae	Algae	0.05	AI mg/L	Population	NOEL	5	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	0.08	AI mg/L	Intoxication	NOEL	2	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Opossum Shrimp	Crustaceans	< 7.8	AI mg/L	Mortality	NOEL	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Bluegill	Fish	0.13	AI mg/L	Mortality	NOEL	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Sheepshead Minnow	Fish	600	AI mg/L	Mortality	NOEL	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Rainbow Trout	Fish	0.037	AI mg/L	Mortality	NOEL	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Rainbow Trout	Fish	0.18	AI mg/L	Mortality	NOEL	4	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Inflated Duckweed	Flowers, Trees, Shrubs, Ferns	0.043	AI mg/L	Population	NOEL	14	EPA 1992	Y
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Northern Quahog Or Hard Clam	Molluscs	0.23	AI mg/L	Intoxication	NOEL	2	EPA 1992	Y

Aziridine homopolymer	Water Flea	Crustaceans	10	AI mg/L	Mortality	NR-LETH	2	Stroganov *et al.* 1977	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoebae	Invertebrates	61	AI mg/L	Mortality	NR-LETH	1	Sutherland and Berk 1996	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	61	AI mg/L	Mortality	NR-LETH	1	Sutherland and Berk 1996	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Ciliate	Invertebrates	61	AI mg/L	Mortality	NR-LETH	1	Sutherland and Berk 1996	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Ciliate Protozoan	Invertebrates	122	AI mg/L	Mortality	NR-LETH	1	Sutherland and Berk 1996	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Ciliate	Invertebrates	488	AI mg/L	Mortality (Delayed)	NR-LETH	<7	Sutherland and Berk 1996	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	62500	AI mg/L	Mortality	NR-LETH	<7	Sutherland and Berk 1996	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	1	AI mg/L	Behavior	NR-LETH	~10.4167	Martin *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	2	AI mg/L	Behavior	NR-LETH	~10.4167	Martin *et al.* 1993	N[6]

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	4	AI mg/L	Behavior	NR-LETH	8.1667	Martin *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	8	AI mg/L	Behavior	NR-LETH	6	Martin *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	1.2	AI mg/L	Mortality	NR-LETH	0.4708	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	2.4	AI mg/L	Mortality	NR-LETH	4.2083	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	4.8	AI mg/L	Mortality	NR-LETH	8.2083	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	2.4	AI mg/L	Mortality	NR-LETH	10.1667	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	0.6	AI mg/L	Mortality	NR-LETH	11.7917	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	1.2	AI mg/L	Mortality	NR-LETH	13.0417	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	0.3	AI mg/L	Mortality	NR-LETH	15.75	McMahon *et al.* 1993	N[6]

Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	0.6	AI mg/L	Mortality	NR-LETH	28.3333	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	0.3	AI mg/L	Mortality	NR-LETH	34.4167	McMahon *et al.* 1993	N[6]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Water Flea	Crustaceans	(>1 to <1.5)	AI mg/L	Mortality	NR-ZERO	2	Cowgill and Milazzo 1991	Y
Aziridine homopolymer	Water Flea	Crustaceans	1	AI mg/L	Growth	NR	30	Stroganov *et al.* 1977	N/A[5]
Aziridine homopolymer	Water Flea	Crustaceans	1	AI mg/L	Mortality	NR	30	Stroganov *et al.* 1977	N/A[5]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	(0.5-2.5)	AI mg/L	Population	NR	1	Srikanth and Berk 1993	N/A[5]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Amoeba	Invertebrates	(0.6-0.7)	AI mg/L	Population	NR	1	Srikanth and Berk 1993	N/A[5]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Asiatic Clam	Molluscs	(150-1800)	AI mg/L	Behavior	NR	23.1667	McMahon *et al.* 1993	N/A[5]
Poly[oxy-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl(dimethyliminio)-1,2-ethanediyl chloride (1:2)]	Zebra Mussel	Molluscs	(0.3-4.8)	AI mg/L	Behavior	NR	34.4167	McMahon *et al.* 1993	N/A[5]

Appendix 3.7.4: Summary of ecotoxicity data from the ECOTOX Knowledgebase for polyethers and copolymers.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Crucian Carp	Fish	> 20000	AI mg/L	Mortality	LC50	4	Bathe *et al.* 1975	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Japanese Medaka	Fish	> 1000	AI mg/L	Mortality	LC50	1	Tsuji *et al.* 1986	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Japanese Medaka	Fish	> 1000	AI mg/L	Mortality	LC50	2	Tsuji *et al.* 1986	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Goldfish	Fish	> 5000	AI mg/L	Mortality	LC50	1	Bridie′ *et al.* 1979	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Atlantic Salmon	Fish	> 1000	AI mg/L	Mortality	LC50	1	Wildish 1974	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Atlantic Salmon	Fish	> 1000	AI mg/L	Mortality	LC50	2	Wildish 1974	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Atlantic Salmon	Fish	> 1000	AI mg/L	Mortality	LC50	4	Wildish 1974	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Rainbow Trout	Fish	> 20000	AI mg/L	Mortality	LC50	4	Bathe *et al.* 1975	Y
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Salmon Louse	Crustaceans	0.1	%	Genetics	NOEC	0.125	Heumann *et al.* 2014	N[3]
2-Methyloxirane, Polymer with oxirane	Dinoflagellate	Algae	2.58	ppb[a]	Population	NR	2	Kutt and Martin 1974	N[4]
2-Methyloxirane, Polymer with oxirane	Dinoflagellate	Algae	12.5	ppb[a]	Mortality	NR	2	Kutt and Martin 1974	Y

alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Green Algae	Algae	100	AI mg/L	Population	NR	12	Chan *et al.* 1981	N[1]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Green Algae	Algae	(3.4-136)	meq	Population	NR	1	Kalinkina *et al.* 1978	N[1]
2-Methyloxirane, Polymer with oxirane	Aquatic Sowbug	Crustaceans	10	AI mg/L	Genetics	NR	NR	Kaim-Malka and Donadey 1978	N[1]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Salmon Louse	Crustaceans	0.1	%	Genetics	NR	1	Heumann *et al.* 2014	N[3]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Marsh Grass Shrimp	Crustaceans	(0.025-0.1)	AI mg/L	Development	NR	NR	Sandifer *et al.* 1975	N[4]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Daggerblade Grass Shrimp	Crustaceans	(0.025-0.1)	AI mg/L	Development	NR	NR	Sandifer *et al.* 1975	N[4]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Aholehole	Fish	20	AI mg/L	Behavior	NR	0.0014	Hiatt *et al.* 1953	N[2]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Atlantic Salmon	Fish	> 1000	AI mg/L	Mortality	NR	4	Wildish 1974	N/A[5]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Ciliate	Invertebrates	1000	AI mg/L	Population	NR	4	Cooley 1970	N/A[5]
alpha-Hydro-omega-hydroxypoly(oxy-1,2-ethanediyl)	Zebra Mussel	Molluscs	1	mCi	Accumulation	NR	0.1667	Dietz and Byrne 1999	N[7]

[a] Listed as AI mg/L in ECOTOX Knowledgebase, ppb in original paper

Appendix 3.7.5: Summary of ecotoxicity data from the ECOTOX Knowledgebase for cellulose and derivatives.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
Cellulose tetranitrate	Green Algae	Algae	579 (138-2400)	AI mg/L	Biochemistry	EC50	4	Bentley *et al.* 1976	Y
Cellulose, Carboxymethyl ether, Sodium salt	Water Flea	Crustaceans	87.26 (46.04-165.37)	AI mg/L	Intoxication	EC50	2	Warne and Schifko 1999	Y
Cellulose, Carboxymethyl ether, Sodium salt	Sand Shrimp	Crustaceans	(330-1000)	AI mg/L	Mortality	LC50	4	Portmann and Wilson 1971	Y
Cellulose, Carboxymethyl ether, Sodium salt	Sand Shrimp	Crustaceans	(1000-3300)	AI mg/L	Mortality	LC50	2	Portmann and Wilson 1971	Y
Cellulose, Carboxymethyl ether, Sodium salt	Crucian Carp	Fish	> 20000	AI mg/L	Mortality	LC50	4	Bathe *et al.* 1975	Y
Cellulose, Carboxymethyl ether, Sodium salt	Rainbow Trout	Fish	> 20000	AI mg/L	Mortality	LC50	4	Bathe *et al.* 1975	Y
Cellulose, Methyl ether	Water Flea	Crustaceans	10000	AI mg/L	Mortality	NR-LETH	1.5	Shcherban 1979	N[6]
Cellulose, Carboxymethyl ether	Rainbow Trout	Fish	32	AI mg/L	Mortality	NR-ZERO	1	Department of Scientific and Industrial Research 1953	Y
Cellulose, Carboxymethyl ether	Rainbow Trout	Fish	32	AI mg/L	Mortality	NR-ZERO	1	Department of Scientific and Industrial Research 1956	Y
Cellulose tetranitrate	Blue-Green Algae	Algae	1000	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Blue-Green Algae	Algae	100	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Blue-Green Algae	Algae	32	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Blue-Green Algae	Algae	1000	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]

Cellulose tetranitrate	Blue-Green Algae	Algae	10	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Diatom	Algae	32	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Diatom	Algae	320	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Diatom	Algae	1000	AI mg/L	Biochemistry	NR	4	Bentley *et al.* 1976	N[1]
Cellulose	Green Algae	Algae	50	AI mg/L	Physiology	NR	4	Schwab *et al.* 2011	N[2]
Cellulose	Green Algae	Algae	50	AI mg/L	Physiology	NR	4	Schwab *et al.* 2011	N[2]
Cellulose	Green Algae	Algae	50	AI mg/L	Population	NR	4	Schwab *et al.* 2011	N[2]
Cellulose tetranitrate	Diatom	Algae	100	AI mg/L	Population	NR	4	Bentley *et al.* 1976	N[1]
Cellulose	Green Algae	Algae	50	AI mg/L	Population	NR	4	Schwab *et al.* 2011	N[2]
Cellulose tetranitrate	Aquatic Sowbug	Crustaceans	1000	AI mg/L	Behavior	NR	2	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Scud	Crustaceans	1000	AI mg/L	Behavior	NR	2	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Water Flea	Crustaceans	1000	AI mg/L	Behavior	NR	2	Bentley *et al.* 1976	N[1]
Cellulose, Methyl ether	Water Flea	Crustaceans	5000	AI mg/L	Mortality	NR	2	Shcherban 1979	N/A[5]
Cellulose, Methyl ether	Water Flea	Crustaceans	5000	AI mg/L	Mortality	NR	4	Shcherban 1979	N/A[5]
Cellulose tetranitrate	Bluegill	Fish	1000	AI mg/L	Mortality	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Channel Catfish	Fish	1000	AI mg/L	Mortality	NR	4	Bentley *et al.* 1976	N[1]
Cellulose tetranitrate	Fathead Minnow	Fish	1000	AI mg/L	Mortality	NR	4	Bentley *et al.* 1976	N[1]
Cellulose, Methyl ether	Common Carp	Fish	(75-179)	AI mg/kg bdwt	Mortality	NR	1.8333	Loeb and Kelly 1963	N/A[5]

Cellulose tetranitrate	Rainbow Trout	Fish	1000	AI mg/L	Mortality	NR	4	Bentley *et al.* 1976	N[1]
Cellulose, Carboxymethyl ether	Rainbow Trout	Fish	(0.5-32)	AI mg/L	Mortality	NR	1	Department of Scientific and Industrial Research 1956	N[1]
Cellulose tetranitrate	Midge	Insects/ Spiders	1000	AI mg/L	Behavior	NR	2	Bentley *et al.* 1976	N[1]

Appendix 3.7.6: Summary of ecotoxicity data from the ECOTOX Knowledgebase for polyvinyl alcohol.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
Polyvinyl alcohol	Common Carp	Fish	(86-118)	AI mg/kg bdwt	Mortality	NR	1.9167	Loeb and Kelly 1963	N[7,8]

Appendix 3.7.7: Summary of ecotoxicity data from the ECOTOX Knowledgebase for silicones.

Chemical Name	Species Common Name	Species Group	Mean conc. (min.-max.)	Conc. units	Effect	Endpoint	Observed Duration (Days)	Reference	Included in dataset in present study?
Dimethyl siloxanes and silicones	Water Flea	Crustaceans	379.6	AI mg/L	Mortality	LC01	2	Hobbs *et al.* 1975	Y
Siloxanes and Silicones	Water Flea	Crustaceans	600	AI mg/L	Mortality	LC01	2	Hobbs *et al.* 1975	Y
Dimethyl siloxanes and silicones	Fowler's Toad	Amphibians	0.25 (0.14-0.4)	AI mg/L	Mortality	LC01	NR	Birge *et al.* 1978	N[9]
Dimethyl siloxanes and silicones	Leopard Frog	Amphibians	0.3 (0.17-0.46)	AI mg/L	Mortality	LC01	NR	Birge *et al.* 1978	N[9]
Dimethyl siloxanes and silicones	Redear Sunfish	Fish	0.23 (0.05-0.62)	AI mg/L	Mortality	LC01	NR	Birge *et al.* 1978	N[9]
Dimethyl siloxanes and silicones	Channel Catfish	Fish	0.04 (0.02-0.09)	AI mg/L	Mortality	LC01	~7	Birge *et al.* 1978	Y
Dimethyl siloxanes and silicones	Fowler's Toad	Amphibians	134.76 (83.97-253.01)	AI mg/L	Mortality	LC50	NR	Birge *et al.* 1978	Y
Dimethyl siloxanes and silicones	Fowler's Toad	Amphibians	7.68 (6.24-9.37)	AI mg/L	Mortality	LC50	NR	Birge *et al.* 1978	Y
Dimethyl siloxanes and silicones	Leopard Frog	Amphibians	17.55 (13.57-22.96)	AI mg/L	Mortality	LC50	NR	Birge *et al.* 1978	Y
Dimethyl siloxanes and silicones	Leopard Frog	Amphibians	6.95 (5.73-8.4)	AI mg/L	Mortality	LC50	NR	Birge *et al.* 1978	Y
Siloxanes and Silicones	Shore Crab	Crustaceans	> 1000	AI mg/L	Mortality	LC50	4	Hobbs *et al.* 1975	Y
Siloxanes and Silicones	Brown Shrimp	Crustaceans	> 1000	AI mg/L	Mortality	LC50	4	Hobbs *et al.* 1975	Y
Dimethyl siloxanes and silicones	Water Flea	Crustaceans	44.5	AI mg/L	Mortality	LC50	2	Hobbs *et al.* 1975	Y
Siloxanes and Silicones	Water Flea	Crustaceans	73.4 (53.2-101)	AI mg/L	Mortality	LC50	2	Hobbs *et al.* 1975	Y

Siloxanes and Silicones	Water Flea	Crustaceans	245 (177-338)	AI mg/L	Mortality	LC50		2	Hobbs *et al.* 1975	Y
Dimethyl siloxanes and silicones	Redear Sunfish	Fish	307.11 (163.26-852.16)	AI mg/L	Mortality	LC50	NR		Birge *et al.* 1978	Y
Dimethyl siloxanes and silicones	Redear Sunfish	Fish	37.79 (26.27-56.73)	AI mg/L	Mortality	LC50	NR		Birge *et al.* 1978	Y
Siloxanes and Silicones	Bluegill	Fish	> 10000	AI mg/L	Mortality	LC50		4	Hobbs *et al.* 1975	Y
Siloxanes and Silicones	Mummichog	Fish	> 1000	AI mg/L	Mortality	LC50		4	Hobbs *et al.* 1975	Y
Dimethyl siloxanes and silicones	Channel Catfish	Fish	5.57 (4.23-7.21)	AI mg/L	Mortality	LC50	~3		Birge *et al.* 1978	Y
Dimethyl siloxanes and silicones	Channel Catfish	Fish	3.16 (2.36-4.15)	AI mg/L	Mortality	LC50	~7		Birge *et al.* 1978	Y
Siloxanes and Silicones	Rainbow Trout	Fish	> 10000	AI mg/L	Mortality	LC50		4	Hobbs *et al.* 1975	Y
Siloxanes and Silicones	Littleneck Clam	Molluscs	> 1000	AI mg/L	Mortality	LC50		4	Hobbs *et al.* 1975	Y
Dimethyl siloxanes and silicones	Water Flea	Crustaceans	5.22	AI mg/L	Mortality	LC99		2	Hobbs *et al.* 1975	N[6]
Siloxanes and Silicones	Water Flea	Crustaceans	8.98	AI mg/L	Mortality	LC99		2	Hobbs *et al.* 1975	N[6]
Siloxanes and Silicones	Water Flea	Crustaceans	300	AI mg/L	Mortality	NR-LETH		2	Hobbs *et al.* 1975	N[6]
Dimethyl siloxanes and silicones	Fowler's Toad	Amphibians	100	AI mg/L	Mortality	NR-LETH	NR		Birge *et al.* 1978	N[6]
Dimethyl siloxanes and silicones	Leopard Frog	Amphibians	100	AI mg/L	Mortality	NR-LETH	NR		Birge *et al.* 1978	N[6]
Dimethyl siloxanes and silicones	Channel Catfish	Fish	100	AI mg/L	Mortality	NR-LETH	~3		Birge *et al.* 1978	N[6]
Siloxanes and Silicones	Mummichog	Fish	100	AI mg/L	Mortality	NR-ZERO		4	Hobbs *et al.* 1975	Y

Siloxanes and Silicones	Shore Crab	Crustaceans	100	AI mg/L	Mortality	NR-ZERO		4	Hobbs *et al.* 1975	Y
Dimethyl siloxanes and silicones	Bluegill	Fish	(0.23-11.84)	AI mg/L	Accumulation	NR	NR		Hobbs *et al.* 1975	N[1]

Appendix 3.8: Summary of the available acute and chronic ecotoxicity data for each polymer group, and the final values used along with choice of assessment factor for derivation of predicted no-effect concentration (PNEC).

Polymer group	Acute data included in dataset	Complete base set (acute data for fish, invertebrates, and algae)?	Chronic data included in dataset	Other data included in dataset	Value used to calculate PNEC (lowest concentration endpoint)	Assessment factor	Notes
Polycarboxylates	Acute data available and compiled previously for fish, algae and crustaceans (HERA 2014a, 2014b)	Yes	Chronic data available and compiled previously for fish, algae and crustaceans (HERA 2014a, 2014b)	n/a	NOEC (crustaceans, 21d) = 3.75 mg L^{-1}	10	Note that the HERA report uses average values for multiple tests on the same species, with values calculated separately for homo- and co-polymers of acrylic acid (P-AA and P-AA/MA). In the present study, the lowest raw data value across both P-AA and P-AA/MA homo- and co-polymers was used for PNEC calculation to give the most conservative PNEC estimate, due to the variability in polymer structure within the group of the present study.
Alcohol ethoxylate salts	Acute data available and compiled previously for fish, algae and crustaceans (HERA 2004)	Yes	Chronic data available and compiled previously for fish, algae and crustaceans (HERA 2004)	n/a	NOEC (crustaceans, 7 days) = 0.06 mg L^{-1}	10	Note that the HERA report calculates individual PNECs for different polymer chain lengths; in the present study, the lowest raw data value across all chain lengths was used for PNEC calculation to give the most conservative PNEC estimate, due to the variability in polymer structure/ chain length within the group of the present study.

Alcohol alkoxylates	Acute data available and compiled previously for fish, algae and crustaceans (HERA 2009)	Yes	Chronic data available and compiled previously for fish, algae and crustaceans (HERA 2009)	n/a	EC10 (algae, duration not reported) = 0.03 mg L^{-1}	10	Note that the HERA report calculates individual PNECs for different polymer chain lengths; in the present study, the lowest raw data value across all chain lengths was used for PNEC calculation to give the most conservative PNEC estimate, due to the variability in polymer structure/ chain length within the group of the present study.
Polyol ethoxylate esters	LC50 (fish, 1-2d; insects, 4h); LD50 (crustaceans, 2d)	No	NOEC (worms, 14d); NR (equivalent to LOEC, crustaceans, 21d)	NOEC (invertebrates, 1h; worms, 3-7d); NR (equivalent to EC10, EC50, crustaceans, 21d; equivalent to NOEC, LOEC, invertebrates, 2.9d)	NOEC (worms, 14d) = 2 mg L^{-1}	100	Although the base set is not available, PNEC was estimated based on available data. Lowest chronic datapoint along with assessment factor of 100 (chronic data for 1 trophic level) used despite incomplete dataset as this gives a more conservative estimate of PNEC from the available data.

Starch and derivatives	n/a	No	n/a	NR-LETH (molluscs, 4d); NR-ZERO (molluscs, 4d; fish, 4d)	NR-ZERO (molluscs, 4d) = 1000 mg L^{-1} AND NR-LETH (molluscs, 4d) = 3000 mg L^{-1}	1000	Although the base set is not complete, PNEC was estimated based on available data. Lower NR-ZERO indicates molluscs are the most sensitive group tested. NR-ZERO and NR-LETH equivalent to 0% and 100% mortality, respectively. Four day study durations indicate acute effects. Therefore acute EC50 (50% organisms affected) can be expected to lie between NR-ZERO and NR-LETH; PNEC thus calculated as range. Assessment factor of 1000 used due to lack of data (incomplete base set).
Polyquaterniums	EC50 (algae, 5d; crustaceans, 2d; plants, 14d; molluscs, 2d); LC50 (crustaceans, 2-4d; fish, 1-4d; molluscs, 2d);	Yes	LOEC (crustaceans, 21d); NOEC (crustaceans, 21d); NOEL (algae, 5d; plants, 14d)	LC10 (fish, 1-2d); LOEC (algae, 1h; invertebrates, 1d); NOEL (crustaceans, 2-4d; fish, 4d; molluscs, 2d); NR-ZERO (crustaceans, 2d)	NOEL (algae, 5d) = 0.001 mg L^{-1}	50	Assessment factor of 50 used as complete base set and chronic effects data for two trophic levels (crustaceans and algae) which include the most sensitive species from the acute studies. Lowest chronic datapoint was therefore used for PNEC calculation.

Polyethers and copolymers	LC50 (fish, 1-4d); NR (equivalent to LC36 and LC59, algae, 2d)	No	n/a	n/a	NR (equivalent to LC36, algae, 2d) = 12.5 ppb = 0.0125 mg L^{-1} AND NR (equivalent to LC59, algae, 2d) = 50.0 ppb = 0.05 mg L^{-1}	1000	Although the base set is not complete, PNEC was estimated based on available data. Acute (two day) data equivalent to LC36 and LC59 available for algae (concentrations of 12.5 ppb and 50.0 ppb resulted in 36 and 59% mortality, respectively; Kutt and Martin 1974). LC50 for algae can therefore be expected to lie between LC36 and LC59; PNEC thus calculated as range using these values (as these were lower than the fish LC50). Assessment factor of 1000 used due to lack of data (incomplete base set).
Cellulose and derivatives	EC50 (algae, 4d; crustaceans, 2d); LC50 (crustaceans, 2-4d; fish, 4d)	Yes	n/a	NR-ZERO (fish, 1d)	EC50 (crustaceans, 2d) = 87.26 mg L^{-1}	1000	Assessment factor of 1000 used as complete base set but no further (chronic) data. Lowest acute datapoint used for PNEC calculation. Although NR-ZERO (fish, 1d) was lower than the lowest acute datapoint, this value was not used to calculate PNEC as NR-ZERO is comparable to NOEC but study duration was acute (one day) therefore not considered comparable to acute or chronic data.

