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BEHAVIOR AND ATTENUATION OF MICROPLASTICS IN ENVIRONMENTAL COMPARTMENTS

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Behavior and attenuation of microplastics in environmental compartments

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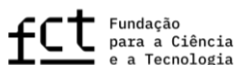
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Statement of Originality

I certify that this work does not contain any material that has been nor will be used for the award of any other degree or diploma in my name or anyone, in any university or institution. In addition, I certify that, to the best of my knowledge, this work does not contain any material previously published or written by another person, except where due reference has been made in the text. Accordingly, all the contents of the work herein presented are exclusively from my own with the collaborations mentioned in the thesis. The full agreement of the co-authors on the inclusion of the manuscripts in the present thesis can be found in Appendix A.

A handwritten signature in black ink, reading "Mariana Nogueira Miranda". The script is cursive and fluid, with the first name "Mariana" being the most prominent.

Mariana Nogueira Miranda

*I believe the wolves went off to a wild and distant place somewhere,
although I don't really know...
because I turned away, and didn't watch them go.*

Never cry wolf (1983)

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Abstract

Microplastics have been recognized as contaminants of emerging concern in the last decade, prompting the research on the microplastic pollution from source to fate. As a relatively new research field, multiple knowledge gaps have been identified and must be tackled to better respond to this challenging and complex environmental problem. This thesis presents the main ideas explored and results obtained from the corresponding PhD project, conducted from February 2018 to January 2023. Two main goals were defined at the beginning of the project: i) examine the behavior of microplastics concerning their aging in the environment and interaction with co-occurring contaminants, and ii) investigate the behavior and attenuation of microplastics in drinking water production from seawater sources. For this, three polymers were selected as the microplastic materials under study for the project: LDPE - low-density polyethylene, PET - poly(ethylene terephthalate), and uPVC - unplasticized poly(vinyl chloride).

First, the DPSIR (driving forces, pressures, states, impacts and responses) framework was applied to the microplastic pollution to organize key information on this topic and define the research questions that would guide the next steps of the project. The responses component of the DPSIR analysis was explored in more detail, providing a literature review up to the first half of 2019 on the upstream (regulatory and policy instruments, environmental education, product design and biodegradable plastics, waste management, and effluent treatment) and downstream (biotechnology tools, drinking water treatment plants, environmental cleanups, and other mitigation technologies and strategies for air, soil and water) responses to microplastic pollution.

The aging of microplastics was assessed after exposing commercial virgin microplastic particles (MPPs) of LDPE, PET or uPVC to ozone, UV-C, artificial solar radiation, and real weathering conditions in a city building rooftop. This allowed to investigate the aging of MPPs under urban environment stressors and identify the subsequent changes in their chemical structure (ATR-FTIR), surface morphology (SEM) and crystallinity (XRD). Additionally, the Carbonyl Index was used as a metric of the oxidation of the MPPs, leading to the quantification of some of the changes in the chemical structure through time. This component of the project allowed to expand the knowledge on the most effective aging agents for each polymer and the consequent modifications on the MPPs, while providing aged MPPs for the following experiments. The aging agents studied were demonstrated to affect the microplastics differently depending on the polymer, with LDPE being aged by all treatments (mostly by ozone and weathering), PET presumed to have been slightly aged by ozone and weathering, and uPVC aged more when exposed to the UV-C treatments and weathering.

The next step focused on exploring the interaction of MPPs with co-occurring contaminants, namely with ten organic micropollutants (OMPs) that include pesticides (alachlor, clofibric acid, diuron, pentachlorophenol) and pharmaceutical substances (citalopram, diclofenac, florfenicol, tramadol, trimethoprim, and venlafaxine). Through sorption batch experiments with virgin and aged (ozone-aged or weathered) MPPs, the sorption kinetics, sorption equilibrium isotherms and the role of the MPPs aging on the sorption capacities were explored. This component of the project gave evidence of the major role that plastic aging can have in the sorption process of OMPs on MPPs, while allowing to identify the affinity between the studied polymers and OMPs, and link the modifications identified for the aged MPPs to their increased sorption capacity for OMPs. Exploring the hypothesis that MPPs can act as vectors for the transport of co-occurring contaminants, phytotoxicity tests were carried out to evaluate the mobility of the OMPs sorbed on the MPPs and the potential effects on germination and early growth of the combo of MPPs and OMPs on two species of plants (*Lepidium sativum* and *Sinapis alba*). The results suggest low or no phytotoxicity effect under the conditions tested, providing some insight into the potential impacts of MPPs on soil-plant systems.

The last component of the PhD project explored the behavior and attenuation of MPPs during a membrane distillation treatment, at a lab-scale, namely by using the direct contact membrane distillation (DCMD) technology. MPPs of uPVC were selected for the DCMD experiments, considering previous results obtained on temperature stress experiments with the different polymeric materials in amber bottles. The DCMD experiments were conducted at two different MPPs loads and at different aging degrees, in filtered seawater. The MPPs modifications were assessed by different characterization techniques regarding their chemical structure (ATR-FTIR), UV-visible absorption, and surface morphology (SEM), while the DCMD system most important parameters (membrane permeability, vapor pressure gradient, permeate interval flux, water recovery, permeate and retentate conductivity and salinity) were analyzed through time to explore the possibility of the MPPs presence decreasing the treated water quality and/or recovery. Additionally, the treated water was analyzed for the presence of MPPs by Raman microscopy. This study is one of the pioneers on microplastics behavior and attenuation when using DCMD, suggesting a very high efficiency ($\geq 99\%$) in removing MPPs from water, and that only high loads of MPPs might have some influence in decreasing the membrane permeability, although no decrease of the water quality was observed for any studied scenario. Some minor aging occurred for the MPPs, with the interesting *pinking* of some of the uPVC samples, but it was concluded that the aging of MPPs can be negligible in a DCMD system, although dependent on the resistance of the polymers to higher temperatures used in the process.

Keywords: Aging; Desalination; Contaminants of Emerging Concern; Membrane Distillation; Microplastics; Micropollutants; Sorption; Phytotoxicity.

Resumo

Os microplásticos foram reconhecidos como contaminantes de preocupação emergente durante a última década, o que levou ao acentuado aumento de investigação dedicada a este tema. Sendo uma área de investigação relativamente nova, várias questões continuam sem resposta, sendo fundamental explorar os vários tópicos que compõem esta linha de investigação de forma a encontrar soluções adequadas para este desafiante e complexo problema ambiental. Esta tese apresenta as principais ideias que foram exploradas e os resultados obtidos no projeto de doutoramento correspondente, realizado de fevereiro de 2018 a janeiro de 2023. No início do projeto foram definidos dois objetivos principais: i) examinar o comportamento dos microplásticos em relação ao seu envelhecimento no meio e interação com outros contaminantes, e ii) investigar o comportamento e atenuação de microplásticos durante a produção de água potável a partir de água do mar. Para isso, três polímeros foram selecionados na forma de microplásticos para o projeto: LDPE - polietileno de baixa densidade, PET - poli(tereftalato de etileno) e uPVC - poli(cloreto de vinilo) não plastificado.

Primeiro, o modelo DPSIR (sigla em inglês para forças motrizes, pressões, estados, impactos e respostas) foi aplicado à poluição por microplásticos, com a finalidade de organizar as principais informações disponíveis sobre esse tópico e determinar as necessidades de investigação que vieram a orientar as próximas etapas do projeto. A componente das respostas do modelo DPSIR foi explorada com mais detalhe, fornecendo uma revisão da literatura até ao primeiro semestre de 2019 sobre as soluções a montante (instrumentos regulatórios e políticas ambientais, educação ambiental, design de produtos e plásticos biodegradáveis, gestão de resíduos e tratamento de efluentes) e a jusante (biotecnologia, estações de tratamento de água, ações de limpeza ambiental, e outras tecnologias e estratégias de mitigação para o ar, solo e água).

O envelhecimento dos microplásticos foi avaliado após a exposição de partículas de microplásticos comerciais virgens (MPP) de LDPE, PET ou uPVC ao ozono, UV-C, radiação solar artificial e às condições climáticas observadas para um telhado de um edifício citadino. Isso permitiu investigar o envelhecimento de MPP sob ação de agentes presentes em ambientes urbanos e identificar as subseqüentes alterações na estrutura química (ATR-FTIR), morfologia de superfície (SEM) e cristalinidade (XRD). Adicionalmente, o Índice Carbonilo foi utilizado como métrica da oxidação dos MPP, levando à quantificação de algumas das alterações na estrutura química ao longo do tempo. Esta componente do projeto permitiu alargar o conhecimento sobre os agentes de envelhecimento mais eficazes para cada polímero e as conseqüentes modificações nos MPP, ao mesmo tempo que permitiu a obtenção de MPP envelhecidos para as experiências seguintes. Foi demonstrado que os agentes de envelhecimento estudados afetaram os microplásticos de várias formas, dependendo do polímero, com o LDPE a ser envelhecido por

todos os tratamentos (principalmente por ozono e no telhado), o PET presumivelmente envelhecido ligeiramente pelo ozono e no telhado, e o uPVC envelhecido sobretudo quando exposto aos tratamentos de UV-C e no telhado.

O passo seguinte centrou-se em estudos de interação dos MPP com outros contaminantes, nomeadamente com dez micropoluentes orgânicos (OMP) que incluem pesticidas (alaclor, ácido clofíbrico, diuron, pentaclorofenol) e substâncias farmacêuticas (citalopram, diclofenac, florfenicol, tramadol, trimetoprim, e venlafaxina). Através da realização de experiências de sorção com MPP virgens e envelhecidos (por ozono ou no telhado), foi possível explorar as cinéticas de sorção, isotérmicas de equilíbrio de sorção, e o papel do envelhecimento dos MPP nas suas capacidades de sorção. Esta componente do projeto evidenciou o papel determinante que o envelhecimento dos plásticos pode ter no processo de sorção de OMP em MPP, ao mesmo tempo que permitiu identificar a afinidade entre os polímeros e os OMP estudados, assim como relacionar as modificações identificadas para os MPP envelhecidos com o aumento da capacidade de sorção para OMP. Explorando a hipótese de que os MPP podem atuar como vetores de transporte de outros contaminantes, foram realizados testes de fitotoxicidade para avaliar a mobilidade dos OMP sorvidos nos MPP e os potenciais efeitos negativos do combo de MPP e OMP na germinação e crescimento inicial de duas espécies de plantas (*Lepidium sativum* e *Sinapis alba*). Os resultados sugerem baixos ou inexistentes efeitos de fitotoxicidade sob as condições testadas, fornecendo algumas informações sobre os potenciais efeitos da presença de MPP nos sistemas solo-planta.

A última componente do projeto explorou o comportamento e atenuação de MPP durante um tratamento de destilação por membranas, à escala laboratorial, nomeadamente através da tecnologia de destilação por membranas de contacto direto (DCMD). Foram selecionados MPP de uPVC para os ensaios de DCMD, com base em experiências previas de exposição dos vários materiais poliméricos a temperaturas mais elevadas em garrafas âmbar. Os ensaios de DCMD foram realizados com duas quantidades de MPP diferentes e com diferentes graus de envelhecimento, em água do mar filtrada. As modificações dos MPP foram avaliadas por diferentes técnicas de caracterização quanto à sua estrutura química (ATR-FTIR), absorção na gama do UV-visível e morfologia da superfície (SEM), enquanto os parâmetros mais importantes do sistema de DCMD (permeabilidade da membrana, gradiente de pressão de vapor, fluxo intervalar de permeado, recuperação de água, e condutividade e salinidade do permeado e retentado) foram analisados ao longo do tempo para explorar a possibilidade de que a presença de MPP pudesse diminuir a qualidade da água tratada e/ou a sua recuperação. Além disso, a água tratada foi analisada quanto à presença de MPP por microscopia Raman. Este estudo foi um dos primeiros a explorar o comportamento e atenuação de microplásticos durante um processo de DCMD, sugerindo uma eficiência muito alta ($\geq 99\%$) na remoção de MPP da água, e que apenas elevadas quantidades de MPP podem ter alguma influência na diminuição da permeabilidade da

membrana, embora nenhuma diminuição da qualidade da água foi observada para qualquer cenário estudado. Foi registado algum envelhecimento dos MPP, com o interessante *pinking* de algumas das amostras de uPVC, mas concluiu-se que o envelhecimento dos MPP pode ser insignificante num sistema DCMD, embora esteja intrinsecamente dependente da resistência dos polímeros às temperaturas mais altas usadas no processo.

Palavras-chave: Envelhecimento; Dessalinização; Contaminantes de Preocupação Emergente; Destilação por membranas; Microplásticos; Micropoluentes; Sorção; Fitotoxicidade.

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Glossary

ΔP	Vapor pressure gradient	kPa
Δt	Time interval	h
ΔW	Mass of the distillate	kg
λ	Wavelength	nm
$\tilde{\nu}$	Wavenumber	cm ⁻¹
ϕ_a	Amorphous area	
ϕ_c	Sum of crystalline peaks areas	
a	Temperature compensation factor	°C ⁻¹
A	Effective area of the membrane	m ²
	(Absorbance in chapter 3)	(n/a)
$adj. R^2$	Adjusted coefficient of determination	
B	Membrane permeability	kg m ⁻² h ⁻¹ kPa ⁻¹
C_0	Initial concentration	µg L ⁻¹
$C_{control}$	Concentration of each OMP in the control bottle	µg L ⁻¹
C_e	Concentration of the sorbate in the aqueous phase at equilibrium	µg L ⁻¹
C_{sample}	Concentration of each OMP in a sample bottle	µg L ⁻¹
CI	Carbonyl Index	
EC	Measured (uncompensated) conductivity	µS cm ⁻¹ or mS cm ⁻¹
EC_{25}	Compensated conductivity	µS cm ⁻¹ or mS cm ⁻¹
J	Permeate flux	kg m ⁻² h ⁻¹
k_1	Sorption rate constant of PFO	h ⁻¹
k_2	Sorption rate constant of PSO	g µg ⁻¹ h ⁻¹
K_d	Equilibrium distribution coefficient	L g ⁻¹
K_f	Freundlich sorption constant	(µg g ⁻¹)(L µg ⁻¹) ^{1/n}
K_l	Langmuir sorption constant	L µg ⁻¹
K_{ow}	Octanol-water partition coefficient	
m	Mass of MPPs added to each bottle	g
$1/n$	Exponential term of Freundlich model	
PI	Polyene Index	
P^v	Water vapor pressure	mmHg or kPa
$q (q_e)$	Sorption capacity (at equilibrium)	µg g ⁻¹
q_m	Maximum sorption capacity of the material	µg g ⁻¹
q_t	Sorption capacity as function of the contact time	µg g ⁻¹
Q	Volumetric flow rate	mL min ⁻¹
R^2	Coefficient of determination	
RSS	Residual sum of the squares	
R_{wp}	Weighted profile residual of the Rietveld refinement	%
t	Contact/experiment time	h
T	Temperature (Transmittance in chapter 3)	°C (n/a)
V	Volume of the solution	L
X_c	Degree of crystallinity	%

List of abbreviations and acronyms

AZO	Anaerobic-Anoxic-Aerobic treatment/method
AGMD	Air Gap Membrane Distillation
ANOVA	Analysis of variance
AOP	Advanced Oxidation Process
APA	<i>Agência Portuguesa do Ambiente</i> (Portuguese Environmental Protection Agency)
ATR	Attenuated Total Reflection
BPA	Bisphenol A
BST	British Summer Time (UTC+1)
CAS	Conventional Activated Sludge
CEC	Contaminant of Emerging Concern
COVID-19	Coronavirus disease caused by the SARS-CoV-2 virus
Csb	Warm-summer Mediterranean climate (Köppen-Geiger classification)
DCMD	Direct Contact Membrane Distillation
DLaTGS	Deuterated and L-alanine-doped triglycine sulfate
DPSIR	Driving forces, Pressures, States, Impacts and Responses
DW	Distilled water
DWTP	Drinking Water Treatment Plant
EC	European Community
ECHA	European Chemicals Agency
EDC	Endocrine-disrupting Chemical
EEC	European Economic Community (Treaty of Rome)
EFSA	European Food Safety Authority
EN	European Norm (European Standard)
EQS	Environmental Quality Standards
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
FSW	Filtered seawater
FTIR	Fourier transform infrared
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
GMT	Greenwich Mean Time (UTC+0)
HDPE (PE-HD)	High-density Polyethylene
HPLC	High-Performance Liquid Chromatography
HVAC	Heating, ventilation and air conditioning
IPMA	Portuguese Institute for Sea and Atmosphere
IR	Infrared
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LDPE (PE-LD)	Low-density Polyethylene
MBR	Membrane Bioreactor
MD	Membrane Distillation
MDL	Method Detection Limit
Micro-FTIR/ μFTIR	FTIR Microspectroscopy
Micro-Raman/ μRaman	Raman microscopy (Raman microspectroscopy)

MPP	Microplastic particle
MQL	Method Quantification Limit
MSFD	EU Marine Strategy Framework Directive
NOAA	National Oceanic and Atmospheric Administration (U.S. Department of Commerce)
OECD	Organization for Economic Co-operation and Development
OMP	Organic micropollutant
PA	Polyamide (Nylon)
PC	Polycarbonate
PCP	Pentachlorophenol
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PFA	Perfluoroalkoxy
PFO	Pseudo-first-order model
PFOS	Perfluorooctane sulfonate
PHA	Polyhydroxyalkanoate
PLA	Poly(lactic acid)
PM	Particulate Matter
POP	Persistent Organic Pollutant
PP	Polypropylene
PS	Polystyrene
PSO	Pseudo-second-order model
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene difluoride)
PW	Purified water
Q-SUN	Xenon test chamber (accelerated weathering)
QUV	Q-panel laboratory ultraviolet (accelerated weathering) testing
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RIC	Resin Identification Code
RT	Rooftop (weathering experiments)
RT1	First tray of the RT weathering experiments (without rainwater)
RT2	Second tray of the RT weathering experiments (with rainwater)
SBR	Sequencing Batch Reactor
SD	Standard deviation
SDG	United Nations Sustainable Development Goal
SEM	Scanning Electron Microscopy
SGMD	Sweep Gas Membrane Distillation
SNIRH	National Water Resources Information System (for Portugal)
SPE	Solid-Phase Extraction
SRM	Selected reaction monitoring
SW	Unfiltered seawater
TDS	Total Dissolved Solids
TS	Temperature Stress
UHPLC-MS/MS	Ultra-high Performance Liquid Chromatography with tandem Mass Spectrometry
UK	United Kingdom
UNEP	United Nations Environment Programme

uPVC (PVC-U)	Unplasticized Poly(vinyl chloride)
UPW	Ultrapure water
USA / US	United States of America
US-EPA	U.S. Environmental Protection Agency
USDA	United States Department of Agriculture
UTC	Coordinated Universal Time
UV	Ultraviolet radiation
UV-Vis	Ultraviolet-visible
VAT	Value Added Tax
VMD	Vacuum Membrane Distillation
WFD	EU Water Framework Directive
WHO	World Health Organization
WWII	World War II (1939-1945)
WWTP	Wastewater Treatment Plant
XRD	X-ray diffraction

1. Introduction

1.1 Overview of the problematic and some knowledge gaps

The increasing abundance and dispersion of plastics in the environment and the better understanding of the resulting impacts have led to the rise of international concern among the public, policy makers and researchers. While the plastic waste polluting the environment has a variety of sizes, chemical compositions, and shapes, microplastics are of special concern because of the current knowledge gaps with respect to the chemical and physical adverse effects on organisms, their distribution, mobility and fate in the different environmental compartments, and the necessary adequate responses to solve this environmental issue.

Consequently, the number of initiatives, regulatory and policy instruments, and scientific publications (GESAMP, 2015) on microplastics had a close to exponential growth in the last decade. Regarding the specific interest of the scientific community on this topic, the trend can be illustrated by Fig. 1.1, which gives the results until 2022 of the search (article title, abstract, keywords) for “Microplastics” on 9th January 2023 on the Scopus database (limited to articles, reviews and book chapters).

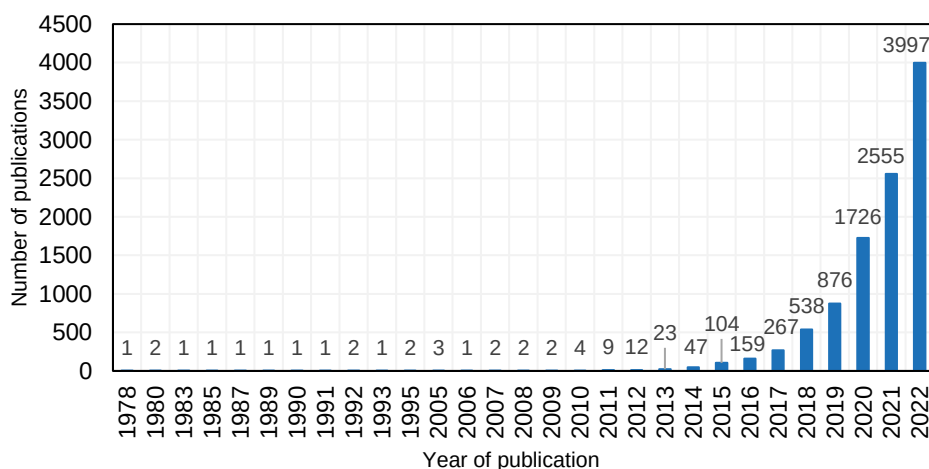


Fig. 1.1. Scopus search on 9th January 2023 on “Microplastics” (1978-2022).

The present PhD thesis project started in 2018, at a time when there was still limited and insufficient data on all the specific research topics within the microplastics field of research, and when most of the articles reported results from monitoring campaigns or individual

assessments on the quantity and type of microplastics present in the environmental compartments, mainly in water and mostly focused on the marine ecosystems although with increasing interest for other aquatic and terrestrial environments in the most recent years (Chapter 2). In parallel, there was an important focus on developing adequate analytical methods to analyze the microplastic (and nanoplastic) pollution in different matrices. Since then, there has been a gradual shift into more fundamental science regarding the behavior and impacts of the microplastics, while also looking into potential responses in order to attenuate the global challenge of the increasing plastic waste in the environment. Nonetheless, as of the end of 2022, the monitorization of microplastics is yet to be included in national programs and there are still regulatory gaps. Therefore, all the reports on the microplastics abundance and characteristics continue to be fundamental in giving enough data to understand the sources and evolution of the current state of the issue, and, therefore, in promoting responses from the policy makers and from the population all over the world.

1.1.1 Plastics: from solution to problem

Plastics are defined by ISO/TR 21960:2020 as a “material which contains as an essential ingredient a high polymer and which, at some stage in its processing into finished products, can be shaped by flow” and has “minor contents of additives”. Also, according to ISO, elastomeric materials, which are also shaped by flow, are not considered to be plastics, and plastics comprise both thermoplastic and thermoset materials. The same document defines polymer as “chemical compound or mixture of compounds consisting of repeating structural units created through polymerization”, comprising both plastics and elastomers.

Some polymers exist naturally, such as cellulose (cell walls of plants), latex (rubber trees and found in a variety of plants) or starch (grains, cereal and potatoes). However, the first synthetic polymer, parkesine (1855), was invented by treating cellulose by Alexander Parkes and later improved by John Wesley Hyatt (1869), leading to the currently known celluloid and responding to an industry challenge to find a substitute for ivory (PlasticsEurope, n.d.; Science History Institute, n.d.). Ivory was, at the time, a highly used and extracted resource for billiards, leading to the slaughter of wild elephants. Other important developments at the time were the rubber technology development with the vulcanization process in the 1820s and the invention of the injection molding in 1872 by the Hyatt brothers (British Plastics Federation, n.d.).

The first fully synthetic polymer and mass-produced plastic, bakelite, was invented later, in 1907, by Leo Baekeland, and opened a new world to the chemical industry with the search for new and better plastics in the following years until today. A significant growth of the plastic industry happened during and after the World War II, since there was a need to preserve scarce

natural resources, with plastics providing adequate substitutes and even improvements for both warfare and daily life applications (Science History Institute, n.d.). After learning and keep discovering new applications for plastics, there was no turning back and the plastic industry kept growing during the following decades.

This growth of the plastic production can be illustrated by Fig. 1.2, which shows the world plastic production (1950-2020) as estimated in the Plastics Europe annual reports (PlasticsEurope, 2021) that include data for thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants. Poly(ethylene terephthalate)-fibers, polyamide-fibers, polypropylene-fibers and polyacryl-fibers are not included, with the exception for 2016-2020 that include polypropylene-fibers. The data for 2021 was not included in Fig. 1.2 since, in the last report (PlasticsEurope, 2022) the polymers not used in the conversion of plastic parts and products are excluded (i.e., for adhesives, sealants, coatings, paints, varnishes, or within the production of cosmetics, medicines or chemicals processes) and post-consumer recycled and bio-based or bio-attributed plastics production quantities are included for the first time. For 2021 it was estimated a global plastic production of 390.7 Mton, of which 352.3 Mton are fossil-based, 32.5 Mton are post-consumer recycled, and 5.9 Mton are bio-based or bio-attributed (PlasticsEurope, 2022).

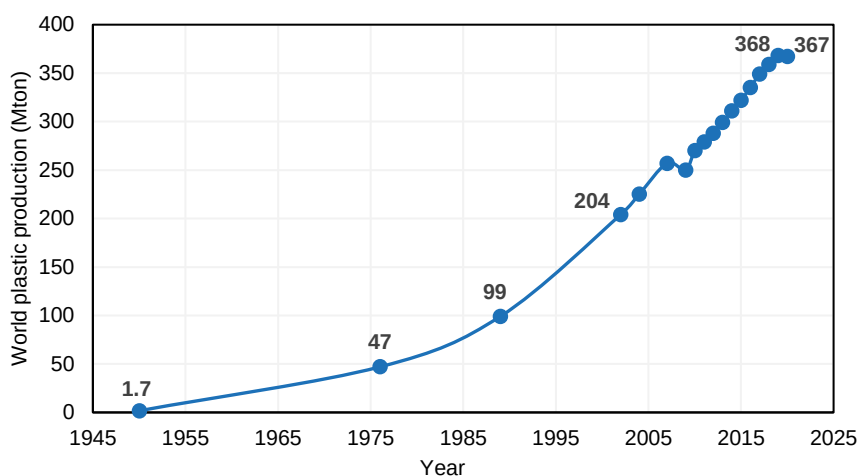


Fig. 1.2. World plastic production from 1950 to 2020
(updated from Miranda et al. (2020) with Plastics Europe 2021 report data).

With a history of more than 100 years, for most of those years, plastics have been regarded as an important revolution to humankind, a way to protect the natural resources and ecosystems from the Human need for progress, and as durable, malleable, lightweight, and cheap (with both good and bad connotation) material that changed for better the way we live. However,

humankind has become dependent on plastics and the excess of their use, lack of regulation or mismanaged disposal, plastic aging with its fragmentation, leaching of plastic additives, and their persistence and accumulation in the environment lead to the plastic pollution problem we face today.

Plastic reputation started to change during the growing environmental consciousness that came with the rise of the environmental movement in the 1960s, and further decreased in the following decades due to the accumulation of waste (Science History Institute, n.d.). In 1972, a paper was published in *Science* reporting weathered plastic particles polluting the Sargasso Sea and raising awareness to the risk of increasing concentration of these particles in the future (Carpenter and Smith, 1972). However, it was only much later that the plastic pollution shocked the world into action.

In the 1990s, people started to be concerned about the potential health hazard of using plastic containers for food and beverage applications when some studies pointed out that bisphenol A (BPA), among other compounds, might have negative effects. BPA is a synthetic organic compound widely used since the 1950s in the production of polycarbonate and epoxy resins. The use of BPA raised concern because it can leach out of the plastic containers into the food or drinks, therefore leading to a dietary intake of BPA, while being a proven endocrine-disruptor (Hahladakis et al., 2023). While there has been controversy regarding the safety of its use, there were calls for it to be restricted or even banned. Currently, the European Food Safety Authority (EFSA) and the European Chemicals Agency (ECHA) are re-evaluating the data, which could lead to the phase-out and ban of BPA in the EU market in the future (EFSA, n.d.; European Commission, 2022a). However, it is still permitted for use in food contact materials in the European Union (EU) under Regulation 10/2011 (European Commission, 2011a), with some restrictions set by Directive 2011/8/EU and Regulation 2018/213.

Finally, plastic pollution, from macro to nano, became one of the most pressing environmental issues in the 2010s, after photographs and video documentaries reached the world population and raised awareness to the state and impacts of this environmental problem, particularly concerning marine litter and how it was affecting wildlife in the oceans. In this last decade, there have been several advances regarding not only the knowledge on the topic, but also the upstream and downstream responses to attenuate plastic pollution (Section 2.6). While plastics are unquestionably important and difficult to replace in certain applications, such as for electronic components, engineering and mechanical parts in vehicles, and medical equipment, the recognition of the consequences of their use calls for a paradigm shift in order to achieve a more sustainable production, use and disposal of plastics.

1.1.2 Microplastics definition

Microplastics are considered as one of the newest contaminants of emerging concern (CECs), but there is still a lack of consensus among the scientific community regarding microplastic multiple aspects, even including the definition of what is the size range for microplastics. Commonly, microplastics have been considered as plastic particles or fibers whose longest diameter or length is less than 5 mm, but different lower limits of the analyzed particles have been reported in the literature. This results mainly from the diversity found in the field and laboratory methods applied, since there is a lack of standardized methods for microplastics identification, quantification and characterization, and because collecting and identifying the plastic nature of such small particles (particularly those under 1 μm) is currently a challenge. For example, marine microplastic studies frequently report microplastics with a particle size range from 333 μm to 5 mm, because Neuston nets with 333 μm mesh are commonly used when sampling microplastics (Arthur et al., 2009; Law and Thompson, 2014).