Polyvinyl alcohol	LC50 (fish, 4d; crustaceans; 4d); EC50 (sea urchin embryo, 2d)	No	NOEC (fish, 28d; crustaceans, 28d; algae, not specified; sea urchin embryo, 2d); LOEC (crustaceans, 28d; algae, not specified; sea urchin embryo, 2d)	n/a	NOEC (crustaceans, 28d) = 2.18 mg L^{-1}	10	No suitable data from ECOTOX Knowledgebase (single datapoint for polyvinyl alcohol; endpoint was not reported, concentration units not transferrable to mg L^{-1}, and study conditions not environmentally relevant (force-feeding experiment)). Literature data from Arfsten *et al.* (2004) and Alonso-López *et al.* (2021) were instead used. Although acute data were not available for algae, chronic data indicated that crustaceans were the most sensitive group and thus an assessment factor of 10 could be used (acute and chronic data for three trophic levels) with the lowest chronic value (NOEC for crustacean).
Silicones	LC50 (amphibians, duration NR; crustaceans, 2-4d; fish, duration NR or 3-7d; molluscs, 4d)	No	n/a	LC01 (crustaceans, 2d; fish, 7d); NR-ZERO (fish, 4d; crustaceans, 4d)	LC50 (fish, 7d) = 3.16 mg L^{-1}	1000	Although the base set is not complete, PNEC was estimated based on available data. Lowest acute datapoint used along with an assessment factor of 1000 due to lack of data (incomplete base set). Although some LC01 data were lower than the lowest acute datapoint, these values were not used to calculate PNEC as LC01 is comparable to NOEC but study durations were not long-term (seven days) or not reported and therefore not considered sufficiently comparable to acute or chronic data.

Appendix 3.9: Predicted and measured environmental concentrations (PEC and MEC) of polymers in surface water from the literature and present study.
Note that where concentrations were measured in wastewater effluent (without direct surface water measurements), a dilution factor of 10 was applied in the present study to obtain comparable concentration estimates for surface water, but values are still recorded as MEC below.

Polymer(s)	Measured or predicted	Value/ mg L^{-1}	Region	Notes	Reference
			Polycarboxylates		
Polycarboxylates	PEC	0.002-0.915	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of polycarboxylate polymers found in UK household products in the present study.	This study
PAA and PAA-MA	PEC	0.09-0.70	United States	PEC for river, 90th percentiles. Sum of values for PAA and PAA-MA from cleaning products in the US. 0.09 mg L^{-1} = mean flow, 0.70 mg L^{-1} = low flow.	DeLeo *et al.* 2020
PAA and PAA-MA	PEC	0.078-0.159	Europe	PEC for water. Sum of values for PAA and PAA-MA used in European household cleaning products. 0.078 mg L^{-1} = regional PEC, 0.159 mg L^{-1} = local PEC.	HERA 2014a, 2014b
PAA-MA	PEC	0.03	Europe	PEC_{SW} for PAA-MA 70,000.	ECETOC 1993
			Alcohol ethoxylate salts		
Alcohol ethoxylate salts	PEC	0.001-0.731	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of alcohol ethoxylate salt polymers found in UK household products in the present study.	This study
Alcohol ethoxylate sulfates	PEC	0.00042-0.05487	Canada	PEC range for 100th percentile to 10th percentile. C = 10-16, EO = unspecified.	ECCC 2019
Alcohol ethoxylate sulfates	PEC	0.003663-0.02279	Europe	Simulation test PEC for surface water. 0.003663 mg L^{-1} = regional PEC, 0.02279 mg L^{-1} = local PEC. C = 12-18, EO = 0-8 or average 2.7.	HERA 2004

Alcohol ethoxylate sulfates	MEC	0.0057-0.0103	United States	0.0057 mg L^{-1} = concentration in river water from selected-ion recording (mass spectrometry) for C = 14,15 and EO = 0-8. 0.0103 mg L^{-1} = concentration in river water from full scan (mass spectrometry) for C = 12-15 and EO = 0-8.	Popenoe *et al.* 1994
Alcohol ethoxylate sulfates	MEC	0.0004-0.0058	United States	x10 dilution factor applied to value for alkyl ethoxylate sulfates present in WWTP effluent. Includes activated sludge and trickling filter. Sum of values for C = 10-18, EO = 1-10.	McAvoy *et al.* 1998
Alcohol ethoxylate sulfates	PEC	0.00093-0.0053	United States	PEC values for 90% river miles < concentration. 0.00093 mg L^{-1} = mean flow, 0.0053 mg L^{-1} = low flow. C = 12-18, EO = 0-8.	Cowan-Ellsberry *et al.* 2014
Alcohol ethoxylate sulfates	MEC	0.0032	Spain	x10 dilution factor applied to value for alcohol ethoxylate sulfates measured in WWTP effluent in Spain (before electron beam irradiation treatment). Sum of values for C = 10-18, EO = 1-10.	Petrovic *et al.* 2007
Alcohol ethoxylate sulfates	MEC	0.0025-0.0029	Spain	Includes concentrations for seawater and estuary in Spain. Sum of values for C = 12,14 and EO = 1-11, and C = 16 and EO = 1-10.	Lara-Martín *et al.* 2006
Alcohol ethoxylate sulfates	MEC	0.0003-0.0012	Netherlands	x10 dilution factor applied to value for alcohol ethoxysulfates present in WWTP effluent from the Netherlands. Sum of values for C = 12-15 (both linear and branched), EO = 0-8.	Matthijs *et al.* 1999
Alcohol ethoxylate sulfates and alkyl sulfates	MEC	0.00001-0.000226	United States	Includes river water concentrations upstream, downstream, far downstream, and at outfall of WWTP, for both alcohol ethoxylate sulfates and alkyl sulfates (NB it is likely that the total alcohol ethoxylate salt PEC from the present study also includes non-ethoxylated alcohol).	Sanderson *et al.* 2006

Alcohol ethoxylate sulfates	MEC	< 0.000222-0.00019	Germany	x10 dilution factor applied to value for concentration of alcohol ethoxylate sulfates in WWTP effluent. C = 12,14 and EO = 0-9.	Freeling *et al.* 2019
Alcohol ethoxylate sulfates and alkyl sulfates	MEC	< 0.0001	Germany	x10 dilution factor applied to value for WWTP effluent concentration of alcohol ethoxylate sulfates. C = 11-18, EO = unspecified.	Schröder *et al.* 1999
			Alcohol alkoxylates		
Alcohol alkoxylates	PEC	0.0008-0.370	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of alcohol alkoxylate polymers found in UK household products in the present study.	This study
Alcohol ethoxylates	MEC	0.0008-0.0509	United States	x10 dilution factor applied to value for alkyl ethoxylates present in WWTP effluent. Includes activated sludge and trickling filter. Sum of values for C = 12-15, average EO assumed to be 9.	McAvoy *et al.* 1998
Alcohol ethoxylates	MEC	0.002-0.037	United States	Includes concentration both upriver and downriver of WWTP in the US (includes both activated sludge and trickling filter). C = 12-15, average EO assumed to be 9.	Fendinger *et al.* 1995
Alcohol ethoxylates	MEC	0.000028-0.0316	United States	x10 dilution factor applied to value for alkyl ethoxylates present in WWTP effluent. Includes activated sludge and trickling filter. Includes novel data and data from previous studies with corrections applied. Sum of values for C = 12-15, EO = 2-18 or average EO = 3.8.	McAvoy *et al.* 2006
Alcohol ethoxylates	MEC	<0.00002-0.031	Japan	Measured concentration in surface water, Japan. C = 12-15, EO = 2-20.	Miura *et al.* 2008
Alcohol ethoxylates	MEC	0.0078-0.0279	Spain	Measured concentration in river water, Spain. Sum of values for C = 12,14,16 and EO = 1-20.	Cantero *et al.* 2005

Alcohol ethoxylates	PEC	0.00006-0.01676	Canada	PEC range for 100th percentile to 10th percentile. C = 6-16, EO = unspecified (but stated as typically 3 to 10-12).	ECCC 2019
Alcohol ethoxylates	PEC	0.000761-0.00993	United States	PEC at WWTP outfall for alcohol ethoxylates. 0.000761 mg L^{-1} = mean flow, 0.00993 mg L^{-1} = low flow.	Sanderson *et al.* 2013
Alcohol ethoxylates	PEC	0.00089-0.0053	United States	PEC values for 90% river miles < concentration. 0.00089 mg L^{-1} = mean flow, 0.0053 mg L^{-1} = low flow. C = 8-18, EO = 3-12.	Cowan-Ellsberry *et al.* 2014
Alcohol ethoxylates	MEC	0.00018-0.0013	Netherlands	x10 dilution factor applied to value for alcohol ethoxylates present in WWTP effluent from the Netherlands. Sum of values for C = 12-15, EO = 2-18.	Matthijs *et al.* 1999
Alcohol ethoxylates	MEC	0.0001-0.0012	Spain	Includes concentrations for seawater and estuary in Spain. Sum of values for C = 12,14 and EO = 1-17, and C = 16 and EO = 1-16.	Lara-Martín *et al.* 2006
Alcohol ethoxylates	MEC	0.000240- 0.001579	United States	Includes river water concentrations upstream, downstream, far downstream, and at outfall of WWTP. Values include alcohol ethoxylate and non-ethoxylated fatty alcohol. C = 12-18, EO = 0-15.	Sanderson *et al.* 2013
Alcohol ethoxylates	MEC	0.000096-0.002271	Europe, Canada	x10 dilution factor applied to value for alcohol ethoxylates present in WWTP effluent in Europe and Canada (mostly activated sludge, but includes values for a trickling filter and a rotating biological contactor). Sum of values for C = 12-18, EO = 0-18.	Eadsforth *et al.* 2006
Alcohol ethoxylates	PEC	0.00101	Europe	Total local dissolved PEC for C = 8-18 and EO = 0-22, derived from monitoring data for C = 12-18 and EO = 0-18.	HERA 2009

Alcohol ethoxylates	MEC	0.0001051-0.0009354	Germany	x10 dilution factor applied to value for alcohol ethoxylates present in WWTP effluent. Sum of values for C = 8-18, EO = 1-20.	Freeling *et al.* 2019
Alcohol ethoxylates	MEC	0.000364	United States	x10 dilution factor applied to value for alcohol ethoxylates present in WWTP effluent from the United States. Sum of values for C = 12-18, EO = 0-18.	Morrall *et al.* 2006
Alcohol ethoxylates	MEC	0.00025	Spain	x10 dilution factor applied to value for alcohol ethoxylates present in WWTP effluent (before electron beam irradiation treatment). Sum of values for C = 10-18, EO = 1-10.	Petrovic *et al.* 2007
Alcohol ethoxylates	MEC	0.0000167	United States	x10 dilution factor applied to value for alcohol ethoxylates present in New York WWTP effluent. C = 12-18, EO = 1-3.	Lara-Martin *et al.* 2014
Alcohol ethoxylates	MEC	<0.000011	United States	Concentration in New York seawater. Sum of values for C = 12-18 and EO = 1-8.	Lara-Martin *et al.* 2011
			Polyol ethoxylate esters		
Polyol ethoxylate esters	PEC	0.067-0.337	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of polyol ethoxylate ester polymers found in UK household products in the present study.	This study
			Starch and derivatives		
Starch and derivatives	PEC	0.063-0.246	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of starch and starch derivative polymers found in UK household products in the present study.	This study
			Polyquaterniums		
Polyquaterniums	PEC	0.005-0.142	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of polyquaternium polymers found in UK household products in the present study.	This study

Polyquaterniums	PEC	0.000039-0.0045	Australia	Predicted environmental concentration for polyquaterniums in Australia across a range of import/manufacture volumes (40-80 tonnes). 0.0045 mg L^{-1} = 21% WWTP removal, 80 tonnes, for all polyquaternium use in Australia; 0.000039 = 73% WWTP removal (considered likely by the author of the study to be the upper limit for the K_0 values of polyquaterniums), 20 tonnes, of polyquaterniums.	Cumming 2008
Polyquaternium-68	PEC	0.00072	Australia	Predicted river concentration of polyquaternium-68 in Australia assuming WWTP removal of 90% and dilution factor of x1.	NICNAS 2009
Polyethers and copolymers					
Polyethers and copolymers	PEC	0.002-0.090	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of polyether polymers and copolymers found in UK household products in the present study.	This study
Polypropylene glycols	MEC	0.212	Poland	Total concentration of polypropylene glycol of chain lengths from 10-17 monomer units in water from the River Warta.	Rychłowska *et al.* 2003
Polyethylene oxides	MEC	< LoD-0.011	Germany	Concentration range across 18 surface water samples from Germany. Concentrations in WWTP effluent reached up to 0.02 mg L^{-1}.	Pauelsen *et al.* 2023
Polypropylene glycols	MEC	0.0004-0.0018	Denmark	x10 dilution factor applied to total measured concentration of polypropylene glycol homologues (3-12 monomer units) in the effluent of two WWTPs in Denmark. Note that ethylene oxide/propylene oxide copolymers were also detected, but not quantified.	Tisler *et al.* 2021

Polyethylene glycols	MEC	0.00015-0.00074	Germany	x10 dilution factor applied to rough estimate of total polyethylene glycol from 4 and 44 monomer units detected in WWTP effluent. Values are "rough estimates" – semi-quantified based on polyethylene glycol standard of 4 monomer units.	Freeling *et al.* 2019
Polyethylene glycols	MEC	0.00063	United States	Concentration in New York seawater.	Lara-Martin *et al.* 2011
Polyethylene glycols	MEC	0.000123-0.0001606	United States	x10 dilution factor applied to value for polyethylene glycols present in New York WWTP effluent.	Lara-Martin *et al.* 2011; Lara-Martin *et al.* 2014
Cellulose and derivatives					
Cellulose and derivatives	PEC	0.016-0.060	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of cellulose and cellulose derivative polymers found in UK household products in the present study.	This study
Polyvinyl alcohol					
Polyvinyl alcohol	PEC	0.003-0.019	United Kingdom	Refined PEC_{SW}, preferred range, for the polyvinyl alcohol polymers found in UK household products in the present study.	This study
Silicones					
Silicones	PEC	0.001-0.012	United Kingdom	Refined PEC_{SW}, preferred range, for the entire group of silicone polymers found in UK household products in the present study.	This study
Polydimethylsiloxane	MEC	<0.005-0.007	United States	Concentration of polydimethylsiloxane in receiving water. All but one sample were below the limit of detection (0.005 mg L^{-1}).	Fendinger *et al.* 1997

Linear siloxanes (L3-L14)	MEC	0.00001687-0.0002683	Greece	x10 dilution factor applied to values for linear siloxanes (sum of minimum and maximum values for L3-L14) present in WWTP effluent in Greece. Cyclic siloxanes were not included due to the fact that these were excluded from the silicones group of the present study.	Bletsou *et al.* 2013
Linear siloxanes (L5-L14)	MEC	0.000013243-0.00012258	China	x10 dilution factor applied to values for linear siloxanes (sum of minimum and maximum values for L5-L14) present in WWTP effluent in China. Cyclic siloxanes were not included due to the fact that these were excluded from the silicones group of the present study.	Li *et al.* 2016

Appendix 3.10: Predicted and measured environmental concentrations (PEC and MEC) of polymers in soil from the literature and present study.

Polymer	Measured or predicted	Value/ mg kg^{-1}	Region	Notes	Reference
			Polycarboxylates		
Polycarboxylates	PEC	0.363-39.1	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of polycarboxylate polymers found in UK household products in the present study.	This study
PAA and PAA-MA	PEC	31.17-35.67	Europe	PEC for soil. Sum of values for PAA and PAA-MA used in detergents. 35.67 mg kg^{-1} wwt = regional PEC, 31.17 mg kg^{-1} wwt = local PEC.	HERA 2014a, 2014b
PAA-MA	PEC	6	Europe	PEC_{SOIL} for PAA-MA 70,000, in mg kg^{-1} y^{-1} (comparable to values given in the present study which were calculated for 1 year of sludge application).	ECETOC 1993
			Alcohol ethoxylate salts		
Alcohol ethoxylate salts	PEC	31.5-95.8	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of alcohol ethoxylate salt polymers found in UK household products in the present study.	This study
Alcohol ethoxysulfates	PEC	0.00166-0.0128	Europe	Simulation test PEC for agricultural soil. 0.0128 mg kg^{-1} wwt = local PEC, 0.00166 mg kg^{-1} wwt = local PEC with 87% anaerobic degradation. Sum of values for C = 12-18 and EO 0-8 or average 2.7.	HERA 2004

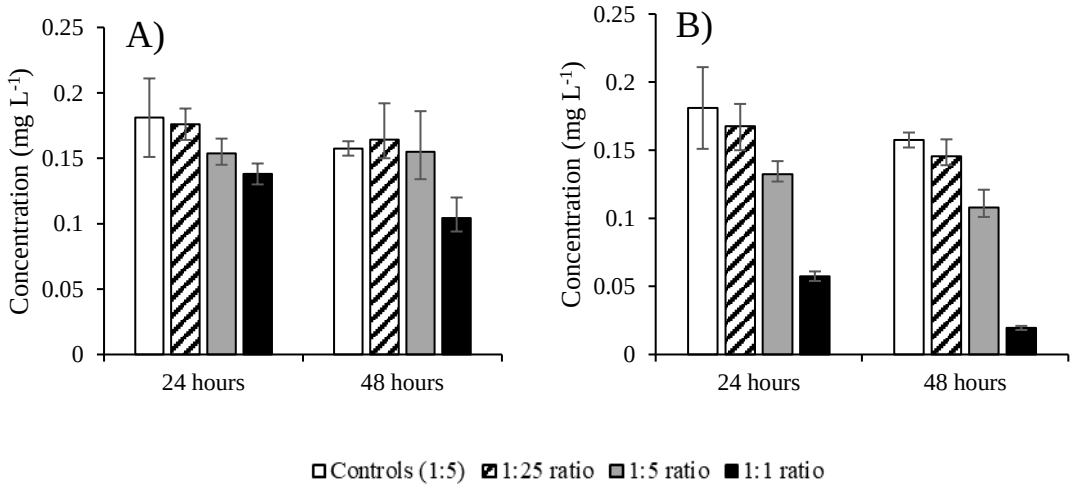
Alcohol alkoxylates					
Alcohol alkoxylates	PEC	23.8-71.3	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of alcohol alkoxylate polymers found in UK household products in the present study.	This study
Alcohol ethoxylates	PEC	0.24	Europe	PEC for soil in mg kg^{-1} wwt. Sum of values for C = 8-18 and EO = 0-22.	HERA 2009
Polyol ethoxylate esters					
Polyol ethoxylate esters	PEC	2.66-13.4	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of polyol ethoxylate ester polymers found in UK household products in the present study.	This study
Starch and derivatives					
Starch and derivatives	PEC	2.50-9.77	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of starch and starch derivative polymers found in UK household products in the present study.	This study
Polyquaterniums					
Polyquaterniums	PEC	0.023-2.34	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of polyquaternium polymers found in UK household products in the present study.	This study
Polyquaternium-68	PEC	0.0055-0.055	Australia	Predicted soil concentration of polyquaternium-68 in Australia from irrigation using WWTP effluent. 0.0055 mg kg^{-1} = 1 year of irrigation, 0.055 mg kg^{-1} = 10 years under repeated irrigation.	NICNAS 2009

Polyethers and copolymers					
Polyethers and copolymers	PEC	0.676-4.87	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of polyether polymers and copolymers found in UK household products in the present study.	This study
Cellulose and derivatives					
Cellulose and derivatives	PEC	0.622-2.37	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of cellulose and cellulose derivative polymers found in UK household products in the present study.	This study
Polyvinyl alcohol					
Polyvinyl alcohol	PEC	0.496-2.98	United Kingdom	Refined PEC_{SOIL}, preferred range, for the polyvinyl alcohol polymers found in UK household products in the present study.	This study
Silicones					
Silicones	PEC	1.80-7.82	United Kingdom	Refined PEC_{SOIL}, preferred range, for the entire group of silicone polymers found in UK household products in the present study.	This study
Polydimethylsiloxane	MEC	<0.41-10.4	United States	Concentration of polydimethylsiloxane measured in sludge-amended soil.	Fendinger *et al.* 1997

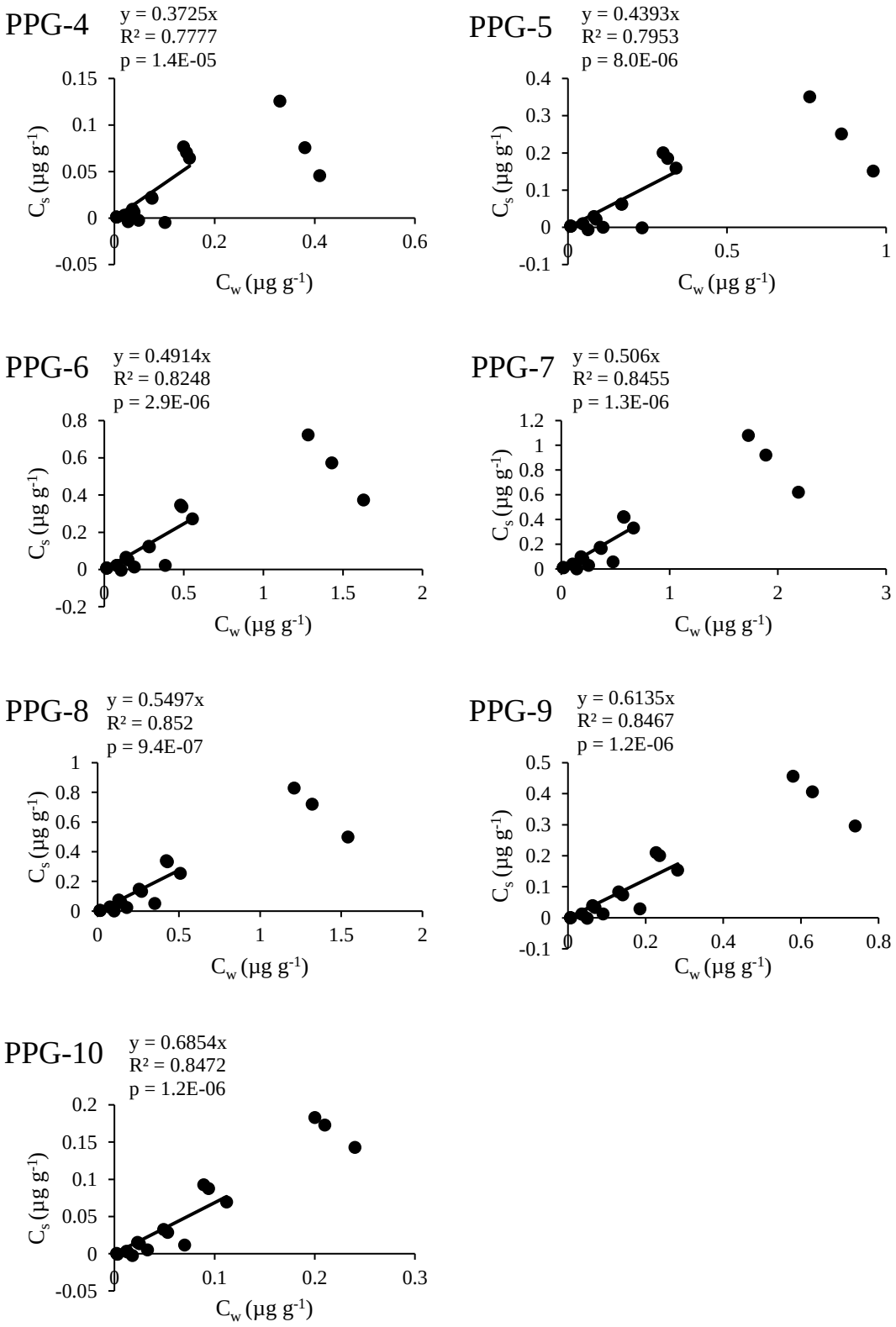
Chapter 4 Appendices

Appendix 4.1: Mobile phase gradients tested for HPLC-MS analysis of PEG-9 (MW_N ca. 400).

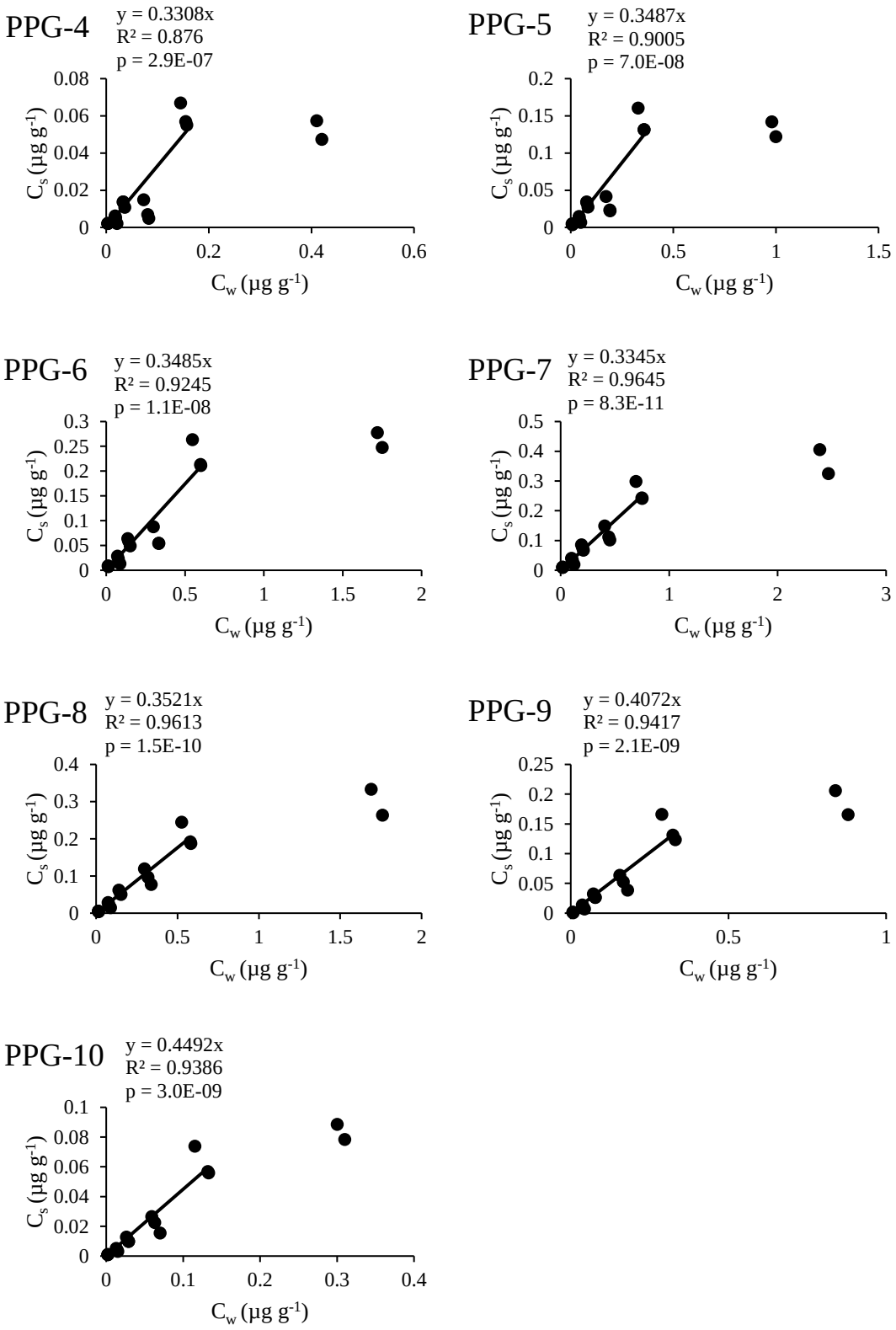
Time (min)	Solvent A (H_2O) (%)	Solvent B (ACN) (%)
Gradient 1		
0	95.0	5.0
25.00	0.0	100.0
30.00	0.0	100.0
30.10	95.0	5.0
Gradient 2		
0	95.0	5.0
20	50.0	50.0
25	50.0	50.0
25.1	95.0	5.0
Gradient 3		
0	95.0	5.0
20	60.0	40.0
25	60.0	40.0
25.1	95.0	5.0



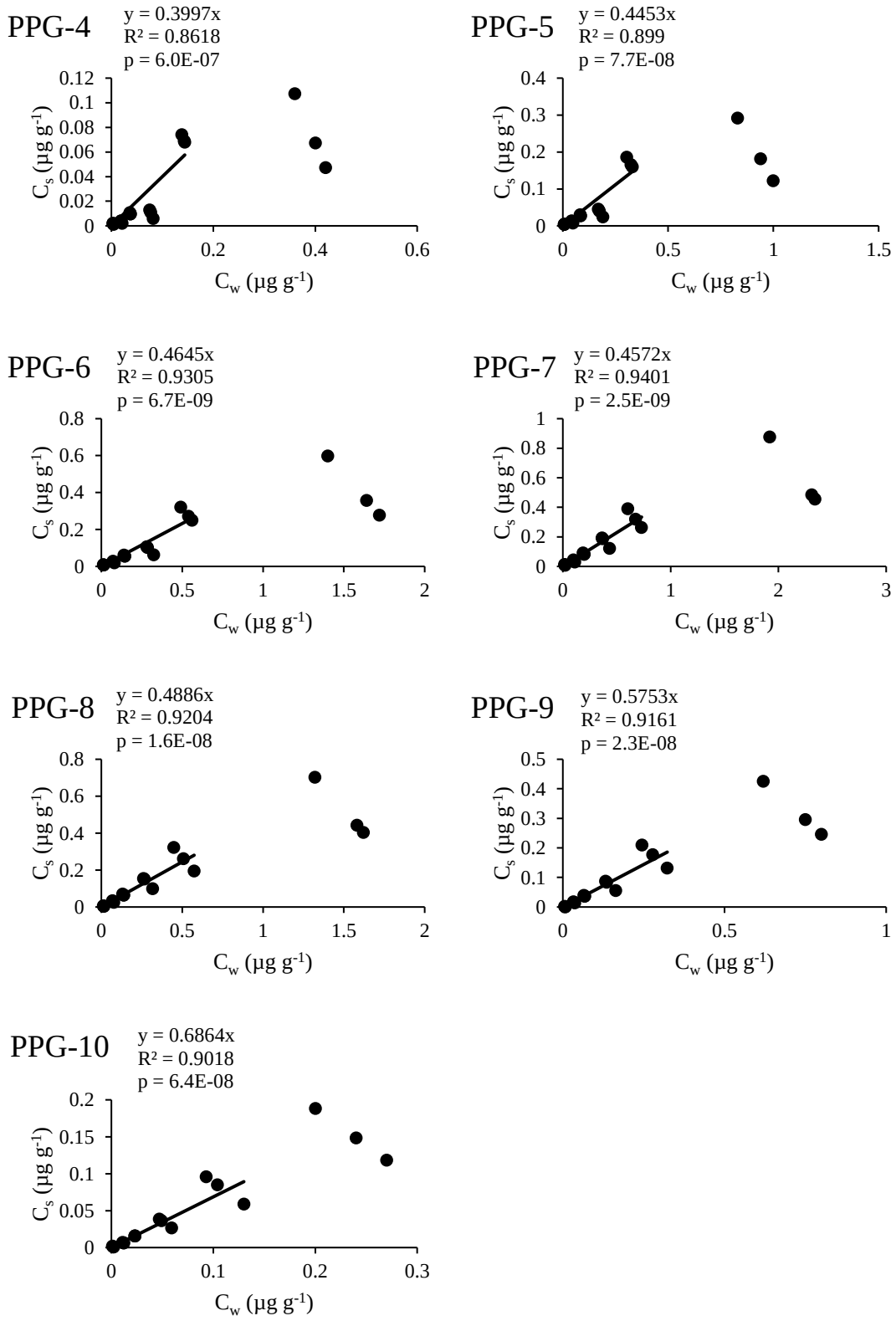
Appendix 4.2: Concentration of PPG-7 homologue after 24 and 48 hours in the presence of A) standard soil 2.1 and B) standard soil 2.4 at different soil:solution ratios, and in the absence of soil (control experiments, equivalent solution to 1:5 ratio).
Error bars show the range of data of replicate experiments.



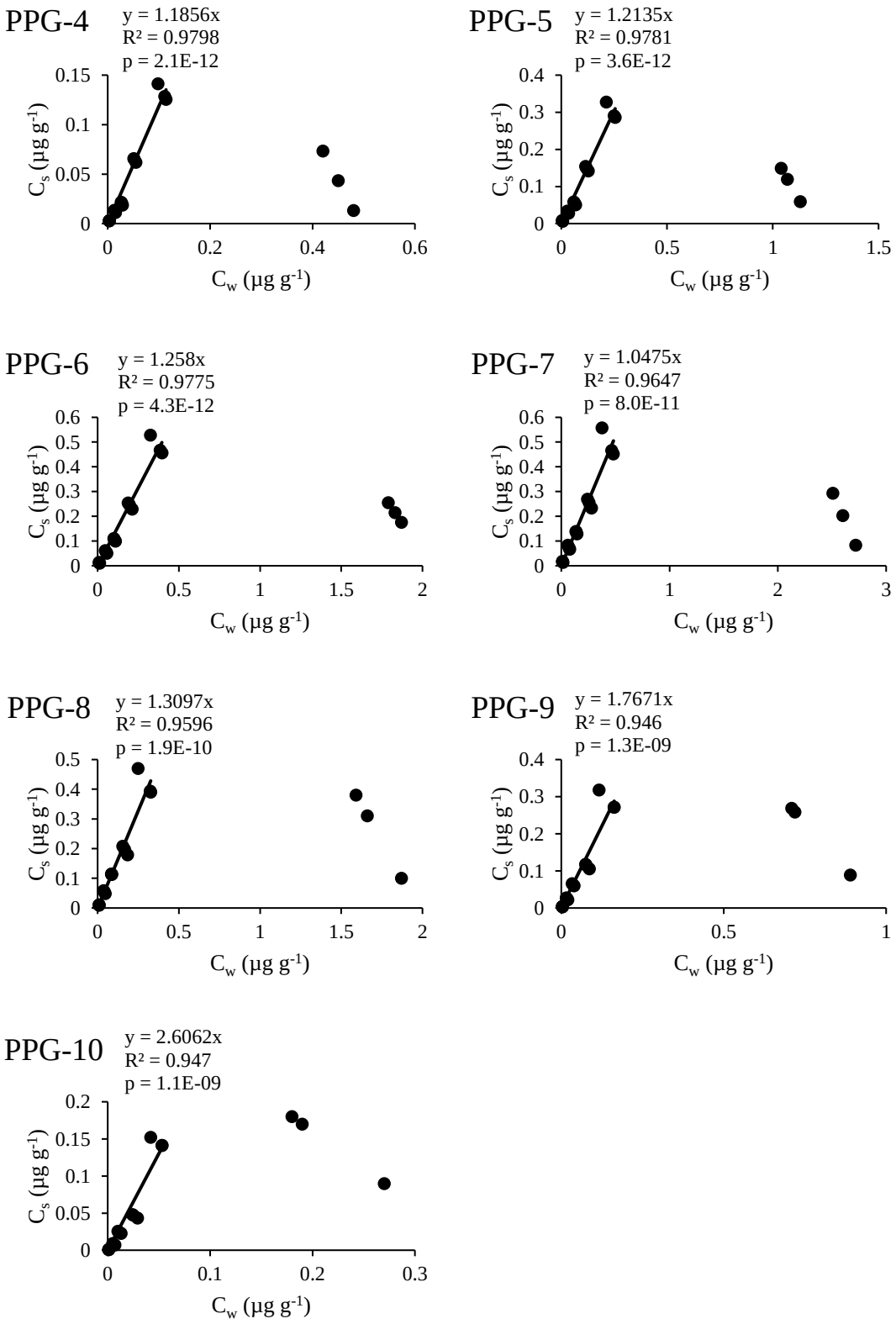
Appendix 4.3: Linear sorption isotherms used to calculate K_d of individual PPG homologues 4-10 for Standard Soil 2.1.
Note that K_d values were calculated using only initial PPG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



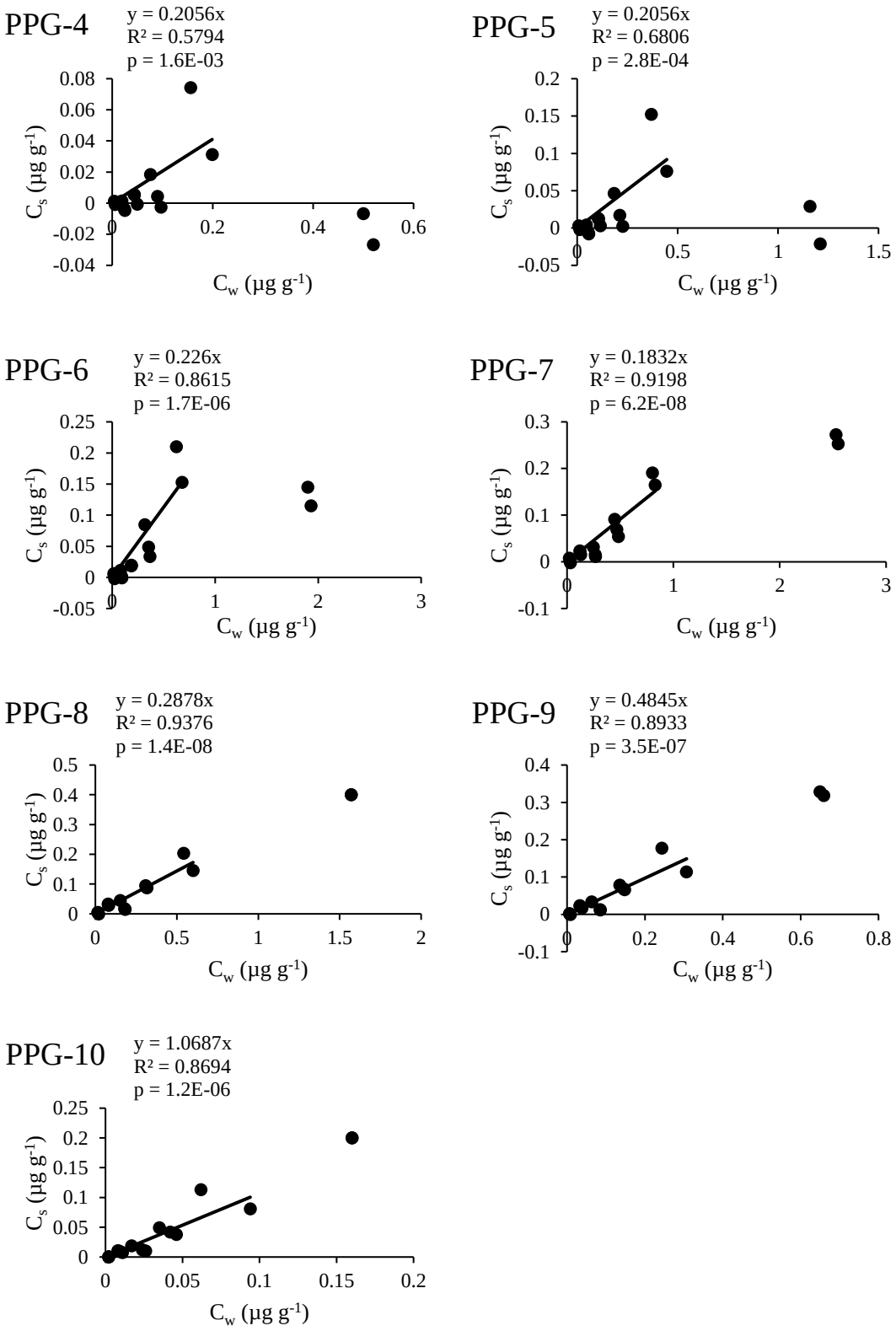
Appendix 4.4: Linear sorption isotherms used to calculate K_d of individual PPG homologues 4-10 for Standard Soil 2.2.
Note that K_d values were calculated using only initial PPG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



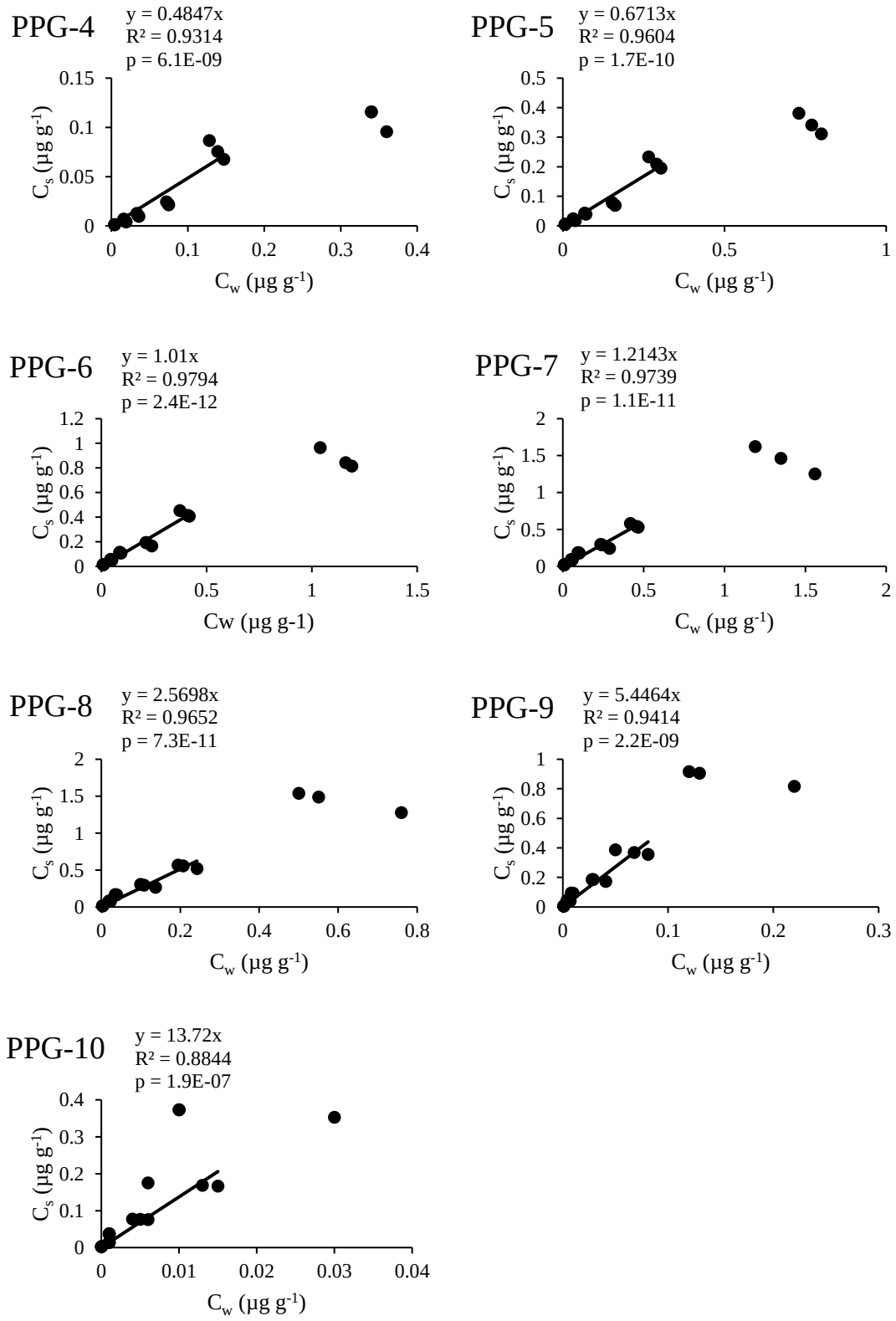
Appendix 4.5: Linear sorption isotherms used to calculate K_d of individual PPG homologues 4-10 for Standard Soil 2.3.
Note that K_d values were calculated using only initial PPG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



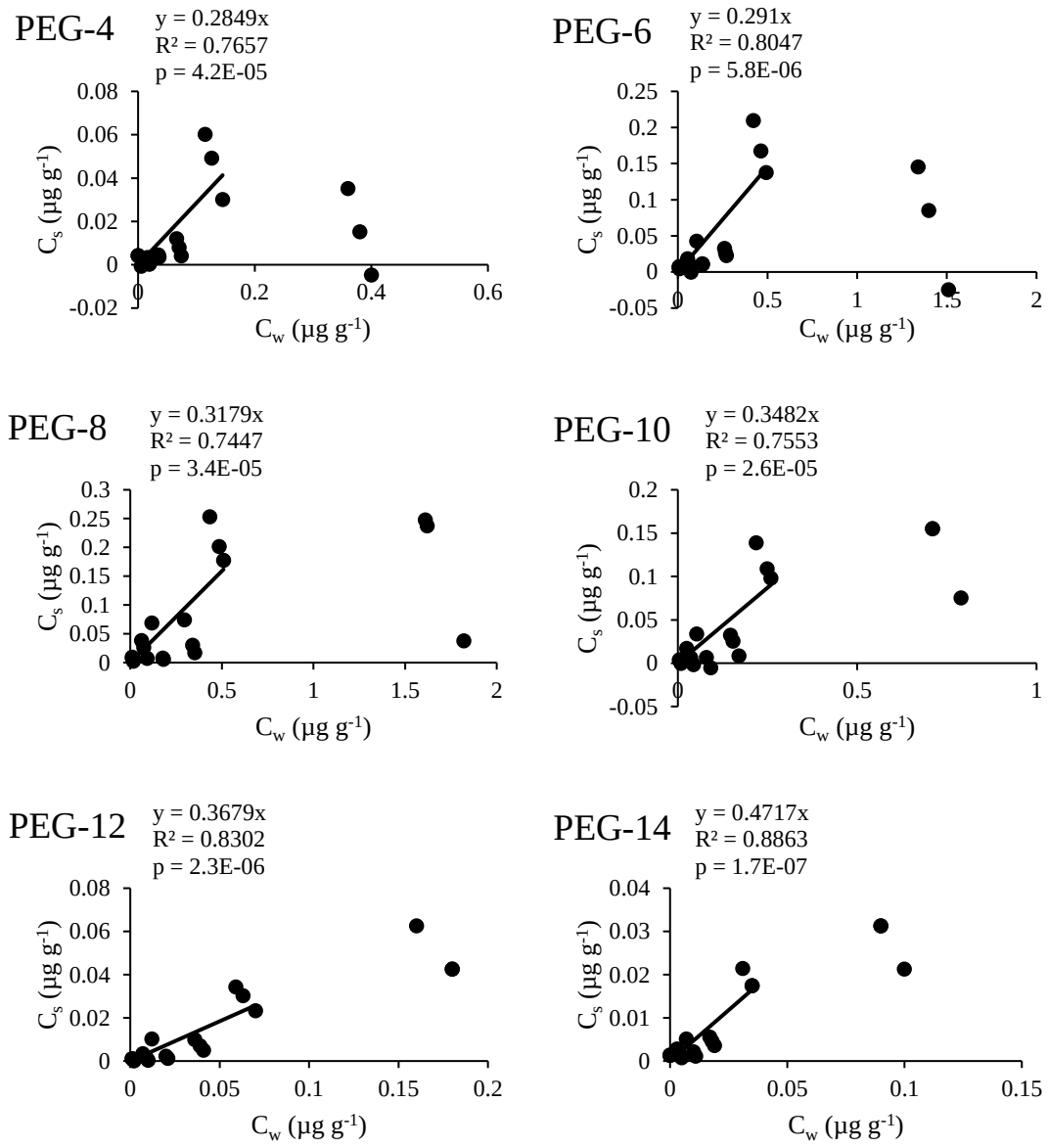
Appendix 4.6: Linear sorption isotherms used to calculate K_d of individual PPG homologues 4-10 for Standard Soil 2.4.
Note that K_d values were calculated using only initial PPG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



Appendix 4.7: Linear sorption isotherms used to calculate K_d of individual PPG homologues 4-10 for Standard Soil 5M.
Note that K_d values were calculated using only initial PPG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.