The highest limit (5 mm) was defined by the US National Oceanic and Atmospheric Administration (NOAA) (Arthur et al., 2009) and is the result of marine litter policy. Nanoplastics, the size-based category below microplastics, are usually defined to include plastic particles with one or more external dimensions with a size ranging from 1 to 100 nm, supporting this size classification on the European Commission nanomaterials definition (European Commission, 2011b). Consequently, several researchers consider the microplastics size range to be 100 nm - 5 mm (Costa et al., 2016). However, due to the increasing challenge with the identification of the polymeric nature of smaller particles, particularly under 1 μm , many researchers have been making the division from micro to nanoplastics at that size. According to ISO/TR 21960:2020:

- Macroplastics are “any solid plastic particle or object insoluble in water with any dimension above 5 mm”;
- Large microplastics are “any solid plastic particle insoluble in water with any dimension between 1 mm and 5 mm”;
- Microplastics are “any solid plastic particle insoluble in water with any dimension between 1 μm and 1 mm”;
- Nanoplastics are “plastic particles smaller than 1 μm ”.

More recently, ECHA and the European Commission proposed in 2022, as part of the draft regulation of intentionally added microplastics in the EU, that microplastics are particles (including fiber-like particles) containing a solid polymer, to which additives or other substances may have been added, and the particles have i) all dimensions in the range $0.1 \mu\text{m} \leq x \leq 5 \text{ mm}$, or ii) a length of $0.3 \mu\text{m} \leq x \leq 15 \text{ mm}$ and length to diameter ratio of > 3 (European Commission and European Chemicals Agency, 2022). Nevertheless, the same document considers that plastic

particles below 0.1 μm pose an equivalent or potentially higher risk to the environment than particles in the size range covered by the above definition. However, these lower limits for particles and fibers now proposed are a consequence of the current analytical constraints in the identification and quantification of particles below 0.1 μm .

Therefore, over the last decade, there has been a lack of consensus on the size-based classification of the plastic particles in the environment by the scientific community. In this thesis, if not specified, microplastics are considered to be plastic particles or fibers whose longest diameter or length is below 5 mm, based on the generally accepted NOAA definition. For the examples explored in the literature review and for the microplastics used in the experimental component of the thesis, the lower limit or size distribution is specified whenever possible to better understand and compare the results.

1.1.3 Contaminants of emerging concern

Contaminants of emerging concern (CECs) - also known as emerging pollutants - encompass a diversified group of substances that, as defined by Directive 2013/39/EU (The European Parliament and the Council of the European Union, 2013), are “currently not included in routine monitoring programs at Union level but which could pose a significant risk requiring regulation, depending upon their potential ecotoxicological and toxicological effects and on their levels in the aquatic environment”. Overall, the CEC classification covers original compounds, metabolites or transformation products that: i) were introduced into the environment recently (e.g., new synthetic industrial compounds), ii) only recently were recognized as potentially harmful for ecosystems, even if identified and quantified before in the environment, or iii) recently were detected due to the advances in analytical techniques, even if present in the environment for some time.

Several compounds have been classified as such over the years, like certain pesticides, pharmaceuticals, nanomaterials, and personal care products, among others (Aryal et al., 2020; Brack et al., 2017; Silva et al., 2020). More recently, this classification was also applied to microplastics due to the increasing knowledge on their abundance, dispersion, persistence, and impacts in the environment (not limited to the aquatic environment) over the last decade (Lambert and Wagner, 2018; Souza Machado et al., 2018; Sridharan et al., 2021; The European Parliament and the Council of the European Union, 2020a). Indeed, the 2022 proposal for an European Union (EU) revised Urban Wastewater Treatment Directive states that “the limit values for the treatment of some pollutants are now outdated compared to technical progress made since 1991 and new pollutants have emerged such as micro-plastics or micro-pollutants, which can be harmful for the environment or public health already at very low level of concentration”

and that “the scientific community, policy makers and the general public see the growing evidence of contaminants of emerging concern, including micro-pollutants such as pharmaceuticals and micro-plastics in water bodies, as an increasingly important issue” (European Commission, 2022b). Consequently, as part of article 17, it is proposed that the member states shall monitor the presence of the several public health parameters in urban wastewater, including CECs (European Commission, 2022b).

1.1.3.1 Organic micropollutants and EU Watch List

Organic micropollutants (OMPs), a group of organic pollutants found at trace concentrations from ng L^{-1} to $\mu\text{g L}^{-1}$ (Stamm et al., 2016), raised concern due to their pseudo-persistence since the conventional treatment technologies were not designed to eliminate them before they enter the environment, as happens for most CECs (Morin-Crini et al., 2022). Specifically, the EU has been developing regulations to cope with the presence of OMPs in the environment. Some OMPs are already classified as priority substances in the field of water policy by Directive 2008/105/EC, amended by Directive 2013/39/EU (The European Parliament and the Council of the European Union, 2013, 2008a), and have environmental quality standards (EQS). However, many are classified as CECs.

Considering the lack of monitoring data for many CECs and the need for a prioritization process to respond more efficiently to this issue, the EU created a dynamic Watch List for a limited number of substances to be temporarily included in, until enough quality information is collected for a further risk assessment and a possible update in the list of priority substances. The three previous editions of the EU Watch List (EU Decision 2015/495, EU Decision 2018/840, and EU Decision 2020/1161) and the current one (EU Decision 2022/1307) include synthetic and natural hormones, non-steroidal anti-inflammatory drugs, antidepressant and antihyperglycemic drugs and their metabolites, antibiotics, antioxidants, insecticides, fungicides, herbicides, and sunscreen agents (European Commission, 2022c, 2020a, 2018a, 2015a). The complete list of substances included in each version of the EU Watch List can be found in Appendix B.

1.1.4 Microplastic behavior in the environment

While microplastics stand out as a threat on their own to the environment and to the public health, it has been acknowledged that they can have increased negative effects because they may act as vectors for the transport of co-occurring contaminants and microorganisms (Auta et al., 2017a; Vieira et al., 2021; F. Wang et al., 2018). Consequently, over the recent years, one of the lines of research in the field of microplastics has been dedicated to understanding their

affinity to sorb other pollutants (e.g., heavy metals and/or organic compounds such as pesticides, pharmaceuticals and personal care products) and then release them when in contact with the organisms' tissues, evaluated with sorption/desorption and ecotoxicological studies (Jiang et al., 2020; F. Wang et al., 2018; Zhang et al., 2019).

The polymer's own characteristics, such as chemical composition, density, crystallinity, oxidation resistance or weatherability, biodegradability, and surface properties, influence the behavior of the microplastic particles (MPPs) in the environment (Andrady, 2017; Singh and Sharma, 2008). Furthermore, it is known that plastic in the environment differs from virgin plastic because: i) it undergoes aging (including weathering and consequent fragmentation), ii) additives are added during the plastic item production, iii) pollutants can be sorbed by the plastic, and iv) there is the possibility of biofilm formation on the surface of the particles (Andrady, 2003; Vroom et al., 2017; Wang et al., 2020).

The interest in the interactions between plastic and organic or inorganic substances is older than the upsurge of microplastics research. Examples include the assessment of different plastics as adequate materials to use for field and laboratory equipment, considering their potential to influence certain analyte concentrations (Hebig et al., 2014; Papiernik et al., 1996), and the use of plastics for medical applications, such as wound dressings host materials (Devetak et al., 2014). However, this research line was focused on their sorption capabilities during their designed lifetime. Such studies did not consider their end-of-life as plastic litter, particularly microplastics with physical and chemical properties that differ from the original plastic due to their modifications through time related to their aging in the environment (Deng et al., 2022; Fotopoulou and Karapanagioti, 2017; Menzel et al., 2022).

The number of publications on microplastics sorption of chemical pollutants had a high growth, particularly since 2015, as detailed in Table 1.1, which lists the raw results of specific search terms related to this PhD work in the Scopus database (20th January 2022). Multiple combinations of different polymers and sorbates have been studied so far, with the conventional plastics being the most studied (particularly polyethylene, polypropylene, and polystyrene) and organic sorbates being more explored, although there are several reports on heavy metals (Agboola and Benson, 2021; Alimi et al., 2022; Liu et al., 2022). Most studies have been conducted with virgin (i.e., new, direct resin produced from the feedstock, without any recycled materials) or pristine (i.e., after production, unused) microplastics, whereas studies performing aging treatments (including weathering), using biofilm-developed microplastics, or using environmental samples, for sorption and/or effect studies, are still insufficient (Alimi et al., 2022; Ding et al., 2022; Guo and Wang, 2019; Hanun et al., 2021; Liu et al., 2020b; Wang et al., 2021).

Table 1.1. Search results in Scopus database (accessed on the 20th January 2022).

Search terms (article title, abstract, keywords)	Years	Number of papers (and references when searching for individual micropollutants) *
microplastics AND sorption OR adsorption OR absorption	1992-2022	863 (<i>distribution by year</i> : 1992:1; 2010:1; 2011:2; 2012:1; 2014:6; 2015:6; 2016:18; 2017:21; 2018:54; 2019:101; 2020:234; 2021:341; 2022:77)
microplastics AND pharmaceuticals OR pesticides	2009-2022	223
microplastics AND pharmaceuticals	2013-2022	113
microplastics AND pesticides	2009-2022	142
microplastics AND heavy metals	2014-2022	366
microplastics AND micropollutants	2012-2022	62
microplastics AND alachlor		0
microplastics AND citalopram		0
microplastics AND clofibric acid		0
microplastics AND diclofenac	2020-2022	8 (Álvarez-Ruiz et al., 2021; Busch et al., 2021; Elizalde-Velázquez et al., 2020 ; Li et al., 2022; Mora et al., 2021; Munoz et al., 2021; Picó et al., 2020; Zhao et al., 2021)
microplastics AND diuron	2020-2021	2 (Godoy et al., 2020 ; Torres and De-la-Torre, 2021)
microplastics AND florfenicol	2018-2021	5 (Guilhermino et al., 2018; Han et al., 2021; Lu et al., 2020; Zhou et al., 2021, 2020)
microplastics AND pentachlorophenol	2019-2020	2 (Loncarski et al., 2020 ; Tubić et al., 2019)
microplastics AND tramadol	2020-2022	2 (Picó et al., 2020; Wagstaff et al., 2022)
microplastics AND trimethoprim	2018-2021	6 (Arias-Andres et al., 2018; Aryal et al., 2020; He et al., 2021; Jia Li et al., 2018; Santana- Viera et al., 2021; Tang et al., 2021)
microplastics AND venlafaxine	2018-2022	3 (Qu et al., 2019, 2018; Yao et al., 2022)

*The most relevant studies (i.e., reporting sorption experiments) are in bold.

1.1.5 Microplastics in drinking water treatments from seawater sources

Although the risk of microplastics and nanoplastics to human health is yet to be established (Sharma et al., 2022; World Health Organization, 2022), the growing amount of reports related to the detection of plastics in food (Garrido Gamarro and Costanzo, 2022; Mamun et al., 2023), beverages (Paul et al., 2020; Sewwandi et al., 2023), air dust (Prata et al., 2020; Soltani et al.,

2022) and on human tissue and biological samples (Kutralam-Muniasamy et al., 2023; Leslie et al., 2022; Ragusa et al., 2022) has been rising concern to their potential toxicological impacts to our species (X. Yang et al., 2022). In particular, the microplastics presence in drinking water is of major importance due to its universal and daily consumption.

The World Health Organization (WHO) identified several data gaps and the highest priority research needs regarding this topic, which include the development of standard methods for microplastics sampling and analysis, more studies on the occurrence and characteristics of microplastics in drinking water, and more data that have to be obtained on the occurrence and fate of microplastics throughout the water supply chain (World Health Organization, 2019). This last research need calls for the analysis of microplastics behavior in the water supply chain, the effectiveness of the water treatments applied, and the microplastics occurrence from the source of raw water to the distribution system or bottling.

Since then, several studies have been published in line with those needs, especially focused on drinking water treatment plants (DWTPs), pipe distribution systems (Mohammadi et al., 2022) and bottled and tap drinking water obtained from surface freshwater or groundwater sources, with seawater receiving far less attention (Gambino et al., 2022; Xue et al., 2022). The most common technologies for the removal of particulate matter and/or organic matter have been reviewed and include coagulation-flocculation and sedimentation, membrane filtration (ultrafiltration, microfiltration and reverse osmosis), and media filtration (sand and granular activated carbon) (Tang et al., 2022; Xue et al., 2022). These studies demonstrate that conventional and advanced DWTPs can remove most of the microplastics from water, but there is still a need for more studies to enhance even more the efficiency of the current drinking water treatment processes (Xue et al., 2022) or to develop new and improved technologies.

Drinking water production from seawater has an important role in reaching the United Nations Sustainable Development Goals (SDGs), and in particular the goal for clean water and sanitation. Considering the need to address drinking water scarcity and the increasing challenge of dealing with more frequent droughts and desertification related to climate change, the development of more and better desalination plants is a crucial step in many regions of the world, with the aim to ensure safe and affordable drinking water supply for the increasing population, without being exclusively dependent on surface freshwater and/or groundwater supply sources.

However, there is a knowledge gap on microplastics behavior and removal during desalination processes, with a search on the Scopus database on 21st of December of 2022 surprisingly giving 7 results only, when searching the article title, abstract and keywords of the documents for “desalination AND microplastics”. Of those documents, some only briefly refer to desalination plants as part of the plastic pollution issue, such as Llorca et al. (2020). Yaranal et al. (2021) reported for the first time the removal efficiency of microplastics from synthetic seawater using

hollow fiber microfiltration membranes, with 99.3% success as assessed using Raman microscopy. Almainan et al. (2021) analyzed tap water sourced from desalinated seawater in Saudi Arabia, revealing low levels of contamination (< 1.8 microplastics L^{-1}) when samples were analyzed by FTIR microscopy. Pérez-Reverón et al. (2022) analyzed, also by FTIR microscopy, brackish water in a desalination plant in Fuerteventura (Canary Islands, Spain) that was treated by filtration with cartridges filters, dual membrane reverse osmosis and chlorination. In this study, the 2.0 ± 2.0 items L^{-1} detected are hypothesized to be contaminations after the treatment and during water storage.

In parallel, the Scopus search for “membrane AND distillation AND microplastics” only gives 2 results, one of them available in Chinese language (Kong et al., 2021) and the other being a review article on fouling mitigation in membrane separation processes (El Batouti et al., 2021). Membrane distillation is a thermally driven separation technology in which water can be extracted from the feed stream through a hydrophobic microporous membrane due to the vapor pressure gradient that is established across the membrane. While there are other processes that can be used for water desalination, membrane distillation offers several benefits, such as a relatively low operating pressure, when compared to pressure-driven membrane processes like ultrafiltration or reverse osmosis, and as consequence resulting in lower equipment costs and increased process safety (Nagy, 2019). Another benefit is the water high separation efficiency, which can theoretically reach 100%, removing undesired substances, particulate matter, and microorganisms. As drawback, membrane distillation needs energy to power the heat and refrigeration sources, although renewable sources of energy can be used to have a more environmentally friendly process (e.g., geothermal or solar energy). Additionally, membrane fouling, pore wetting, and mineral scaling can pose some problems depending on the feed stream (Horseman et al., 2021), and the process concentrates some undesired compounds in the retentate (as other membrane processes), and does not eliminate them. However, the last disadvantage can be turned into a benefit if one or more undesired compounds with commercial value can be extracted and isolated from the retentate.

1.2 Thesis objectives and selection of microplastics

Taking into account the state of the art at the beginning and during the PhD project, the research goals were defined in order to contribute to fill some of the knowledge gaps in the field of microplastics. To that end, from February 2018 to January 2023 studies were conducted to enlighten the behavior of microplastics in different environmental compartments, in particular regarding their aging and interaction with co-occurring contaminants such as organic

micropollutants, and to analyze their behavior and attenuation when applying water treatment technologies used in desalination processes.

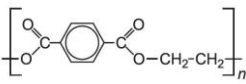
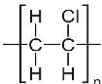
The main goals that the PhD project aimed to achieve were:

- 1) Increase the current knowledge on microplastics behavior under different environmental conditions: their physicochemical and biological interactions, mobility and fate. Under this goal, there are two main subjects under study:
 - a. Microplastics aging and degradation mechanisms in urban environments due to exposure to solar radiation, advanced oxidation processes (AOPs) such as those using ozone and UV radiation, and other weathering and erosion processes. The modified microplastics, under laboratory-controlled conditions, were characterized in order to identify their modifications, but also used for the second part of this goal. Aimed progress: deepen the existing knowledge on microplastics characteristics and sorption potential after aging, by simulating their degradation under environmental conditions and specific treatment technologies lacking evaluation.
 - b. Microplastics interaction with co-occurring contaminants, namely organic micropollutants. The microplastic particles tested, through sorption batch experiments, include both virgin microplastic samples and the microplastics obtained after aging treatments. Aimed progress: the identification of key contaminants that co-occur with microplastics and have higher affinity to be sorbed on them, potentially increasing their impacts on biota and human health.
- 2) Study of microplastics attenuation in drinking water production from seawater sources. This goal also includes the study of the behavior, primarily the potential aging, of microplastics during desalination processes such as membrane distillation. Aimed progress: understand the microplastics behavior in one very poorly studied scenario, and how desalination treatments fare at keeping microplastics from the treated water and how they are affected by the presence of microplastics in the system feed stream.

For the duration of the PhD project, three polymers were selected and enough microplastics of those polymers were acquired at the beginning of the experimental component of the project in order to achieve the above identified goals. The selected polymers (Table 1.2) are three of the most used plastics that are consistently found as pollutants in the environment (Geyer et al., 2017; Jones et al., 2020; Zhang et al., 2022): LDPE - low-density polyethylene, PET - poly(ethylene terephthalate), and uPVC - unplasticized poly(vinyl chloride). Additionally, it was identified at the beginning of the PhD project that PET was much less studied concerning aging

and sorption experiments than polyethylene, polypropylene, and polystyrene. LDPE was selected since it is the polymer that produces globally more waste (Geyer et al., 2017) and, because being one of the most studied, allows to compare the results obtained with the literature. Finally, with the selection of uPVC, the three polymers have, in theory, different levels of resistance to different aging stressors, giving a better representation of the variety of polymers that contribute to the microplastic pollution in the environment.

Table 1.2. Selected polymer for the PhD project.

Characteristic	Low-density polyethylene (LDPE)	Poly(ethylene terephthalate) (PET)	Unplasticized poly(vinyl chloride) (uPVC) ¹
Resin identification code (RIC)			
	$(C_2H_4)_n$	$(C_{10}H_8O_4)_n$	$(C_2H_3Cl)_n$
Chemical structure			
Type	polyolefin, thermoplastic, fossil-based or bio-based	polyester, thermoplastic, fossil-based or bio-based	thermoplastic, fossil-based or bio-based
Developed	1933	1940s	1838/1872/1913 ²
Main applications	packaging, agricultural film	textile, packaging	building applications such as pipe, and window/door frames

¹ Unplasticized PVC, also known as rigid PVC. If plasticizers, such as phthalates, are added is known as flexible PVC and has other applications.

² PVC was unofficially first discovered in 1838/1872, but it was only patented in 1913.

1.3 Thesis outline

The present thesis compiles and presents the results obtained during the PhD project, being organized in 6 chapters.

Chapter 1: This first chapter provides a general introduction to the topic, identifies some research gaps based on the state-of-the-art, and states the objectives of the work.

Chapter 2: The second chapter includes a review of microplastic pollution structured as the DPSIR framework. The “responses” component of the DPSIR is developed further than the rest, providing the state-of-the-art at the beginning of the PhD on the available or under development upstream and downstream responses to microplastic pollution. An additional section was added to this chapter (Section 2.8), to evaluate and reflect the developments and highlights that occurred from 2019 to 2022 and that were not included in the review.

Chapter 3: The third chapter is aligned with the first goal of the thesis and explores the microplastic aging under urban environment stressors, particularly regarding the modifications in the chemical structure, surface morphology and crystallinity.

Chapter 4: The fourth chapter is a direct continuation of the previous and, through sorption batch experiments, explores the role of the plastic aging degree on the potential sorption of organic micropollutants by microplastics, identifies affinities between the selected polymers and ten organic micropollutants, which include pharmaceutical substances and pesticides, and analyzes the potential of microplastics behaving as transport vectors for organic micropollutants, particularly for soil-plant systems through phytotoxicity tests.

Chapter 5: The fifth chapter is aligned with the second goal of the thesis. It uses some of the knowledge acquired in the previous ones to study a more applied scenario for microplastics, namely for desalination processes using membrane distillation for drinking water production. In this chapter, the direct contact membrane distillation (DCMD) technology is explored on the subject of microplastics behavior during desalination treatments and how the technology performs when microplastics are present.

Chapter 6: The final chapter includes the main conclusions of the thesis and recommendations for future work on the specific topics studied.

Some of the work included in the thesis is based on manuscripts already published within the scope of the PhD project, namely chapters 2 to 4.

The dissemination of results, all references, and appendices are located at the end of the thesis.

2. A DPSIR analysis on microplastic pollution in the environmental compartments



This review organizes key information about microplastic pollution through a DPSIR (driving forces, pressures, states, impacts and responses) analysis, namely the current knowledge on the sources of microplastics in the environment, the abundance, mobility and fate of microplastics distributed across the different environmental compartments, as well as their socio-economic and environmental impacts. The available or developing upstream and downstream responses to the microplastic pollution are also reviewed as part of the DPSIR analysis. These include the regulatory and policy instruments, environmental education campaigns, product design, the development of biodegradable plastics, environmental cleanups, waste management, drinking water and wastewater treatment plants, and other treatment technologies and processes. Whenever possible, the current trends and discerning gaps in the research conducted so far by the scientific community are identified, giving some clues to what is going to be the future research on this topic and into new lines of research.



This chapter is based on the following reference (original version available online as indicated in the thesis section “Dissemination of results”), and in accordance with the Elsevier copyright permission guidelines that state that “authors can include their articles in full or in part in a thesis or dissertation for non-commercial purposes”:

Miranda, M. N., Silva, A. M. T., & Pereira, M. F. R. (2020). Microplastics in the environment: A DPSIR analysis with focus on the responses. *Science of The Total Environment*, 718, 134968. <https://doi.org/10.1016/j.scitotenv.2019.134968>

2.1 Introduction

The present chapter explores the research topic of microplastics in the environment through a DPSIR analysis and a literature review of potential responses to this problematic, including the analysis of the treatment technologies and processes that are currently being applied or in development to attenuate the microplastics impacts and reduce their pervasive nature and global dispersion. With that purpose, the literature was covered until the first half of 2019. Therefore, this chapter captures an overview state of the art on microplastic pollution in the different environmental compartments at the beginning of the PhD project and was the main source of inspiration for the research questions that were tackled with the experimental component of the PhD project in the following years, which are explored in the remaining chapters. Because there were several developments and new findings between this literature review and 2023, a supplementary section (2.8) was added to this chapter with some highlights for that period.

As stated, in order to organize key information about microplastics in the environment, this review is structured as a DPSIR analysis. DPSIR stands for driving forces, pressures, states, impacts and responses, and it is the causal framework adopted by the European Environmental Agency to describe the interactions between society and the environment. This analysis can be used to express a complex environmental problem by establishing simple causal relations. Social and economic developments exert pressure on the environment and, as a consequence, the environment state changes. This leads to impacts on the human health and activities as well as on ecosystems, what may stimulate a societal response that acts on the driving forces, pressures, state and/or impacts, in order to adapt to or mitigate the problem (Smeets and Weterings, 1999).

The Fig. 2.1 summarizes the DPSIR analysis applied to microplastic pollution and can be used as a supporting schematic to the remaining discussion in this chapter. As shown, the analysis was used to organize key information on microplastic pollution, reviewing the current knowledge on the driving forces, pressures, states, impacts, and responses. It should be noted that a much more extensive literature review was done for the responses to the microplastic pollution, taking into consideration both the goals set for the PhD project but also the urgent need for solutions to this environmental problem.

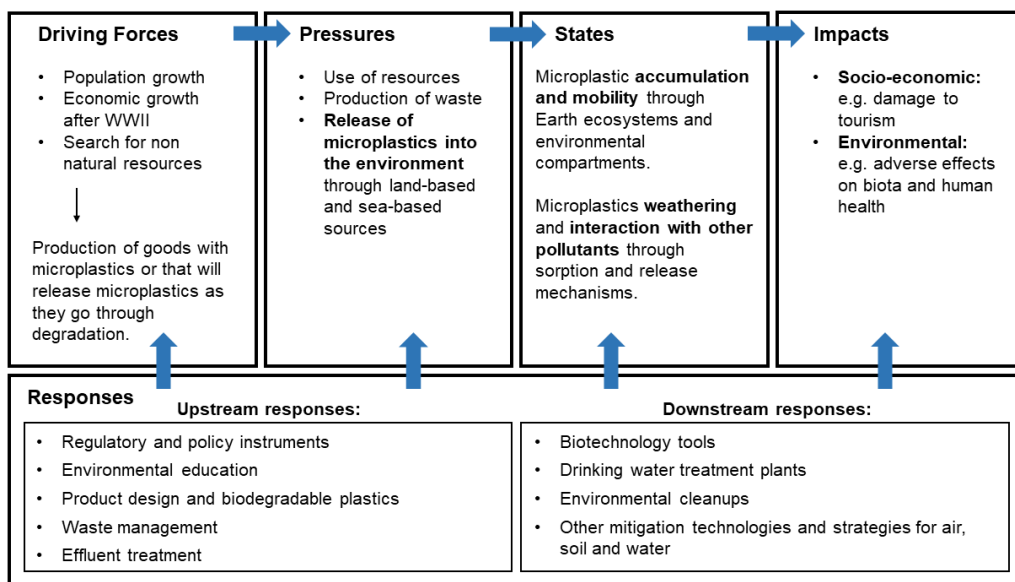


Fig. 2.1. DPSIR analysis for microplastic pollution.

2.2 Driving forces

Plastics are one of the most popular materials in modern times. They are widely used in a variety of economic sectors (packaging - the largest market, construction, transportation, healthcare, agriculture and electronics, among others) and are almost unavoidable in every household and goods. Since the development of the rubber technology in the 19th century, several polymers and chemical additives have been developed and improved for increased mechanical strength and weight reduction, among others (Wagner and Lambert, 2018). The plastics that currently dominate the market are: poly(ethylene terephthalate) (PET), polyethylene (PE) of high and low density, poly(vinyl chloride) (PVC), polypropylene (PP), polystyrene (PS) and polyurethane (PUR) (GESAMP, 2015). The appeal of plastics comes from a combination of characteristics such as low cost, versatility, durability and resistance, what led to an exponential growth of the plastic industry production since the World War II (World Economic Forum et al., 2016) (Chapter 1 - Fig. 1.2). Moreover, the Plastics Europe 2018 report estimated that the world plastic production, excluding fibers of PET, polyamide (PA) and polyacryl, increased from 335 to 348 million ton from 2016 to 2017, of which 64.4 million ton correspond to the European production in 2017, the second largest producer behind China (PlasticsEurope, 2018).

Microplastics can be manufactured as such (e.g., in cosmetic products), fitting into the primary microplastics category. The secondary microplastics are formed from the degradation and

fragmentation of larger plastic materials. Therefore, in order to better understand the microplastic pollution, it is necessary to analyze not only the direct sources of microplastics into the environment, but also all plastic waste that is not currently disposed of and the plastic materials that, through use, release microplastics.

2.3 Pressures

The increase in plastic production led to the pressure of a higher input of microplastics into the environment through a variety of sources. These microplastic sources are frequently classified as land-based or sea-based, particularly because the engagement on microplastic pollution gained significantly more momentum with the recognition of the marine litter problem. Nevertheless, it is a valid classification for the microplastic pollution as a whole. The main microplastic sources are listed in Table 2.1.

Some studies try to quantify the environmental input behind each source or a combination of (micro)plastics sources, particularly into the ocean. Jambeck et al. (2015) estimated that about 4.8 to 12.7 million metric tons of land-based mismanaged plastic waste entered the ocean, from a total of 275 million metric tons plastic waste generated in 192 coastal countries in 2010. In parallel, it is estimated a global release of 1.5 million tons per year of primary microplastics into the ocean, in a projection that ranges from 0.8 to 2.5 million tons per year depending on whether or not an optimistic or pessimistic scenario is adopted (Boucher and Friot, 2017). Regarding the microplastics main sources, tire and road wear particles and the synthetic textiles released by laundering are accounted for the largest land-based sources (Siegfried et al., 2017). The global releases of microplastics are expected to fluctuate significantly among different regions, with the largest regional releases being estimate to be in Asia, North America and Europe (Boucher and Friot, 2017).

Table 2.1. Main sources of primary and secondary microplastics in the environment

Source classification	Source ^c
Land-based (> 80%) ^a	• Mismanaged waste (Jambeck et al., 2015) • Municipal and illegal landfills • Commercial handling or maintenance on plastic items • Medical applications of plastic beads or spheres • Industrial products or process emissions (outfall, gas emissions and solid waste) • Abrasive media in metal works and other processes • Construction sites and building maintenance • Excavation of plastics contaminated soil • Freshwater (lakes and rivers) leisure activity and recreational boating • Discharge from storm water drains • Untreated or insufficiently treated municipal wastewater (including WWTP^b inability to remove all the microplastics originated in personal care products and textile fibers from washing clothes) (Hernandez et al., 2017; Kay et al., 2018) • Application of treated sludge from WWTPs in agriculture (Mahon et al., 2017) and other soil amendments such as compost (Bläsing and Amelung, 2018) • Agriculture practices such as plastic mulching and irrigation (Bläsing and Amelung, 2018) • Indoor dust emissions from commercial or public buildings (e.g., abrasion on furniture) • Accidental release (e.g., tire wear and tear (Kole et al., 2017), paint weathering and fires)
Sea-based (< 20%) ^a	• Seaside leisure activity and recreational boating • Fishery and aquaculture • Harbors (e.g., dredging plastic contaminated sediment) • Shipping • Maintenance on plastic painted maritime surfaces and plastic treated surfaces (e.g., ships high-pressure wash and bridges maintenance) • Offshore mining and extraction • Illegal dumping at sea

^a Estimated contribution of the total input.

^b Wastewater treatment plants.

^c Other data sources: European Commission (2011), Sundt et al. (2014), Essel et al. (2015), Auta et al. (2017a), Horton et al. (2017), Wagner & Lambert (2018), Karbalaie et al. (2018), (Prata, 2018a).

2.4 States

Each environmental system evolves as the microplastic inputs and outputs change. Microplastics move between the different compartments, go through degradation processes and interact with other pollutants and with biota (Fig. 2.2). In order to better understand the environment state, as well as the impacts, regarding the microplastic pollution, research studies and monitoring campaigns are crucial. The available data shows that microplastics are widely scattered on Earth, even in more remote locations such as the arctic ice and the bottom of the ocean, and that have recognized adverse effects on biota. Nevertheless, much more studies are necessary to fill the

gaps regarding the temporal and spatial distribution, mobility, natural degradation and physicochemical and biological interactions, long-term fate and effects on biota and human health.

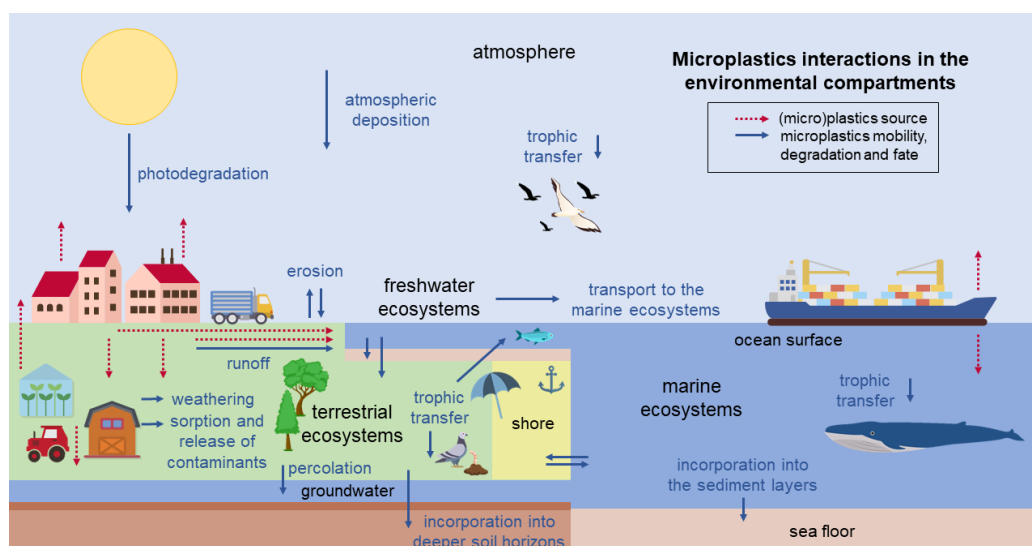


Fig. 2.2. Microplastics interactions in the environmental compartments.

The ecosystems that have captured more interest when it comes to microplastics research are the aquatic environments, above all the **marine ecosystems**: coastal environments, seas and the ocean. The marine studies already conducted report microplastics in water surface, water column, sediments and organisms, and were carried out in different regions: North America, South America, Antarctica, Asia, Oceania, Europe and southern Africa coasts; Persian and Mexican Gulf; Atlantic and Pacific oceans; North, Mediterranean, Adriatic, Baltic, Tyrrhenian and Bohai seas; and Polar Regions (GESAMP, 2015; Rezania et al., 2018). Regarding the transport pathways, gyres play an important role for surface transport, while the oceanic currents and biota influence the vertical transport (GESAMP, 2015). Because microplastic particles have a combination of characteristics such as very small size and low density, they are more easily transported across larger distances by currents, making them transport vectors for co-occurring pollutants and microorganisms. Since considerable spatial variability has been verified in the reported abundances, there is particular interest in identifying the regional or local hot spots of (micro)plastic occurrence to assess the risks. One of those identified locations is the Great Pacific Garbage Patch in the North Pacific Ocean Gyre, where it has been estimated the occurrence of 1.7 trillion floating particles of microplastics ($> 500 \mu\text{m}$) (94% of the plastic debris items), representing 8% of the total plastic mass in that area (Lebreton et al., 2018). Other potential plastic sinks that are being considered are the Arctic sea ice (Peeken et al., 2018; Geilfus et al.,

2019) and the deep sea sediments. Concerning the plastic fate, Eunomia (2016) estimated an average plastic concentration of 0.74 kg km^{-2} floating (with 18 kg km^{-2} being the highest concentration found floating or near the ocean surface, in the North Pacific gyre), 2000 kg km^{-2} at the shore and 70 kg km^{-2} at the sea floor. That translates to a global estimate of 27 to 66.7 million tons of plastic, of which 1% is at the ocean surface, 5% at the shore and 94% at the sea floor.

For **freshwater ecosystems**, which include rivers, reservoirs and lakes, groundwater, estuaries and other transitional waters, there are fewer studies concerning the microplastics abundance when comparing to the marine ecosystems. These studies assess the amount of microplastics in sediment (bed/bottom and banks/shore), water surface and water column, and presence in freshwater biota. Nevertheless, since the land-based sources of microplastics are the primary contributors to the microplastic pollution, these ecosystems are starting to get more attention. Horton et al. (2017) and Li et al. (2018) selected relevant freshwater studies that sampled microplastics in sediment and water in order to compare the amounts that have been reported. Although there are limitations when doing so, since there are no standardized methods to sample, isolate and analyze microplastics. The microplastic pollution levels reported differ significantly among different regions and type of water body, with e.g., concentrations ($> 50 \mu\text{m}$) in water ranging from 900 to 2800 items m^{-3} for Dongting Lake and 1250 to 4650 items m^{-3} for Hong Lake, both in China (W. Wang et al., 2018), and concentrations ($100 < \text{particles} < 2000 \mu\text{m}$) in water ranging from 3.52 to 32.05 items m^{-3} in 12 different surface freshwater bodies in Hungary (Bordós et al., 2019).

The microplastics that enter freshwater ecosystems will not remain stationary and will be transported from and to land, as well as to the ocean (e.g., regular river input, floods and storms). This mobility is influenced by hydrology (e.g., river flow) and morphology (e.g., vegetation and erodibility), as well by human activities such as dam construction. The microplastics characteristics change throughout the transport because of their potential degradation (e.g., weight loss, changes in tensile strength and breakdown of molecular structure), biofilm formation and further fragmentation, changing their transport rate and sorption capacity and consequently their bioavailability and fate (Wagner and Lambert, 2018). The microplastics that remain in freshwater ecosystems are probably concentrated at lakes and reservoirs due to their high residence time, while rivers are more temporary sinks. Finally, where microplastics find the right deposition conditions, they will sink through the water column and eventually become buried, and so higher concentrations of plastic particles are expected to be found within the sediments at the lake bottom and river bed (Corcoran et al., 2015; Nel et al., 2018).

Among the Earth's spheres, the **atmosphere** is the least studied regarding microplastic pollution, with very few reports assessing the levels of microplastics in outdoor or indoor air quality. One of these few studies was conducted by Dris et al. (2016) that investigated the microplastics ($> 50\ \mu\text{m}$) atmospheric fallout (dry and wet deposition) during several months in two different areas near Paris (France), reaching 2 to 355 particles $\text{m}^{-2}\ \text{day}^{-1}$ with an average of 110 ± 96 particles $\text{m}^{-2}\ \text{day}^{-1}$ in an urban area and 53 ± 38 particles $\text{m}^{-2}\ \text{day}^{-1}$ in a sub-urban area, with almost all particles collected being fibers (29% of the analyzed fibers were synthetic). It was estimated an annual fallout of 3 to 10 tons of synthetic fibers at the scale of the Parisian agglomeration area (about $2500\ \text{km}^2$). Therefore, atmospheric deposition can be a substantial microplastics input into aquatic and terrestrial ecosystems. After deposition, they can continue their transport between different compartments and ecosystems or directly impact organisms due to the risk of inhalation. Similarly to the other environmental compartments, microplastics in the atmosphere are believed to go through photo-oxidative degradation, as well as wind shear and abrasion against other particulate matter, what makes them more bioavailable (Gasperi et al., 2018).

At indoor environments, microplastics can be in the air but also associated with dust, with measured ($50 - 4850\ \mu\text{m}$) indoor air concentrations reaching $0.4 - 59.4$ fibers m^{-3} (compared to $0.3 - 1.5$ fibers m^{-3} at the reference outdoor site) and accumulating to $190 - 670$ fibers mg^{-1} of settled dust (Dris et al., 2017). The fibers deposition rate was estimated as $1586 - 11130$ fibers $\text{m}^{-2}\ \text{day}^{-1}$ in indoor environments, with 33% of the fibers being classified as synthetic by this study.

Studies that focus on microplastics distribution, mobility and fate in **terrestrial ecosystems** are scarce, even though evidence has been rising that plastics are abundant in soil and that these ecosystems may be major sinks for microplastics (Bläsing and Amelung, 2018). As an example, Zhang & Liu (2018) assessed the microplastics ($0.05 - 10\ \text{mm}$) contamination at $0 - 5\ \text{cm}$ and $5 - 10\ \text{cm}$ layers of soil in four cropped areas and one riparian forest buffer zone in China. The results showed concentrations ranging from 7100 to 42960 particles kg^{-1} (mean 18760 particles kg^{-1}), 95% of the particles presenting a size range of $0.05 - 1\ \text{mm}$. No pattern was found regarding the concentrations between the two layers of soil analyzed at each location, while the concentrations were significantly different between different land uses and locations studied. The land use is precisely one of the most important factors to consider when understanding soil microplastics contamination, since agricultural practices such as the application of sewage sludge on soil or industrial activities in urban areas play a determinant role as sources of plastic to the soil.

A review article on the current knowledge on sources, occurrence and fate of microplastics in soils was written by Hurley & Nizzetto (2018). Briefly, plastics accumulated on soil can be transported across soil systems due to erosion by water and wind, which may lead to their burial, or transport to water systems (including groundwater) or the atmosphere. Biota can transport

microplastics (Rillig et al., 2017) but also contribute for their degradation and fragmentation (e.g., through bioturbation), what may also occur due to human activities (e.g., agricultural practices) and because of the exposure to sunlight and other environmental conditions. Microplastics that are buried into deeper soil layers, being incorporated into the soil, can stay accumulated there for long periods, where they are stored and preserved in the soil horizons, not being easily degraded (Bläsing and Amelung, 2018). Floods, landslides and certain human activities (e.g., construction) can remobilize microplastics and bring them back to the soil surface.

2.5 Impacts

The current knowledge on the microplastics impacts is not extensive but has been increasing. Socio-economic impacts are more easily identified and include the damage to leisure and recreational activities (e.g., surf at the seaside), the costs associated with cleaning plastic waste from the environment and costs to tourism, fisheries and shipping sectors (The European Parliament and the Council of the European Union, 2019a).

Environmental impacts are more difficult to assess but comprise the adverse effects on biota and on human health, as well as changes in the ecosystems functioning (biological, geochemical and physical processes and components of the system). Microplastics can interact directly with biota in the environment and, consequently, can potentially lead to adverse effects through the different exposure pathways: inhalation, ingestion and dermal contact. This results from the omnipresence and persistence of microplastics in the possible exposure media: air, water, food, dust, soil and sediments, among others. The extent to which organisms are exposed to physical stress depends on the microplastic size and shape. Additionally, other microplastics characteristics such as their chemical composition, sorbed and leaching chemicals, and additives can lead to toxic effects, which are more difficult to assess (Wagner and Lambert, 2018). Because some organisms show low or non-existent rate of internal degradation or excretion of microplastics, this leads to microplastics trophic transfer, what may result in bioaccumulation or biomagnification (Wright et al., 2013). In parallel, microplastics can affect abiotic qualities of the environment, such as the distribution of chemicals, the light penetration into the water column, and sediment characteristics, potentially affecting the biogeochemical cycles (Eerkes-Medrano et al., 2015).

Understanding the specific effects that microplastics have on different organisms has been one of the most intensively explored areas on microplastics research in recent years, particularly for aquatic organisms. The following ecotoxicological effects are documented across several groups of organisms: mortality, neurotoxicity, genotoxicity, cytotoxicity, behavior effects such as the

reduction of the predatory performance and efficiency, physical effects such as growth rate reduction, oxidative stress, reduction of reproductive fitness, alteration of enzymes, and changes in blood and hemolymph parameters (Sá et al., 2018). Studies on the interactive ecotoxicological effects of microplastics with other contaminants are less common and have been performed mainly on fish. The list of contaminants that has been already investigated includes persistent organic pollutants (POPs), endocrine-disrupting chemicals (EDCs), metals, antibiotics and herbicides (Sá et al., 2018).

The ecological effects of airborne microplastics and microplastics in soil are less understood and the data available is very limited. Airborne microplastics have the capacity to enter the respiratory system, and plastic fibers have been observed in human pulmonary tissue. This may lead to airway and interstitial lung diseases by mechanisms of dust overload, oxidative stress, translocation and gene mutation, as well as to contribute to the incidence of cardiopulmonary diseases among the population (Gasperi et al., 2018; Prata, 2018b). Microplastics in soils can be ingested, egested and transferred by soil organisms, as well as leach chemicals that accumulate in them. Much that is currently known is due to experiments with earthworms, which are model organisms for soil ecosystems. Earthworms can transport microplastics in soil, be affected due to bioaccumulation and show sub-lethal effects on growth and immune system response, among others. Nevertheless, these are very complex ecosystems, meaning that more organisms need to be considered for these studies (e.g., plants and insects) (Chae and An, 2018).

Other than the direct exposure to the microplastics in the environment, food and drinking water contaminated with microplastics constitute risks to human health. Some studies assessed the microplastics levels in sea products, such as that reported by Karami et al. (2017) that analyzed commercial salts from different countries, and in drinking water, such as that published by Schymanski et al. (2018) that quantified microplastics in water stored in plastic bottles, glass bottles and beverage cartons. Waring et al. (2018) reviewed the currently available studies in order to understand if the plastics constitute a threat to human health, concluding that the plastic contamination of the food chain is unlikely to cause serious toxicity if very high exposure levels are not reached, although it cannot be excluded under special circumstances (e.g., long-term ingestion of contaminated food). Nonetheless, the microplastics impacts on humans are mostly unknown and much more specific research is needed.

2.6 Responses

With the increased concern over the impacts of the plastic pollution on biota, especially on aquatic organisms, and the potential effects on human health, multiples strategies have been developed, at different levels, to reduce and manage the plastic pollution.

2.6.1 Upstream responses

In this review, upstream responses comprise the preventive strategies and technologies, action plans and regulatory agreements to reduce the plastic inputs. These responses act on the sources of the plastic pressures on the environment (q.v. 2.2 and 2.3), affecting economic sectors such as the plastic industry, but also the consumer practices, waste management and effluent treatment. Therefore, the developed strategies can be more or less specific, considering the source that is being tackled.

2.6.1.1 Regulatory and policy instruments

The regulatory and policy instruments related to (micro)plastics are applied at international, regional and national levels (Wagner and Lambert, 2018). At international level stand conventions, agreements, regulations, strategies, action plans, programs and guidelines created by e.g., the United Nations, such as the “Global Programme of Action for the protection of marine environment from land-based activities” (UNEP, 1996). The regional level comprises e.g., the Marine Strategy Framework Directive (2008/56/EC) (The European Parliament and the Council of the European Union, 2008b), among other European Union (EU) directives and United States (USA) regulations (Table 2.2 for a list of the EU directives and other regulatory and policy instruments pertaining to the microplastic pollution issue). At all levels there have been significant advances in the last decade, although microplastics are still not explicitly addressed in most of the instruments available in environmental law regarding water quality, air quality, waste management, among others.

Some of the most well-known land-based policies are directed towards the reduction of plastic carrier bags, with the policy tools available classified as regulatory instruments (ban), economic instruments (levy on suppliers, retailers or consumers) or a combination of both (UNEP, 2018a). The Directive (EU) 2015/720 (The European Parliament and the Council of the European Union, 2015), that amends Directive 94/62/EC regarding the reduction of the consumption of lightweight plastic carrier bags, urged the EU member states to take measures to achieve a sustained reduction in the consumption of lightweight plastic carriers bags on their territory, including through the use of national reduction targets and maintaining or introducing economic instruments and marketing restrictions. The Directive establishes that the member states have to restrict the use of lightweight plastic bags by introducing measures that result in the achievement of at least one of the two goals proposed: a) meeting the consumption targets defined by EU for 2019 and 2025, or b) ensuring that lightweight plastic carrier bags are not provided free of charge at the point of sale of goods or products by 31 December 2018.

For instance, in Portugal, the Green Taxation Reform (Law n.º 82-D/2014) was enforced in February 2015 (Governo de Portugal - MAOTE, 2014), which included a tax on lightweight plastic carrier bags (0.08 € + VAT per bag), with the goal to decrease the 2014 average consumption of 466 lightweight plastic bags per person per year to 50 bags per person per year in 2015 and 35 bags per person per year in 2016. Martinho et al. (2017) analyzed the effect of the Portuguese plastic bag tax on the consumer behavior in two cities to learn how it was received and the perceived effectiveness of the tax 4 months after its implementation. The results of this study showed a 74% reduction of single-use plastic bag consumption, while the use of reusable plastic bags increased by 61% after the tax was implemented. According to the Portuguese Environmental Agency, there was a reduction of 94% on the production of lightweight plastic bags and a consumption reduction of 95%, between January and October 2015 (Pinheiro, 2016). In 2019, several national and multinational retailers announced that the lightweight plastics carrier bags would stop being commercialized until the end of the year in Portugal and substituted by paid paper or fabric options. In parallel, a new law-project was approved in July 2019 (Projeto de Lei 1187/XIII, 2019), on the alternatives to the very lightweight plastic carrier bags (wall thickness below 15 µm) and to foam food containers (e.g., made of PS) at food points of sale in Portugal.

Another example is the legislative ban of plastic microbeads used in rinse-off personal care products in some countries like the USA in 2015 and the UK in 2018. The course since the first scientific evidence of microbeads environmental harm, through anti-microbeads activism, to the political action is covered by Dauvergne (2018), who tries to explain the uneven phaseout of microbeads via social science analysis.

On November 2018, a background paper on “Microplastic Pollution: The Policy Context” was published (European Commission’s Scientific Advice Mechanism, 2018), providing a synthesis of legislation, regulation and policies relevant to microplastics. Similarly, on December 2018, the United Nations Environment Programme (UNEP) and the World Resources Institute published a report entitled “Legal limits on single-use plastics and microplastics: a global review of national laws and regulations” (UNEP, 2018b) overviewing the policy instruments and progress on the topic of the regulation of manufacture, import, sale, use and disposal of selected single-use plastics and microplastics.

Nevertheless, considering that plastic pollution has been identified as priority issue by policy makers, much more developments are expected to happen in the following years, with regulatory and policy instruments being enforced or updated frequently.

Table 2.2. EU regulatory and policy instruments pertaining to the microplastics pollution issue.

Instrument	Environmental compartment	Scope within the (micro)plastics pollution issue
Sewage Sludge Directive (Directive 86/278/EEC)	Soil and water	(Micro)plastics are not explicitly addressed by the directive.
Urban Waste Water Treatment Directive (Directive 91/271/EEC)	Water	(Micro)plastics are not explicitly addressed but the directive is currently under evaluation.
Landfill Directive (Directive 1999/31/EC)	Air, soil and water	While the adopted revisions (Directive (EU) 2018/850) require that landfill waste disposal must be reduced significantly, neither plastic nor microplastics are explicitly addressed.
Water Framework Directive (Directive 2000/60/EC) (WFD)	Water (freshwater)	(Micro)plastics are not explicitly addressed, but a future revision is expected to update the directive regarding this issue.
Regulation (EC) N° 1907/2006 - REACH	Air, soil and water	Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). “Polymers are exempted from the provisions on registration of Title II of REACH (Article 2(9)). The manufacturer or importer of a polymer is therefore generally not required to provide to the Agency any information related to the intrinsic properties of the polymer itself, with the exception of its classification and labelling when applicable (Regulation (EC) N° 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP)).” (European Chemicals Agency, 2012) REACH Article 6 states the conditions that lead to the obligation of registration.
Marine Strategy Framework Directive (MSFD) (Directive 2008/56/EC)	Water (seawater)	Addressed through the 10 th qualitative descriptor for determining good environmental status: “Properties and qualities of marine litter do not cause harm to the coastal and marine environment.” It does not explicitly target microplastics.
Waste Framework Directive (Directive 2008/98/EC)	Air, soil and water	The directive includes general recycling targets for waste from households and possibly other origins with similar streams, which includes plastic. It does not explicitly target microplastics.
Air Quality Directives (Directive 2004/107/EC and Directive 2008/50/EC)	Air	(Micro)plastics are not explicitly addressed, although microplastics that fit into PM ₁₀ and PM _{2.5} size thresholds are covered.
Eco-design Directive (Directive 2009/125/EC)	Air, soil and water	Microplastics are not explicitly addressed by the directive. Mentions the “use of component and material coding standards for the identification of components and materials suitable for reuse and recycling (including marking of plastic parts in accordance with ISO standards)”.

Behavior and attenuation of microplastics in environmental compartments

Fisheries Control Regulation (Council Regulation (EC) N° 1224/2009)	Water	The 2018 proposal for a revision of the Fisheries Control Regulation will introduce daily electronic reporting for all vessels and remove the exemption of small vessels from the obligation to carry retrieval equipment. It does not explicitly target microplastics.
The Industrial Emissions Directive (Directive 2010/75/EU)	Air, soil and water	An integrated approach that considers the whole environmental performance of industrial processes (e.g., emissions to air, water and land, generation of waste, use of raw materials, energy efficiency and noise). Plastic materials production is one of the industrial activities identified.
Regulation on plastic materials and articles intended to come into contact with food (Commission Regulation (EU) N° 10/2011)	Soil and water	“Plastic materials and articles shall not transfer their constituents to food simulants in quantities exceeding 10 milligrams of total constituents released per dm ² of food contact surface (mg dm ⁻²).” It also specifies the thresholds according to the form and composition of each plastic. The regulation is regularly amended with the last version dating January 2019.
Green Paper on a European Strategy on Plastic Waste in the Environment (COM/2013/0123 final)	Air, soil and water	It had the purpose of launching a broad reflection on possible responses to the public policy challenges posed by plastic waste which were not specifically addressed in EU waste legislation at the time. Microplastics are defined and specified as a challenge, mentioning as well the chemicals in and adsorbed to them.
Directive 94/62/EC on Packaging and Packaging Waste, with the last revision on May 2018	Soil and water	Lays down measures aimed at preventing the production of packaging waste and at reducing their final disposal. Directive (EU) 2015/720 (known as Plastic Bags Directive) amends the Directive 94/62/EC regarding the reduction of the consumption of lightweight plastic carrier bags.
Closing the loop - An EU action plan for the Circular Economy (COM/2015/0614 final)	Air, soil and water	Identifies plastics as one of the priority areas and states that “The Commission will adopt a strategy on plastics in the circular economy, addressing issues such as recyclability, biodegradability, the presence of hazardous substances of concern in certain plastics, and marine litter.” As well that, “The Commission is proposing, in the revised legislative proposals on waste, a more ambitious target for the recycling of plastic packaging”.
Drinking Water Directive (Directive 98/83/EC) with a proposal for a revised directive (COM/2017/0753 final - 2017/0332 (COD)) with amendments by the European Parliament legislative resolution of 28 March 2019	Water	Although there is no mention in the old Drinking Water Directive (98/83/EC), the review of the directive, from February 2018, addresses microplastic contamination through article 8 regarding hazard assessment of bodies of water used for the abstraction of water intended for human consumption. It is stated that “microplastics are of particular concern due to the negative effects on marine and freshwater environments, aquatic life, biodiversity, and possibly to human health since their small size facilitates uptake and bioaccumulation by organisms, or toxic effects from the complex mixture of chemicals these particles consist of”.

A European Strategy for Plastics in a Circular Economy (COM/2018/028 final)	Air, soil and water	Aimed at “transforming the way plastic products are designed, used, produced and recycled in the EU.” It proposes concrete actions designed to contribute for a more circular plastic economy including that “all plastic packaging on the EU market will be recyclable by 2030, the consumption of single-use plastics will be reduced and the intentional use of microplastics will be restricted”.
Proposal for a reviewed tire labelling regulation (COM(2018) 296 final - 2018/0148 (COD))	Air, soil and water	To repeal Regulation (EC) N° 1222/2009. It states that “Tire abrasion is a major source of microplastics released into the environment. No test has yet been developed that would allow the mileage or abrasion rate of tires to be measured reliably. It is therefore proposed to consider using delegated powers to include these parameters in the future, once an appropriate test standard is finalized.”
Directive 2019/883 on port reception facilities for the delivery of waste from ships	Water (seawater)	This directive repeals Directive 2000/59/EC and amends Directive 2010/65/EU. It “aims to protect the marine environment against the negative effects from discharges of waste from ships using ports located in the Union, while ensuring the smooth operation of maritime traffic, by improving the availability and use of adequate port reception facilities and the delivery of waste to those facilities.” Microplastics do not fall directly within the scope of this Directive.
Directive 2019/904 on the reduction of the impact of certain plastic products on the environment	Air, soil and water	The objectives of this Directive are “to prevent and to reduce the impact of certain single-use plastic products, products made from oxo-degradable plastic and fishing gear containing plastic on the environment and on human health, and to promote the transition to a circular economy, including the fostering of innovative and sustainable business models, products and materials, thus also contributing to the efficient functioning of the internal market”. Microplastics do not fall directly within the scope of this Directive.
Towards an EU Product Policy Framework contributing to the Circular Economy (roadmap stage)	Air, soil and water	Initiative that aims to “examine options and actions for a more coherent policy framework of the different strands of work of EU product policy in their contribution to the circular economy”. It will build on ongoing or recent initiatives such as the revision of the waste legislation or the check on the EU Ecolabel and the Eco-Management and Audit Scheme.

2.6.1.2 Environmental education

One of the most important strategies to reduce microplastics inputs is environmental education towards the population increased awareness on this environmental problem. Several governmental and international agencies like the National Oceanic and Atmospheric Administration (NOAA), the European Commission and the UNEP have increased their efforts to reach the citizens in order to explain plastic pollution, particularly marine litter, and give some alternatives to reduce plastics in the daily life, as well as educate people to acquire better practices regarding waste management. In parallel, many non-governmental organizations have started awareness movements and some individual initiatives, with more local effects, have emerged. These initiatives rely strongly on volunteering work and on concepts such as citizen science and open access to the project data, although they frequently have specialized members to give scientific ground to the project. Some examples include Plastic Tides and Surfrider Foundation. Through the news, documentaries and photography, some very impactful images of the ocean pollution current scenario reached the urban clusters, that otherwise would remain unfamiliar and distant to this environmental issue. Examples comprise the 2016 “A Plastic Ocean” and the 2017 “Albatross” documentaries.

A study that applied social and behavioral research methods to assess the effectiveness of environmental and ocean literacy initiatives (Ashley et al., 2019) reported that, after viewing an educational film, the participants of the study (general public and 11-15 years old school pupils) demonstrated a significant increase in self-reported knowledge on microplastic pollution and an increased intention to change their behavior to e.g., reduce the use of products containing microplastics. While some practices were already well implemented by the participants, such as separating plastics for recycling, actions that specifically targeted microplastics constituted mostly new behavior options. Consequently, the institution of education tools related to (micro)plastic pollution in education channels can have a very positive impact, especially when showing to a still unaware audience the known impacts of this environmental issue and correspondent available and feasible behavioral changes to attenuate it.

2.6.1.3 Waste management

At the plastic products end-of-life, the plastic will be recycled, incinerated and/or go through an energy recovery process, landfilled or incorrectly discarded when dumped in uncontrolled sites or littered in the environment. According to the estimative by Geyer et al. (2017), between 1950 and 2015, the cumulative waste generation of primary and secondary (recycled) plastic waste amounted to 6300 Mton of which approximately 12% have been incinerated and 9% have been recycled (of which 10% were recycled more than once). The plastic recycling rate increased

from 1950 to today, but plastic recycling and incineration were negligible before 1980 (Geyer et al., 2017), and only 14% of the total plastic packaging waste (packaging amounted 47% of the 302 Mton plastic waste generated) was collected for recycling in 2015 (Fig. 2.3) (UNEP, 2018a). Therefore, an increased circularity and correct waste management of plastics are needed in order to reduce the inputs of (micro)plastics into the environment.