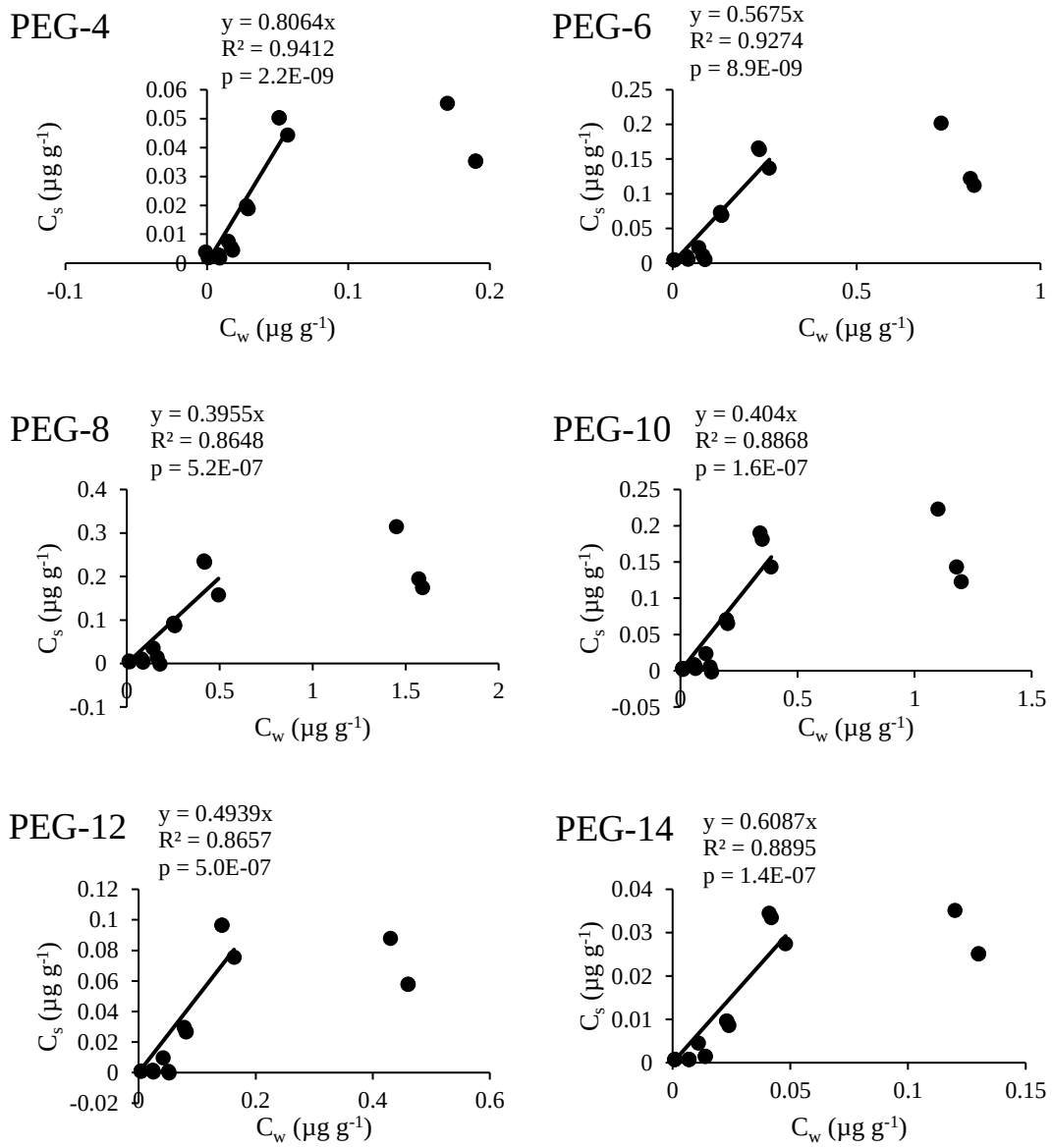


Appendix 4.8: Linear sorption isotherms used to calculate K_d of individual PPG homologues 4-10 for Standard Soil 6S.
Note that K_d values were calculated using only initial PPG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



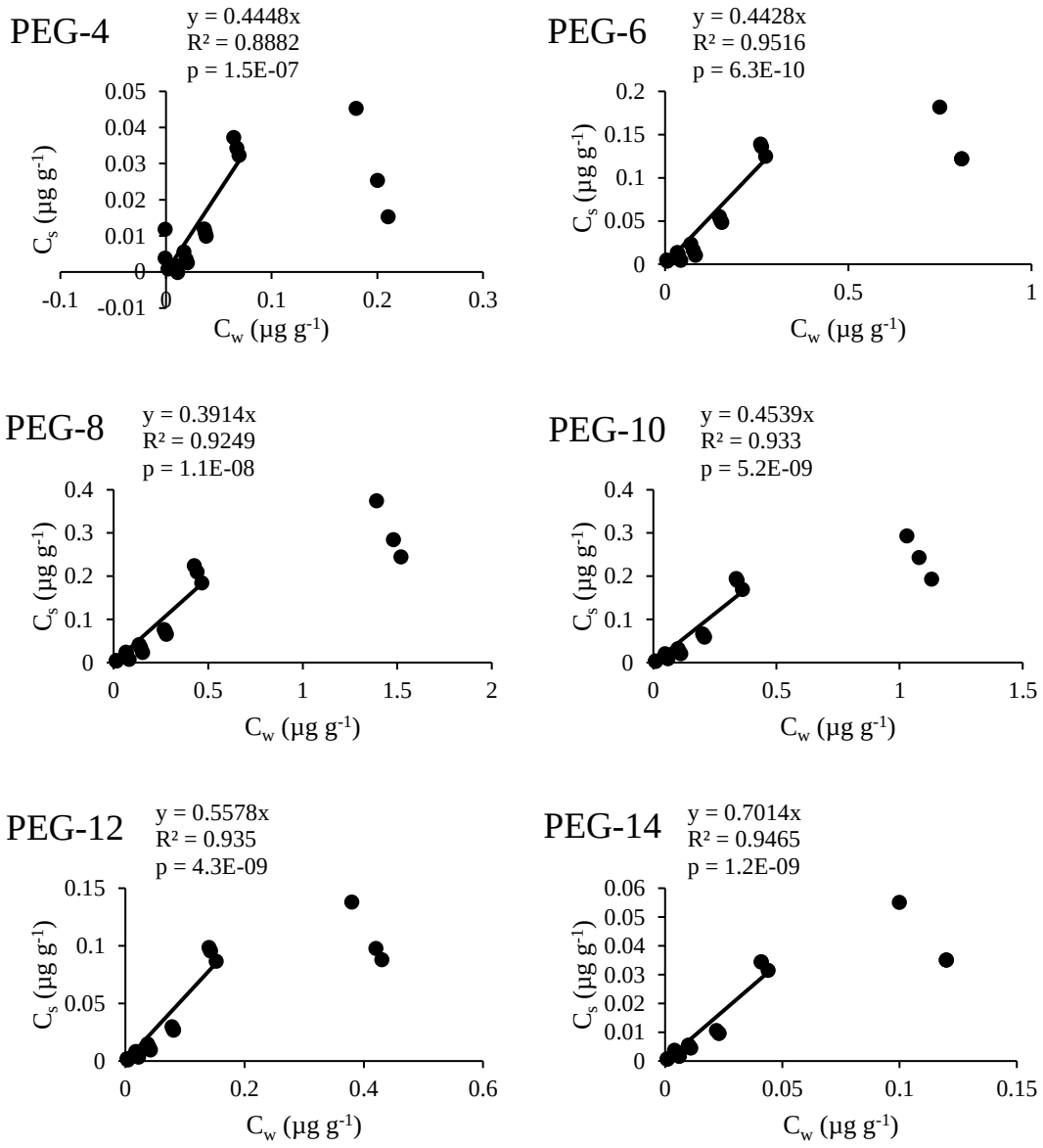
Appendix 4.9: Linear sorption isotherms used to calculate K_d of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.1.

Note that K_d values were calculated using only initial PEG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.

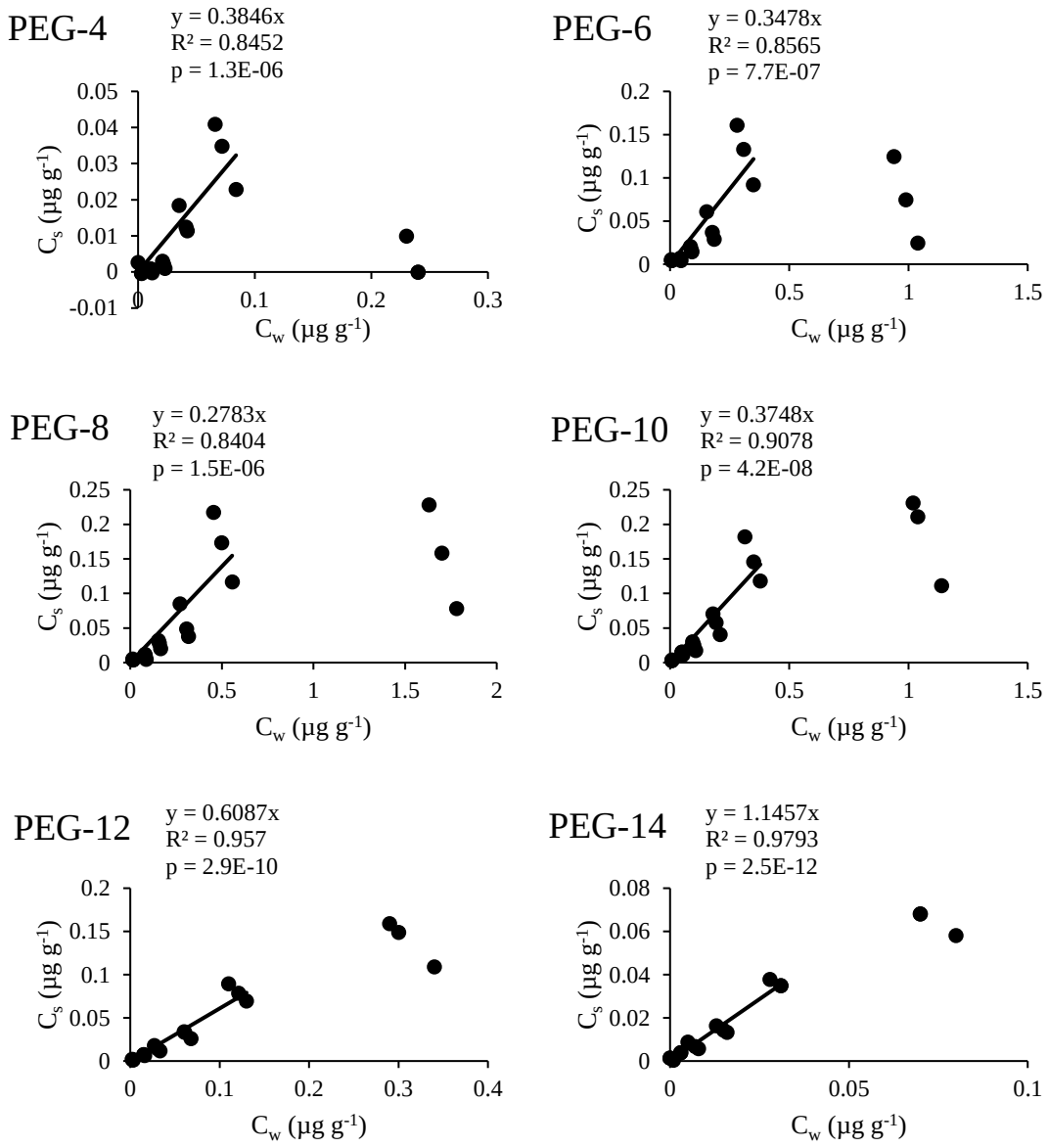


Appendix 4.10: Linear sorption isotherms used to calculate K_d of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.2.

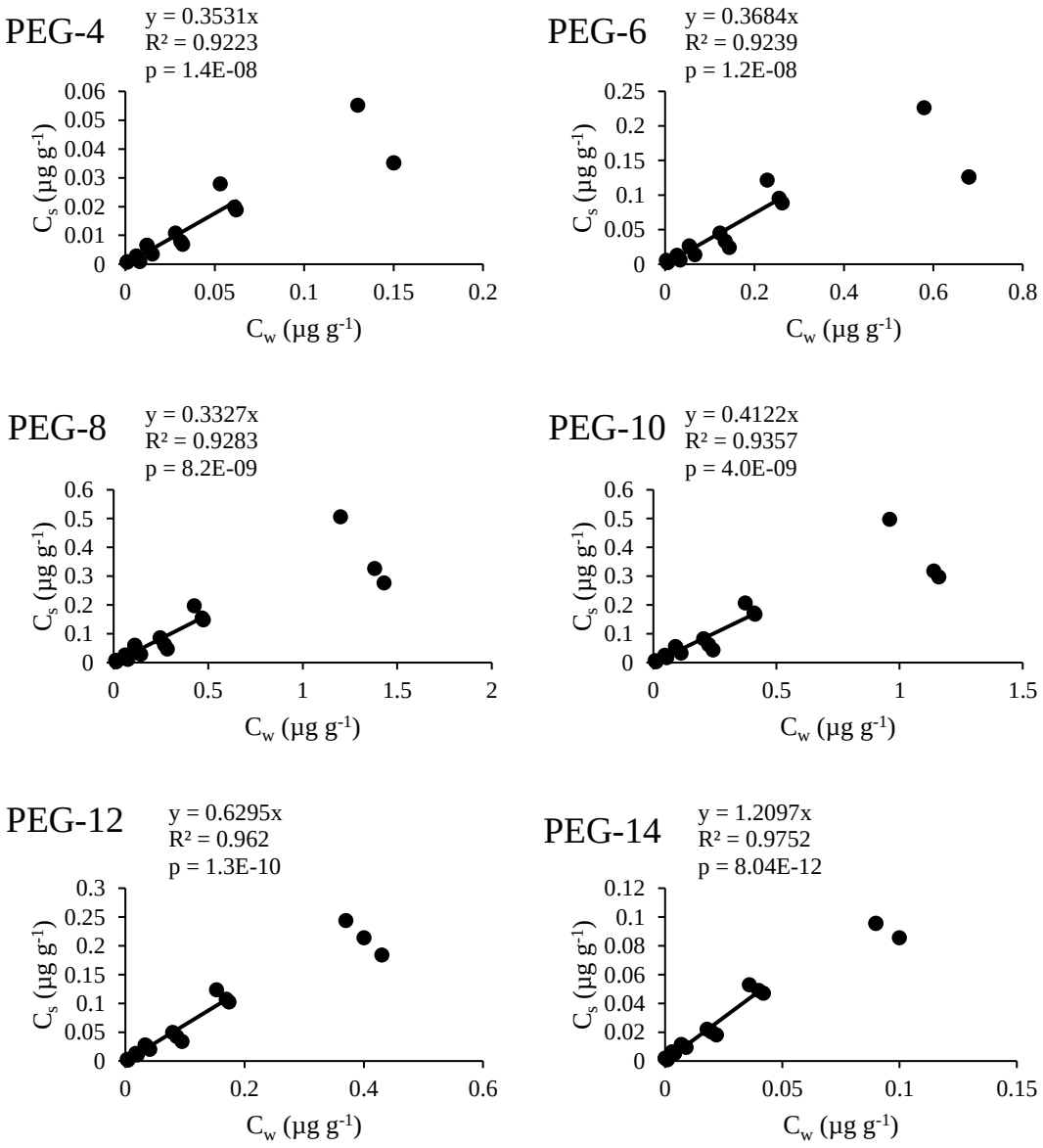
Note that K_d values were calculated using only initial PEG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



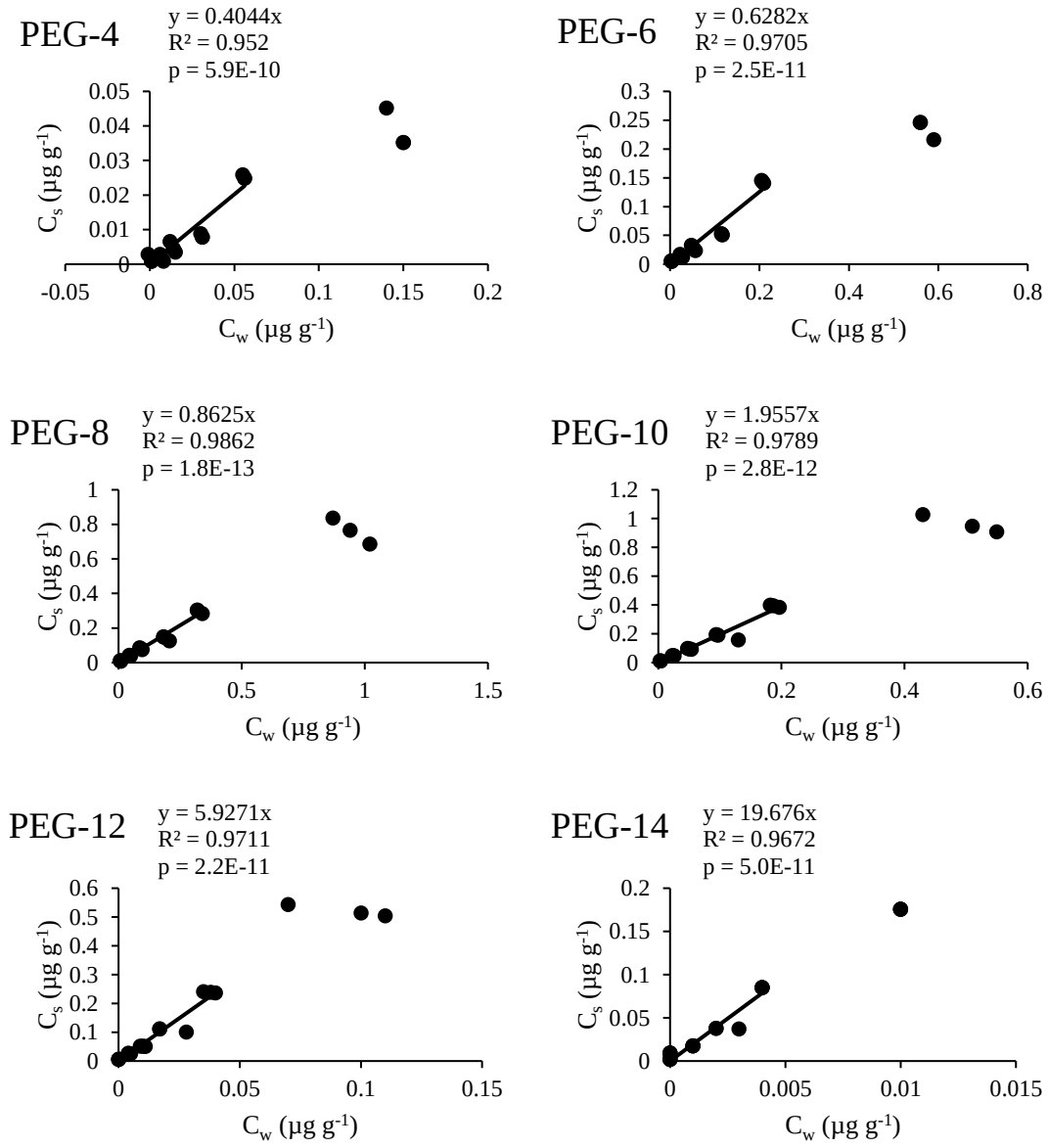
Appendix 4.11: Linear sorption isotherms used to calculate K_d of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.3.
Note that K_d values were calculated using only initial PEG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



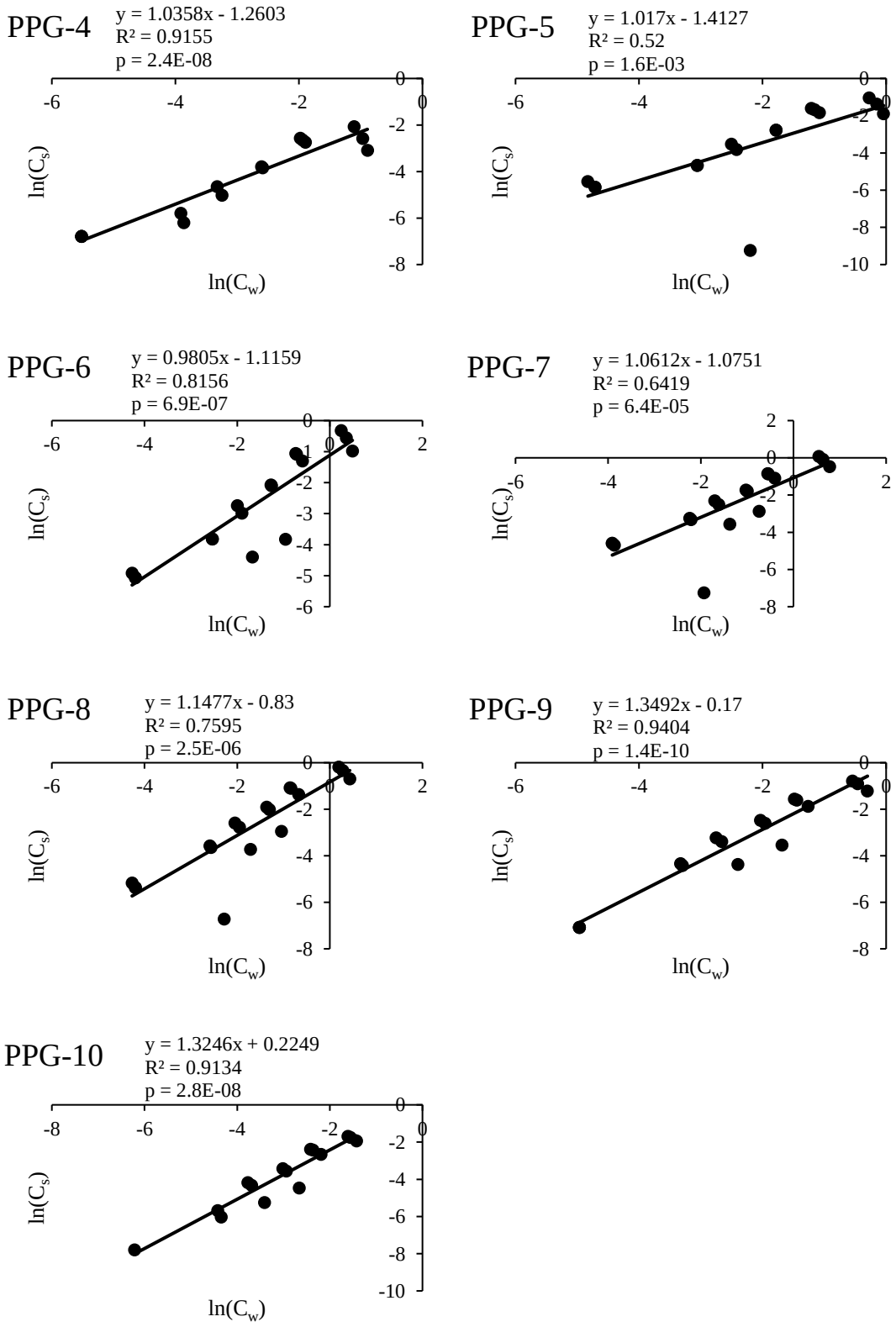
Appendix 4.12: Linear sorption isotherms used to calculate K_d of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.4.
Note that K_d values were calculated using only initial PEG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