The 2016's World Economic Forum "The new plastic economy: rethinking the future of plastics" explores this idea of implementing a circular economy to plastics in order to: i) create an effective after-use plastics economy by improving the economics and uptake of recycling, reuse and controlled biodegradation for targeted applications; ii) drastically reduce leakage of plastics into natural systems and other negative externalities; and iii) decouple plastics from fossil feedstocks by exploring and adopting renewably sourced feedstocks. As such, the continuous development of improved recyclable or compostable plastics and respective waste management, while avoiding single-use plastics, should be a part of the package of solutions to fight the plastic pollution in the environment.

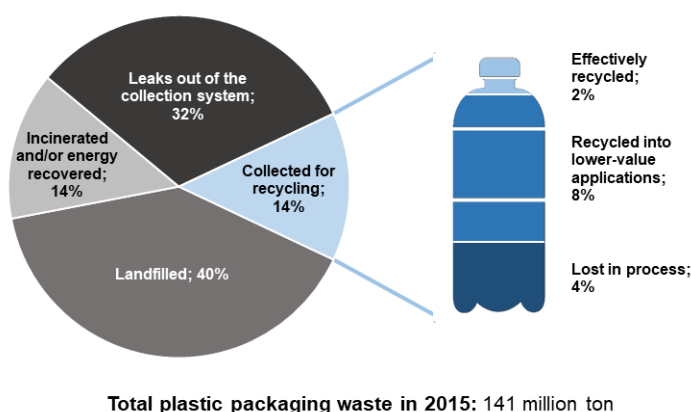


Fig. 2.3. End of life of 2015 global plastic packaging waste, based on the 2013 global flows of plastic packaging materials (Geyer et al., 2017; World Economic Forum et al., 2016).

Plastic recycling, in which the waste plastics are recovered and reprocessed into useful products, can be classified as primary, secondary, tertiary or quaternary recycling, depending if the final product has performance characteristics more or less equivalent to those of the virgin plastic or even if it is converted into chemicals or fuels (Merrington, 2017). Typically, the plastics are processed, melted, extruded, pelletized and, then, can be used to make a new product. However, plastic recycling can be a complex process due to the variety of plastic materials and their consequent mixture. Plastics made from a single polymer can be more easily identified and separated from the mixture, as those identified by the Resin Identification Codes (RICs): PET,

HDPE, PVC, LDPE, PP and PS (Table 2.3). These plastic materials can be collected, transported to a facility where they are separated by polymer type, washed and dried, and then fragmented and possibly pelletized, while some additives can be added to achieve the desired characteristics. It should be noted that not all the plastic materials identified with the RICs are recycled, the least recycled of these six polymers being PVC. Some plastics labeled as “others” (RIC: 7) can be recycled, like nylon and polycarbonate (PC), although the thermoset plastics cannot be remolded upon heating and are currently limited to be ground and incorporated into an uncured monomer as a filler or to be used in compression molding (Merrington, 2017). On the other end, mixed plastics usually cannot be combined into a single material with good mechanical properties and need to be separated by polymer type through manual, density, optical, spectroscopic, and/or electrostatic, among other separation processes, or made compatible with each other by adding surface-active agents (compatibilizers) (Merrington, 2017). Nevertheless, it is not only a question of whether the plastic material can be recycled or not, but also if the resulting material will be attractive economically and if there is a market for it.

Table 2.3. Percentage of global primary plastic waste generation in 2015, according to polymer type

Polymer type or additive	Plastic acronym and RIC	2015 primary waste generation		Examples of applications ^b
		(Mton) ^a	(%)	
Low-density polyethylene	LDPE or PE-LD (RIC: 4)	57	19	Bags for fresh products, stretch film, coatings for paper milk cartons, hot and cold beverage cups, toys
Polypropylene	PP (RIC: 5)	55	18	Containers for yogurt and take-out meals, medicine bottles, bottle caps and closures, appliances, battery cases
Polyester, polyamide, and acrylic fibers	-	42	14	Clothing articles, home furnishing and textiles, upholstery padding, tire reinforcement, safety belts
High-density polyethylene	HDPE or PE-HD (RIC: 2)	40	13	Bottles for drinks (e.g., milk), groceries bags, cereal box liners, extruded pipes and conduits, wire and cable covering
Poly(ethylene terephthalate)	PET or PETE (RIC: 1)	32	11	Bottles for drinks (e.g., water), food jars, microwavable food trays, textiles, films
Polystyrene	PS (RIC: 6)	17	6	Food service disposables, hinged take-out containers, protective foam packaging, packaging loose fill, building insulation
Additives	-	17	6	Used to enhance the properties of the material
Polyurethane	PUR or PU	16	5	Foam used in cushions, thermal insulation, computer casing, shoe soles, artificial heart valves
Poly(vinyl chloride)	PVC or V (RIC: 3)	15	5	Blister packs, shrink wrap, pipes, railing, blood bags and medical tubing
Other	(RIC: 7)	11	4	
Total		302	100	

^a Data source: Geyer et al. (2017)^b Data source: American Chemistry Council

Intrinsically connected to higher plastic recycling rates is the correct disposal of plastic waste, since each country or even region has its own waste management system in place with different collection systems. For example, for beverage packaging waste management, the bottles or cans: i) can have a deposit and be transported back to the producer to be refilled; ii) can have an one-way deposit with which the producer can get back the materials or alternatively they are sent directly to the recycling company to produce new bottles; or iii) be one-way without deposit, meaning that, at most, a fee will be paid to an organization to handle the waste or the producer will have nothing to do with their product after becoming waste. Deposit systems lead to high collection rates and a higher quality of the material sent for recycling (even in accordance with food safety and quality regulations), apart from being a tool to implement **Extended Producer Responsibility**, a way to cut the cost of waste management and to reduce the exploitation of natural resources. Countries like Germany, Sweden, Denmark, the Netherlands, Norway and Finland have deposit systems implemented for refillable containers, while other countries like the United Kingdom are currently studying its implementation or considering its introduction.

Other plastic waste treatment options, such as **incineration with energy recovery**, **gasification**, **pyrolysis**, and **refuse-derived fuel** production, can be economically attractive for some countries since they present a way to eliminate plastics while making possible to have monetary return with energy or chemical fuels production (Ocean Conservancy, 2015). Nevertheless, these technologies have some setbacks, such as the gas emissions that have to be treated before being released into the environment, and are a fallback from the EU Solid Waste Management Hierarchy as well as a deviation from the desired circular economy for plastics.

2.6.1.4 Product design and biodegradable plastics

Of the range of measures that can be implemented throughout the plastics value chain, product design is an upstream measure that affects the conception of plastic products and that can be aimed at using more sustainable materials. Through **eco-design**, environmental criteria can be used to reduce each plastic product environmental impact during its life cycle. Therefore, it can benefit not only the product production, but also its distribution, sale, use, reuse, recovery, recycle and elimination. Although other materials can be tested to replace plastics, one of the focus of the industry has been on developing new plastic materials with better environmental performance, such as the biodegradable plastics.

The viewpoint paper by Kubowicz & Booth (2017) points out some of the challenges and misconceptions associated with the **plastics biodegradability**, including how biodegradable plastics are considered an undesired contaminant within the recycling streams of conventional plastics and how they can be seen as a step back from the circular economy because of the loss

of a potential resource when the plastic is mineralized in industrial composting facilities. Furthermore, not all the plastics currently promoted as “biodegradable” are better than conventional plastics. The oxo-degradable plastics, commonly said to be biodegradable, are conventional plastics containing additives (prodegradants) that accelerate the oxidation process, what makes them more rapidly fragment into microplastics when exposed to the combined effect of sunlight and oxygen. On the other end, the biodegradable plastics, which are approved as such by standard specifications and test methods, can be fully mineralized during reasonable timeframes under controlled conditions, but not always under natural conditions. Likewise, the industrial compostable plastics, in compliance with the European standard EN 13432 or EN 14995, can be decomposed in a composting process for organic waste within a certain time at controlled conditions, which are optimal when compared to the natural biodegradation conditions in the soil, freshwater and seawater, and the atmosphere. Therefore, one of the main challenges for biodegradable plastics is the lack of materials that can be completely degraded in a short period under natural environmental conditions but still be able to retain their properties while being used by the consumers.

Another misconception centers on the use of the term bioplastics, which can refer to either bio-based plastics or to biodegradable plastics. Bio-based plastics are defined by the European standard EN 16575, establishing that the product is derived from biomass. To exemplify, polyhydroxyalkanoates (PHAs) and cellophane are bio-based biodegradable plastics, while bio-PE is a bio-based non-biodegradable plastic (van den Oever et al., 2017). While bio-based biodegradable products can seem more appealing regarding the most recent environmental concerns of both climate change and plastic pollution, each product should be analyzed through **Life Cycle Assessment (LCA)** in order to understand the best option that balances the positive and negative impacts concerning different criteria like carbon emissions and land use.

Thus, plastic products with good environmental performance can be identified through LCA and labelled accordingly in order to promote the consumer demand for products that cause less stress on the environment. For that purpose, one can resort to **ecolabelling**, which has been used as a valuable tool by some governments to encourage better environmental consumer practices and for businesses to identify and establish markets for their products and services, including plastic products. A variety of labels are available in different regions with more or less meaning for the consumer, as it is the case with United States Department of Agriculture (USDA) Certified Biobased label or the EU Ecolabel.

2.6.1.5 Effluent treatment

There has been an increasing number of studies that analyze the efficiency of **wastewater treatment plants** (WWTPs) at removing microplastics, and the flow rate released to the environment, especially when compared to the number of drinking water treatment plant (DWTP) studies (q.v. 2.6.2.2). This is a consequence from the increasing concern that WWTPs are releasing large amounts of microplastics to the rivers and to the ocean, considering the volumes of wastewater processed each day (Ziajahromi et al., 2016; Mrowiec, 2018; Kazour et al., 2019). These studies are the first step to improve the WWTP response to microplastic pollution, as they increase our understanding of the best technologies available, as well as the interactions and aging that microplastics undergo during the treatment processes (Enfrin et al., 2019). Therefore, in this review, the current knowledge on the wastewater treatment processes and technologies that can be used to remove microplastics is analyzed as an upstream response.

The research projects conducted so far on microplastics removal efficiency through conventional WWTPs pinpoint that the first treatment stages are crucial in removing microplastics (Magni et al., 2019; Murphy et al., 2016), with pre-treatment and primary treatment processes being able to reduce the concentration up to 98% (micro particles size analyzed > 20 μm) (Talvitie et al., 2017b). The biological treatment (activated sludge) can further decrease the concentration of the micro particles in 7-20%, while a tertiary treatment with a biologically active filter does not have a significant impact on the removal of micro particles (Talvitie et al., 2017b).

When comparing the conventional activated sludge (CAS) process with a pilot-scale membrane bioreactor (MBR) for treating the same primary effluent, Lares et al. (2018) reported a slightly better removal of microplastics (collected using a 250 μm sieve) with the MBR system (99.4% reduction from the initial WWTP influent) in comparison with the overall CAS-based WWTP process (98.3%). Talvitie et al. (2017a) reported a 99.9% microplastics (> 20 μm) content reduction in the primary effluent when using the same pilot-scale MBR (with a membrane pore size of 0.4 μm), achieving a concentration of 0.005 ± 0.004 microplastics L^{-1} . Other biologic treatments were analyzed for their efficiency in removing microplastics (> 106 μm), including the anaerobic-anoxic-aerobic treatment (A2O), sequencing batch reactor (SBR) and the Media process with a sequence of three bioreactors followed by two aerobic tanks, with efficiencies $\geq 98\%$ for all of these three processes (Lee and Kim, 2018).

Regarding the different tertiary treatment technologies available, Talvitie et al. (2017a) assessed their efficiency to remove microplastics (> 20 μm) from secondary effluent, specifically: discfilter with 40 to 98.5%, rapid sand filtration with 97% and dissolved air flotation with 95%.

Similarly to DWTPs (q.v. 2.6.2.2), the smaller particles are the most difficult to remove efficiently through WWTP processes: most of the particles > 100 μm can be removed during the

pre-treatment, the micro particles with a size ranging from 20 (lowest size analyzed) to 100 μm becoming predominant (> 70%) in the effluent (Talvitie et al., 2017b). This resulted in an estimated flow rate of about 200 to 790 million micro particles entering the marine environment per day and, of those, 1.7 to 140 million particles of microplastics being released each day with the effluent of a WWTP in Finland. In another study, a similar amount was estimated for a tertiary (sand filter treatment and disinfection) WWTP in Italy, with an average 160 million microplastics (> 10 μm) being release each day after a treatment with 84% efficiency (Magni et al., 2019). Among the microplastics, fibers and fragments are the most abundant shapes in wastewater, while the most frequent polymers identified are polyesters, PS, PE and PP (Lv et al., 2019; Xu et al., 2019).

In the solid's treatment line of a WWTP (Talvitie et al., 2017b), some microplastics are recycled back in the reject water, while most are removed from the system in the dried sludge. Considering that in some countries the treated sludge is reused in agriculture and, therefore, it is a potential land source of microplastic pollution, the effects of the sludge treatments on the microplastics characteristics and abundance should be further investigated. Mahon et al. (2017) analyzed WWTP sludge samples from seven plants in Ireland, comparing different treatments for solids prior to their land application: anaerobic digestion, thermal drying or lime stabilization. The results showed that anaerobic digestion sludge samples had lower abundances of microplastics (collected using a 250 μm sieve), suggesting that the microplastics may undergo degradation processes during this treatment due to the activity of the microorganisms. The thermal drying sludge samples showed that the microplastics suffered melting and blistering. Finally, the lime stabilization sludge samples indicated that the process shears the microplastic particles, because not only the samples had significantly higher abundances of smaller size classes of microplastics but also because the particles showed signs of shredding and flaking.

2.6.2 Downstream responses

In light of the alarming rate at which plastics have been accumulating in the environment and the complexity in understanding and dealing with all the inputs of primary and secondary microplastics, different approaches are being developed in order to attenuate their environmental (and socio-economic) impact after their input into the environment. With that goal, the current knowledge on the separation and degradation pathways for plastics is being expanded. These pathways include biological and/or physicochemical processes, where hydrolysis and oxidation are considered the primary polymer degradation mechanisms. In environmental exposure conditions, photo-degradation is seen as one of the primary mechanisms of polymers degradation (Fotopoulou and Karapanagioti, 2017), although the most common plastics have a very low degradation rate in the environment.

The downstream responses, which comprise the treatment processes and technologies to separate and eliminate (micro)plastics from polluted environmental compartments, are reviewed in this section.

2.6.2.1 Biotechnology tools

Together with the production of biodegradable plastics, already explored in this report (q.v. 2.6.1.4), the use of organisms capable of degrading plastics constitutes a promising biotechnology strategy (A. B. Silva et al., 2018, Urbanek et al., 2018). Organisms, such as some species of worms and microorganisms, are capable of partially mineralizing petrochemical polymers naturally, even if at a low rate. Complementary to biodegradation, a physicochemical pre-treatment such as UV or gamma irradiation, ozonation, thermal degradation, physical stress, or the addition of pro-oxidants can be used to improve the biodegradation rate and yield.

As an example of these type of studies, Tian et al. (2017) analyzed the degradation of PS by the fungus *Penicillium variable* and evaluated the potential of an ozonation pretreatment to enhance the degradation efficiency. The results showed that this polymer can be slowly mineralized by the fungus, while the ozonation pre-treatment enhanced the biodegradation. Other organisms used in similar studies include: the fungus *Zalerion maritimum* tested for PE degradation (Paço et al., 2017); *Bacillus* strains tested for PE, PET, PP and PS degradation after a UV pre-treatment (Auta et al., 2017b); the larvae of *Tenebrio molitor* with PS (Yang et al., 2018); the bacterium *Ideonella sakaiensis* that secretes PETase to digest PET (Austin et al., 2018); the bacteria *Bacillus sp.* and *Rhodococcus sp.* with PP (Auta et al., 2018); among others.

Although considered a promising strategy, biodegradation has some limitations such as that plastic biodegradation occurs at low rates when in natural conditions and that this type of treatment must be conducted in adequate facilities to control both the organism's growth as well as ensuring that microplastics are effectively eliminated and not simply further fragmented. On the other end, it could be a way to produce added-value products from plastic waste while attenuating the plastic pollution (Wierckx et al., 2015), but more research on the area is needed before plastic waste can be seen as a resource or biodegradation treatments as efficient.

2.6.2.2 Drinking water treatment plants

Very few studies focus on the microplastics efficiency removal at DWTPs, and their respective content in drinking water. In one of those first studies, Pivokonsky et al. (2018) analyzed the microplastics (> 1 µm) content in samples of freshwater from different sources that directly enter three DWTPs in Czech Republic, as well as the corresponding treated water samples, collected

for 3 random days (every 8 h) in the winter. The results (Table 2.4) gave some light into the DWTP efficiency, showing an improved removal when a two-stage separation is employed (DWTP 2 and DWTP 3) by using either sedimentation + sand filtration or flotation + sand filtration, with additional granular activated carbon filtration.

Mintenig et al. (2019) analyzed the supply chain and treatment of drinking water obtained from ground sources. The water treatment consisted of water aeration and filtration, after groundwater well extraction, the treated water being stored in a tank before distribution. The amounts of microplastics ($> 20 \mu\text{m}$) detected resulted in an average of $0.7 \text{ microplastics m}^{-3}$, indicating low contamination, especially when compared to the drinking water obtained from surface freshwater sources. However, the slight fluctuations of the amounts of microplastics detected were not enough to conclude on where the water contamination occurred.

Table 2.4. Drinking water treatment plants studied by Pivokonsky et al. (2018) and corresponding average number of microplastic particles at the DWTP inlet and outlet.

DWTP	Freshwater source	Treatment applied	Average microplastics in raw water (L^{-1}) ^a	Average microplastics in treated water (L^{-1}) ^a	Average removal (%)
DWTP 1 (usual capacity 3700 L s^{-1})	Large valley water reservoir	Coagulation-flocculation and sand filtration	1473 ± 34	443 ± 10	70
DWTP 2 (usual capacity 100 L s^{-1})	Small water reservoir	Coagulation-flocculation, sedimentation, sand and granular activated carbon filtration	1812 ± 35	338 ± 76	81
DWTP 3 (usual capacity 90 L s^{-1})	River	Coagulation-flocculation, flotation, sand filtration and granular activated carbon filtration	3605 ± 497	628 ± 28	83

^a Plastic particles $> 1 \mu\text{m}$ and $< 5 \text{ mm}$; The identification of the microplastic particles was achieved with representative samples by confirmation techniques: particles $> 10 \mu\text{m}$ were analyzed using micro-FTIR and particles in the size range $1\text{-}10 \mu\text{m}$ were analyzed with micro-Raman.

Other DWTP treatments were analyzed by Ma et al. (2019), that focused on the PE ($< 5 \text{ mm}$) removal when using common coagulants and ultrafiltration membranes. The results revealed that the Al-based coagulant ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) performed better than a Fe-based one ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), although a low efficiency ($< 10\%$) was observed with conventional dosages (0.5 mM). By changing the floc properties with pH variations or by adding polyacrylamide, the PE removal efficiency increased (achieving 61% for smaller particles) when using a higher coagulant dosage (5 mM), while water conditions such as ionic strength, natural organic matter and turbidity have little influence. The

ultrafiltration experiments with a poly(vinylidene difluoride) (PVDF) membrane (pore size of 30 nm) indicated that it is a highly efficient technology to remove PE particles, although membrane fouling increased with the coagulant dosage.

Similarly to WWTPs (q.v. 2.6.1.5), it was observed that the microplastic particles bigger than 100 μm can be successfully removed during the water treatment, as well as most of the 50-100 μm particles. The prevailing size categories of 1-5 μm (around 25-60% of microplastics) and 5-10 μm (around 30-50%) (Pivokonsky et al., 2018) are size categories that are usually not studied due to limitations in identifying and quantifying microplastics smaller than 20 μm . Contrary to the trend with most treatments, Ma et al. (2019) verified that coagulation was more efficient for smaller PE particles (< 0.5 mm).

Other microplastic characteristics such as their shape (e.g., fragments, spheres, fibers) and composition (e.g., PET, PE, PP) are expected to influence the microplastics removal efficiency of the multiple drinking water treatment technologies available. Nevertheless, further research is necessary to define the most suitable sequence of treatment processes for the efficient removal of smaller size categories of plastic particles, what may help to improve the DWTP design in order to consider this type of emerging contaminants that was not taken into account in the past.

2.6.2.3 Environmental cleanups

Few scientific publications have been released regarding the strategies and technologies available for microplastic cleanup from the environment. Nevertheless, in recent years, several cleanup initiatives have been carried out that resulted primarily from the population increased awareness of plastic pollution. As an example, the 2017 Ocean Conservancy's *International Coastal Cleanup* managed to involve nearly 800 thousand volunteers that removed more than 20 million pieces of waste from the ocean, beaches and waterways around the world (Ocean Conservancy, 2018). As it is pointed out by Loizidou et al. (2018), coastal cleanups have an important role as a response to plastic pollution since they help to remove persistent plastics from selected locations, and also help to identify the main sources of marine litter (e.g., cigarette butts, plastic beverage bottles, plastic bottle caps, food wrappers and plastic grocery bags are the top 5 items collected at the cleanups) and raise awareness among the population.

While cleanups usually do not target microplastics, they reduce the number of secondary microplastics that would potentially be created by the degradation of larger plastic litter. Kataoka & Hinata (2015) evaluated beaches cleanup effects by using linear system analysis. The aim of this study was to understand how to plan the cleanups in order to decrease the total mass of toxic metals that could leach from the plastics to the beach and to prevent their fragmentation

into microplastics. The results showed that the cleanups are more effective at beaches with the plastic average residence time higher than the period of temporal variability of the input flux of plastics, and also when they occur near the peak time when the remnants of plastics reach the local maximum.

Regarding the removal of surface plastic from the ocean, the project *Ocean Cleanup* is one of the most ambitious ongoing projects. The idea behind it is developing a passive u-shaped system, which moves with the currents and collects the plastic. The first system consisted of a 600 m long floater with a 3 m deep net attached below, giving the system buoyancy as well as preventing the plastic from escaping underneath it. The plastic to be removed, beginning from the Great Pacific Garbage Patch (central North Pacific Ocean), is intended to be recycled and sold, with the revenue being invested to expand the project to the other four ocean gyres (South Pacific, North and South Atlantic and Indian). The first system (001) was launched on September 2018, to the North Pacific Ocean and, after being tested and later returned to shore, an upgraded design (001/B) was developed and deployed on June 2019, being currently under tests. However, the paper published by Sherman & van Sebille (2016), on marine surface microplastic transport modeling, concluded that the plastic removal might be more effective, in both removing more microplastics and reducing potential impacts to the ecosystem, when the passive systems are deployed close to the coastline instead of within the plastic accumulation zones at the center of each gyre, particularly when located off the coast of China and in the Indonesian archipelago. By locating the collection systems close to the plastic pollution sources, the (micro)plastics can be removed before they can cause higher impact to the marine ecosystem and the system can collect a higher amount of microplastics since the flux of microplastics showed to be more significant than the concentration.

Schneider et al. (2018) explored a frequently forgotten, but important, question that consists of how the marine litter collected in cleanups or scientific studies is treated or used post collection and analysis. While academia usually does not specify the waste end-of-life, landfilling and energy recovery seem to be the common pathways for non-scientific projects, with some trying to recycle and reuse some of the collected items. Therefore, in order to improve the positive impact of plastic collected from the environment, the waste treatment options need to be further assessed within this matter.

2.6.2.4 Other mitigation technologies and strategies

A new approach was tested, at a lab-scale, by Herbort et al. (2018a, 2018b) to remove microplastics from **aquatic systems** by using sol-gel induced agglomeration reactions that result in adhesive particle growth around and between the microplastics particles, which can be more easily separated from the aqueous matrix by filtration processes. The results showed that, in the sol-gel process, the alkoxy-silyl functionalized molecules synthesized led to the agglomeration of microplastic particles such as PE and PP in water, which were later easily separated.

Although **indoor and outdoor air contamination** by microplastics has been receiving very little attention from the academia, some studies such as that conducted by Dris et al. (2017) called attention for the amount and effects of microplastics on the air we breathe, raising the concern and opening space for the development or adaptation of existing air treatment devices to reduce the contamination levels. Consequently, brands such as *Blueair* started selling air purifiers that are publicized to remove airborne microplastics down to 0.1 μm (99.97%) in order to improve the indoor air quality (Blueair, n.d.).

Remediation of soil and sediments contaminated with microplastics has received slightly more attention than the treatments targeting the air compartment, but requires, nevertheless, much more studies that focus on it and especially outside of sediments contamination at the coastal ecosystems. The (micro)plastics accumulated at the topsoil can go through degradation processes due to exposure to direct UV radiation and higher oxygen availability and temperature, while both soil and terrestrial organisms can contribute by biodegradation routes and as transport vectors. Weathering due to rain is another degradation agent, leading as well to the microplastics potentially leaching into the groundwater. Additionally, some agricultural practices, such as crop rotation or tillage (mechanical stirring to prepare the soil), may lead to plastic waste fragmentation into microplastics, as well as their sink into deeper soil horizons (He et al., 2018). However, most degradation drivers are absent or weak in deeper soil horizons, making plastic natural degradation a very slow process in soil and this compartment a sink that can potentially accumulate microplastics until they reach levels that can affect the ecosystem (Bläsing and Amelung, 2018). While the focus at responding to soil plastic contamination has been mainly on preventive strategies (Gionfra, 2018), natural attenuation of plastic waste by bioremediating microorganisms is, at this point, the most studied soil remediation technique. As examples, Ali et al. (2014) studied the PVC biodegradation ability by different fungal isolates in soil burial experiments and Nowak et al. (2016) evaluated the degree of degradation of modified PVC with recycled poly(lactic acid) (PLA) in garden soil and in a mixture of garden soil with soil contaminated with hydrocarbons.

2.7 Conclusions

This chapter reviewed the knowledge and research gaps of microplastic pollution in the environment, at the beginning of the PhD project. Therefore, taking into consideration the literature until the first half of 2019, the main conclusions on the state of the art of microplastic pollution in the environmental compartments were as stated below.

Through a DPSIR analysis, it was prominent that the driving forces and pressures of microplastic pollution are mostly known, but there is still a lack of quantitative data on the microplastics inputs and fluxes. This leads to a wide range of values when trying to estimate the global or regional production of primary and secondary microplastics and their input into the environment.

Similarly, there are significant variations on the reported content of microplastics in the different environmental compartments and ecosystems. For this reason, standardization of field and laboratory methods is needed, as well as many more studies on the temporal and spatial distribution, mobility, natural degradation, physicochemical and biological interactions, and long-term fate of microplastics in the environment.

The current knowledge of the effects of microplastics on biota follows the trend seen throughout this overview that shows that microplastics research is at a more advanced stage on aquatic ecosystems, particularly marine ecosystems, than on terrestrial ecosystems and on the atmosphere. Thus, a greater diversity of organisms needs to be considered for this type of studies, such as plants and insects. Although it is known that microplastics can enter the human body and potentially have effects on human health, there are still limited data to support the suspected negative impacts.

The responses to the microplastic pollution have been mainly upstream responses, with multiple new regulatory and policy instruments coming into force around the world and the adaptation of existing ones to also cover plastic and microplastic pollution. Environmental education has been playing a decisive role, creating additional pressure for the governments to act on this environmental issue and evolving into diverse initiatives, such as environmental cleanups. While the industry looks at alternatives to replace the conventional plastics and the scientific community has been looking at biotechnology tools as the most promising, there are still gaps regarding the knowledge of the efficiency of existing treatment technologies in eliminating microplastics. These and new technologies are key to avoid the release of microplastics into the environment through the emissions of industrial facilities and wastewater treatment plants, but also need to be considered in drinking water treatment plants, that have received far less attention. Although it is frequently perceived that source reduction is more important than downstream responses, both approaches are needed to reduce the estimated large amounts of microplastics and their impacts during the next decades.

2.8 Recent developments

Since the review presented in this chapter was completed (first half of 2019), several developments were made in the research field of microplastics, and regarding the regulatory and policy instruments. Therefore, in this section, some highlights are briefly described.

Research on the state and impacts of microplastics in terrestrial ecosystems and especially in freshwater environments has gained substantially more attention in recent years, making it a little more balanced with marine environments (Raza et al., 2022; H. Yang et al., 2022). Airborne microplastics, which contribute to the pollution of both aquatic and terrestrial ecosystems, however, still receive less interest (Zhao et al., 2023).

Considering all the uncertainties related to the impact of nanoplastics and microplastics to the human health and the recent advancements in analytical methods, several studies were conducted and published in the last four years, reporting the detection of plastic particles or fibers on human tissue and biological samples: blood (Leslie et al., 2022), lung tissue (Jenner et al., 2022), breastmilk (Ragusa et al., 2022), liver, kidney, spleen, skin, placenta, saliva, feces, among others (Kutralam-Muniasamy et al., 2023). These studies provide evidence of human exposure to microplastics through inhalation, ingestion, and skin contact (World Health Organization, 2022; X. Yang et al., 2022). However, there is a lack of standardization for the protocols employed and still numerous knowledge gaps about the interactions of microplastics and carried pollutants with human biology (Kutralam-Muniasamy et al., 2023). Consequently, it is expected that this specific topic within the microplastics research field will continue to grow in the following years.