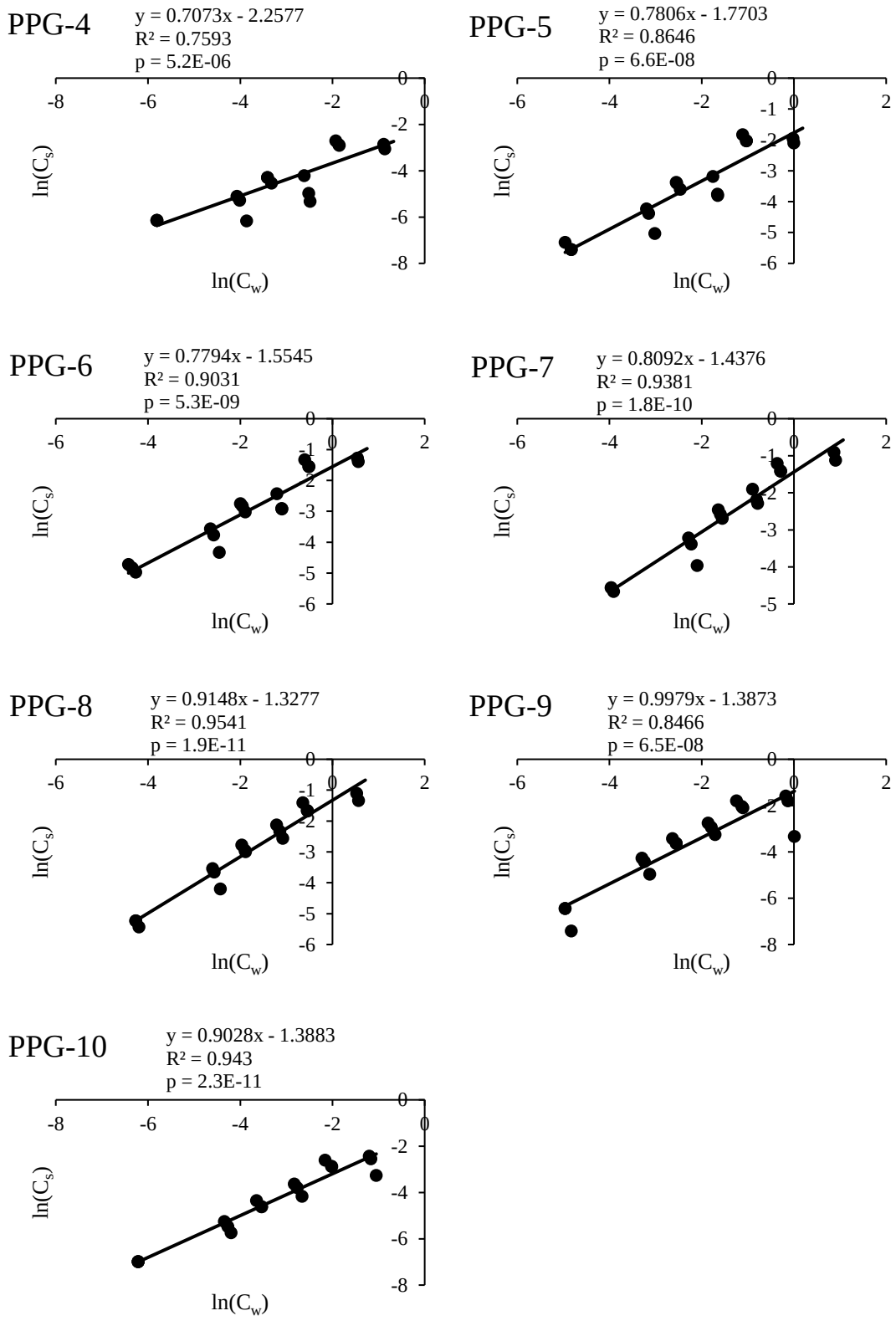
Appendix 4.13: Linear sorption isotherms used to calculate K_d of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 5M.
Note that K_d values were calculated using only initial PEG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



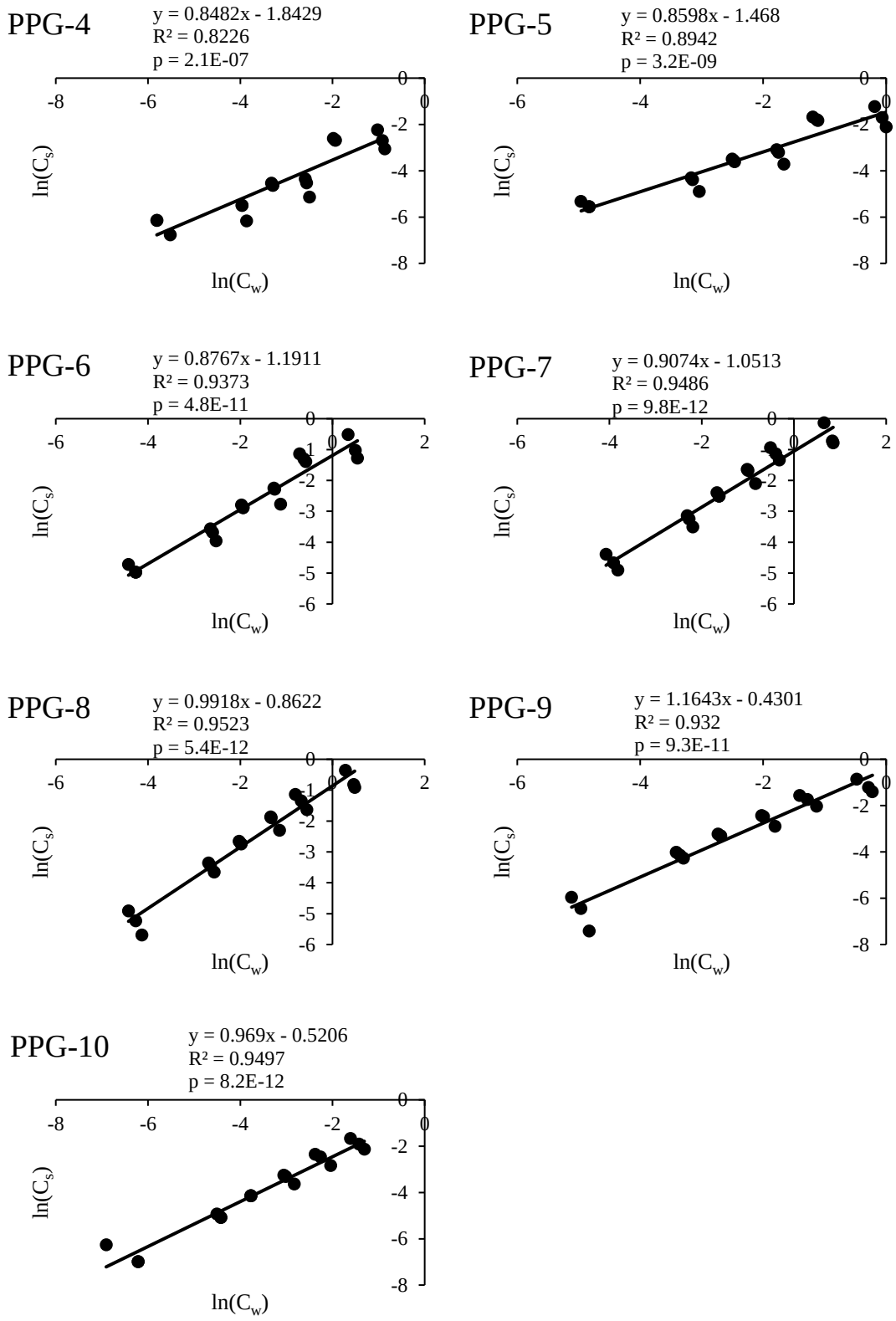
Appendix 4.14: Linear sorption isotherms used to calculate K_d of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 6S.
Note that K_d values were calculated using only initial PEG concentrations between 0.1 and 4 mg L^{-1} due to deviations from linearity at 10 mg L^{-1} for some polymer chain lengths and soils.



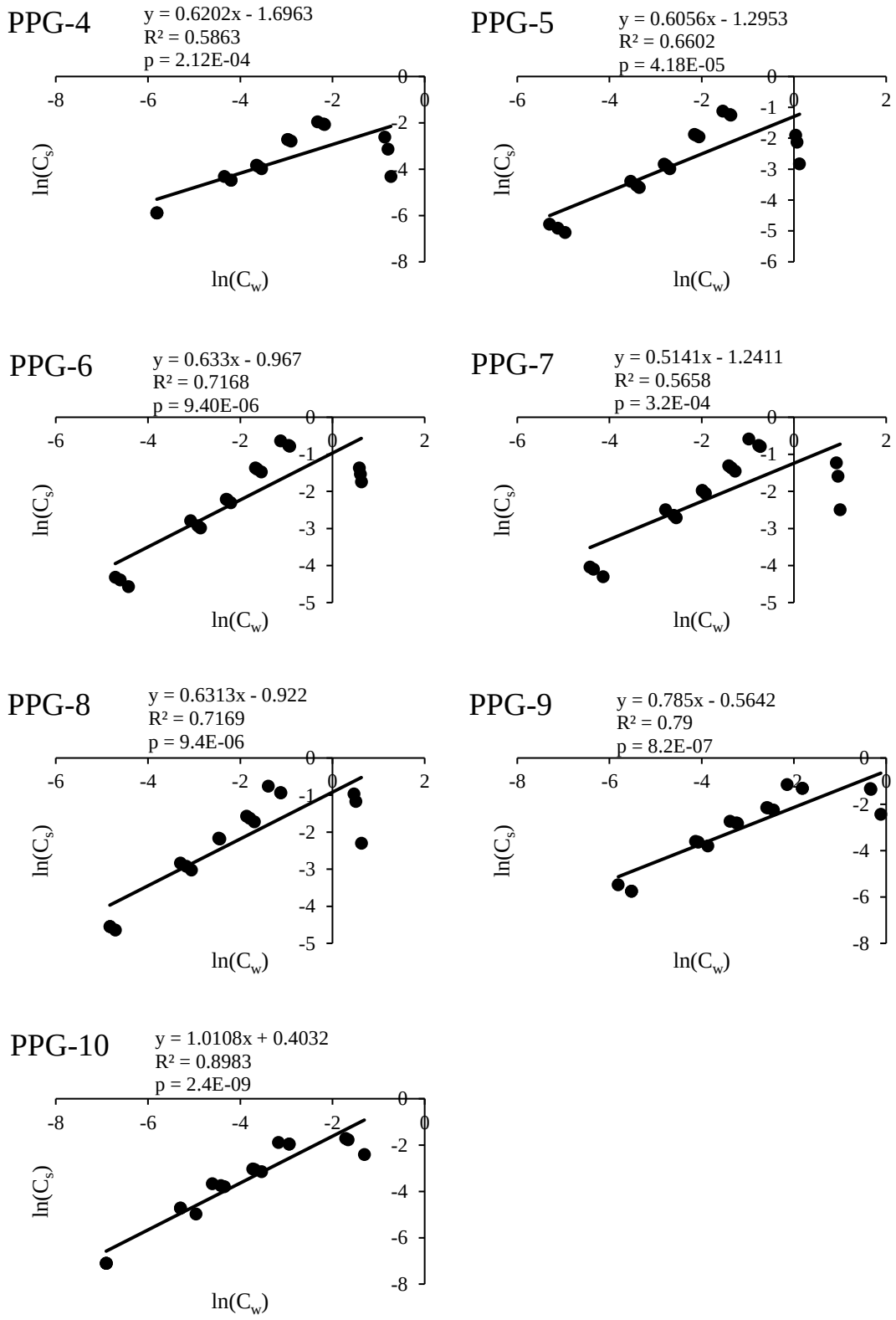
Appendix 4.15: Freundlich sorption isotherms used to calculate K_F of individual PPG homologues 4-10 for Standard Soil 2.1.
Note that 0 values (arising from ln of negative value) were removed from analyses.



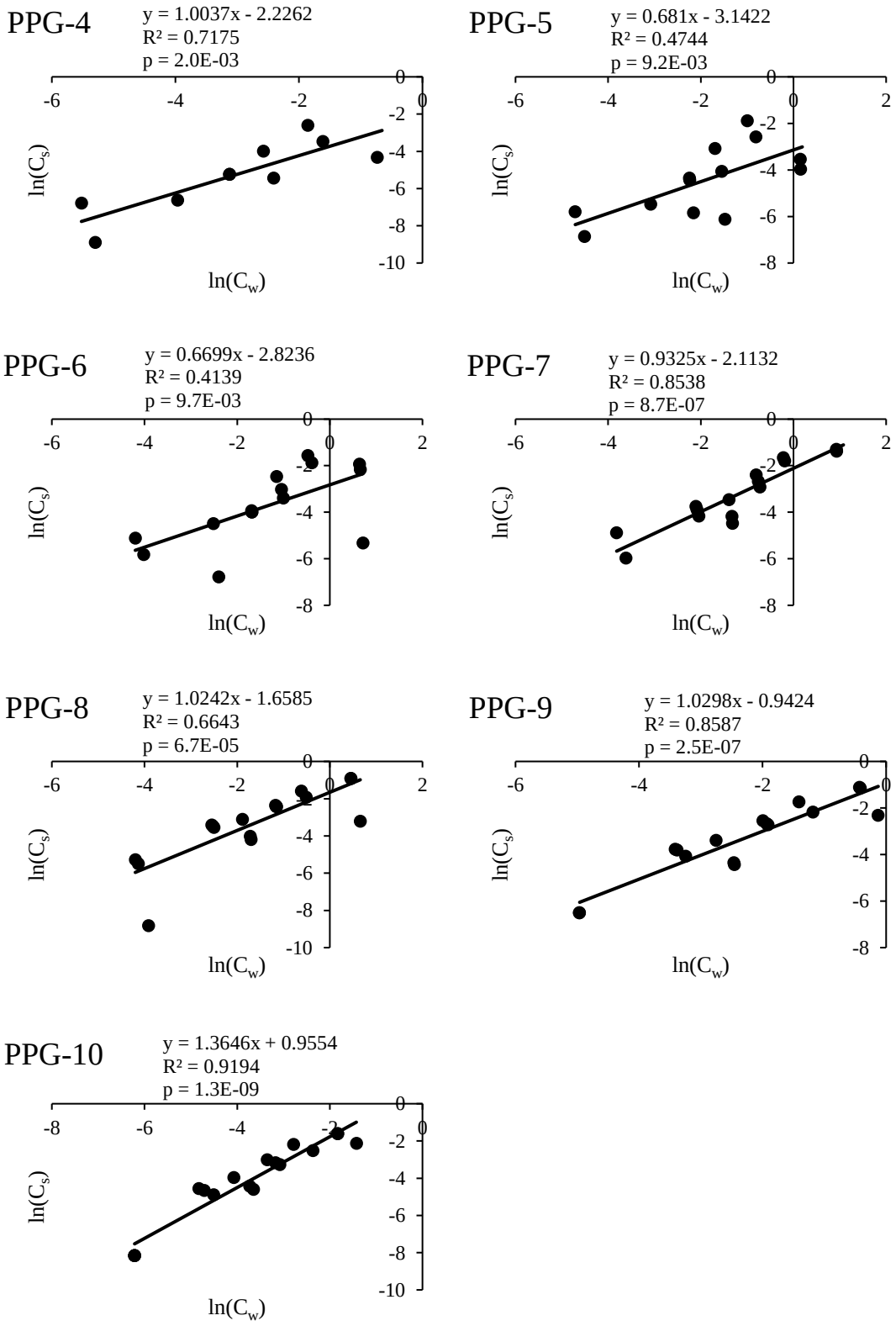
Appendix 4.16: Freundlich sorption isotherms used to calculate K_F of individual PPG homologues 4-10 for Standard Soil 2.2.
Note that 0 values (arising from ln of negative value) were removed from analyses.



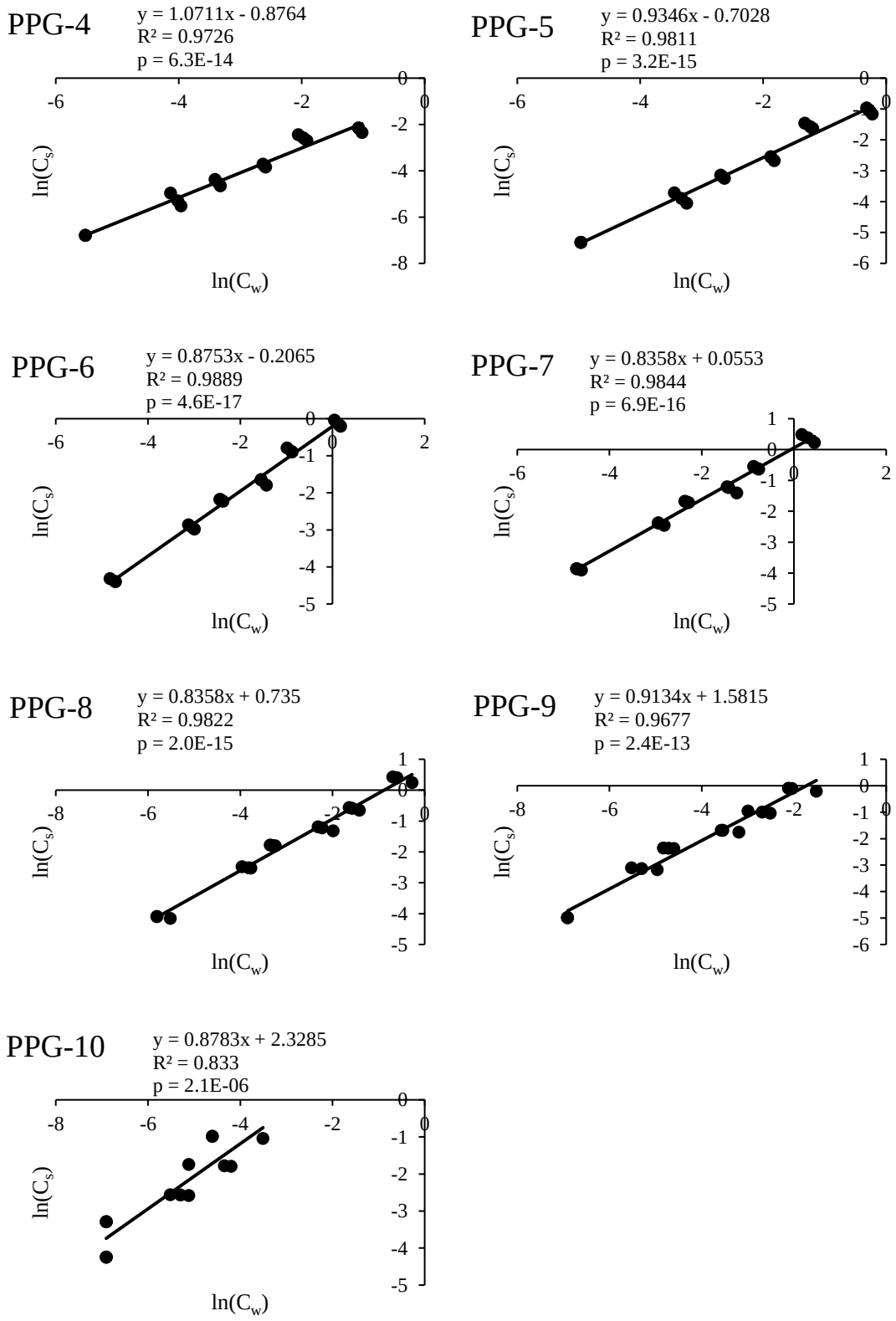
Appendix 4.17: Freundlich sorption isotherms used to calculate K_F of individual PPG homologues 4-10 for Standard Soil 2.3.
Note that 0 values (arising from ln of negative value) were removed from analyses.



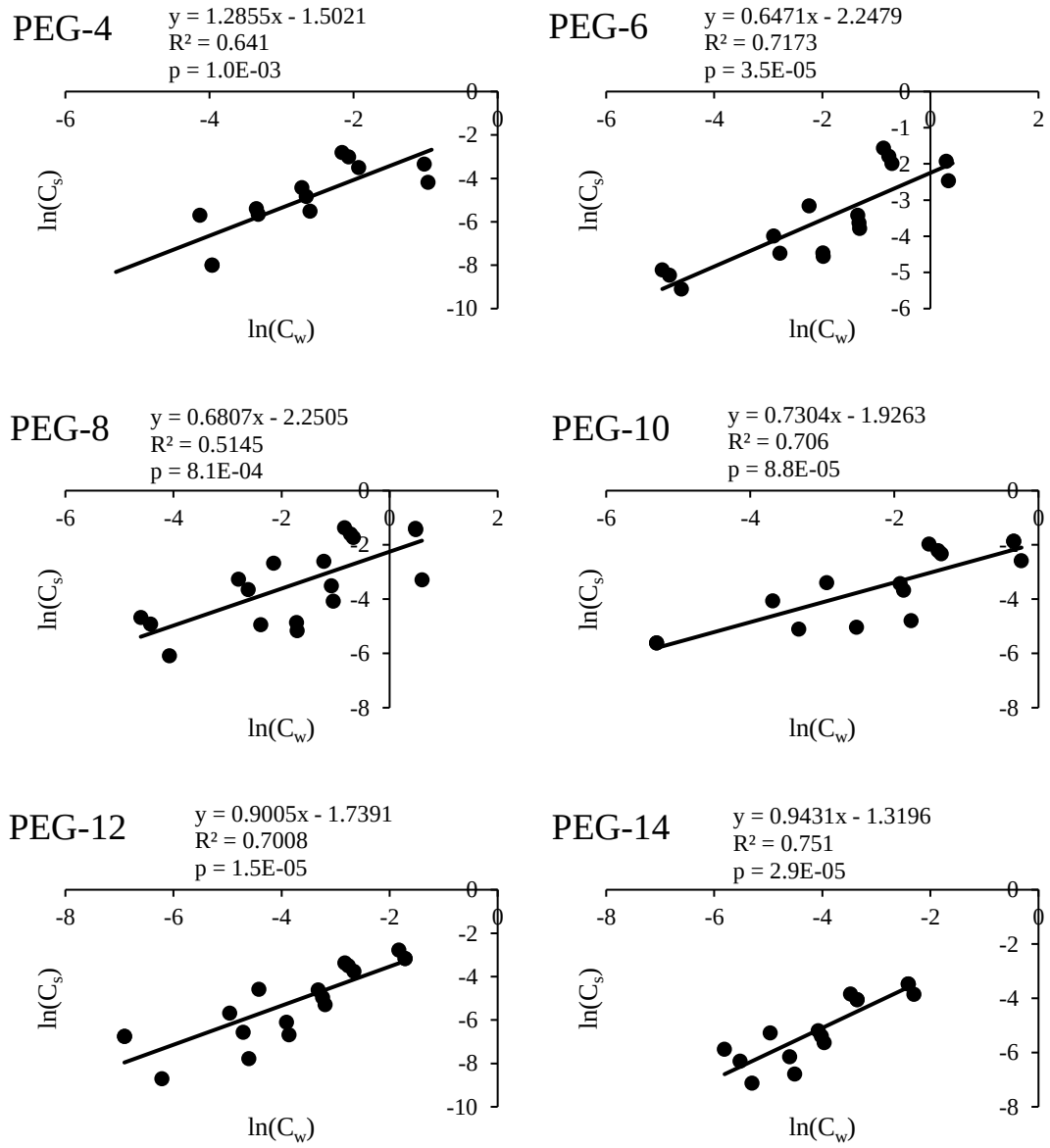
Appendix 4.18: Freundlich sorption isotherms used to calculate K_F of individual PPG homologues 4-10 for Standard Soil 2.4.
Note that 0 values (arising from ln of negative value) were removed from analyses.