In line with this rising concern about microplastics impacts on human health, WHO and the Food and Agriculture Organization of the United Nations (FAO) published the reports “Microplastics in drinking-water” (World Health Organization, 2019), “Microplastics in food commodities - A food safety review on human exposure through dietary sources” (Garrido Gamarro and Costanzo, 2022), and “Dietary and inhalation exposure to nano- and microplastic particles and potential implications for human health” (World Health Organization, 2022). These reports review the literature and identify knowledge gaps and the highest priority research needs to better assess human health risks from microplastics (and nanoplastics) in e.g., drinking water and food, therefore contributing to spotlight these topics to the scientific community and policy makers.

Concerning the recent developments in EU regulatory and policy instruments, the following instruments were published or are being prepared:

- **European Green Deal** (European Commission, 2019): addresses plastic and microplastic pollution, in line with the EU Plastics Strategy (European Commission, 2018c). “**A new Circular Economy Action Plan**” (COM/2020/98 final), from March 2020 (European Commission, 2020b), is one of the main building blocks of the European Green Deal and also directly addresses (micro)plastic pollution.
- **Regulation EU 2019/1009** (The European Parliament and the Council of the European Union, 2019c) laying down rules on the making available on the **market of EU fertilizing products** and amending Regulations (EC) N° 1069/2009 and (EC) N° 1107/2009 and repealing Regulation (EC) N° 2003/2003: states that biodegradability criteria for polymers need to be assessed, ensuring the polymer decomposition in natural soil conditions and aquatic environments with at least 90% of the organic carbon being converted into carbon dioxide in a maximum period of 48 months after the product end-of-life, and safeguarding that there is no accumulation of plastics in the environment.
- **Biodiversity Strategy for 2030** (European Commission, 2020c): states that “biodiversity is suffering from the release of nutrients, chemical pesticides, pharmaceuticals, hazardous chemicals, urban and industrial wastewater, and other waste including litter and plastics. All of these pressures must be reduced.”
- **Regulation EU 2020/740 on tire labelling** (The European Parliament and the Council of the European Union, 2020b): directly addresses microplastics, linking the abrasion of tires during use as a significant source of microplastics.
- **Regulation EU 2020/2174 on shipments of waste** (European Commission, 2020d): new rules on the shipments of plastic waste are implemented in the EU Waste Shipment Regulation, including the ban of the exporting of hazardous plastic waste and plastic waste that is hard to recycle from the EU to non-OECD countries.
- **Revised EU Drinking Water Directive 2020/2184** (The European Parliament and the Council of the European Union, 2020a): directly addresses microplastics, classifying them as CECs. It states that by 2024, a methodology is going to be adopted to measure microplastics and to include them on the EU Watch List.
- **Chemicals Strategy for Sustainability** (European Commission, 2020e): aims to better protect citizens and the environment and boost innovation for safe and sustainable chemicals. Directly addresses plastics and plasticizers, stating the need to invest in innovative technologies to address the presence of legacy substances in waste streams. The “**Restrictions Roadmap under the Chemicals Strategy for Sustainability**” (European Commission, 2022a) provides the Rolling List, which will be regularly reviewed and consists of three pools of substances or group of substances currently

pointing towards the regulatory hypothesis of restriction. The 2022 version includes BPA in pool 0 (substances in the current pipeline for restrictions) and PVC and its additives in pool 1 (planned restrictions), among others.

- **Pathway to a healthy planet for all - EU action plan: 'Towards zero pollution for air, water and soil'** (European Commission, 2021): includes the target to reduce “by 50% plastic litter at sea and by 30% microplastics released into the environment” as one of the zero pollution targets for 2030.
- **Proposal for a revised Urban Wastewater Treatment Directive** (European Commission, 2022b): directly addresses the microplastic pollution, classifying “micro-plastics” as CECs. The time horizon of 2040 was chosen for certain objectives, including that microplastics emissions should be “reduced by 9%, mainly through actions on improved management of rain waters”. In article 21, a new obligation is introduced to monitor the presence of microplastics in urban runoff, storm water overflows, and outlets of urban WWTPs (including in sludge).
- **Proposal for a Directive amending the Water Framework Directive, the Groundwater Directive and the Environmental Quality Standards Directive** (European Commission, 2022d): the proposal targets microplastics, aiming to included them in the Watch List although a methodology for monitoring has to be developed first.
- **Draft proposal to restrict intentionally added microplastics** (European Commission and European Chemicals Agency, 2022): this restriction would comprise synthetic polymer microparticles below 5 mm and fiber-like particles below 15 mm that are used in products on intention and may result in environmental release. It could ban the use of microplastics in cosmetics, cleaning products, pesticides, and sports fields, amongst others. According to the draft, the “Commission considers it appropriate to exclude natural, degradable and soluble polymers from the definition of synthetic polymer microparticles.”

In parallel, the United Nations have been working towards a “Plastic Treaty”, negotiating in order to have a new legally binding global instrument on plastic pollution by 2024, according to the resolution adopted on March 2022 (UNEP, 2022). This instrument would reflect “the wide range of approaches, sustainable alternatives and technologies available to address the full life cycle of plastics”, and “the need for enhanced international collaboration to facilitate access to technology, capacity-building, and scientific and technical cooperation” (UNEP, 2022).

Apart from the regulatory and policy instruments, other developments occurred with the goal to better respond to the microplastic pollution. One of the lines of research has been in the development of biodegradable plastics or materials that can substitute conventional plastics.

However, there has been a lot of controversy in recent years on which plastics classify as biodegradable because of the compartments in which the plastic must be biodegradable, the rate of degradation in the environment, and if the testing framework is appropriate (Viera et al., 2021). For example, poly(lactic acid) (PLA) has been considered in the past as a biodegradable plastic; however, several researchers have been defending that it should not be classified as such because it is only biodegradable in controlled conditions such as in composting industrial facilities (Al-Khairy et al., 2022). In parallel, the soluble polymers have also created some challenges and controversy, since microplastics are usually considered to be only solid particles or fibers, making soluble polymers a “loophole” in plastic pollution policy, and also less studied regarding their behavior in the environment.

Different technologies have been assessed for their efficiency in microplastics removal or degradation, as upstream or downstream responses for the different environmental compartments. Those that received more attention in the last years have been the ones used in WWTPs (Gao et al., 2023). The development of new or improved technologies has been more focused on biotechnology, such as PETase and MHETase enzymes engineering used for PET degradation into mono(2-hydroxyethyl)terephthalic acid (MHET) and then into ethylene glycol and terephthalic acid (Kumar et al., 2023), or technologies based on photocatalysis, adsorption, or filtration (Pan et al., 2023). Additionally, some industries have been working on reducing the release of microplastics from the use of their products, as is the case with technologies to capture microplastic fibers released when using washing machines, e.g., developing improved filters (Masselter et al., 2023).

3. Microplastics behavior: aging under urban environment stressors



In this chapter, the changes in the chemical structure, surface morphology and crystallinity are reported for three different polymers (LDPE, PET and uPVC) in microplastic form, after being artificially exposed to different aging agents that can affect microplastics in urban environments: ozone, UV-C, and solar radiation. In parallel to the laboratory experiments, the microplastics were exposed to real weathering conditions for three-months in a building rooftop located in the city of Porto (Portugal). By analyzing the (virgin and aged) microplastic samples periodically through ATR-FTIR spectroscopy and estimating the Carbonyl Index, it was possible to sketch the aging degree evolution through time and identify the most aggressive agents for each polymer regarding the changes in their chemical structure. SEM and XRD measurements allowed to complement the ATR-FTIR results, giving a more complete picture of the effects of each treatment on each polymer and suggesting that ATR-FTIR measurements are not sufficient to correctly evaluate the aging degree of microplastics. The changes observed in the microplastic particles studied support the theory that microplastics in the environment undergo aging and change their characteristics through time, potentially affecting their behavior and intensifying their impacts.



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3.1 Introduction

Thanks to the contribution of decades of polymer degradation research (most of which not specific to microplastics), it is known that the aging of microplastic particles (MPPs) can be due to the combined effect of several polymer degradation mechanisms, led by either abiotic or biotic pathways. Abiotic degradation includes processes such as photo-oxidative degradation, thermal degradation, hydrolysis, catalytic degradation, mechanical stress, and exposure to chemically aggressive agents (e.g., ozone). The abiotic pathways can lead to increased surface area for microbial colonization or reduce the polymer molecular weight, and therefore enhance biodegradation (Singh and Sharma, 2008). Thus, these pathways usually precede the biotic pathways, with biodegradation possible because of the activity of some cellular or extracellular enzymes (Gewert et al., 2015).

While the degradation mechanisms and pathways for plastics are well described in the polymer literature, these previous studies are more focused on the stability of the material during its designed lifetime, with fewer studies exploring its end-of-life as plastic litter and the aging processes contribution to the MPPs behavior in the environment, as the contaminants of emerging concern they are now recognized for (Brandon et al., 2016; Gewert et al., 2015; P. Liu et al., 2019). The aging processes are usually considered to be very slow in the natural environment, with the complete degradation (mineralization) of the plastic being currently estimated to take up to centuries or even thousands of years in marine environments or in soil, depending on the polymer and the circumstances in which the degradation mechanisms are active and how they interact (Andrady, 2015; Kyrikou and Briassoulis, 2007; Lundquist et al., 2000; O’Brine and Thompson, 2010). However, in an urban context, apart from the weathering agents, there are other agents that can contribute to enhance MPP aging. For example, the exposure to advanced oxidation technologies and other treatments in drinking water and wastewater treatment plants, in industrial and urban waste (solid waste, effluents and soil) treatments, and in cleaning and disinfection in e.g., hospital and food processing settings have the potential to increase the aging rate and lead to the fragmentation of plastics and land-based microplastics. The MPPs might not be completely eliminated during these treatments and be later released into the environment with chemical and physical modifications, that might influence their sorption of other contaminants and interaction with biota (Fred-Ahmadu et al., 2020; Liu et al., 2020a; Mao et al., 2020). Therefore, the land-based MPPs that reach the oceans might have already started their aging due to these urban environment stressors, while the study of the aging of MPPs has been more focused on the degradation mechanisms that occur only when MPPs are already in marine and coastal environments (Biber et al., 2019; Zhang et al., 2021).

Therefore, the research presented in this chapter aimed at contributing to the current knowledge on the modifications that can result from aging processes and that can impact the MPP behavior.

The targets are the aging stressors present in urban environments, because they have received far less attention, and to explore the hypothesis that land-based microplastics can go through pronounced aging due to urban environment stressors before reaching the oceans. Additionally, since many sorption and ecotoxicological studies have been conducted in the last decade with virgin microplastics, the present study tackles the need to establish relevant artificial aging treatments for each polymer that can be performed in controlled conditions to simulate environmental aging and to obtain aged MPPs to use in other studies. For that, two types of experiments were conducted: i) the MPPs were exposed to different aging stressors that can affect land-based microplastics: ozone, UV-C, and solar radiation (simulated); and ii) weathering experiments were conducted in an urban environment, allowing to evaluate the combined effect of real conditions of solar radiation, air humidity and temperature, and the effect of the precipitation pattern. The aged samples were analysed by different characterization techniques, making possible to detect changes in the chemical structure, surface morphology and crystallinity of the MPPs.

3.2 Material and methods

3.2.1 Microplastic particles

Three different polymers were selected for this work based on their common high consumption by society and persistence on the environment (GESAMP, 2015; Geyer et al., 2017), and their distinct resistance to UV: low-density polyethylene (LDPE), poly(ethylene terephthalate) (PET) and unplasticized poly(vinyl chloride) (uPVC). MPPs made from the selected polymers were acquired in the powder form from Goodfellow (UK), and all the experiments were done with the same lot of each polymer to ensure material consistency. The main characteristics as provided by Goodfellow are listed in Table 3.1. However, the particle size distribution of each polymer was analyzed as described in Section 3.2.1.1, resulting in the mean sizes of the particle diameter of 509 μm for LDPE, 161 μm for PET and 159 μm for uPVC. The polymers were used as received by the supplier.

Table 3.1. Some characteristics provided by Goodfellow (UK) on the acquired microplastic materials.

Characteristic	Low-density polyethylene (LDPE)	Poly(ethylene terephthalate) (PET)	Unplasticized poly(vinyl chloride) (uPVC)
Type	powder	powder	powder
Maximum size (μm)	300	300	250
Density (g cm^{-3})	0.92	1.3 - 1.4	1.4
Resistance to UV	poor	fair	good
Water absorption over 24 h (%)	< 0.015	0.1	0.03 - 0.4
Color	Natural *	Natural *	Natural *

* Natural color is the color of the polymer without any pigment added as colorant. The three polymers studied show a translucent off-white coloration.

3.2.1.1 Particle size distribution

The virgin MPPs were analyzed in duplicates with the Beckman Coulter LS230 (Beckman Coulter, USA) using a diffraction sample cell, allowing the quantification of particles with diameters from 0.375 to 2000 μm . The fluid used for the suspension of the particles in the equipment was distilled water for PET and uPVC, and ethanol for LDPE (due to its density being lower than that of water). Before the analysis, a background measurement was performed with the suspension fluid used. The amount of sample to add for the analysis is automatically determined by the system, therefore the MPPs were added until the system determined that an appropriate concentration was reached. In a first analysis, it was verified that LDPE particles would conglomerate and, consequently, the analysis was repeated after the sample went into the ultrasound bath for 0.5 min.

The statistics of the results were obtained directly with the equipment software (LS software program) that calculates a variety of statistical quantities to characterize the particle size distribution. They were calculated as they would be for a frequency distribution, with the volume percent in a certain size channel being analogous to the frequency of occurrence of a certain value. The main outputs on the arithmetic statistics are summarized in Table 3.2 and Fig. 3.1. Additionally, these results were compared and validated with the images (Appendix D - SEM images) obtained during the Scanning Electron Microscopy (SEM) analysis, as explored in Section 3.2.4.

Table 3.2. Particle size (diameter) distribution for virgin microplastic powders: statistics.

Statistic	Low-density polyethylene (LDPE)	Poly(ethylene terephthalate) (PET)	unplasticized poly(vinyl chloride) (uPVC)
Mean (μm)	509	161	159
Standard deviation (μm)	221	79	43
Coefficient of variation (%)	43	49	27
d10 (μm)	319	68	109
d50 median (μm)	473	150	156
d90 (μm)	721	273	216
Mode (μm)	471	169	154

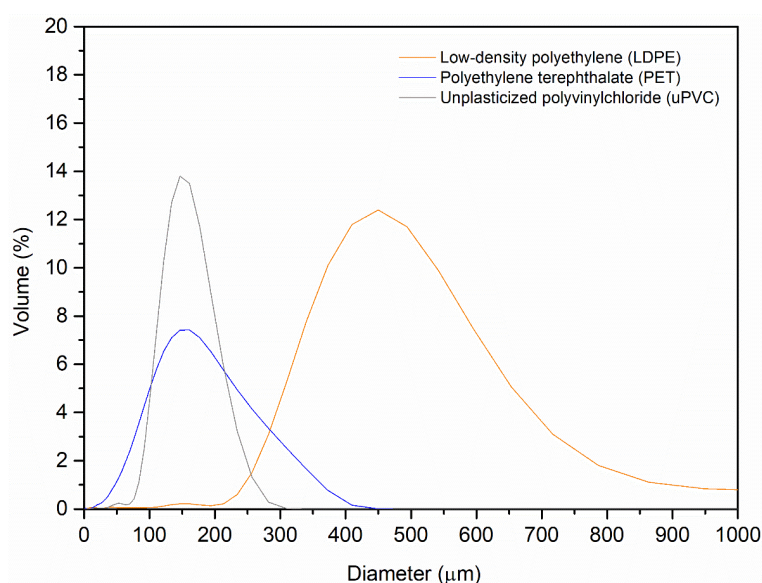


Fig. 3.1. Differential distribution of particle size (diameter) by volume % for virgin microplastic powders.

3.2.2 Simulated treatments setups

With the goal to study the MPP aging due to different agents in an urban environment, several simulated treatments were selected and conducted in laboratory-controlled conditions: ozone treatments, UV-C exposure, and solar radiation exposure.

3.2.2.1 Ozone treatments

For the simulated ozone treatments, two different setups were used to understand the effects on MPPs when i) they are suspended in water and in contact with dissolved ozone, e.g., in the disinfection stage of a water treatment station (Pulicharla et al., 2020; Zhang and Chen, 2020); and ii) they enter in direct contact with ozone gas, e.g., in air treatments such as those used in the food industry (Deng et al., 2020; Giménez et al., 2021) or hospital air disinfection (Dubuis et al., 2020). A schematic representation of each configuration is shown in Fig. 3.2a and Fig. 3.2b, respectively.

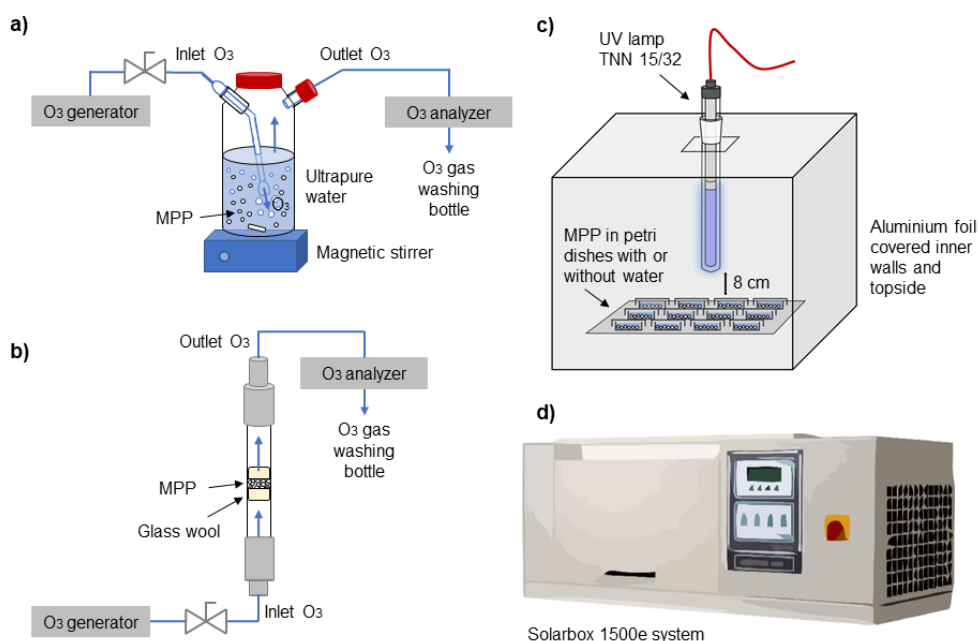


Fig. 3.2. Microplastic particles (MPPs) simulated treatments setups: a) dissolved ozone in ultrapure water with suspended MPPs, b) ozone gas direct treatment, c) MPPs dry or suspended in ultrapure water under UV-C radiation, d) simulated solar radiation exposure inside the Solarbox system.

Each polymer was tested in triplicate experiments. The water selected was Milli-Q ultrapure water. Additionally, both the liquid and gas reactors were always covered with aluminum foil during each experiment, to avoid the influence of the light in the MPP degradation. As a starting point, the exposure time selected was 60 min, accounted for when the ozone inlet (with a previously stabilized concentration) was connected to the liquid or gas reactor.

The first configuration tested (Fig. 3.2a) consists in a glass reactor with 600 mL of ultrapure water with 2 g of MPPs in suspension and a circulation system for ozone gas. The ozone gas reaches the reactor with a 50 g Nm^{-3} concentration and a flow rate of $150 \text{ Ncm}^3 \text{ min}^{-1}$. This concentration and flow rate were selected to have an excess flow of ozone, ensuring that enough ozone is fed to the system for the maximum aging of the MPPs. Entering the system by a glass/ceramic diffuser submerged in the water, the ozone is dissolved in the water and contacts with the MPPs. The excess gas can exit the system through the reactor outlet. The remaining ozone concentration is analyzed at the exit by an ozone analyzer and, afterwards, proceeds into a washing bottle filled with potassium iodide solution to remove the ozone. The suspension was continuously stirred to promote the ozone interaction with the MPPs. After each experiment, the solution was filtered using a glass filtration kit with 47 mm borosilicate glass microfiber filters (Fioroni, France) with a pore size of $1.2 \mu\text{m}$. The filters were preserved in 60 mm soda-lime glass Petri dishes and were dried in a desiccator in the dark, before being analyzed by Attenuated Total Reflection (ATR) - Fourier transform infrared (FTIR) spectroscopy.

The second configuration tested (Fig. 3.2b) consists in a glass column with 2 g of MPPs, supported by lab-grade glass wool fibers, and a circulation system for ozone gas. The ozone gas reaches the column with the same 50 g Nm^{-3} concentration and a flow rate of $150 \text{ Ncm}^3 \text{ min}^{-1}$, as the first configuration. Likewise, the circulation system for ozone gas is very similar to the one used with the first configuration, with the main differences being that no diffuser is used and the ozone inlet is directly connected to the column at the start of the experiment. At the end of each experiment, the MPPs are removed from the column and stored in 60 mm soda-lime glass Petri dishes, before being analyzed by ATR-FTIR spectroscopy.

The ozone generator used for all experiments was the Enaly 1KNT-24 (Enaly, China), while the ozone analyzer used was the BMT 964 (BMT Messtechnik GmbH, Germany). The tubes used to transport the ozone gas were made from perfluoroalkoxy (PFA) 1/8 flexible tubing with metal tube fittings, from Swagelok. The magnetic stirring bar used had a polytetrafluoroethylene (PTFE) encasement. Otherwise, most of the components of each configuration were made from glass, to avoid introducing unwanted microplastics in the system.

Regarding control samples, an experiment without ozone was performed with each polymer in the first setup and used as the reference material when comparing the IR spectra. These experiments replicate all the procedure adopted except that no ozone was fed to the system. For all the remaining configurations, the reference materials used were the virgin microplastics and, consequently, no control samples were obtained.

The experimental conditions and ozone concentrations were recorded and are included in Table 3.3.

Table 3.3. Experimental conditions and ozone concentrations for ozone aging experiments.

Experiment	Polymer	Polymer mass (g)	Average IN O ₃ (g Nm ⁻³)	Average OUT O ₃ (g Nm ⁻³)	Flow rate (Ncm ³ min ⁻¹)	Agitation (rpm)
Ozone dissolved in water (1 h exposure)	LDPE	2.00	50.3	20.3	152	1100
	LDPE control		-	-		
	PET		50.0	22.0	152	300
	PET control		-	-		
	uPVC		49.4	34.4	150	650
	uPVC control		-	-		
Ozone gas direct treatment (1 h exposure)	LDPE	2.00	50.4	46.1	151	-
	PET		50.4	49.2	148	-
	uPVC		50.1	49.3	148	-

3.2.2.2 UV-C exposure

UV-C treatments can be used as an efficient food preservation technology, such as for microbial reduction in milk (Ward et al., 2019), as well as in water and wastewater treatment applications, such as hospital laundry wastewater treatment (Zotesso et al., 2017). Consequently, the MPPs present in these settings, e.g., microfibers released during laundry (Napper and Thompson, 2016), can go through aging processes due to exposure to UV-C radiation. Additionally, UV-C radiation has been used as a disinfection strategy in healthcare settings, e.g., in HVAC (heating, ventilation and air conditioning) systems and installed on the ceiling of operating rooms, with this technology gaining even more attention recently due to multidrug resistance in bacteria and because of the COVID-19 pandemic (Ethington et al., 2018; Lauritano et al., 2020).

In order to assess the aging of MPPs under UV-C exposure, the setup represented in Fig. 3.2c was assembled using a box with aluminum foil covered inner walls and topside. 60 mm Petri dishes (bottom made of soda-lime glass and top made of quartz) were placed on an aluminum tray. An UV-C lamp in a quartz tube was secured vertically 8 cm from the Petri dishes with a clamp holder on a support stand. The UV lamp used was the Heraeus TNN 15/32 (Heraeus, Germany), which is a low-pressure 15 W mercury vapor lamp with an emission line at 253.7 nm (Table 3.4).

Quartz was used for Petri dishes top since it transmits most of the radiation with wavelengths higher than 200 nm, while if a soda-lime glass Petri dish top was used it would absorb the wavelengths below 360 nm. These wavelengths are relevant to the study (namely for the UV-C experiments, simulated solar radiation experiment and rooftop weathering experiments), since they correspond to a component of the solar spectral irradiance, specifically to UV (short-wave UV-C: 100-280 nm, middle-wave UV-B: 280-315 nm, long-wave UV-A 315-400 nm), which is known for increasing synthetic polymers degradation (Andrady, 2017; Andrady et al., 2003; Wang et al., 2016). The comparison between the ultraviolet-visible spectrum for both Petri dish materials

used can be found in Fig. 3.3. The Petri dishes tops were necessary to avoid contaminating the samples with MPPs from the environment.

Table 3.4. Relative spectral energy distribution of the Heraeus TNN 15/32 UV-C lamp (Heraeus, Germany) as given by the supplier.

Wavelength in nm	Relative spectral energy distribution
248	0.1
254	100
265	0.9
276	0.1
280	0.1
289	0.1
297	0.6
302	0.4
313	2.8
334	0.1
366	2.2
405/8	1.6
436	1.1
546	1.6
577/9	0.5

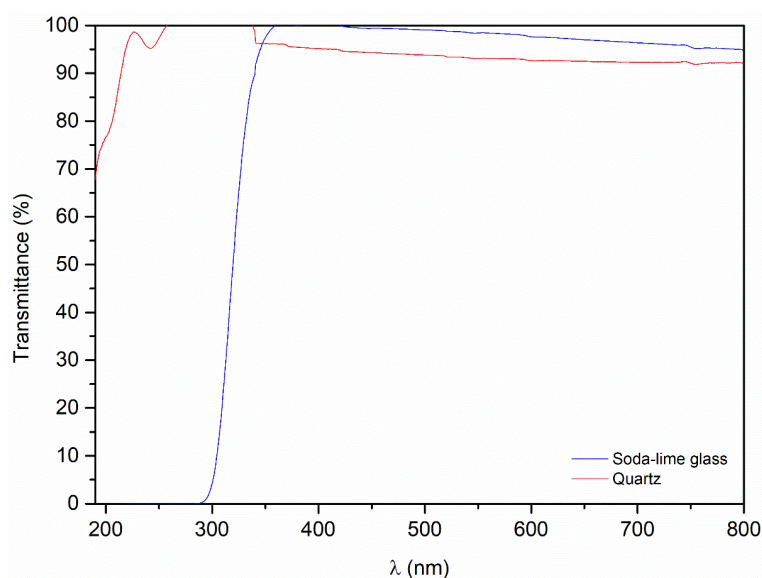


Fig. 3.3. Ultraviolet-visible (UV-Vis) spectra for the soda-lime glass (bottom) and quartz (top) Petri dishes used in the UV-C radiation, solar radiation and rooftop weathering experiments. The optical transmittance of the materials was followed by UV-Vis spectroscopy using a JASCO V-560 spectrophotometer (JASCO, Japan).

Two sets of experiments were conducted with the UV-C setup: i) 0.1 g of MPPs were subject to a maximum of 96 h of exposure to UV-C radiation, and ii) 0.1 g of MPPs in a suspension of 3 mL of Milli-Q ultrapure water were subject to a maximum of 96 h of exposure to UV-C radiation. Each Petri dish had 0.1 g of a single polymer and was under UV-C radiation for consecutive periods of 6 h each different day until the desired exposure time of 12, 24, 36, 48, 60, 72, 84, or 96 h. The water level in each Petri dish for the second set of experiments was kept by adding more ultrapure water, since it started evaporating during the experiment, albeit slowly. Each Petri dish was very carefully manually stirred after each period of 6 h of exposure, to ensure that all MPPs were being irradiated.

After each sample reached the desired time of exposure, the sample was dried in a desiccator in the dark and, then, stored in the dark until the end of the experiment in order to have all samples analysed together by ATR-FTIR spectroscopy. The experimental conditions are listed in Table 3.5.

Table 3.5. Experimental conditions for the UV-C exposure experiments.

Experiment	Exposure time (h)	Polymer	Polymer mass (g)	Temperature	Water added (mL)
UV-C	12, 24, 36, 48, 60, 72, 84, 96	LDPE	0.100	Room temperature	-
		PET			
		uPVC			
		LDPE			
UV-C + H ₂ O		PET	0.100		3
		uPVC			

3.2.2.3 Simulated solar radiation exposure

A simulated solar radiation exposure experiment was conducted to compare results with the rooftop weathering experiments. The simulated experiment allowed to assess the solar radiation influence on MPP aging separately from the effect of the air temperature and humidity variations. Additionally, it allowed to obtain MPP samples that were aged at controlled experimental conditions, specially concerning the constant solar irradiance used throughout the experiment.

The photodegradation of the MPP samples was carried out using a Solarbox 1500e system (CO.FO.ME.GRA, Italy) (Fig. 3.2d), which uses as irradiation source a 1500 W xenon lamp equipped with a cut-off soda-lime glass UV filter with infrared reflection coating to simulate outdoor exposure. The system was programmed to deliver 500 W m⁻² light irradiance, of which 416 W m⁻² reached the Petri dishes that contained the MPP samples, as measured by a UV-Vis

spectroradiometer (USB2000+, Ocean Optics / Ocean Insight, USA) (Fig. 3.4 for a comparison of the rooftop and Solarbox solar irradiance measurements). This light irradiance selected allows to perform the photodegradation experiments faster than under natural solar conditions.