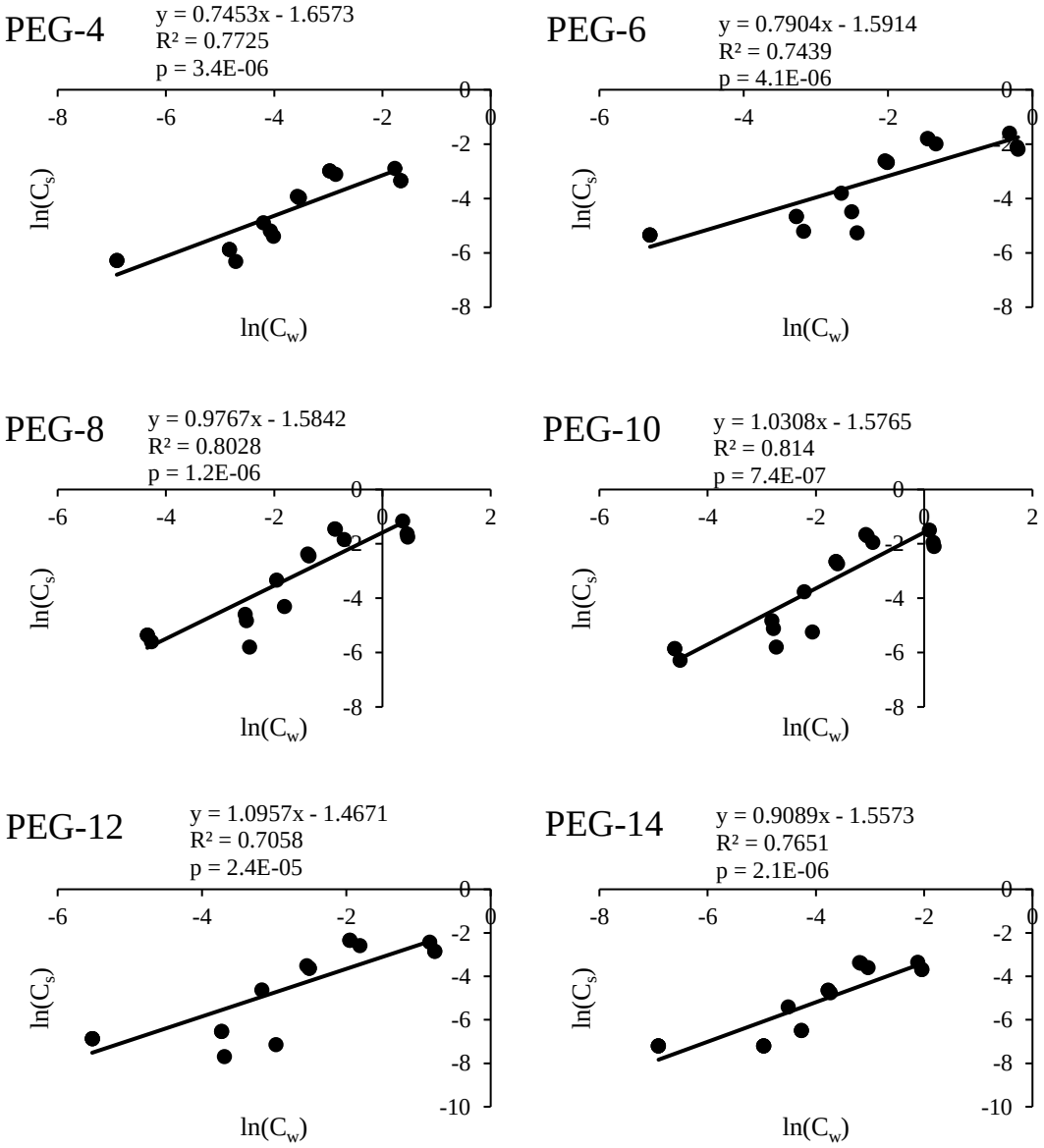
Appendix 4.19: Freundlich sorption isotherms used to calculate K_F of individual PPG homologues 4-10 for Standard Soil 5M.
Note that 0 values (arising from ln of negative value) were removed from analyses.



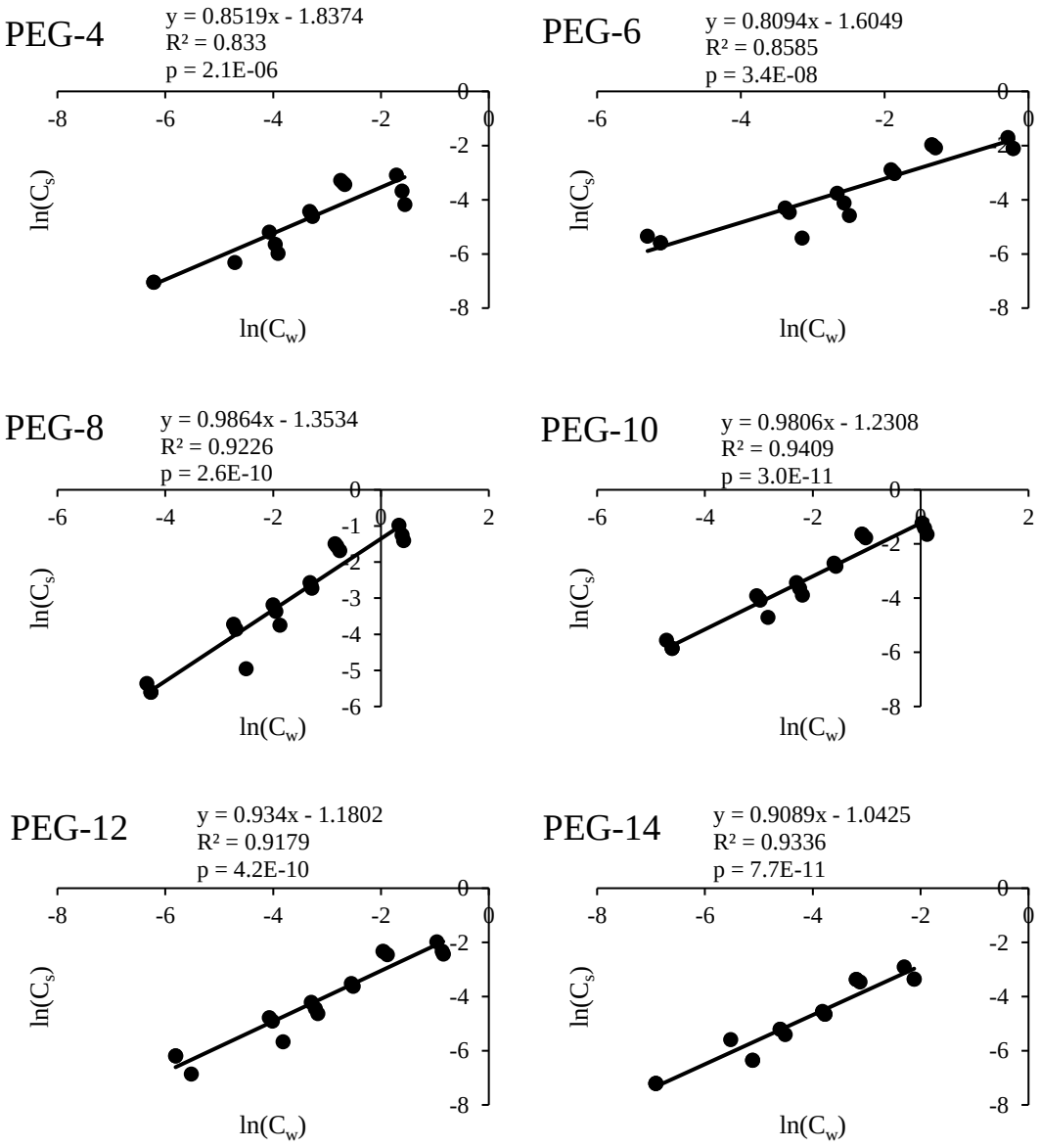
Appendix 4.20: Freundlich sorption isotherms used to calculate K_F of individual PPG homologues 4-10 for Standard Soil 6S.
Note that 0 values (arising from ln of negative value) were removed from analyses.



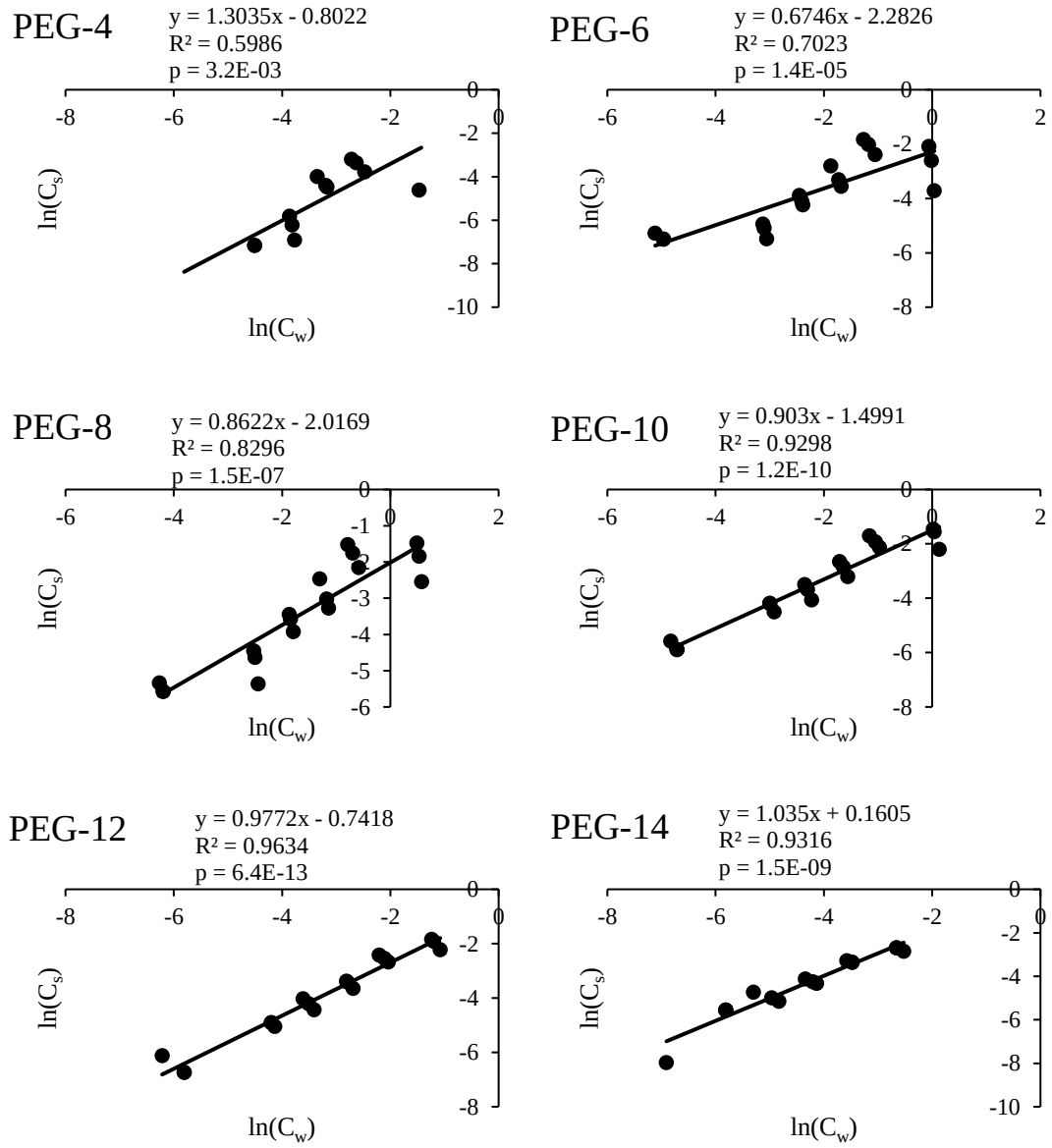
Appendix 4.21: Freundlich sorption isotherms used to calculate K_F of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.1.
Note that 0 values (arising from ln of negative value) were removed from analyses.



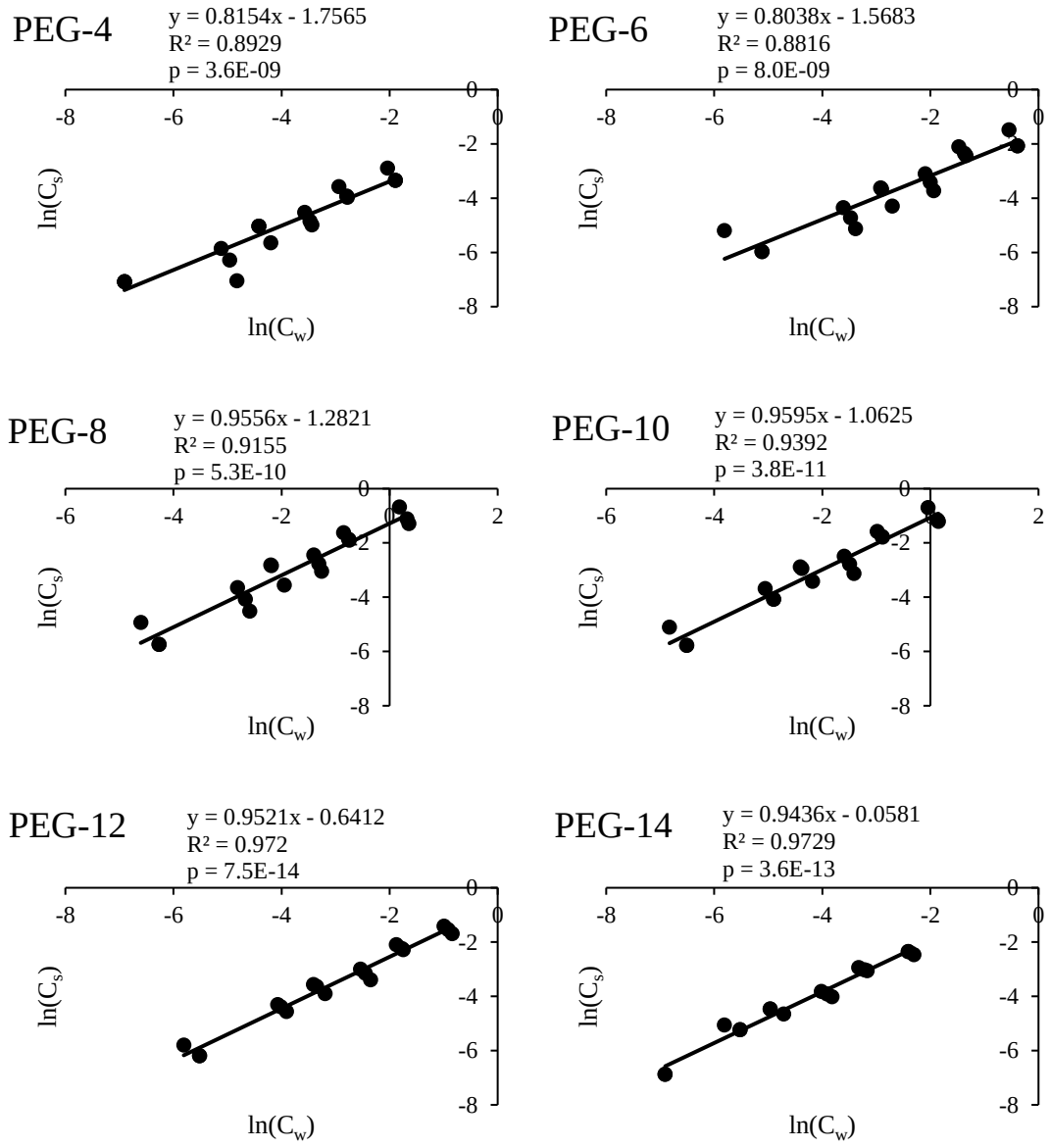
Appendix 4.22: Freundlich sorption isotherms used to calculate K_F of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.2.
Note that 0 values (arising from ln of negative value) were removed from analyses.



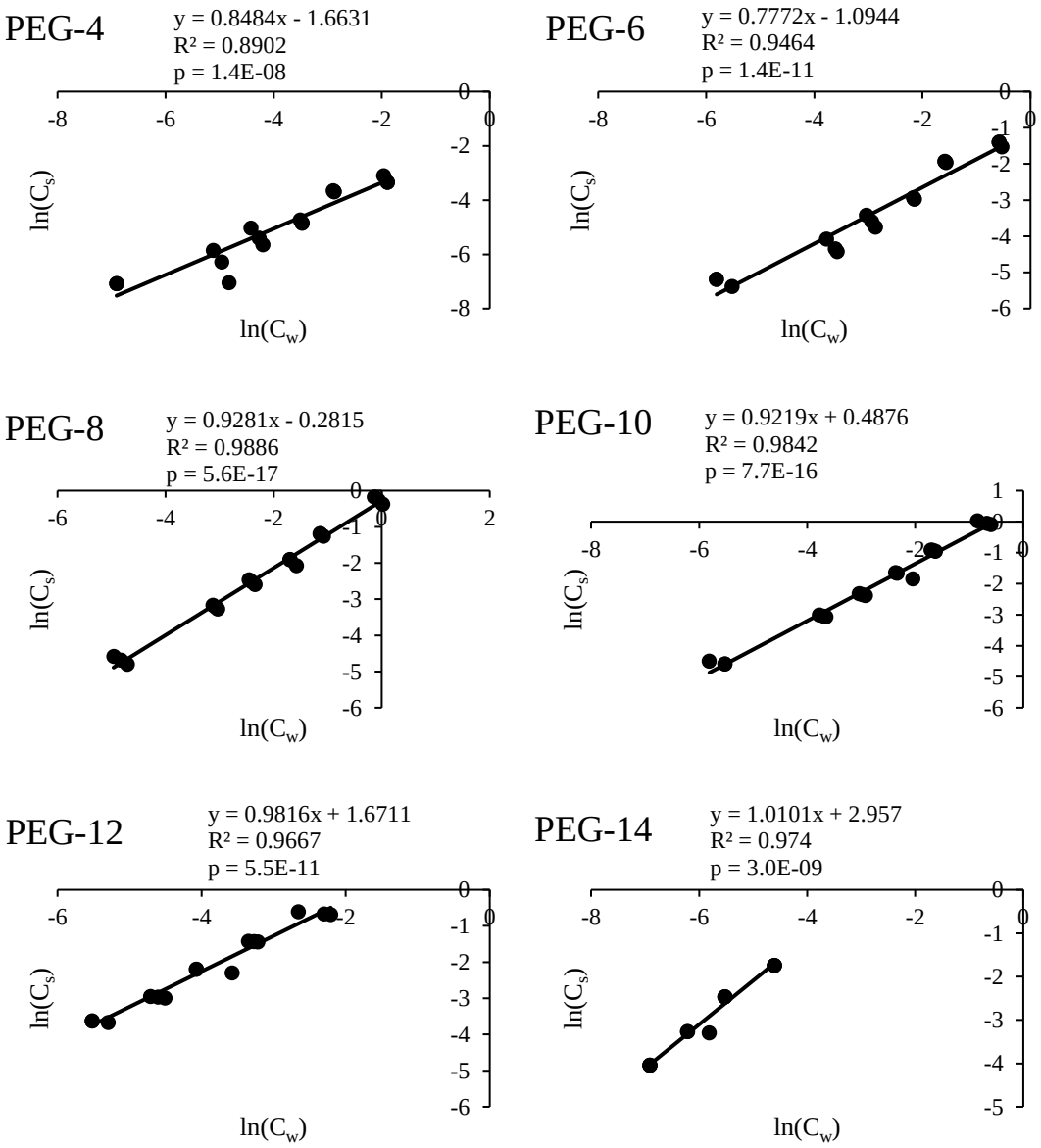
Appendix 4.23: Freundlich sorption isotherms used to calculate K_F of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.3.
Note that 0 values (arising from ln of negative value) were removed from analyses.



Appendix 4.24: Freundlich sorption isotherms used to calculate K_F of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 2.4.
Note that 0 values (arising from ln of negative value) were removed from analyses.



Appendix 4.25: Freundlich sorption isotherms used to calculate K_F of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 5M.
Note that 0 values (arising from ln of negative value) were removed from analyses.



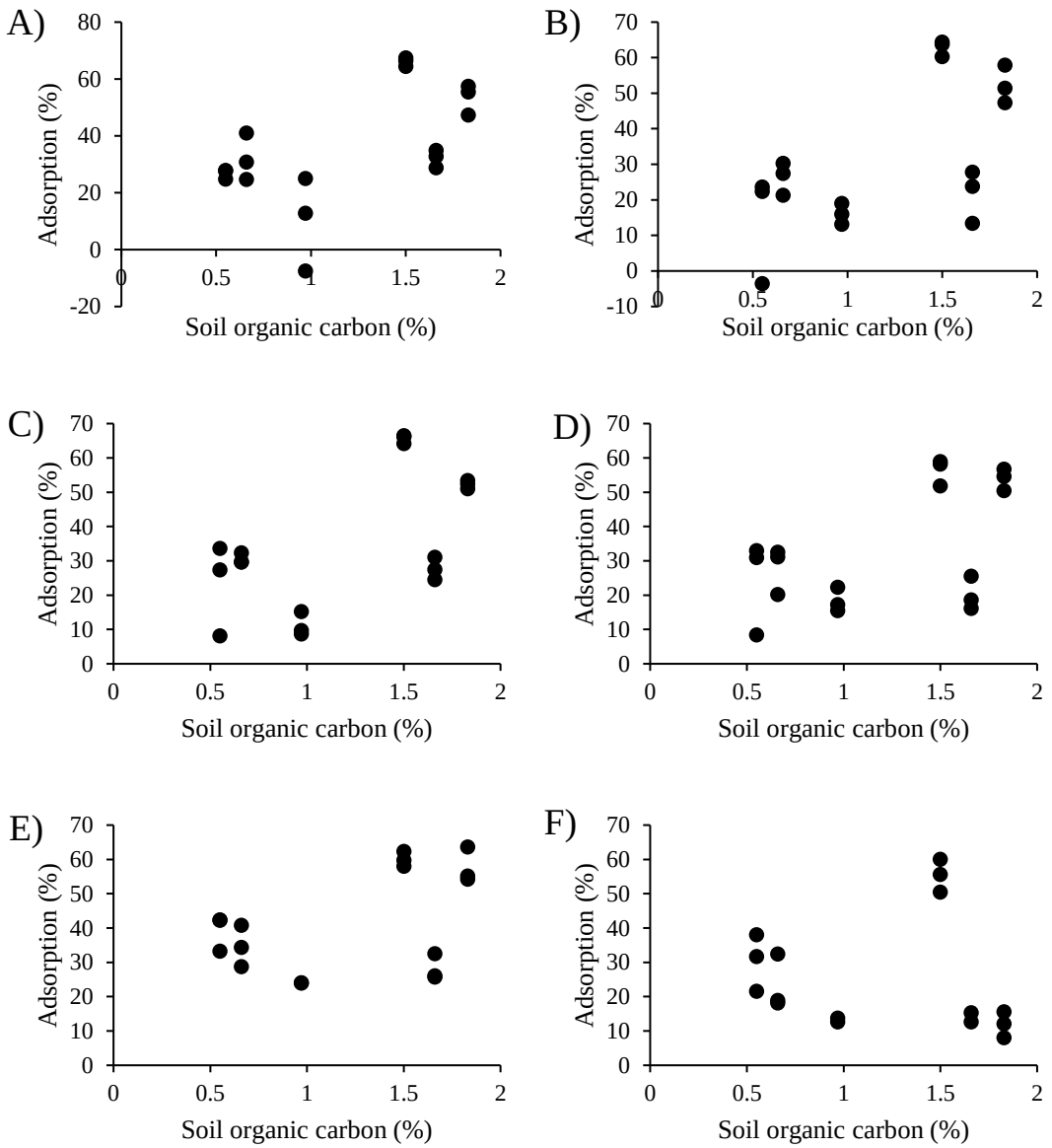
Appendix 4.26: Freundlich sorption isotherms used to calculate K_F of individual PEG homologues 4-14 (only even numbered homologues are shown as examples) for Standard Soil 6S.
Note that 0 values (arising from ln of negative value) were removed from analyses.

Appendix 4.27: Values of Spearman's rank correlation coefficient (R_s) for percentage adsorption of the PPG mixture (chain lengths 4-10, for each initial polymer concentration) versus soil properties, with corresponding significance results. Statistically significant positive correlations (positive R_s) are highlighted in green.