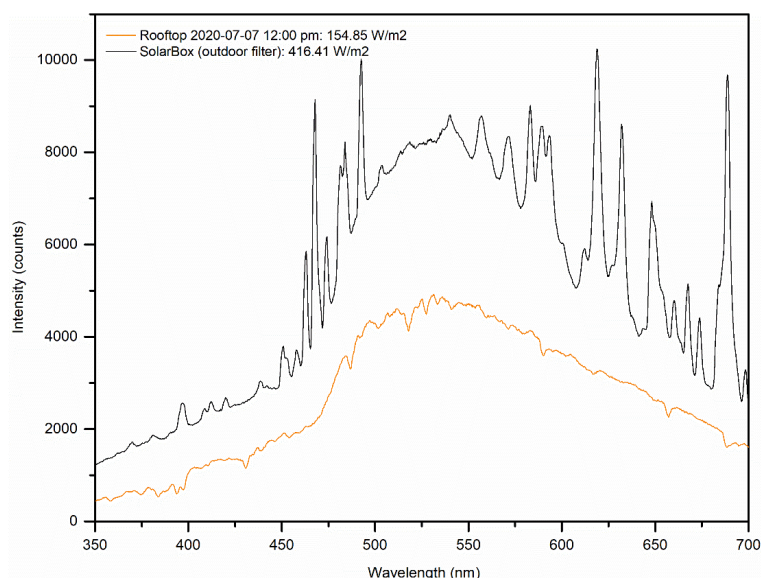


Fig. 3.4. Irradiance measurements determined using a UV-Vis spectroradiometer (USB2000+, Ocean Optics / Ocean Insight, USA).

The MPP samples inside Petri dishes (bottom made of soda-lime glass and top made of quartz like in the UV-C experiments) were exposed to the simulated solar radiation with the same concern of carefully manually stirring each Petri dish after each period of 6 h of exposure. About 0.5 g of each polymer MPPs, in triplicate, were irradiated inside the Solarbox for periods of 6 h day^{-1} until the desired accumulated exposure time of 120 h. At every 24 h of exposure time, a small subsample of each of the 9 MPP samples was collected with a steel micro spatula and stored in the dark in a 5 mL amber glass vial until the end of the experiment, in order to have all samples analyzed together by ATR-FTIR spectroscopy. This resulted in triplicated samples for the three polymers and for the exposure times of 24, 48, 72, 96 and 120 h.

Since the goal of this experiment was to study the individual effect of solar radiation on MPP aging, the temperature reached inside the Solarbox was a concern, as it could promote the degradation of the polymers. It was measured temperatures of around 36 °C inside the system using a type-K thermocouple probe with a Total-Range thermometer (Traceable, USA). Therefore, a small temperature stress test was also conducted, for which 0.5 g of each polymer was added inside a Petri dish (all soda-lime glass) wrapped in the outside with aluminum foil and

kept in the laboratory oven at the controlled temperature of 45 °C for 96 consecutive hours. After cooling, the samples were analyzed by ATR-FTIR spectroscopy and visually inspected. No changes were detected with the temperature stress test for any of the polymers, as discussed further in this chapter. The summary of the experimental conditions of this test and the simulated solar radiation exposure are listed in Table 3.6.

Table 3.6. Experimental conditions for the simulated solar radiation exposure experiment and temperature stress test.

Experiment	Exposure time (h)	Polymer	Polymer mass (g)	Temperature	Water added (mL)
Simulated solar radiation using SolarBox	24, 48, 72, 96, 120	LDPE	0.500	Around 36 °C for 6 h day ⁻¹	-
		PET			
		uPVC			
Temperature test	96	LDPE	0.500	45 °C	-
		PET			
		uPVC			

3.2.3 Rooftop (RT) weathering experiments

In order to study the MPP aging under real conditions of weathering, regarding temperature, sunlight, and humidity variations, and maximize solar exposure of these samples, a simple experimental setup was designed, assembled and installed at the rooftop of the Chemical Engineering Department of the Faculty of Engineering of the University of Porto. These experiments were conducted for three months from 18th of May to 17th of August of 2020, making it 13 full weeks. These three months were selected based on the period when the length of the day, as measured by the average sunlight hours per day, is higher in Porto: May to August (Observatório Astronómico de Lisboa, 2020). Consequently, the MPPs were exposed to the maximum time of solar radiation per day in Porto in 2020, as well as to some of the highest air temperatures registered that year in the city. Therefore, while these experimental conditions are specific to the climate of Porto (temperate climate, type Csb under the Köppen-Geiger climate classification) and cover only a fourth of the year, they were selected to maximize the aging of the MPPs by weathering in a three-month period in Porto.

The setup, as depicted in Fig. 3.5 and Fig. 3.6, incorporates three main components: a filtration and collection system for rain and two trays set without inclination (perforated to drain the rainwater), where microplastics undergo aging. One of the challenges in designing the setup was to avoid using plastic materials, to minimize the input of other microplastics in the system, and consequently most of the materials used are made of steel, wood or glass.



Fig. 3.5. Rooftop weathering experimental setup: rainwater filtration and collection system (above) and perforated trays with microplastic particles in Petri dishes (below).

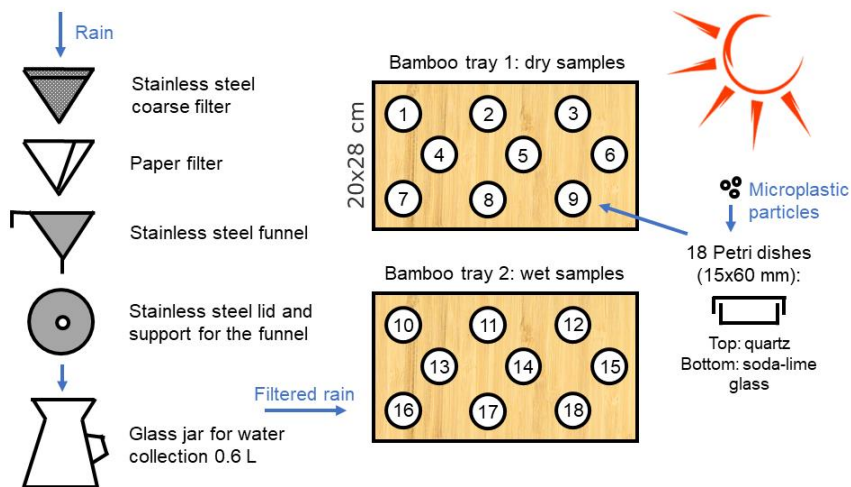


Fig. 3.6. Rooftop weathering experimental setup: schematic.

The goals pursued with the filtration system were to collect rainwater to be added to the Petri dishes on one of the trays, while minimizing the virgin MPP contamination with environmental MPPs, due to atmospheric deposition, and transport by water, wind and biota. For that, it includes a sequence of two filters, a stainless-steel funnel (maximum diameter of 125 mm) that supports them, a stainless-steel lid that seals the filtered water storage and also supports the funnel, and the glass jar that can stock up to 0.6 L of filtered rainwater. The first filter, made from stainless-steel, has two main purposes: i) to protect the paper filter below it from

weathering, and ii) to retain the coarser particles that can potentially deposit in the system and, consequently, lead to the faster clogging of the paper filter. For the second filter, it was selected a VWR paper filter with 240 mm of diameter and a pore size of 20-45 μm . Research findings on the size distribution of microfibers and other microplastic particles in atmospheric fallout samples show that the number of MPPs decreases substantially when their size decreases below 100 μm , with the plastic nature of smaller MPPs being very difficult to identify (Brahney et al., 2020; Dris et al., 2016). Therefore, it was expected that microplastics below 45 μm would not constitute a measurable interference on the experiments results.

The two perforated bamboo trays used in the setup contain and protect the 60 mm Petri dishes and allow easy transport when needed. For each tray, 9 Petri dishes bottoms (soda-lime glass) were glued to the tray, while the Petri dishes tops (quartz) were secured with duct tape, to ensure their content protection from wind, rainwater, and birds. The number of Petri dishes in each tray allows for the exposure of the 3 polymers (LDPE, PET and uPVC) separately and in triplicate with each experiment (Table 3.7).

Table 3.7. Experimental conditions for the rooftop weathering experiments.

Tray	Polymer	Polymer mass (g)	Rainwater added to each Petri dish (mL)
Rooftop tray 1 (RT1)	LDPE	0.500	No rainwater added
	PET		
	uPVC		
Rooftop tray 2 (RT2)	LDPE	0.500	0.75 mL (1 st June), 5.00 mL (12 th June), 5.00 mL (29 th June), 5.00 mL (17 th August)
	PET		
	uPVC		

The virgin MPPs (0.5 g in each Petri dish) were placed to undergo aging under natural solar exposure and temperature variations in the first tray (RT1), while the second tray (RT2) also allows to study the influence of the presence of water. With that goal, the filtered rainwater collected with the filtration system was manually added to the Petri dishes in the second tray, following the precipitation pattern, while ensuring that all the other parameters are the same. From 18th of May to 17th of August of 2020, thirteen samples were collected in triplicate for each polymer and tray (RT1 and RT2) using a steel micro spatula at the end of each week of weathering, at around 5 pm (GMT summer time or BST). All the samples collected were dried in a desiccator in the dark for at least a week and, then, stored in the dark in 5 mL amber glass vials until the end of the experiments to be then analyzed by ATR-FTIR spectroscopy. Rainwater was added 4 times throughout the duration of the experiments to a maximum of 5 mL in each Petri dish in tray RT2, as listed in Table 3.8. The filtration system paper filter was replaced and stored on 29th June and 17th August, but no damage was detected. The Petri dishes quartz tops were frequently cleaned in the outside with a wet cloth to ensure that dust did not block the

sunlight, and each tray was very carefully manually shaken frequently to ensure that all MPPs were being irradiated.

Table 3.8. Data on the rainwater collected by the filtration system in the rooftop.

Week	Days	Weather station precipitation (mm)	Rainwater collected (mL)	Rainwater added to RT2 Petri dishes (mL)	pH
2	31 st May to 1 st June	1.4	7.0 ± 0.2	0.75	5
4	11 th to 12 th June	8.2	134 ± 2	5.00	5
4	12 th to 13 th June	0.6	-	a	-
5	16 th June	0.9	-	a	-
6	24 th June	0.1	none	-	-
6	26 th to 28 th June	3.5	53.6 ± 1.0	5.00	5
13	14 th to 17 th (until 11 am) August	8.6	166 ± 2	5.00	5
13	17 th August (after 11 am)	7.7	-	a	-

^a No water was added because the Petri dishes from tray RT2 had already the maximum amount of water stipulated of 5 mL/Petri dish.

Meteorological public data available at the Portuguese Institute for Sea and Atmosphere (IPMA) website (Portuguese Institute for Sea and Atmosphere I. P., 2020) was recorded daily to create an air temperature, precipitation, air relative humidity, and UV index record for the closest active meteorological station (Porto - Massarelos). The meteorological record is represented in Fig. 3.7, Fig. 3.8, and Fig. 3.9.

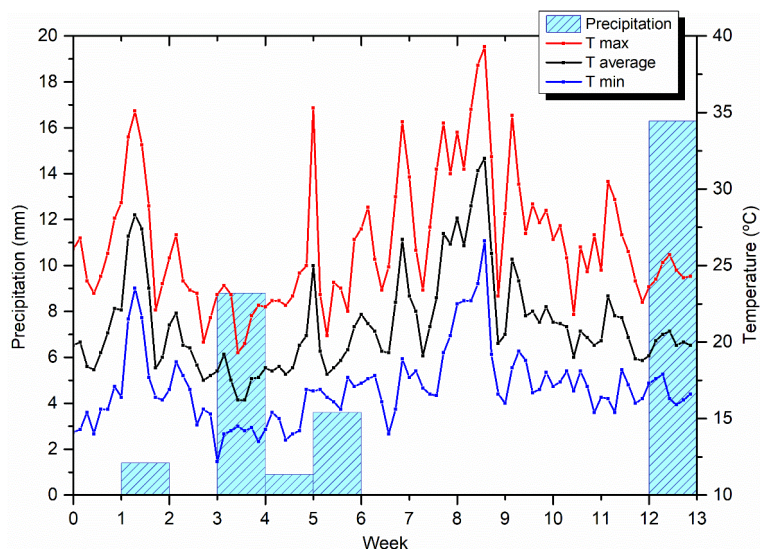


Fig. 3.7. Daily maximum, average and minimum air temperature and weekly accumulated precipitation recorded from 18th May to 17th August 2020, for Porto – Massarelos IPMA weather station.

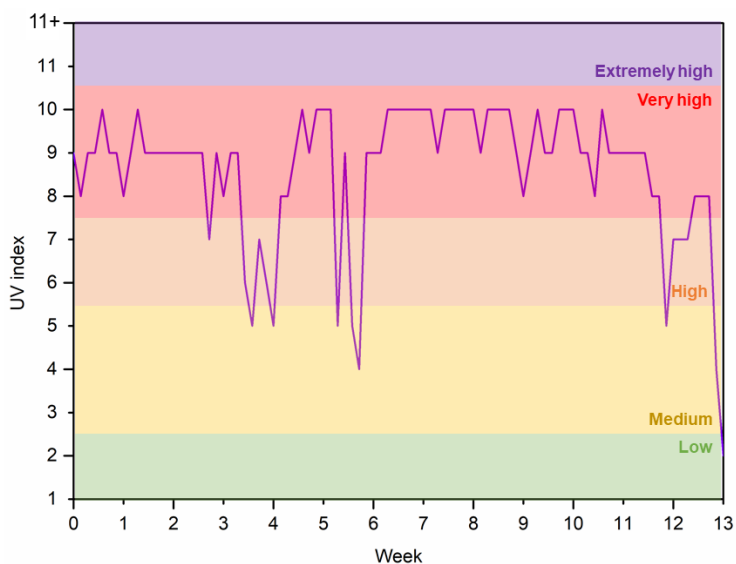


Fig. 3.8. UV index calculated daily by IPMA from 18th May to 17th August 2020 for Porto city.

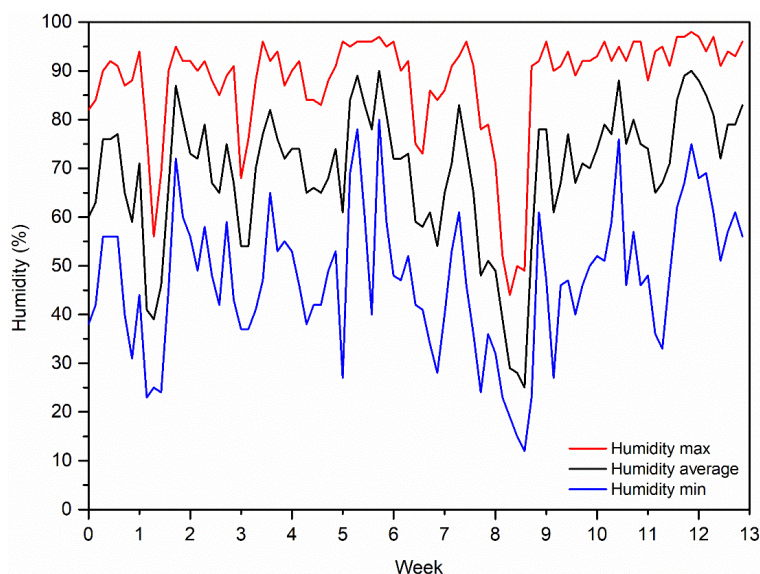


Fig. 3.9. Daily maximum, average and minimum air relative humidity recorded from 18th May to 17th August 2020, for Porto – Massarelos IPMA weather station.

3.2.4 Characterization of MPP samples

Microplastics samples were characterized by Fourier transform infrared (FTIR) spectroscopy with an Attenuated Total Reflection (ATR) sampling technique, Scanning Electron Microscopy (SEM), and X-ray diffraction (XRD) analysis. All the samples were analyzed with ATR-FTIR spectroscopy, but only selected samples were analyzed by XRD and SEM techniques. Additionally, one sample of aged LDPE MPPs was analyzed by Raman microscopy (μ Raman), as explained in 3.3.2. For every characterization technique used, a virgin/pristine sample of each polymer was analyzed to detect changes in the MPPs due to the aging treatments/weathering.

3.2.4.1 ATR-FTIR spectroscopy

ATR-FTIR measurements were made using a FTIR-6800 spectrometer equipped with a DLaTGS detector (JASCO, Japan) with a MIRacle single reflection horizontal ATR attachment (PIKE Technologies, USA), with a ZnSe crystal. Each measurement was performed with a 4 cm^{-1} resolution of the $4000 - 600\text{ cm}^{-1}$ region, with 128 scans/sample. Background (empty and clean system) was done every two samples analyzed. The baseline correction was accomplished with the Spectra Manager software with points at 4000, 3000 (only for uPVC), 2000 and 600 cm^{-1} .

3.2.4.2 Raman microscopy

The Raman microscopy (μ Raman) measurements were made using a WITec alpha300 R confocal Raman microscope (WITec, Germany) that uses a WITec UHTS 300 VIS spectrometer (600 lines/mm grating) coupled with a FI CCD detector (spectral resolution of $0.8 \text{ cm}^{-1}/\text{pixel}$, 1650×200 pixels, -60°C), at a magnification of 100x with the selection of the Zeiss EC Epiplan-Neofluar Dic 100x/0.9 objective. The spectra were recorded using 18 mW of laser power and the 532 nm excitation wavelength, with 30 accumulations and an integration time of 0.5 s per spectrum. The data processing was achieved with the Project FIVE software for background subtraction and graphical representation.

3.2.4.3 SEM analysis

SEM analysis was performed in low vacuum mode, using a high resolution (Schottky) environmental scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis: FEI Quanta 400 FEG ESEM (FEI Company, USA) / EDAX Genesis X4M (EDAX - AMETEK, USA). All the MPP samples were previously coated with an Au/Pd thin film, by sputtering, using the SPI Module Sputter Coater equipment (SPI, USA).

3.2.4.4 XRD analysis

XRD analysis was conducted with a PANalytical X'Pert MPD apparatus (PANalytical, Netherlands) equipped with an X'Celerator detector and secondary monochromator ($\text{Cu K}\alpha \lambda = 0.154 \text{ nm}$, 40 kV, 30 mA; data recorded at a 0.017° step size, 100 s step^{-1}).

The diffractograms were analyzed to obtain each sample degree of crystallinity, using the HighScore 4.8 software. A baseline was defined adjusting the bending factor and granularity parameters. First, the total area under the peaks was calculated and, second, the bending factor and granularity were adjusted so that the baseline passes through the base of the crystalline peaks. This second time, the area under the peaks was calculated as the “sum of crystalline peaks areas” (ϕ_c). The amorphous area (ϕ_a) is the difference between the total area and the crystalline area. After obtaining the sum of the crystalline peaks and the amorphous component for each sample diffractogram, the degree of crystallinity (X_c) was estimated as defined by Eq. 3.1 (for LDPE and PET) and Eq. 3.2 (for uPVC, $C/A = 1.51$) (Obande and Gilbert, 1989).

$$X_c \text{ (LDPE and PET)} = \frac{\phi_c}{\phi_c + \phi_a} \times 100 \quad \text{Eq. 3.1}$$

$$X_c (uPVC) = \frac{1}{\frac{C}{A} \times \frac{\phi a}{\phi c} + 1} \times 100 \quad \text{Eq. 3.2}$$

For LDPE, three main crystalline peaks were identified in the diffractograms, at the positions 19.9°, 21.4° and 23.7°, which are in line with the literature (Li et al., 2019; Papajani et al., 2015). For PET, six main crystalline peaks were assigned: 16.4°, 17.6°, 21.6°, 22.8°, 26.1° and 32.4°, similarly to Farrow and Preston (1960). While for uPVC, five main crystalline peaks were identified: 15.5°, 16.9°, 18.7°, 24.6° and 40.3°, similarly to Obande and Gilbert (1989).

3.2.5 Carbonyl Index

The IR (infrared) spectra obtained for LDPE and uPVC samples were used to estimate the Carbonyl Index (*CI*), since the ATR-FTIR technique can measure the formation of several by-products containing carbonyl functionalities on the surface of the particles that result from the oxidation of the material (Andrady, 2017; Barbeş et al., 2014). The *CI* is determined by calculating the ratio of the carbonyl peak relative to a reference peak (Almond et al., 2020). Therefore, the *CI* was used in this work as a metric for the oxidation of polymers, enabling the quantification of some of the changes in the chemical structure of the material. This approach is particularly interesting for this work, since one absorption peak with a maximum height at the wavenumbers 1712 - 1722 cm⁻¹, corresponding to the carbonyl groups, can be easily identified for two of the polymers selected (LDPE and uPVC), different intensities being observed for the different aging processes tested and exposure times. The *CI* was not estimated for PET because this polymer has a characteristic IR absorption peak of strong intensity at 1714 cm⁻¹ band due to stretching of C=O of the carboxylic acid group (Edge et al., 1996; Tobin, 1957).

As described by Almond et al. (2020), there is no universal method for determining *CI* currently. The methodology changes with some researchers choosing to calculate the *CI* as the ratio of the two peaks maximum absorbance height or of the two peaks absorbance areas. Additionally, the reference peak selected for each polymer is different among different studies, and researchers also vary the methodology adopted by using transmission or absorbance mode with ATR-FTIR spectroscopy. For this study, the ATR-FTIR measurements were conducted in transmission mode and the maximum height of the selected peaks was converted from transmittance (*T*) to absorbance (*A*) by Eq. 3.3. After testing different peaks as reference and considering only those that do not show any change in shape regardless of the several treatments tested, the absorbance of the methylene group (-CH₂-) symmetric stretching vibration was selected as reference peak for both polymers. The *CI* was calculated as shown by Eq. 3.4.

$$A = \log_{10} \frac{1}{T(\text{maximum height})} \quad \text{Eq. 3.3}$$

$$CI = \frac{A_{\text{carbonyl group (1712-1722)}}}{A_{\text{methylene group (2848 for LDPE or 2844 for PVC)}} \quad \text{Eq. 3.4}$$

The statistical analysis of the *CI* results included the calculation of the average *CI* for the triplicate samples (n=3), the respective standard deviation (SD) and, whenever a pattern or trend was observed, a regression analysis. Additionally, the *CI* results (UV-C, UV-C with humidity and Solarbox; and the rooftop weathering experiments) were compared for the same exposure times using One-Way ANOVA and the post hoc Tukey test (OriginPro 9 software).

3.3 Results and Discussion

3.3.1 ATR-FTIR and Carbonyl Index

The characterization of the MPP samples with ATR-FTIR spectroscopy allowed to verify some modifications in the chemical structure of the particles of the three selected polymers, particularly the severity of oxidation caused by the aging processes tested. The full set of spectra of the polymers exposed to the different treatments can be found in Appendix C - ATR-FTIR spectra.

With respect to both LDPE and uPVC, it was possible to clearly identify for several samples one absorption peak with maximum height at the band 1712 - 1722 cm⁻¹ (Fig. 3.14 and Fig. 3.19). This peak resulted from the formation of carbonyl species (C=O) due to physicochemical processes that affected the particles during the aging experiments. As expected, the carbonyl absorbance peak intensity was verified to be proportional to the exposure time. This consequence of the MPP aging was translated to aging kinetics by quantifying the oxidation intensity with the *CI*.

3.3.1.1 LDPE

For LDPE (*CI*_{LDPE, virgin} = 0.004 ± 0.001), the ozone treatments (1 h) were verified to be the most aggressive among the simulated treatments, as assessed by the ATR-FTIR spectra and *CI* (Table 3.9). As shown in Fig. 3.10a, the average *CI* for the direct treatment with ozone gas reached a value of 0.100 ± 0.002, while the treatment with ozone dissolved in ultrapure water resulted in

an average CI of 0.028 ± 0.001 . During the treatment with dissolved ozone in ultrapure water, hydroxyl radicals ($HO^\bullet$) may be generated from the decomposition of ozone (Faria et al., 2006; Sotelo et al., 1987), which could boost the aging process since these radicals are very reactive and have a stronger oxidation potential than ozone. Additionally, due to the presence of water, hydrolysis could also take place and contribute to the oxidation of the polymer (Massey et al., 2007). Therefore, the aging mechanisms for the experiment with ozone dissolved in ultrapure water include direct reactions with ozone, but also potentially indirect reactions with secondary oxidants, namely hydroxyl radicals, and hydrolysis. Considering the results and that much more ozone was consumed during the experiment with ozone dissolved in water (Table 3.3), it can be concluded that LDPE aging with a direct treatment with ozone gas is more severe in the oxidation of the surface of the particles, at room temperature and neutral pH.

 Table 3.9. Carbonyl Index (CI) for LDPE samples: simulated treatments.

Treatment	Exposure time (h)	Average CI	Standard deviation (SD)
Virgin	0	0.004	0.001
Ozone gas	1	0.100	0.002
Dissolved ozone	1	0.028	0.001
LDPE in stirred UP water	1	0.005	
UV-C	0	0.006	
	12	0.008	0.001
	24	0.010	0.001
	36	0.011	0.001
	48	0.015	0.001
	60	0.017	0.001
	72	0.018	0.001
	84	0.022	0.002
	96	0.027	0.002
	0	0.002	
UV-C with humidity	12	0.006	0.001
	24	0.008	0.001
	36	0.010	0.001
	48	0.011	0.001
	60	0.013	0.001
	72	0.016	0.001
	84	0.017	0.001
	96	0.020	0.001
	0	0.003	
Solarbox	24	0.008	0.001
	48	0.013	0.002
	72	0.022	0.001
	96	0.033	0.003
	120	0.044	0.004

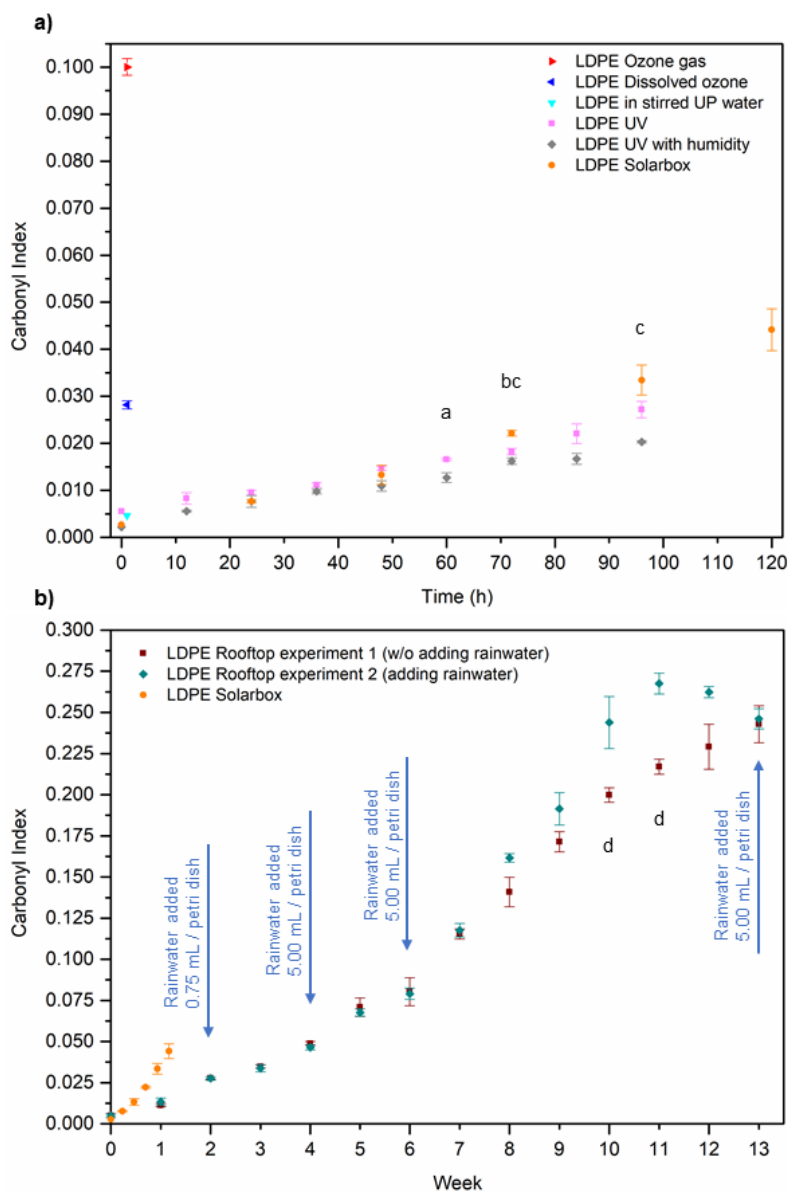


Fig. 3.10. Carbonyl Index (CI) for LDPE samples aged a) with the simulated treatments and b) by the rooftop weathering experiments. Error bars represent the standard deviation (SD) (n=3). The letters a, b, c and d indicate that the difference of the means between treatments (a: UV-C and UV-C with humidity; b: UV-C and Solarbox; c: UV-C with humidity and Solarbox; d: rooftop weathering experiments 1 and 2) with same exposure time is significant at the 0.05 level.

LDPE under UV-C radiation shows an increasing oxidation degree with time, with the average CI as high as 0.027 ± 0.002 for the experiment without water (96 h) and 0.020 ± 0.001 for the experiment with water (96 h). Similarly to the ozone experiments, the presence of water (at room temperature and neutral pH) does not seem to increase the oxidation of LDPE under UV-C radiation, when evaluating the aging degree with the CI (the difference between the treatments is only significant for an exposure time of 60 h). The slightly lower CI for the experiment with water can be ascribed to the partial absorption of the UV radiation by water (Mason et al., 2016; Quickenden and Irvin, 1980). When a regression analysis (Fig. 3.11 and Fig. 3.12) is applied to the CI results plotted as a function of the exposure time, it is necessary to resort to a 2nd order polynomial model for the UV-C experiment ($R^2 = 0.959$), while a linear model is sufficient for the UV-C experiment with the MPPs suspended in ultrapure water ($R^2 = 0.946$).

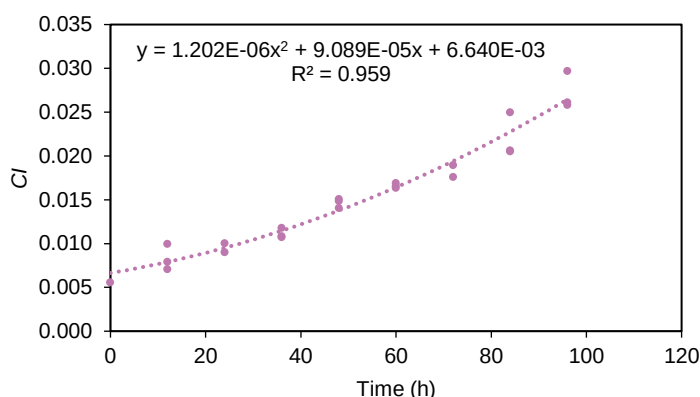


Fig. 3.11. Carbonyl Index for LDPE under UV-C radiation.

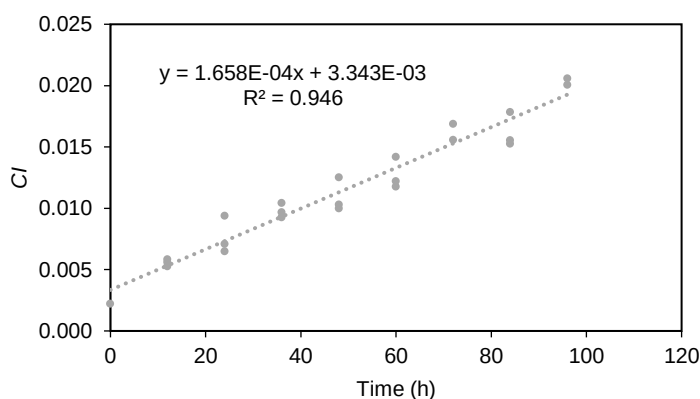


Fig. 3.12. Carbonyl Index for LDPE suspended in water under UV-C radiation.

The experiment with simulated solar radiation using the Solarbox resulted in a *CI* pattern similar to those observed in the beginning of the UV-C experiments, but diverged after 48 h of exposure (the difference between the Solarbox treatment and the UV-C treatments is significant for 72 h and 96 h of exposure), i.e., leading to higher *CI* values for the same exposure times. The maximum average *CI* obtained was 0.044 ± 0.004 for 120 h of exposure. The *CI* results obtained at different exposure times in the Solarbox are best described by a 2nd order polynomial model ($R^2 = 0.966$) (Fig. 3.13). One possible cause for the higher level of oxidation observed with the Solarbox in comparison to that achieved with UV-C could be due to the temperatures reached inside the Solarbox (36 °C). However, since the temperature stress test of 45 °C for 96 h did not result in any measurable change in the ATR-FTIR spectrum, the level of oxidation cannot be justified by a simple action of the temperature. The combined effect of solar radiation with temperature cannot be thus excluded, higher temperature variations being expected to promote an increased aging degree of the LDPE MPPs (Andrady, 2003; Andrady et al., 2003).

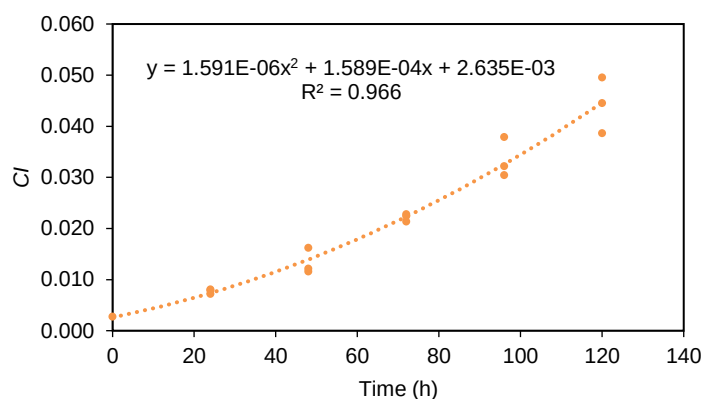


Fig. 3.13. Carbonyl Index for LDPE under solar radiation (Solarbox).

As shown in Fig. 3.10b, during the 3 months of the RT weathering experiments, LDPE reached a higher degree of oxidation when compared to any of the simulated treatments conducted (Fig. 3.10a). The maximum average *CI* of 0.268 ± 0.006 for 11 weeks of weathering was observed with addition of rainwater, while the experiment without addition of rainwater resulted in maximum average *CI* of 0.243 ± 0.011 for the maximum exposure time tested of 13 weeks (Table 3.10). Both weathering experiments have very similar *CI* results for the first 7 weeks of weathering, with the addition of rainwater contributing to higher *CI* for the samples of weeks 8 to 12 (Fig. 3.10b) (the difference between the treatments is only significant during weeks 10 to 11). Throughout the last two weeks of the weathering experiments (week 12 and 13), the *CI* decreased

for the LDPE samples that were in contact with rainwater, with the final average *CI* (week 13) being identical to the one obtained for the samples for which no rainwater was added. This decrease of the *CI* is in line with the decrease of the air temperature and UV index (from 8-10 to 2-9, Fig. 3.8) during the last two weeks of the experiments. The decrease of the *CI* for these samples, and the deceleration of the *CI* growing for the samples without rainwater during the last two weeks, can be both explained by the reduction in the weekly production of carbonyl functionalities due to the weaker oxidation of the surface of the particles, whereas the oxidation products continue to go through photodegradation with generation of CO₂ (Andrady, 2017; Fernando et al., 2007). Therefore, for some of the samples under certain conditions, the degradation of the oxidation products could be higher than the formation of these products, leading to an overall reduction of the estimated *CI*. Furthermore, since it rained during the last week, the addition of water to the samples might have washed away some of the oxidation products containing carbonyl species, helping in the decline of the *CI* for these samples.

 Table 3.10. Carbonyl Index (*CI*) for LDPE samples: rooftop experiments.

Exposure time (weeks)	Rooftop experiment 1		Rooftop experiment 2 (with rainwater)	
	Average <i>CI</i>	Standard deviation (SD)	Average <i>CI</i>	Standard deviation (SD)
0	0.005	0.001	0.005	0.001
1	0.011	0.001	0.013	0.002
2	0.028	0.001	0.028	0.001
3	0.035	0.001	0.034	0.002
4	0.049	0.001	0.046	0.002
5	0.071	0.006	0.068	0.002
6	0.080	0.008	0.079	0.003
7	0.115	0.003	0.118	0.004
8	0.141	0.009	0.162	0.003
9	0.171	0.006	0.191	0.010
10	0.200	0.004	0.244	0.016
11	0.217	0.005	0.268	0.006
12	0.229	0.014	0.262	0.003
13	0.243	0.011	0.246	0.006

In order to compare the results of the first week (during the second half of May) of the RT weathering experiment without adding rainwater with the results obtained with the simulated solar radiation treatment with the Solarbox, the exposure time of the simulated experiment was converted to weeks of exposure in the outdoor by considering that the week 18th - 25th May 2020 in Porto city had on average 14.7 h day⁻¹ of sunlight (Observatório Astronómico de Lisboa, 2020). As shown in Fig. 3.10b, the average *CI* obtained for the simulated solar radiation treatment is higher than the average *CI* obtained for the weathering experiment samples, with 1.2 weeks

(120 h) of simulated solar exposure ($CI = 0.044 \pm 0.004$) showing a CI close to the result of 4 weeks of RT weathering ($CI_{RT1, \text{week } 4} = 0.049 \pm 0.001$). That was expected since the MPP samples were exposed to a constant high irradiance (416 W m^{-2}) and temperature in the simulated solar radiation experiment, while the irradiance at 12 pm in one of the hottest days and with high UV index (UV index = 10) of July was measured as 155 W m^{-2} at the rooftop.

Apart from the absorption peak that resulted from the formation of carbonyl species (C=O), there were some other substantial modifications in the chemical structure of LDPE that were detected by ATR-FTIR spectroscopy (Fig. 3.14), particularly for the RT weathering experiments samples:

- i) new absorption band at $3673 - 2960 \text{ cm}^{-1}$ (O-H bonds, possibly due to the decomposition/formation of functional groups of hydroperoxides and/or alcohols) (Gugumus, 1989; Massey et al., 2007);
- ii) distortion of the LDPE medium intensity characteristic absorption peaks at 1468 cm^{-1} (CH_2 bending deformation) and at 718 cm^{-1} (CH_2 rocking deformation);
- iii) increased intensity of the characteristic absorption peak at 1377 cm^{-1} (CH_3 symmetric bending deformation);
- iv) increase of absorption intensity and new absorption peaks at the $1468 - 717 \text{ cm}^{-1}$ band, with a maximum height peak at 1176 cm^{-1} (wagging deformation) and at 909 cm^{-1} (vinyl groups).

For the samples from the Solarbox experiment, it was detected the absorption peaks at 1176 cm^{-1} (wagging deformation) and at 909 cm^{-1} (vinyl groups). In the case of the ozone gas experiment, it was possible to detect the absorption peak at 965 cm^{-1} (vinylene groups), also detected for the samples of the RT weathering experiments. Moreover, in the triplicates of the samples from the UV-C experiment with water (particularly for 96 h of exposure), new absorption bands at 1595 cm^{-1} (possibly due to carbonyl groups), and at 1176 cm^{-1} (wagging deformation) were observed, as well as an increased intensity of the peak at 1080 cm^{-1} (C-C stretching deformation amorphous regions). The absorption peak at 888 cm^{-1} (vinylidene groups) was detected for most of the samples in early stages of oxidation, being known to decrease preceding the development of vinyl groups during the photo-oxidation of polyethylene (Arnaud et al., 1984).

The distortion identified in the LDPE characteristic peak at 1468 cm^{-1} , detected in the samples exposed to simulated solar radiation and to the RT weathering, excluded its use as the reference peak for the estimation of the CI. Indeed, this absorption peak and the one at 718 cm^{-1} are frequently used as reference peaks for the CI calculation in many studies with polyethylene (Almond et al., 2020), but could not be selected as such in the present study due to their distortion when LDPE was exposed to some treatments and long periods of weathering. While

the bases of the strong intensity characteristic absorption peaks of CH₂ asymmetric (2915 cm⁻¹) and symmetric (2848 cm⁻¹) stretching were altered, the height of both peaks maintained its characteristics, making possible their use as reference peaks when calculating the *CI* with the height of the absorption peaks. The CH₂ symmetric stretching peak was selected as reference peak in this study for LDPE.

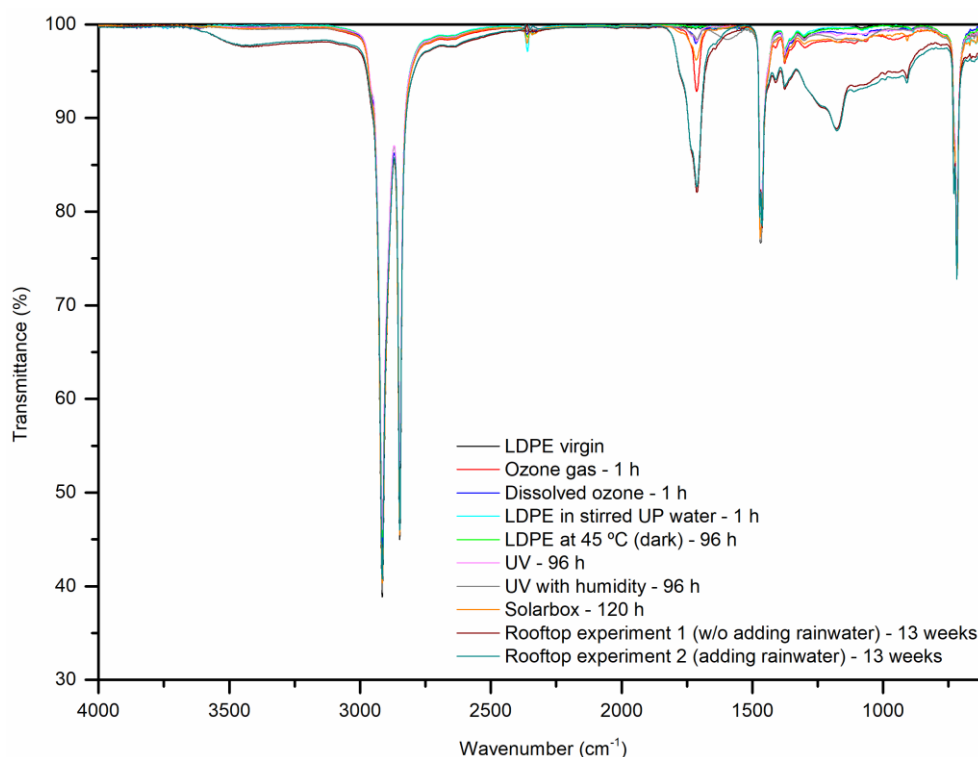


Fig. 3.14. ATR-FTIR complete set of spectra for LDPE.

3.3.1.2 PET

Comparing the ATR-FTIR spectra obtained for the PET samples under different aging treatments (Fig. 3.15), it is difficult to detect changes for most of the samples, with exception for the samples that were exposed to the direct treatment with ozone gas (1 h) and that were exposed to 13 weeks of RT weathering and in contact with rainwater. As explained previously in Section 3.2.5, PET has a characteristic IR absorption peak of strong intensity at 1714 cm⁻¹ (stretching of C=O of the carboxylic acid group), making it difficult to assess the oxidation degree of the polymer based on the formation of carbonyl species. Based only on the results obtained with ATR-FTIR spectroscopy, it is only possible to conclude that the two previous referred treatments

were able to lead to chemical structure changes in PET MPPs, detected as the widening of the 1714 cm^{-1} peak base, but it cannot be excluded that the other treatments aged PET. Additionally, it was detected a new absorption band at $3615 - 3115\text{ cm}^{-1}$ (O-H bonds) for the samples of 13 weeks of RT weathering experiment with rainwater, what could be the combined result of photochemical and hydrolytic degradation of the polymer, since these are considered the main degradation pathways for PET in the environment (Bond et al., 2018).

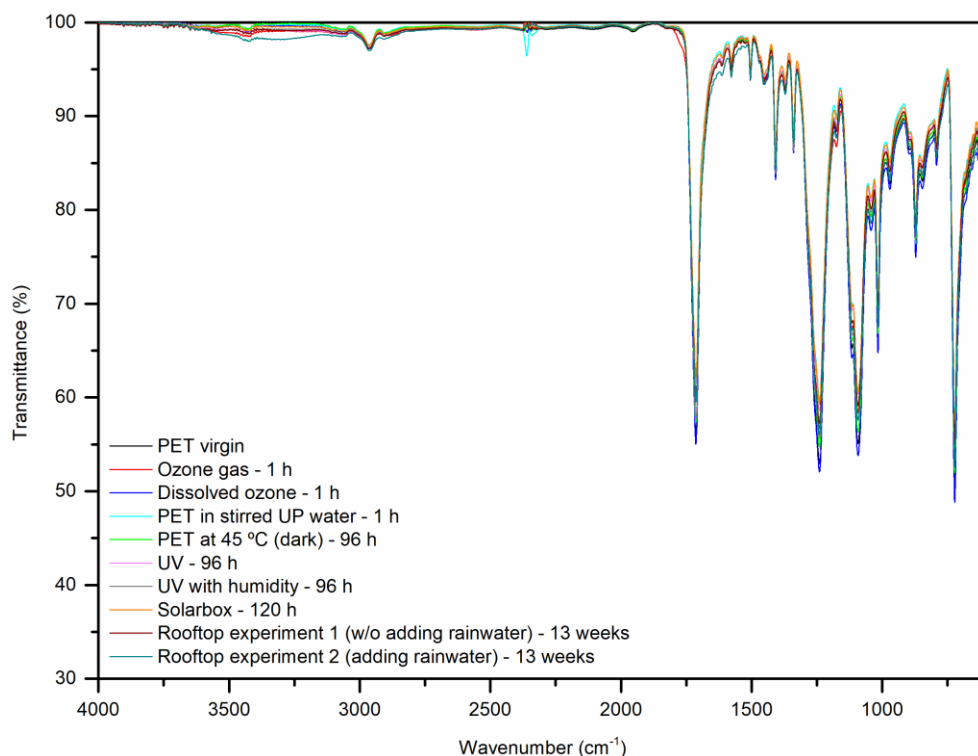


Fig. 3.15. ATR-FTIR complete set of spectra for PET.

3.3.1.3 uPVC

Analyzing the aging treatment effects on uPVC MPPs ($CI_{\text{uPVC, virgin}} = 0.73 \pm 0.15$) by ATR-FTIR spectroscopy and with the CI (Table 3.11 and Table 3.12), it is verified that the UV-C treatments (Fig. 3.16a) were the most aggressive on the chemical structure of the material, with the CI reaching average values of 9.34 ± 0.47 (96 h) for the experiment without water and 8.37 ± 0.23 (96 h) for the experiment with ultrapure water. As seen for the LDPE samples, the presence of water (at room temperature and neutral pH) does not seem to increase the oxidation of the MPPs when assessing their aging degree with the CI (results significantly lower for 12 h, 48 h, 72 h and 84 h of exposure). When applying a regression analysis (Fig. 3.17 and Fig. 3.18) to the CI results

as a function of the exposure time, the conclusion is that a 2nd order polynomial model is necessary for the UV-C experiment ($R^2 = 0.973$), while a linear model is sufficient for the UV-C experiment with the MPPs suspended in ultrapure water ($R^2 = 0.942$).

Table 3.11. Carbonyl Index (*CI*) for uPVC samples: simulated treatments.

Treatment	Exposure time (h)	Average <i>CI</i>	Standard deviation (SD)
Virgin	0	0.73	0.15
Ozone gas	1	0.85	0.06
Dissolved ozone	1	0.68	0.05
uPVC in stirred UP water	1	0.73	
UV-C	0	0.88	
	12	1.79	0.18
	24	3.44	0.67
	36	4.37	0.34
	48	6.00	0.60
	60	7.31	0.17
	72	8.10	0.27
	84	8.97	0.08
	96	9.34	0.47
	0	1.03	
UV-C with humidity	12	2.89	0.48
	24	3.11	0.21
	36	4.12	0.64
	48	4.46	0.39
	60	6.21	0.78
	72	7.20	0.19
	84	7.89	0.15
	96	8.37	0.23
Solarbox	0	0.55	
	24	0.85	0.02
	48	0.85	0.11
	72	0.96	0.04
	96	1.08	0.05
	120	1.09	0.04

The other simulated treatments tested (Fig. 3.16a) did not affect the *CI* of the uPVC MPPs, namely the ozone treatments ($CI_{\text{uPVC, ozone gas}} = 0.85 \pm 0.06$ and $CI_{\text{uPVC, dissolved ozone}} = 0.68 \pm 0.05$), or had very little impact on it, as it is the case with the simulated solar radiation exposure experiment with the Solarbox equipment ($CI_{\text{uPVC, 120h SB}} = 1.09 \pm 0.04$) (results significantly different from the UV-C treatments for all exposure times). No satisfactory model was found, when doing a regression analysis, between the slow increase of the *CI* with exposure time for the simulated solar radiation experiment.

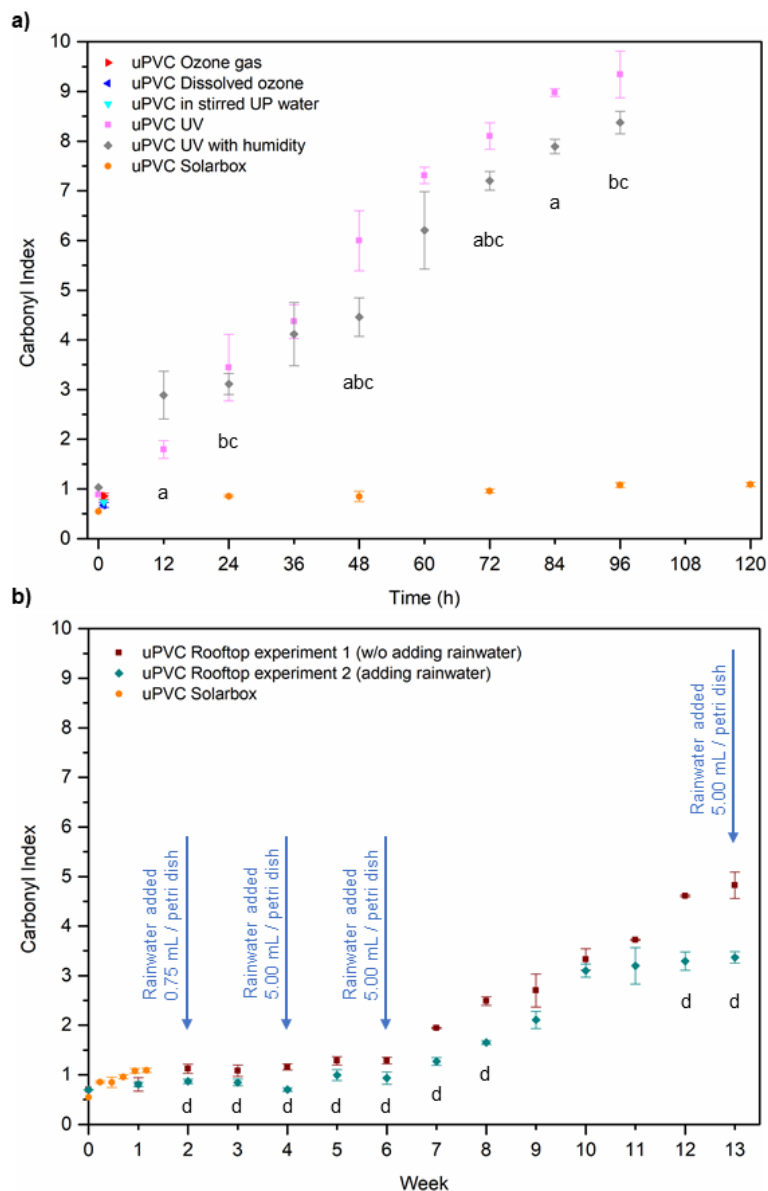


Fig. 3.16. Carbonyl Index (CI) for uPVC samples aged a) with the simulated treatments and b) by the rooftop weathering experiments. Error bars represent the standard deviation (SD) (n=3). The letters a, b, c and d indicate that the difference of the means between treatments (a: UV-C and UV-C with humidity; b: UV-C and Solarbox; c: UV-C with humidity and Solarbox; d: rooftop weathering experiments 1 and 2) with same exposure time is significant at the 0.05 level.

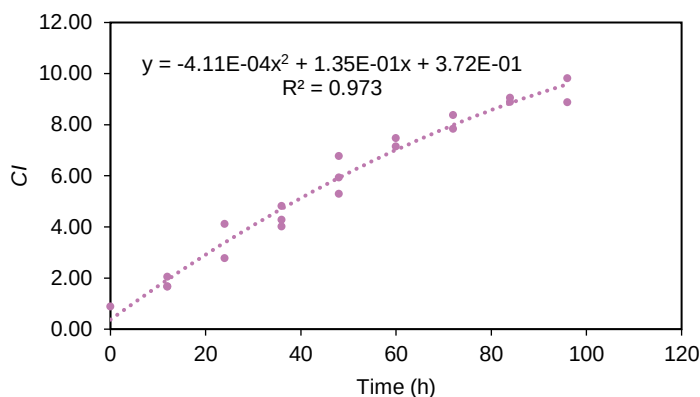


Fig. 3.17. Carbonyl Index for uPVC under UV-C radiation.

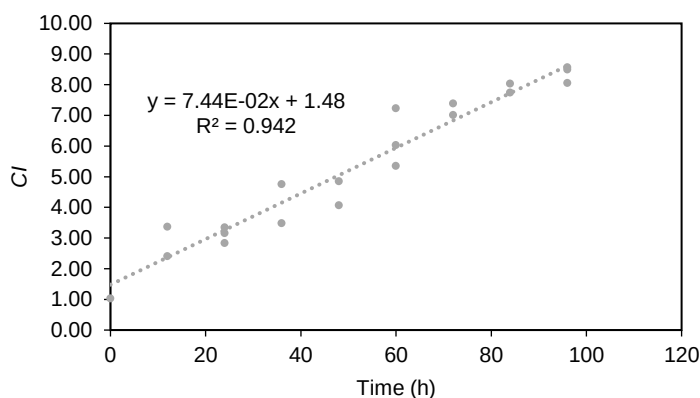


Fig. 3.18. Carbonyl Index for uPVC suspended in water under UV-C radiation.

During the RT weathering experiments (Fig. 3.16b), it was observed a slow increase of the *CI* for uPVC MPP samples for the first 6 weeks of weathering. During weeks 7 to 11, both samples (with and without rainwater) showed an increase of the carbonyl species production rate, which was expected considering that it was during these weeks that the UV index was the highest (UV index > 8) and that UV radiation seems to be one of the main aging agents for uPVC. Towards the end of the experiments, the average *CI* continued to increase but at a slower rate, particularly during the last week when the UV index dropped to 2 (low). Throughout the 13 weeks of the experiments, the samples to which was added rainwater following the precipitation pattern always had lower average *CI* when comparing to the experiment without added rainwater (significantly different for all exposure times except for weeks 1 and 9 to 11). That was even more discernible during the last two weeks, considering that, after week 10, the *CI* almost

stabilized for the samples with rainwater. The highest average *CI* detected for both experiments was reached at the end of the 13 weeks of weathering, with a *CI* of 4.82 ± 0.27 for the experiment without rainwater and 3.37 ± 0.12 for the experiment with rainwater addition.

Table 3.12. Carbonyl Index (*CI*) for uPVC samples: rooftop experiments.

Exposure time (weeks)	Rooftop experiment 1		Rooftop experiment 2 (with rainwater)	
	Average <i>CI</i>	Standard deviation (SD)	Average <i>CI</i>	Standard deviation (SD)
0	0.70	0.01	0.70	0.01
1	0.81	0.13	0.81	0.04
2	1.12	0.09	0.87	0.04
3	1.08	0.11	0.85	0.07
4	1.16	0.06	0.70	0.04
5	1.28	0.08	0.99	0.11
6	1.29	0.07	0.93	0.13
7	1.94	0.01	1.27	0.08
8	2.49	0.09	1.65	0.04
9	2.70	0.33	2.11	0.17
10	3.33	0.21	3.10	0.13
11	3.72	0.01	3.20	0.37
12	4.61	0.02	3.29	0.18
13	4.82	0.27	3.37	0.12

Comparing the simulated solar radiation exposure results to the weathering achieved at the rooftop for the uPVC samples, it is observed that the simulated solar radiation exposure results in higher *CI* values than those of the first week of weathering. The cause for this is thought to be the same as what was previously identified for LDPE samples, although the difference between the average *CI* for the simulated experiment and the weathering experiments was not as substantial as it was for LDPE. This happens because LDPE is more affected by the irradiance at the wavelength range of solar radiation than uPVC, that is more aged by short-wave radiation such as UV-C.

There were few sizeable changes detected by ATR-FTIR spectroscopy apart from the formation of carbonyl species. One of those changes was detected as a higher absorption at the band $3650 - 3000 \text{ cm}^{-1}$ (O-H bonds) for both types of UV-C experiments samples, particularly for higher exposure times (Fig. 3.19). It should be noted that several samples of aged uPVC, and particularly those irradiated with UV-C and exposed to 3 months of weathering, underwent yellowing discoloration, with visual observation of the samples suggesting that the yellowing is correlated to the exposure time. This characteristic is usually attributed to the formation of conjugated polyenes due to the PVC photothermal degradation and can be detected by ATR-FTIR spectroscopy with a new peak with a maximum at 1620 cm^{-1} and that can be used to calculate

the Polyene Index (*PI*) in a similar method to the *CI*, by normalizing the result with a reference peak (Andrady et al., 1998; Merah et al., 2013). The polyene absorption peak (maximum at 1635 - 1625 cm^{-1}) was indeed observed in the uPVC spectra, on the right shoulder of the carbonyl group absorption peak, and matching the evolution of the MPPs coloration observed for the samples exposed to UV-C and weathering.