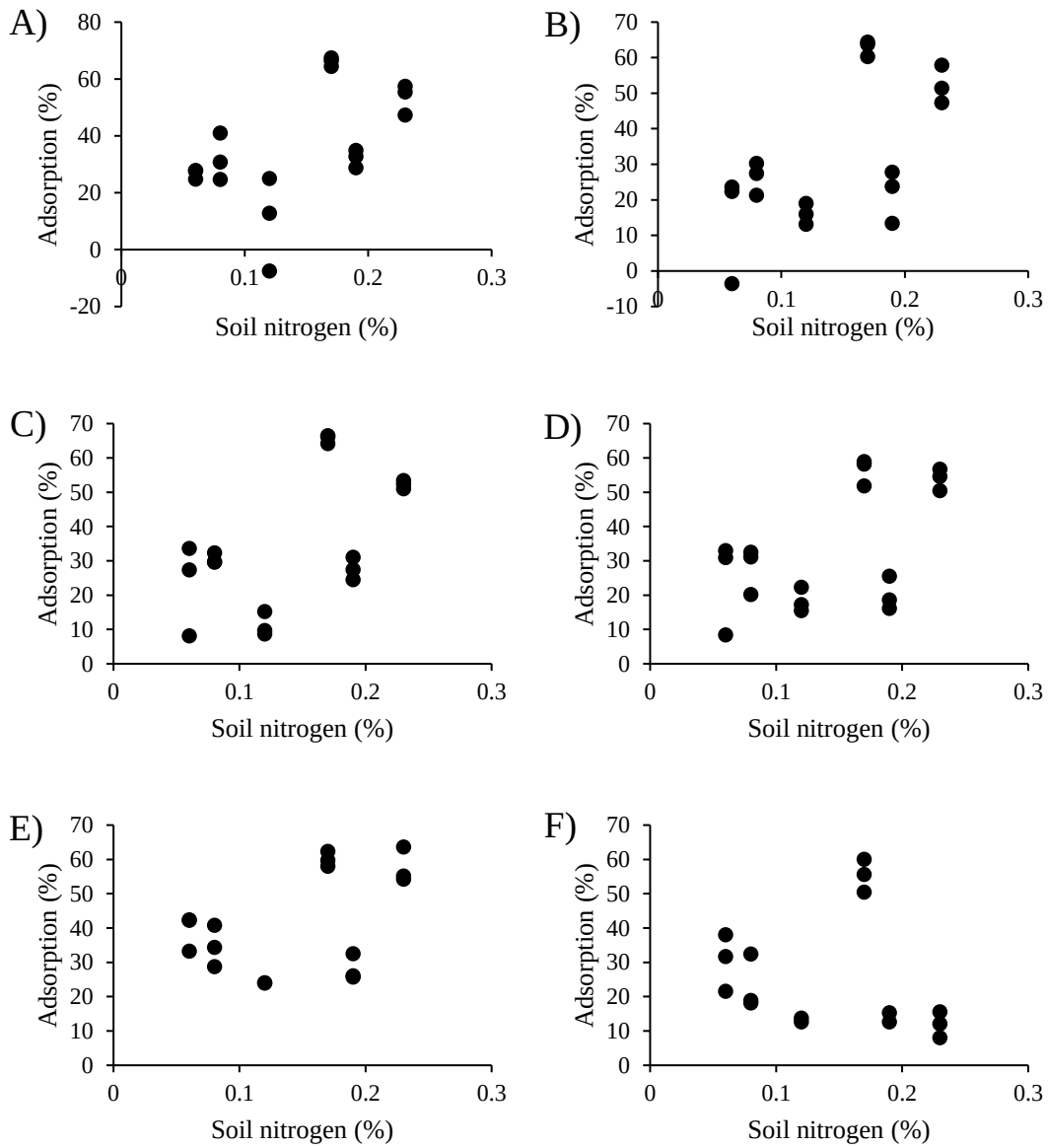
Initial polymer concentration (mg L^{-1})	N	R_s	T statistic	DF	p value
Soil organic carbon (%C)					
0.1	18	0.57	2.80	16	0.01
0.5	18	0.49	2.22	16	0.04
1	18	0.44	1.94	16	0.07
2	18	0.35	1.52	16	0.15
4	17	0.25	1.02	15	0.32
10	16	-0.47	2.00	14	0.07
Soil nitrogen content (%N)					
0.1	18	0.57	2.80	16	0.01
0.5	18	0.49	2.22	16	0.04
1	18	0.44	1.94	16	0.07
2	18	0.35	1.52	16	0.15
4	17	0.25	1.02	15	0.32
10	16	-0.47	2.00	14	0.07
Soil pH					
0.1	18	0.18	0.71	16	0.49
0.5	18	0.27	1.14	16	0.27
1	18	0.21	0.86	16	0.40
2	18	0.29	1.22	16	0.24
4	17	0.23	0.90	15	0.38
10	16	-0.42	1.71	14	0.11
Soil cation exchange capacity (meq/100g)					
0.1	18	0.64	3.30	16	0.004
0.5	18	0.64	3.36	16	0.004
1	18	0.59	2.94	16	0.010
2	18	0.57	2.80	16	0.013
4	17	0.47	2.08	15	0.06
10	16	0.01	0.03	14	0.97
Soil particle size distribution (% < 0.002 mm)					
0.1	18	0.64	3.30	16	0.004
0.5	18	0.64	3.36	16	0.004
1	18	0.59	2.94	16	0.010
2	18	0.57	2.80	16	0.013
4	17	0.47	2.08	15	0.06
10	16	0.01	0.03	14	0.97

Appendix 4.28: Values of Spearman's rank correlation coefficient (R_s) for percentage adsorption of the PEG mixture (chain lengths 4-14, for each initial polymer concentration) versus soil properties, with corresponding significance results. Statistically significant positive correlations (positive R_s) are highlighted in green.

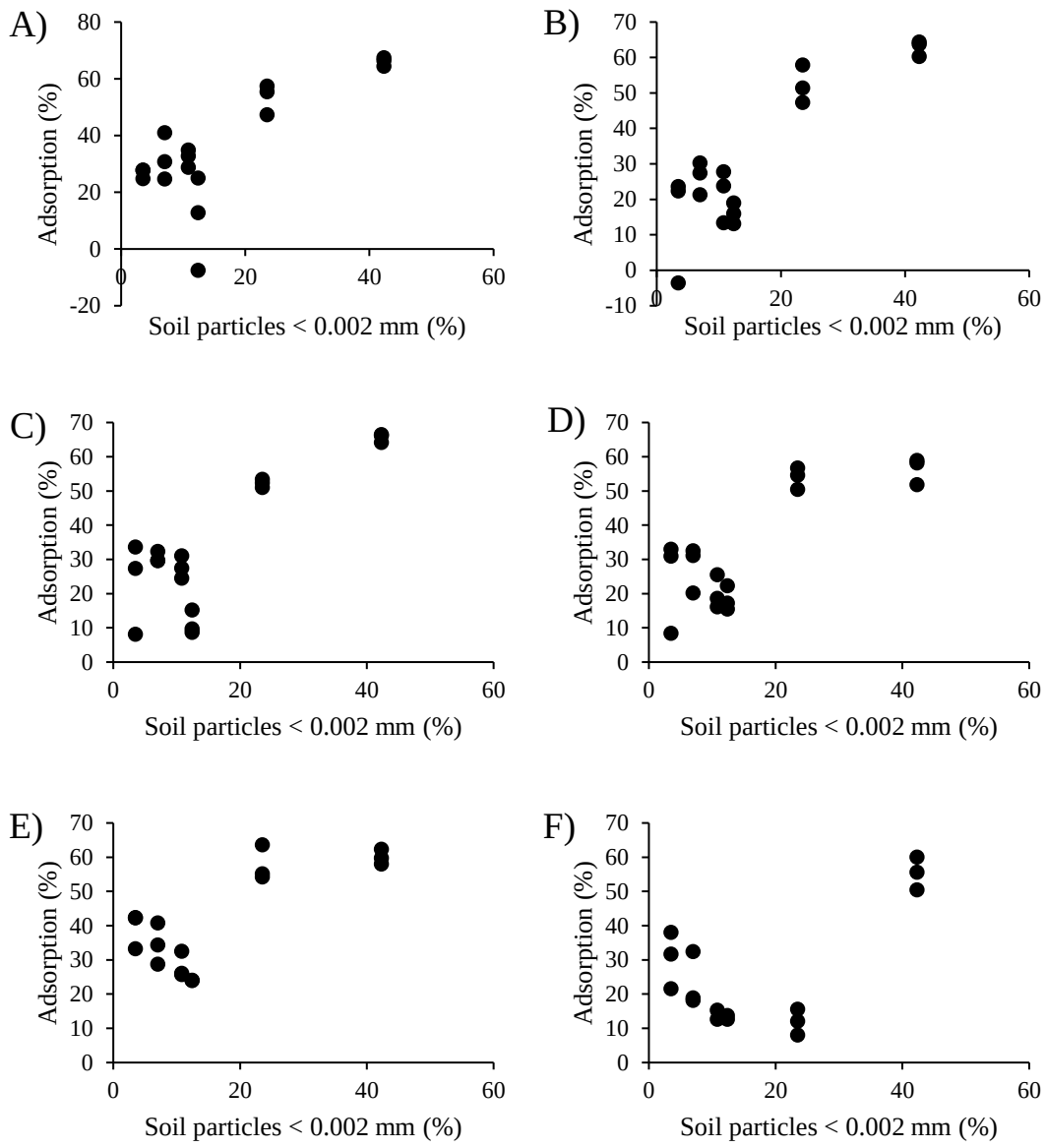
Initial polymer concentration (mg L^{-1})	N	R_s	T statistic	DF	p value
Soil organic carbon (%C)					
0.1	18	-0.11	0.43	16	0.67
0.5	18	-0.13	0.54	16	0.59
1	18	-0.03	0.14	16	0.89
2	18	0.44	1.97	16	0.07
4	18	0.22	0.91	16	0.37
10	18	-0.01	0.04	16	0.97
Soil nitrogen content (%N)					
0.1	18	-0.11	0.43	16	0.67
0.5	18	-0.13	0.54	16	0.59
1	18	-0.03	0.14	16	0.89
2	18	0.44	1.97	16	0.07
4	18	0.22	0.91	16	0.37
10	18	-0.01	0.04	16	0.97
Soil pH					
0.1	18	-0.08	0.33	16	0.74
0.5	18	0.31	1.31	16	0.21
1	18	0.39	1.68	16	0.11
2	18	0.27	1.14	16	0.27
4	18	0.01	0.05	16	0.96
10	18	0.40	1.73	16	0.10
Soil cation exchange capacity (meq/100g)					
0.1	18	0.28	1.15	16	0.27
0.5	18	0.45	2.01	16	0.06
1	18	0.52	2.46	16	0.03
2	18	0.65	3.41	16	0.004
4	18	0.43	1.90	16	0.08
10	18	0.53	2.50	16	0.02
Soil particle size distribution (% < 0.002 mm)					
0.1	18	0.28	1.15	16	0.27
0.5	18	0.45	2.01	16	0.06
1	18	0.52	2.46	16	0.03
2	18	0.65	3.41	16	0.004
4	18	0.43	1.90	16	0.08
10	18	0.53	2.50	16	0.02



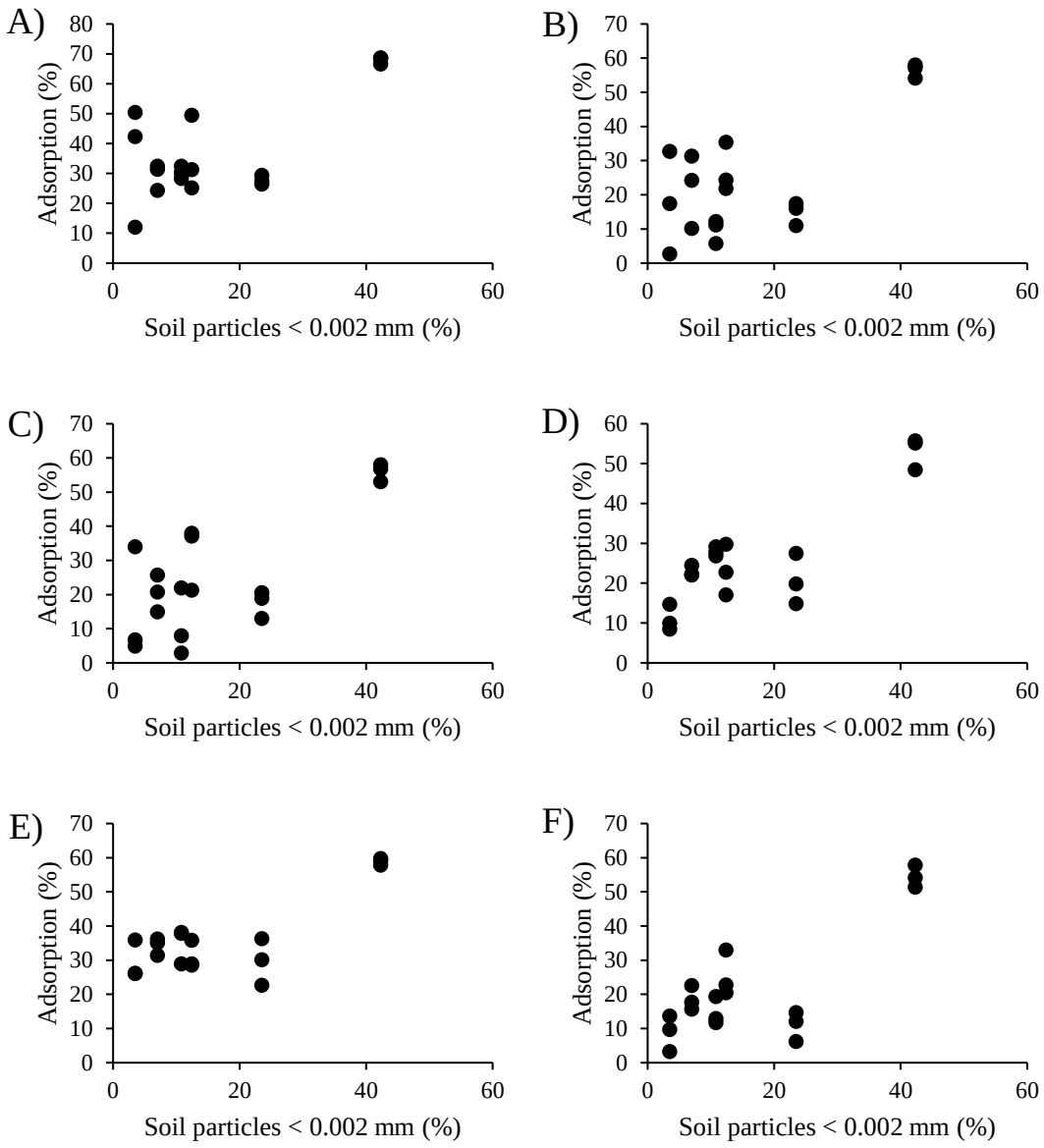
Appendix 4.29: Percentage of PPG mixture (chain lengths 4-10) of initial concentrations A) 0.1, B) 0.5, C) 1, D) 2, E), 4, and F) 10 mg L^{-1} adsorbed to soils with varying organic carbon content.



Appendix 4.30: Percentage of PPG mixture (chain lengths 4-10) of initial concentrations A) 0.1, B) 0.5, C) 1, D) 2, E), 4, and F) 10 mg L^{-1} adsorbed to soils with varying nitrogen content.



Appendix 4.31: Percentage of PPG mixture (chain lengths 4-10) of initial concentrations A) 0.1, B) 0.5, C) 1, D) 2, E), 4, and F) 10 mg L^{-1} adsorbed to soils with varying particle size distributions.



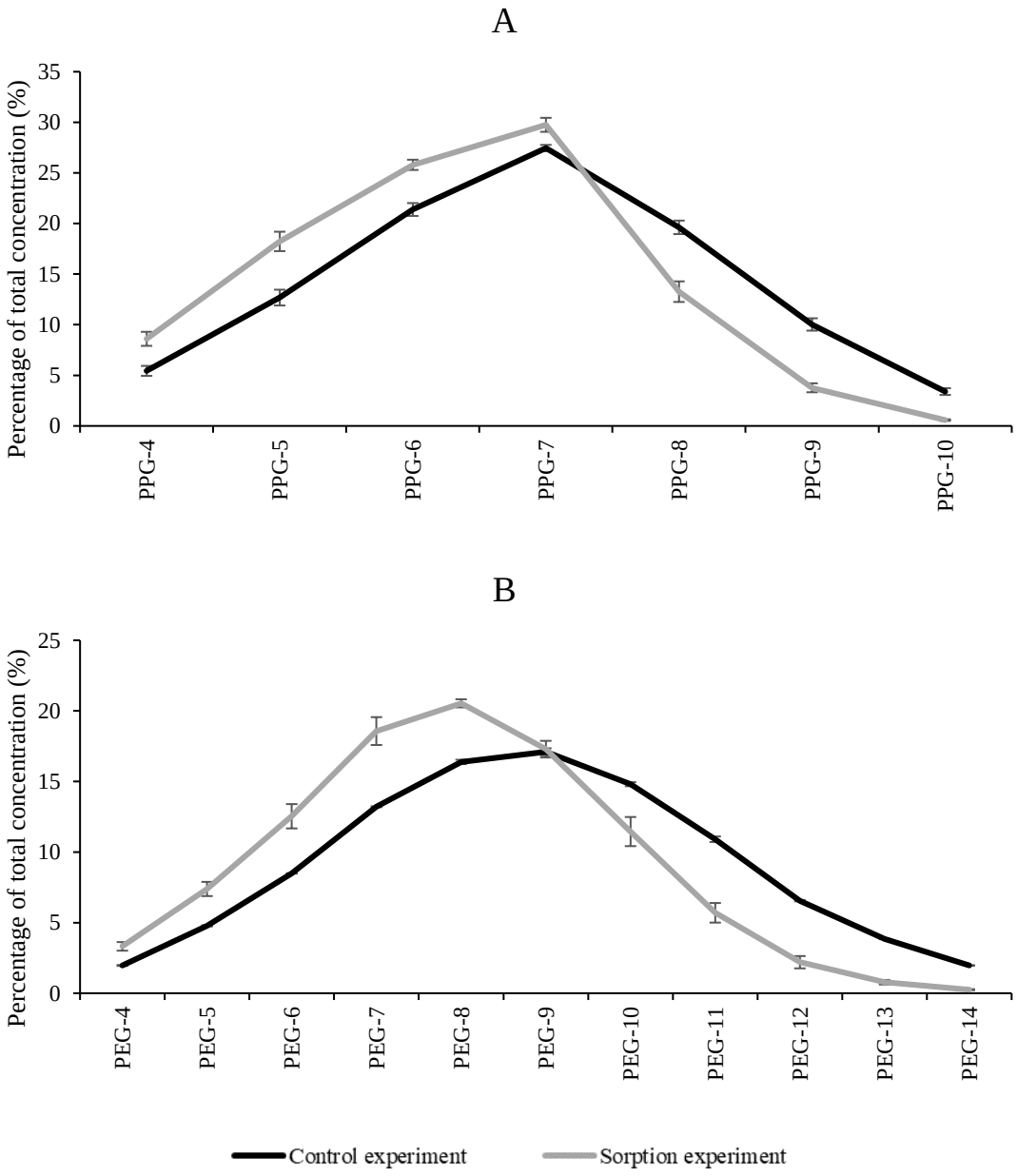
Appendix 4.32: Percentage of PEG mixture (chain lengths 4-14) of initial concentrations A) 0.1, B) 0.5, C) 1, D) 2, E), 4, and F) 10 mg L^{-1} adsorbed to soils with varying particle size distributions.

Appendix 4.33: Values of Spearman's rank correlation coefficient (R_s) for percentage adsorption of PPG homologues (at each initial polymer concentration) versus polymer chain length (from 4 to 10 monomer units) for each soil type, with corresponding significance results. Statistically significant positive correlations (positive R_s) are highlighted in green, whilst statistically significant negative correlations (negative R_s) are highlighted in red.

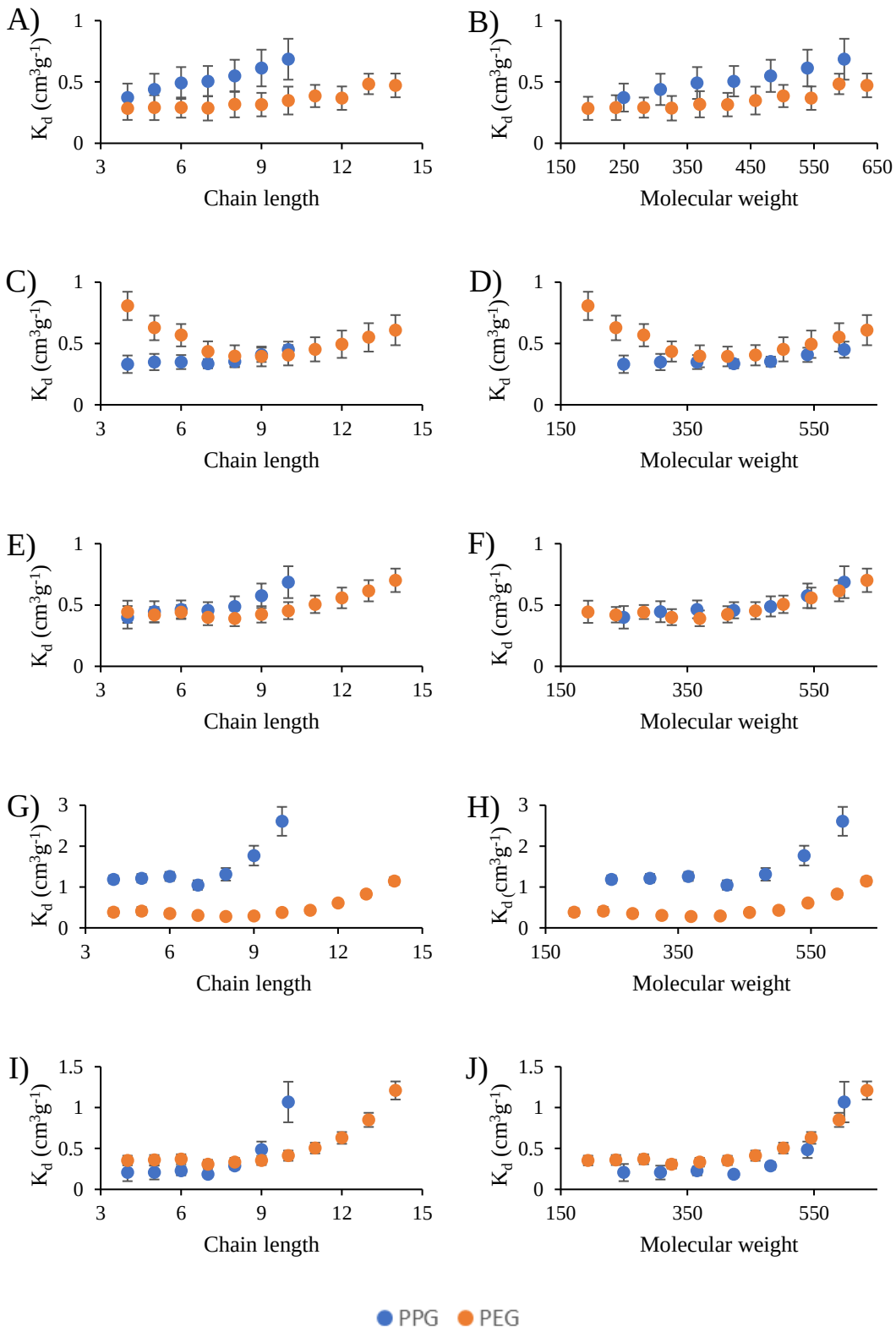
Initial polymer concentration (mg L^{-1})	N	R_s	T statistic	DF	p value
Soil 2.1					
0.1	21	-0.49	2.45	19	0.02
0.5	21	0.29	1.33	19	0.20
1	21	0.49	2.46	19	0.02
2	21	0.53	2.76	19	0.01
4	21	0.67	3.92	19	0.001
10	21	0.77	5.34	19	3.8E-05
Soil 2.2					
0.1	21	-0.80	5.76	19	1.5E-05
0.5	21	0.24	1.06	19	0.30
1	21	0.09	0.40	19	0.70
2	21	0.71	4.42	19	3.0E-04
4	21	0.24	1.06	19	0.30
10	14	0.88	6.33	12	3.8E-05
Soil 2.3					
0.1	21	-0.33	1.51	19	0.15
0.5	21	0.89	8.30	19	9.7E-08
1	21	0.98	20.28	19	2.5E-14
2	21	0.85	7.01	19	1.1E-06
4	21	0.23	1.04	19	0.31
10	21	0.72	4.52	19	2.4E-04
Soil 2.4					
0.1	21	-0.36	1.70	19	0.11
0.5	21	0.68	4.05	19	6.8E-04
1	21	0.93	11.20	19	8.3E-10
2	21	0.42	2.02	19	0.06
4	21	0.69	4.14	19	5.6E-04
10	21	0.61	3.32	19	0.004
Soil 5M					
0.1	21	0.15	0.68	19	0.51
0.5	21	0.95	13.49	19	3.5E-11
1	21	0.64	3.61	19	0.002
2	21	0.88	8.11	19	1.4E-07
4	14	0.58	2.44	12	0.03
10	14	0.99	20.18	12	1.3E-10
Soil 6S					
0.1	21	1.00	56.50	19	1.2E-22
0.5	21	0.99	35.34	19	8.5E-19
1	21	0.99	34.60	19	1.3E-18
2	21	0.98	23.34	19	1.9E-15
4	21	0.98	20.97	19	1.3E-14
10	21	0.99	27.39	19	9.8E-17

Appendix 4.34: Values of Spearman's rank correlation coefficient (R_s) for percentage adsorption of PEG homologues (at each initial polymer concentration) versus polymer chain length (from 4 to 14 monomer units) for each soil type, with corresponding significance results. Statistically significant positive correlations (positive R_s) are highlighted in green, whilst statistically significant negative correlations (negative R_s) are highlighted in red.

Initial polymer concentration (mg L^{-1})	N	R_s	T statistic	DF	p value
Soil 2.1					
0.1	33	0.26	1.50	31	0.14
0.5	33	0.28	1.60	31	0.12
1	32	0.21	1.19	30	0.24
2	33	0.70	5.47	31	5.7E-06
4	33	0.40	2.40	31	0.02
10	33	0.79	7.18	31	4.5E-08
Soil 2.2					
0.1	33	-0.48	3.01	31	0.005
0.5	33	-0.68	5.18	31	1.3E-05
1	33	-0.29	1.66	31	0.11
2	33	-0.46	2.90	31	0.007
4	33	-0.14	0.80	31	0.43
10	33	-0.10	0.58	31	0.57
Soil 2.3					
0.1	33	-0.03	0.19	31	0.85
0.5	33	0.35	2.06	31	0.05
1	33	0.60	4.14	31	2.5E-04
2	33	0.64	4.65	31	5.8E-05
4	33	0.73	5.99	31	1.2E-06
10	33	0.70	5.50	31	5.2E-06
Soil 2.4					
0.1	33	0.33	1.96	31	0.06
0.5	33	0.90	11.39	31	1.3E-12
1	33	0.82	8.07	31	4.1E-09
2	33	0.56	3.81	31	6.2E-04
4	33	0.56	3.78	31	6.7E-04
10	33	0.90	11.36	31	1.4E-12
Soil 5M					
0.1	33	0.18	1.00	31	0.32
0.5	33	0.74	6.16	31	7.8E-07
1	33	0.72	5.79	31	2.2E-06
2	33	0.66	4.85	31	3.3E-05
4	33	0.76	6.57	31	2.5E-07
10	33	0.77	6.72	31	1.6E-07
Soil 6S					
0.1	33	0.74	6.09	31	9.6E-07
0.5	33	0.98	31.50	31	4.2E-25
1	33	0.98	25.86	31	1.5E-22
2	33	0.99	45.85	31	4.7E-30
4	33	0.99	55.30	31	1.5E-32
10	33	1.00	61.88	31	4.8E-34



Appendix 4.35: Change in homologue distribution following sorption of A) PPG and B) PEG to soil 6S, showing homologue distribution in control experiments (2 mg L^{-1}) and homologue distribution following sorption to soil 6S (initial concentration 2 mg L^{-1}). Error bars show 95 % confidence intervals calculated from experiments run in triplicate.

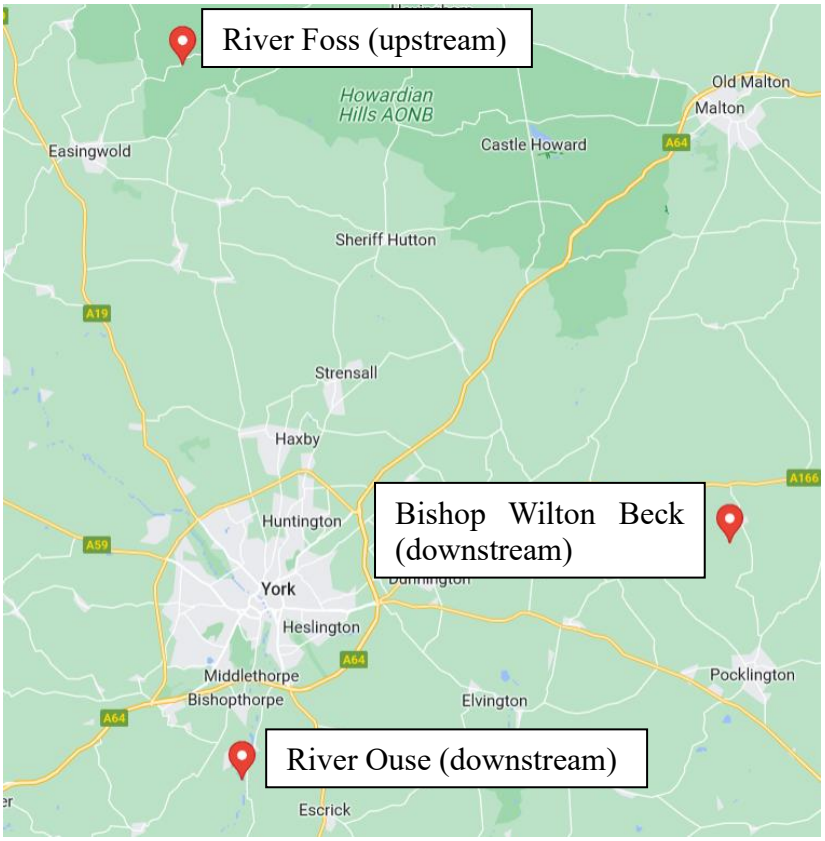


Appendix 4.36: Relationship between linear sorption coefficient (K_d) and chain length (A, C, E, G, I) and molecular weight (B, D, F, H, J) for PEG (orange) and PPG (blue) with Lufa-Speyer standard soils 2.1 (A + B), 2.2 (C + D), 2.3 (E + F), 2.4 (G + H), and 5M (I + J).
Error bars show 95% confidence intervals for K_d calculated from regression analysis.

Chapter 5 Appendices

Appendix 5.1: Details of sampling locations for the three environmental water samples which were not used in biodegradation experiments.

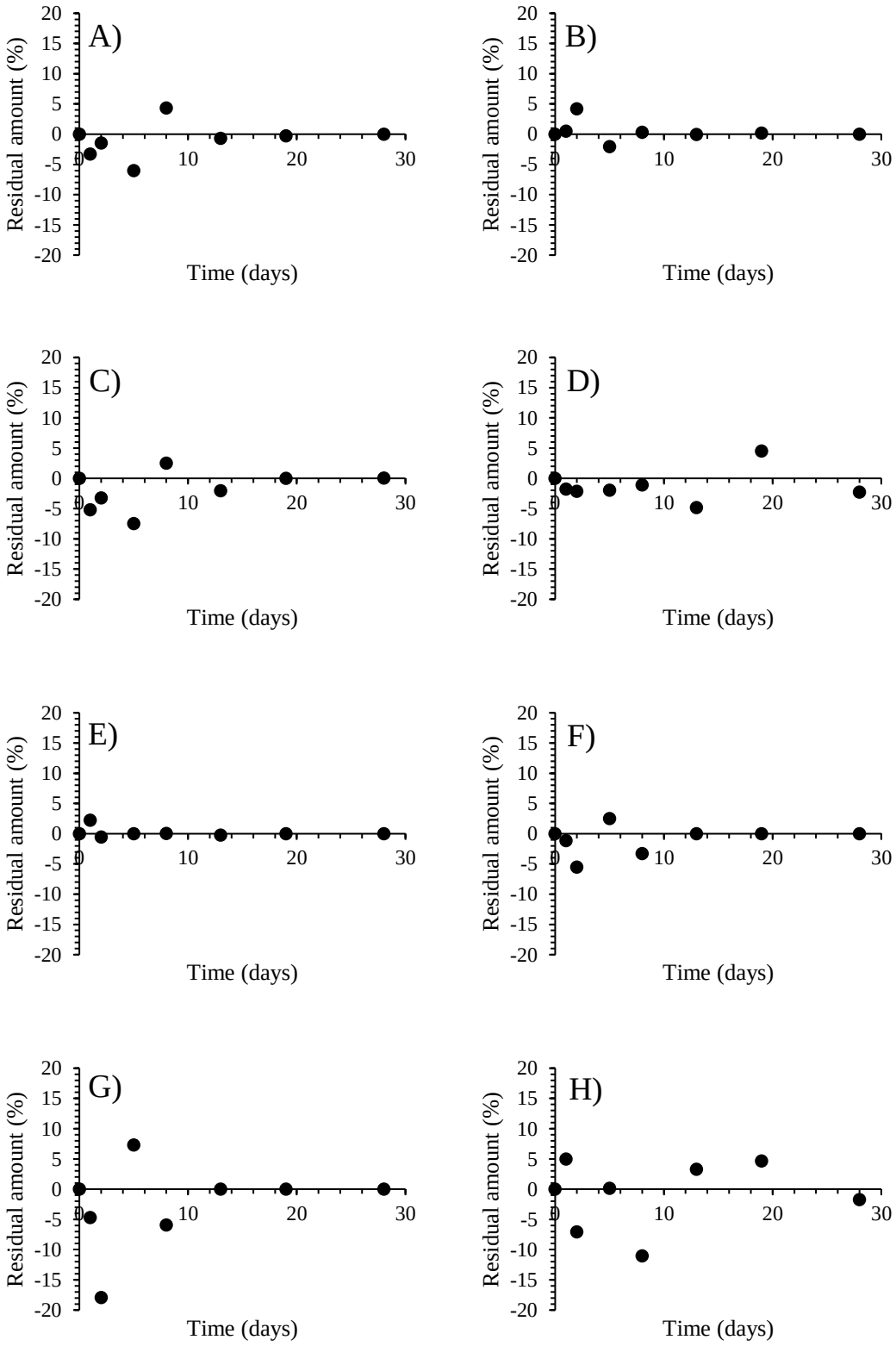
Location (coordinates)	Water body	Site description
53.892363, -1.096898	River Ouse	River Ouse (large river which runs through the city of York), sampled at Naburn Lock downstream from the city of York and Naburn wastewater treatment plant, downstream from a weir.
54.153801, -1.134401	River Foss	River Foss (medium river which runs through the city of York), sampled on Milking Hill downstream of Oulston Reservoir and close to the river source, upstream from any input from wastewater treatment.
53.978710, -0.792914	Bishop Wilton Beck	Small beck running through the village of Bishop Wilton, sampled downstream from the associated wastewater treatment plant.



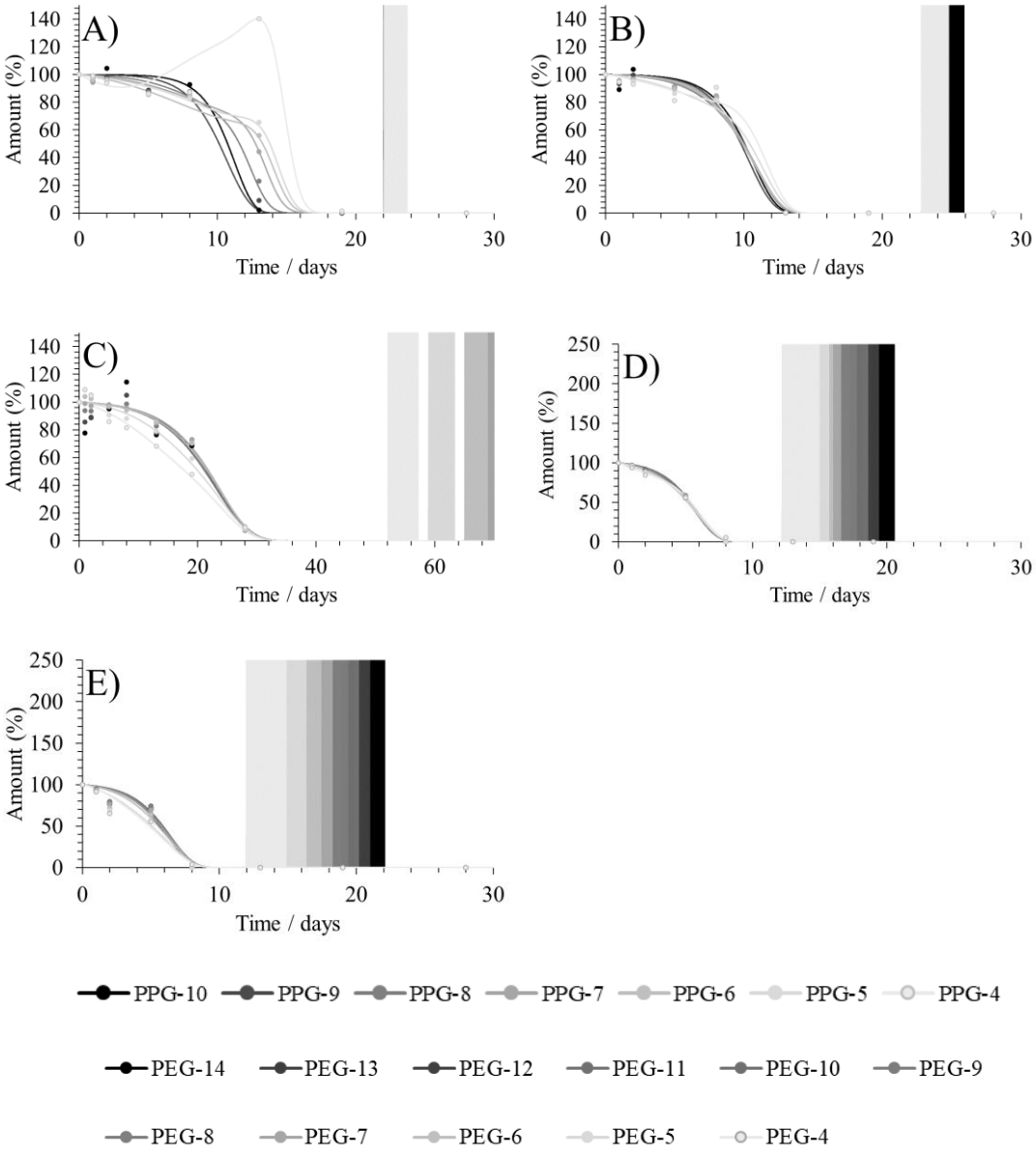
Appendix 5.2: Sampling locations of the three water types not selected for use in biodegradation experiments.

Appendix 5.3: Average measured values of water parameters of environmental water samples not used for the biodegradation study. 95% confidence intervals calculated from analytical replicates are shown in brackets.
Elemental composition measurements were measured and averaged in triplicate by the instrument and thus confidence intervals are not given for these measurements.

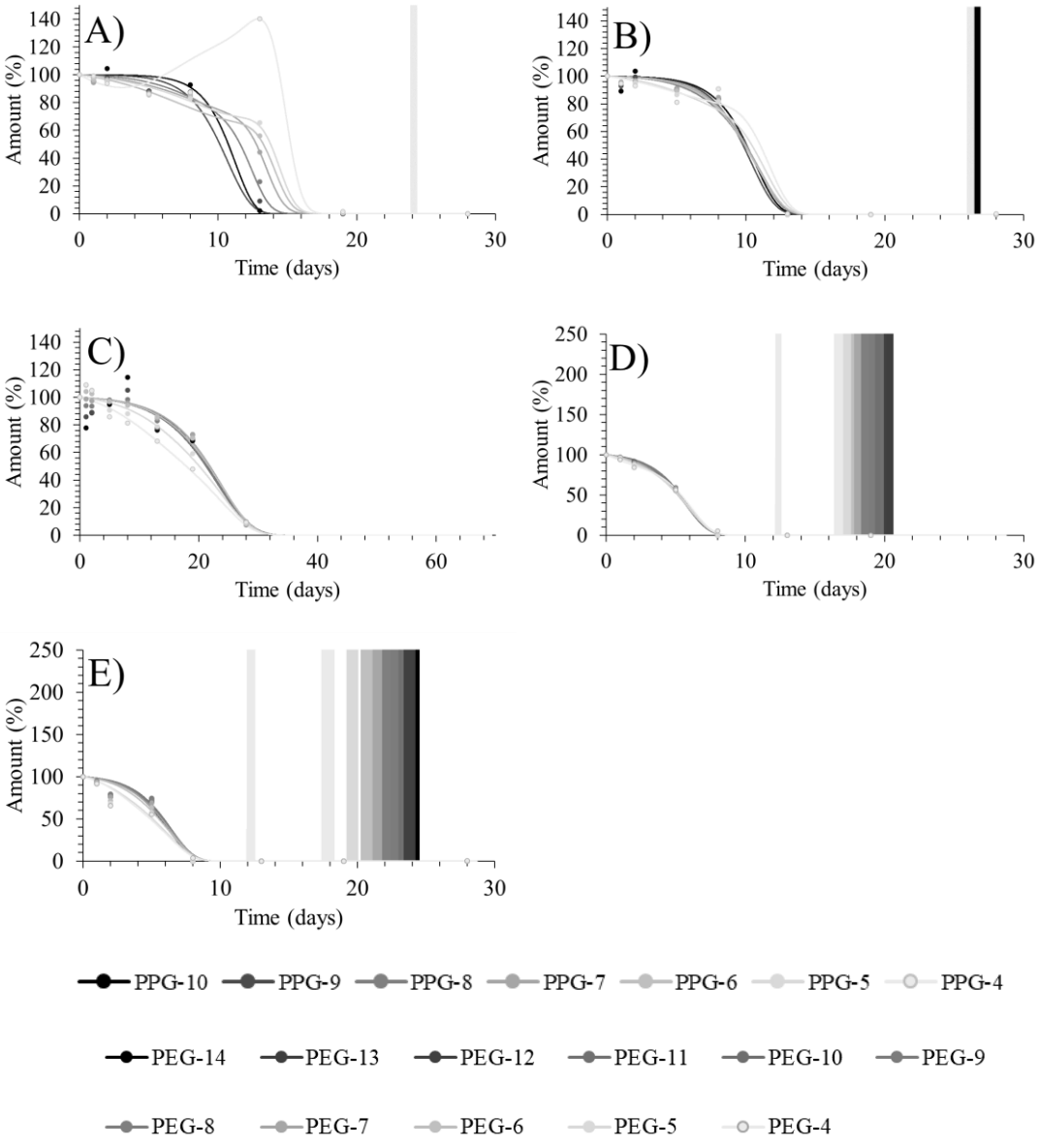
Parameter	**Unit**	**River Ouse**	**Bishop Wilton Beck**	**River Foss**
pH	n/a	7.58 (±0.05)	7.86 (±0.01)	7.99 (±0.03)
Conductivity	µS cm^{-1}	652.7 (±1.8)	553.9 (±1.8)	546.5 (±1.3)
DOC	mg L^{-1}	5.814 (±0.037)	5.831 (±0.200)	4.918 (±0.112)
Magnesium	mg L^{-1}	15.983	6.172	7.672
Calcium	mg L^{-1}	79.930	86.505	89.387
Sodium	mg L^{-1}	26.053	13.620	12.370
Potassium	mg L^{-1}	6.768	7.488	2.745
Phosphorous	mg L^{-1}	0.704	0.837	0.015
Copper	mg L^{-1}	0.009	0.011	0.008
Zinc	mg L^{-1}	0.005	0.003	0.001
Iron	mg L^{-1}	0.012	0.019	0.023
Manganese	mg L^{-1}	0.002	0.001	0.003
Chromium	mg L^{-1}	0.002	0.002	0.002
Nickel	mg L^{-1}	0.000	0.000	0.000
Fluoride	mg L^{-1}	0.211 (±0.001)	0.079 (±0.000)	0.063 (±0.001)
Chloride	mg L^{-1}	40.477 (±0.152)	20.961 (±0.023)	29.223 (±0.011)
Nitrite	mg L^{-1}	0.061 (±0.004)	0.487 (±0.007)	0.000
Nitrate	mg L^{-1}	16.334 (±0.096)	37.685 (±0.148)	10.280 (±0.035)
Sulphate	mg L^{-1}	78.881 (±0.126)	44.524 (±0.073)	51.221 (±0.085)
Phosphate	mg L^{-1}	1.273 (±0.013)	1.931 (±0.049)	0.016 (±0.026)
Hardness (calculated)	mg L^{-1}	265.4	241.4	254.8



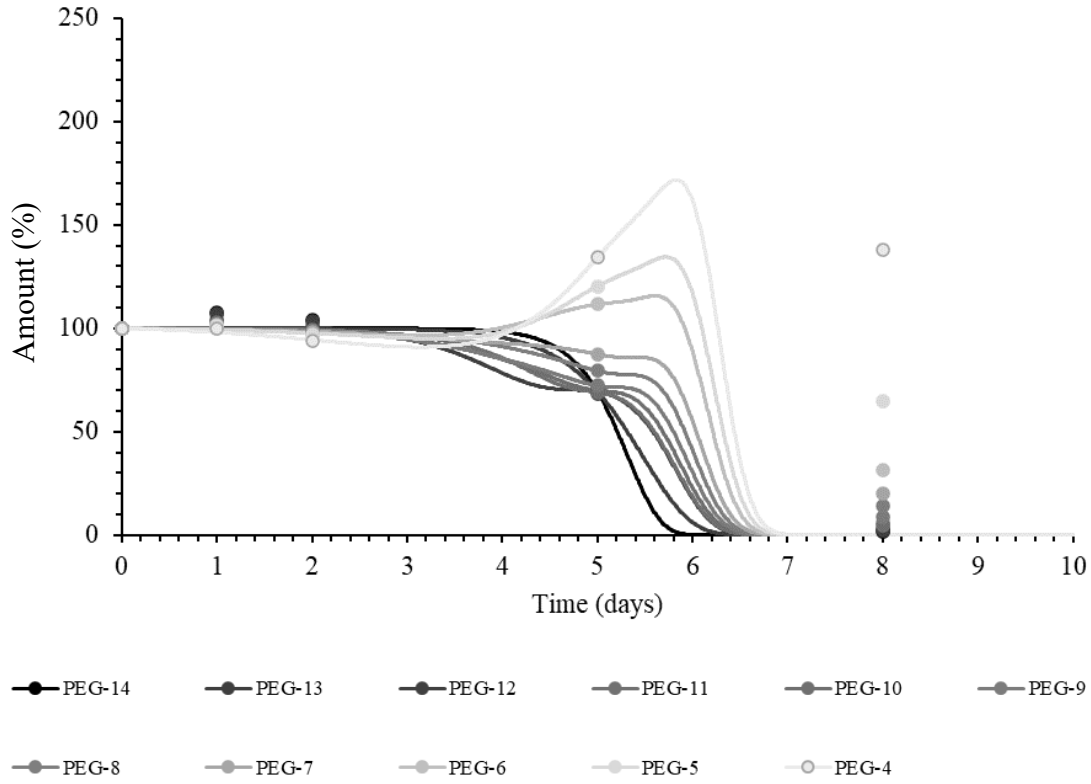
Appendix 5.4: Residual plots showing difference between experimentally measured concentrations and optimised logistic model at each timepoint for A) PPG in River Ouse water; B) PPG in River Foss water; C) PPG in Bishop Wilton Beck water; D) PPG in Yearsley Lake water; E) PEG in River Ouse water; F) PEG in River Foss water; G) PEG in Bishop Wilton Beck water; and H) PEG in Yearsley Lake water.



Appendix 5.5: Degradation kinetics for individual homologues showing the full modelled time range (0-30 days for river water, 0-70 days for lake water) in cases where models broke down at longer timepoints. Graphs show data for water for A) PPG in the River Ouse; B) PPG in the Bishop Wilton Beck; C) PPG in Yearsley Lake; D) PEG in the River Foss; and E) PEG in Bishop Wilton Beck, shown as visually derived logistic model curves (lines) and experimentally measured concentrations at each time point (circles).



Appendix 5.6: Degradation kinetics for individual homologues in water for A) PPG in the River Ouse; B) PPG in the Bishop Wilton Beck; C) PPG in Yearsley Lake; D) PEG in the River Foss; and E) PEG in Bishop Wilton Beck, shown as derived logistic model curves (lines) and experimentally measured concentrations at each time point (circles), decreasing the time increment in modelled data from 10 minutes to 1 minute after time t = 12.5 days.



Appendix 5.7: Degradation kinetics for individual PEG homologues in water from the River Ouse, shown as derived logistic model curves obtained using the Microsoft Excel solver add-in (lines) and experimentally measured concentrations at each time point (circles).

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