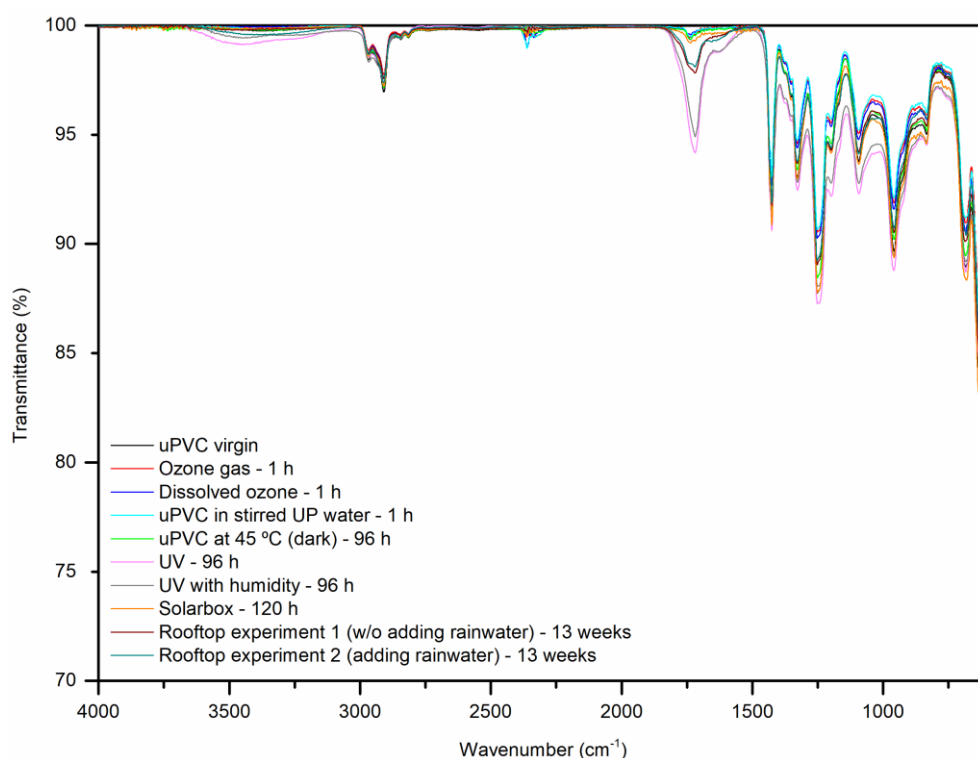


Fig. 3.19. ATR-FTIR complete set of spectra for uPVC.

3.3.2 SEM analysis and Raman microscopy

Samples obtained for the higher time of exposure of each treatment were analyzed by SEM. For most of the aging treatments conducted no major morphological changes were detected, with exception for the RT weathering samples of LDPE and one of PET weathering samples (Appendix D - SEM images, for the complete set).

The aging and overall degradation of thermoplastics exposed to mechanical stress and/or chemically aggressive environments have been associated with the formation of a microcrack network within a surface layer of the degraded polymer, initiating the plastic fracture (Choi et al., 2005). As shown in Fig. 3.20, 13 weeks of RT weathering led to the formation of a network of randomly distributed cracks and signs of deformation (parallel cracks, top left of Fig. 3.20d) on the surface of the LDPE MPPs without (Fig. 3.20b) and with the addition of rainwater following the precipitation pattern (Fig. 3.20c). All these morphologic changes observed on the surface of LDPE can provide preferential areas for foreign substances or organisms to become lodged in the particles (Cooper and Corcoran, 2010), increasing their potential as transport vectors for co-occurring pollutants and microorganisms in the environment. Furthermore, since the initiation of oxidative degradation in plastics is known to be localized in a thin surface layer and that develops around the initiation points, these morphologic changes can accelerate the aging of the polymer, particularly since the cracks can grow into deeper layers of the particle providing a site for fragmentation (Andrady, 2017).

The LDPE sample that was in contact with rainwater shows the formation of more cracks, which are deeper than those formed on the surface of the LDPE MPPs without the addition of rainwater. In this sample, it was also detected the growth of what is believed to be microorganisms on the surface (detailed in Fig. 3.20d). This hypothesis is supported by the μ Raman analysis performed on this LDPE sample (RT2, 13 weeks), in which the foreign elements on the surface of the particle (Fig. 3.21) showed fluorescence (Fig. 3.22) and got burned under the laser, similarly to Radić (2019), and displayed a completely distinct spectrum when compared to the spectra of the pristine and aged LDPE. This microbial colonization was only detected for LDPE in contact with rainwater and, despite all samples being handled in the same settings, it cannot be excluded the possibility of an accidental contamination during the 13 weeks of the experiment.

Although the LDPE final *CI* and ATR-FTIR spectra obtained for the weathering experiments with and without the addition of rainwater were similar (Section 3.3.1.1), the SEM analysis confirms that the effects of the two experiments on the LDPE MPPs were different and that MPP samples with similar *CI* can be at different stages of aging. Even though the results suggest that rainwater played a role in the aging process of LDPE MPPs, it is difficult to conclude if the higher level of morphological changes observed in the MPPs that were in contact with rainwater is the result of the direct effect of the presence of rainwater, or an indirect result because it contributed to

the colonization of the MPPs by microorganisms that could also have enhanced the aging process through biotic pathways, or a combination of both.

One of the possible explanations for rainwater helping the aging process can be due to the acidity of the water (pH = 5), since the presence of ultrapure water (neutral pH) in the other experiments did not increase the *CI* or led to evident morphological changes on the surface of the particles for those samples, comparing to the corresponding samples without water. Furthermore, pH has been considered an important factor that affects the hydrolytic stability of a polymer, with potential acceleration of the degradation process due to the catalytic effect of the acid or base, although hydrolysis can occur in a neutral environment (pH = 7) (Speight, 2018). Additionally, the variation of the air temperature throughout the duration of the RT weathering experiments might also contribute to the aging effect of the rainwater, since the *CI* results suggest that when the water is added the degradation slows down but during the water evaporation process and following weeks it accelerates.

It is difficult to assess if flaking occurred for any polymer studied, due to the initial irregularities on the surface of the particles. Nevertheless, in one of PET RT weathering samples, namely the one corresponding to 13 weeks of weathering without the addition of rainwater, it was discernible the flaking of some areas of the PET MPPs (Fig. 3.20f).

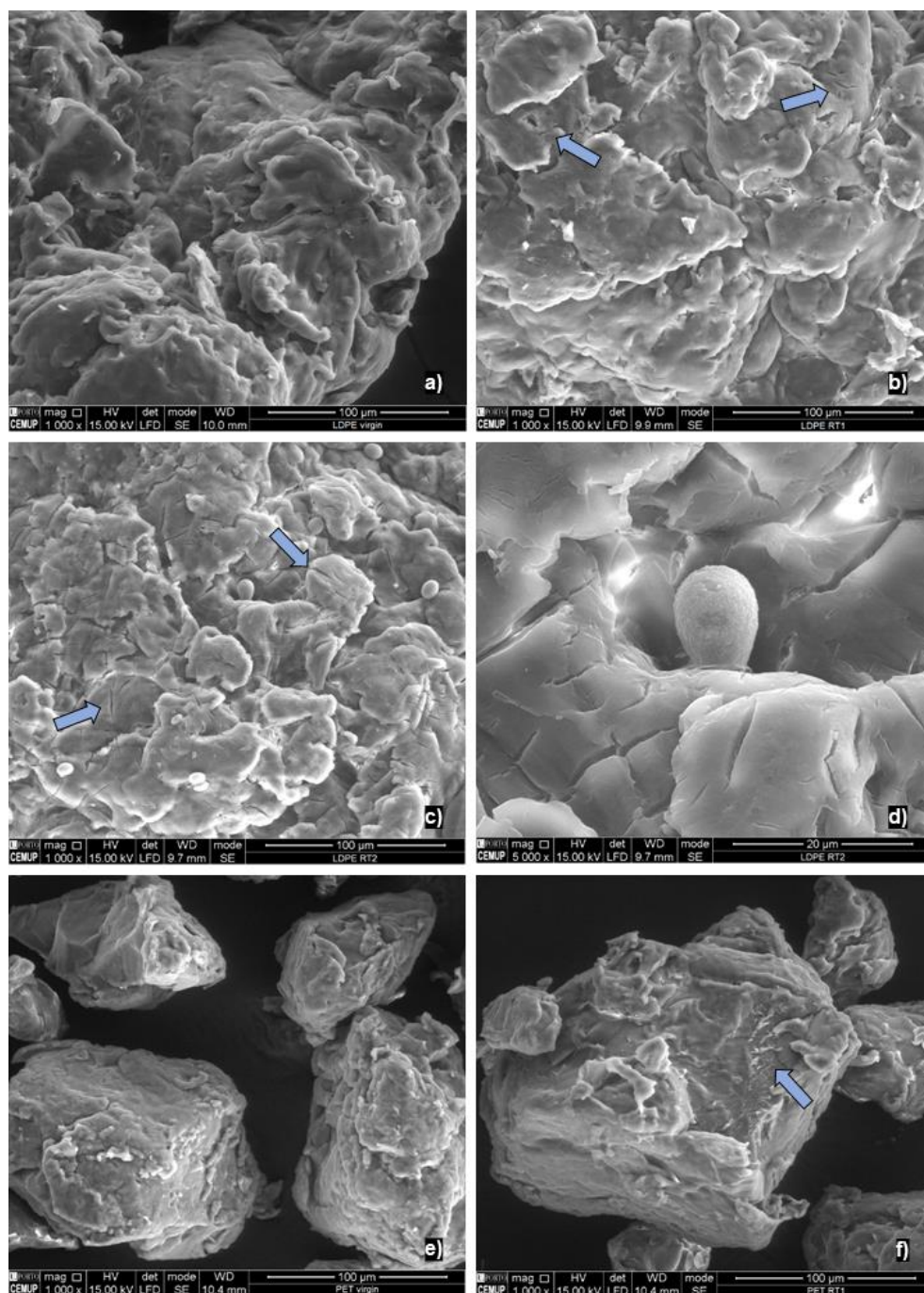


Fig. 3.20. SEM images: a) virgin LDPE, b) LDPE rooftop weathering RT1 (13 weeks), c) LDPE rooftop weathering RT2 (with rainwater) (13 weeks), d) LDPE rooftop weathering RT2 detail (13 weeks), e) virgin PET, f) PET rooftop weathering RT1 (13 weeks).

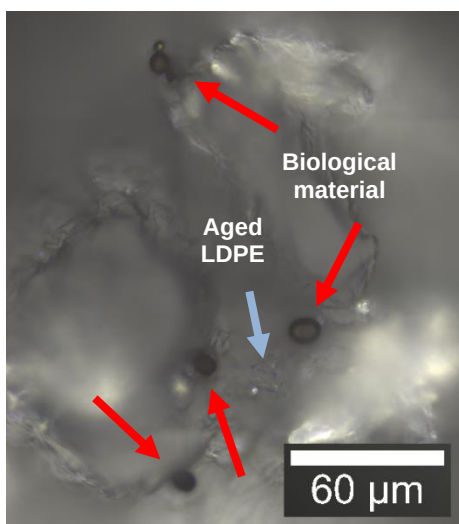


Fig. 3.21. μ Raman image of the area of LDPE RT2 (13 weeks) sample analyzed.

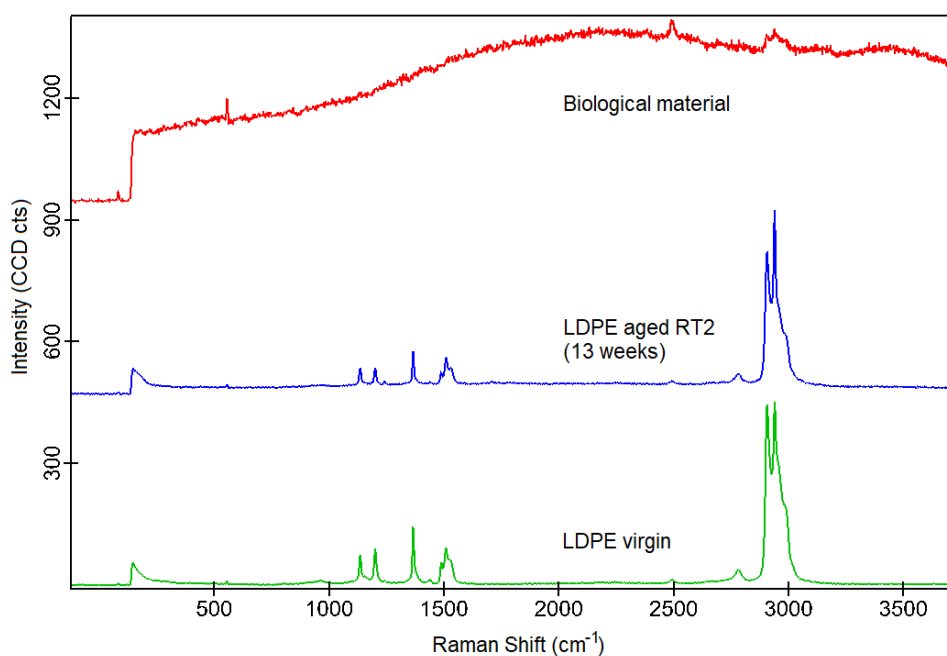


Fig. 3.22. μ Raman spectra for LDPE.

3.3.3 XRD analysis and degree of crystallinity

Similarly to the SEM analysis, samples obtained for the higher time of exposure of each treatment were analyzed by the XRD technique (Appendix E - XRD diffractograms). As detailed in Section 3.2.4.4, the degree of crystallinity of the samples was obtained by integration of the areas of the crystalline peaks, using the XRD diffractograms. The results, listed in Table 3.13, show that the degree of crystallinity of most of the LDPE samples increased or was maintained compared to the corresponding virgin MPPs, while PET crystallinity stayed mostly unchanged. The uPVC crystallinity decreased slightly for most of the samples aged but increased when the microplastics were exposed to dissolved ozone in water.

Table 3.13. LDPE, PET and uPVC degree of crystallinity obtained with XRD analysis.

Experiment	% Crystallinity (X_c)		
	LDPE	PET	uPVC ¹
Virgin	34.3	29.1	21.7
O ₃ gas (1 h)	33.0	30.2	17.5
O ₃ dissolved (1 h)	35.6	30.6	25.4
UV-C (96 h)	34.2	31.5	18.2
UV-C with humidity (96 h)	32.0	31.2	18.3
Solarbox (120 h)	39.0	32.6	22.1
RT weathering 1 (13 weeks)	40.3	30.4	17.8
RT weathering 2 (rainwater) (13 weeks)	42.1	28.5	19.5

¹ uPVC degree of crystallinity was calculated similarly to Obande and Gilbert (1989), using a C/A value of 1.51.

For LDPE, the results suggest that the samples exposed to solar radiation treatments (Solarbox and weathering) were those that increased more their crystallinity (of 34% to 39 - 42%). This increase of crystallinity could be explained by the amorphous component being the one preferentially degraded, as previously described for photo-oxidation and weathering (Andrady, 2017; Halle et al., 2017). Additionally, due to photo-oxidation and/or thermo-oxidation, chain scission occurs, making the amorphous chains more mobile and free to further crystallize by chemi-crystallization, what can also lead to the growth of crystal dimensions (Guadagno et al., 2001; Guo and Wang, 2019). Furthermore, these results are in line with those obtained with SEM, since the weathering treatment with addition of rainwater is also the most aggressive for LDPE MPPs according to this technique. On the contrary, considering the ATR-FTIR and *CI* results, it was expected that the other photo-oxidation treatments tested, namely UV-C treatments, would have a bigger impact on the crystallinity of the samples. UV radiation (more than temperature) has been identified as an important contributor to the secondary crystallization of polyethylene in other studies (Guadagno et al., 2001), leading to an increase in the crystallinity. Nevertheless,

the time of exposure should be taken into consideration and 96 h under UV-C radiation might not be sufficient to detect sizable changes in the degree of crystallinity of the LDPE samples by XRD. As expected, the two ozone treatments did not impact the crystallinity of LDPE, considering the short time of exposure.

The most evident increase of crystallinity for PET was detected for the samples that were exposed to simulated solar radiation (from 29% to 33%), with the rest of the treatments having very little impact on the crystallinity degree of PET MPPs. Similarly to the LDPE samples, no evident change was observed for the PET samples exposed to ozone. The most probable causes for the increase of crystallinity of the PET samples are identical to those explored for LDPE, with chemi-crystallization and the preferential degradation of the amorphous regions contributing to the increase in crystallinity (Sang et al., 2020). This very slow increase of the PET crystallinity under photo-oxidative treatments is in line with what was observed by Aljoumaa and Abboudi (2016), whose research on PET bottles indoor/outdoor aging showed as well a very slow increase of the PET crystallinity in the first 200 days of the experiment, accelerating to a faster increase during the remaining of the experiment (of a total of 670 days). Here, it was observed that artificial aging using the Solarbox and UV-C lamp shows a slightly higher impact on PET crystallinity than the RT weathering experiments. This suggests that the radiation intensity could be a more relevant aging agent regarding the crystallinity degree than the cumulative exposure time, although only a longer set of experiments and periodic analysis by XRD could enlighten on that possibility. Nevertheless, it should be noted that other studies with accelerated weathering systems (QUV and Q-SUN systems), that mimic radiation, humidity and temperature variations have detected a decrease in the crystallinity of PET (Sang et al., 2020), suggesting that the aging of PET could lead to the increase or decrease of the crystallinity of this polymer.

Here, the presence of water did not lead to discernible differences in the degree of crystallinity of the PET samples, although the crystallinity of the sample of the RT weathering experiment with the addition of rainwater suffered from a faintly decrease. As shown in other studies (Arhant et al., 2019; Ballara and Verdu, 1989), PET undergoes hydrolysis when immersed in water but at higher temperatures (e.g., 100 °C) than those observed here, with higher temperatures contributing to higher increases of the crystallinity degree during hydrolysis. Nevertheless, as pointed out by Sang et al. (2020), it is not yet understood what factors promote one pathway over the other when photolysis and hydrolysis are combined, as in this study.

For uPVC, the results suggest that most of the treatments lead to decreases in the degree of the crystallinity of the polymer. The exceptions were the Solarbox and the dissolved ozone in water treatments, which resulted in a similar value to the virgin sample and an increase of the crystallinity (from 22% to 25%), respectively. Even though it is expected that the PVC crystallinity increases with exposure time, Yang et al. (2014) observed that during the first 120 h of PVC

accelerated weathering in a QUV system, the degree of crystallinity decreased slightly, increasing to values higher than those obtained by the original samples after 480 h of exposure (of a total of 1920 h). This could explain why here it was observed a slightly crystallinity decrease for the samples aged by UV-C, when the ATR-FTIR data points out UV-C treatments as the most aggressive for uPVC. Nevertheless, uPVC is a very amorphous polymer making it more difficult to assess changes in the crystallinity of the samples by XRD and, in the case of this study, not possible to establish a defined trend for the differences observed.

3.4 Conclusions

The research presented in this chapter allowed to identify and better understand the modifications on the chemical structure, surface morphology, and crystallinity, that MPPs undergo when submitted to different treatments that simulate the effect of some of the agents that can contribute to the aging of MPPs in urban environments. The aging stressors studied, namely ozone, UV-C, solar radiation, and weathering agents, were confirmed to cause modifications to LDPE, PET and uPVC MPPs, validating the hypothesis that land-based microplastics can undergo pronounced aging due to urban environment stressors before reaching the oceans. In spite of the experiments exposure times only allowing us a glimpse of the modifications that can occur through time, the aging treatments performed in this work provide a way to obtain, in controlled conditions, aged MPPs (particularly for LDPE) that can be used in other types of studies in order to work with MPPs more similar to those found in the environment.

The main conclusions for each polymer MPP aging are as follows:

- LDPE MPPs were affected by all treatments, but particularly by ozone and during the rooftop weathering experiments. SEM analysis showed that 13 weeks of rooftop weathering led to the formation of cracks on the surface of the LDPE MPPs, that were more pronounced for the samples that were in contact with the rainwater added following the precipitation pattern. This polymer was shown to be more susceptible to crystallinity changes than PET and uPVC for the treatments and exposure times tested.
- PET MPPs were affected at least by the treatment with direct contact with ozone gas and by 13 weeks of rooftop weathering with rainwater, although it is difficult to assess the aging degree using ATR-FTIR data. SEM analysis hint that there might be flaking of some areas of the PET MPPs after 13 weeks of weathering without the addition of rainwater, while XRD analysis suggests that modifications occur when exposed to simulated solar radiation, with an increase of the PET crystallinity, but that it is a very slow process. PET MPP aging is more challenging to obtain and correctly identify in the laboratory, but it might also indicate that PET MPPs in the environment are closer to the pristine polymer

than other polymers, such as LDPE and uPVC, when exposed to the same agents and for the same time.

- uPVC MPPs were affected by the UV-C treatments and, to a lesser degree, in the rooftop weathering experiments. Although XRD and SEM analysis did not contribute greatly to the assessment of the polymer aging for the exposure times considered, the degree of yellowing observed for this polymer matches the conclusions reached by analyzing the ATR-FTIR spectra, presenting a way to do a preliminary assessment of its aging degree.

The three main techniques used to study the aging of the MPPs allowed to identify different modifications, with ATR-FTIR spectroscopy giving most of the information gathered and the Carbonyl Index being a good metric to assess LDPE and uPVC MPP aging. However, SEM and XRD give important complementary data, allowing to better understand the effect of the different aging agents and degradation pathways on MPPs, and showing that the Carbonyl Index should not be used alone to assess the aging degree of MPPs.

4. Microplastics behavior: potential as transport vectors of organic micropollutants



This chapter presents the results of sorption experiments conducted using virgin and aged (by ozone treatment or rooftop weathering) microplastic particles of LDPE, PET, or uPVC. The organic micropollutants (OMPs) selected as sorbates comprise a diversified group of priority substances and contaminants of emerging concern, including pharmaceutical substances and pesticides, analyzed at trace concentrations (each $\leq 100 \mu\text{g L}^{-1}$). Sorption kinetics and equilibrium isotherms were obtained, as well as the confirmation that the aging degree of microplastics plays a major role in their sorption capacities. The results show an increased sorption of several OMPs on aged microplastics when compared to pristine samples, i.e., the sorption capacity increasing from one or two sorbed substances (maximum $3 \mu\text{g g}^{-1}$ per sorbate) up to nine after aging (maximum $10 \mu\text{g g}^{-1}$ per sorbate). The extent of sorption depends on the OMP, polymer and the effectiveness of the aging treatment. The modifications (Chapter 3) between virgin and aged microplastics were linked to the increased sorption capacity of certain OMPs, allowing to better understand the different affinities observed. Additionally, phytotoxicity tests were performed to evaluate the mobility of the OMPs sorbed on the microplastics and the potential effects (on germination and early growth) of the combo on two species of plants (*Lepidium sativum* and *Sinapis alba*). These tests suggest low or no phytotoxicity effect under the conditions tested but indicate a need for further research on the behavior of microplastics on soil-plant systems.



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Miranda, M. N., Ribeiro, A. R. L., Silva, A. M. T., & Pereira, M. F. R. (2022). Can aged microplastics be transport vectors for organic micropollutants? - Sorption and phytotoxicity tests. *Science of The Total Environment*, 850, 158073. <https://doi.org/10.1016/j.scitotenv.2022.158073>

4.1 Introduction

Since the rise of microplastics as pollutants of emerging concern, the sorption capacity of microplastics and their potential to carry co-occurring pollutants have been under the scrutiny of the scientific community. Consequently, the hypothesis that microplastics may act as vectors for transporting substances and microorganisms has been raised and is under debate (Dong et al., 2021; Thompson et al., 2004; Verla et al., 2019; Wang et al., 2021; Yu et al., 2021). Furthermore, it has been identified the possibility of a microplastics trojan horse effect, in which the sorbed pollutants (and additive chemicals) are released from the microplastics and transferred into the biota tissues after exposure to this combination through e.g., ingestion (González-Soto et al., 2019; UNEP, 2016). Organic micropollutants (OMPs), a group of organic pollutants found at trace concentrations (Stamm et al., 2016), may occur in the same environmental compartments as the microplastics and, therefore, have the potential to be sorbed to them (Aryal et al., 2020; Yu et al., 2021).

Therefore, the main goal of the research presented in this chapter was to test the hypothesis that MPPs can be transport vectors of OMPs, with particular attention to the role played by the MPP aging degree on the sorption capacities of MPPs. Ozone-aged and weathered MPPs of LDPE, PET, and uPVC obtained and characterized for the previous chapter (Chapter 3) were selected for the sorption experiments, aiming to represent more realistic MPPs, particularly from an urban environment. These three polymers showed different degrees of resistance to the aging processes applied, making them a good choice to this study considering the diversity of microplastics that can be found in the environment and that will not have equal sorption capacities. The choice of sorbates fell on 10 OMPs: 6 pharmaceutical substances (florfenicol, trimethoprim, diclofenac, tramadol, citalopram, and venlafaxine) and 4 pesticides (alachlor, clofibric acid, diuron, and pentachlorophenol). These OMPs were selected based on: i) their inclusion in the list of priority substances in the field of water policy (alachlor, diuron and pentachlorophenol) (The European Parliament and the Council of the European Union, 2013); or ii) their potential as candidates to join that list due to their targeting as relevant CECs by the EU Watch List or by the scientific community (Choi et al., 2020; Gorito et al., 2022; Kye et al., 2020; Y. Yang et al., 2022). Some studies have reported the detection of these OMPs and MPPs in the same environmental samples and ecosystems (Mora et al., 2021; Picó et al., 2020). However, while several publications demonstrate the sorption of pharmaceutical substances and/or pesticides on microplastics, few reports focus on the sorbates selected for the present study (Chapter 1 - Table 1.1), particularly regarding the influence of the MPP aging in the sorption process. Therefore, sorption experiments were conducted to explore the sorption kinetics of 10 OMPs on each virgin polymer, as well as the effect of aging on sorption. The equilibrium sorption isotherms for the most sorbed pollutant (pentachlorophenol) on MPPs of LDPE or PET were also

studied. Furthermore, phytotoxicity tests were used to identify potential effects of the OMP-sorbed MPPs on seed germination and early growth of two species of plants (*Lepidium sativum* and *Sinapis alba*), simulating a possible transport and transfer of OMPs by MPPs from source to fate systems and the OMP mobility between different environmental compartments.

4.2 Material and methods

4.2.1 Microplastic particles (MPPs)

MPPs made from LDPE (average particle diameter of $509 \pm 221 \mu\text{m}$), PET ($161 \pm 79 \mu\text{m}$) and uPVC ($159 \pm 43 \mu\text{m}$) were purchased in powder form from Goodfellow (UK) at the beginning of the PhD work. The main characteristics of the virgin MPPs are included in Section 3.2.1 of the previous chapter. Aliquots of these virgin MPPs were i) artificially exposed for 1 h to ozone gas or ii) exposed to natural weathering conditions for 3 months on a building rooftop, to study the MPP modifications by aging in an urban environment, as described in the previous chapter (3.2.2 and 3.2.3). The weathered samples from the previous chapter were selected for this one because they correspond to the most aged samples obtained for LDPE, while showing also relevant aging for uPVC. The ozone-aged samples were selected because the results from the previous chapter suggested that it was one of the most aggressive treatments for PET.

Therefore, four types of MPPs of each polymer, previously characterized (3.2.4 - methodology and 3.3 - results), were used: virgin, ozone-aged (ozone gas), RT1 weathering (without rainwater), and RT2 weathering (with rainwater).

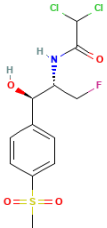
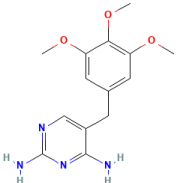
4.2.2 Organic micropollutants (OMPs)

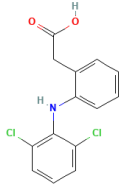
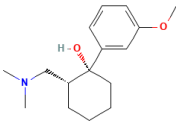
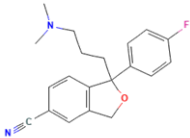
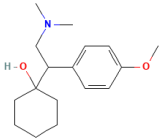
HPLC (LC-MS) grade methanol (HiPerSolv Chromanorm, VWR) was used to prepare a stock solution (ca. 1000 mg L^{-1} , stored at -18°C) of each OMP selected: alachlor, citalopram, clofibric acid, diclofenac, diuron, florfenicol, pentachlorophenol (PCP), tramadol, trimethoprim, and venlafaxine. The OMPs were purchased from Sigma-Aldrich (Germany) or Supelco (Germany) in powder form. Table 4.1 and Table 4.2 respectively comprise a detailed list of the reagents and a list of the classification, chemical structure, CAS number, molecular weight, $\log K_{ow}$, pK_a and water solubility of the 10 OMPs. Two working solutions were prepared by dilution in methanol (to ensure the OMPs complete dissolution and their stability when stored) of the individual stock solutions: i) MIX10 - a solution prepared with 5 mg L^{-1} of each of the 10 OMPs, and ii) PCP solution - a 5 mg L^{-1} solution of pentachlorophenol. The working solutions were stored at -18°C .

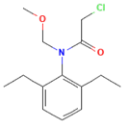
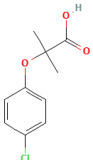
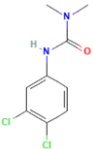
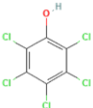
Table 4.1. Organic micropollutants: list of reagents used.

Compound	Supplier and reference	CAS number	Molecular weight (g mol ⁻¹)
Alachlor (analytical standard)	Sigma-Aldrich 45316-250MG	15972-60-8	269.77
Citalopram hydrobromide (certified reference material; pharmaceutical secondary standard)	Supelco PHR1640-1G	59729-32-7	405.30
Clofibric acid 97%	Sigma-Aldrich 197777-50G	882-09-7	214.65
Diclofenac sodium salt ≥ 98%	Sigma-Aldrich D6899-10G	15307-79-6	318.13
Diuron (analytical standard)	Sigma-Aldrich 45463-250MG	330-54-1	233.09
Florfenicol (analytical standard, for drug analysis)	Sigma-Aldrich F1427-500MG	73231-34-2	358.21
Pentachlorophenol 97%	Sigma-Aldrich P2604-5G	87-86-5	266.34
Tramadol hydrochloride ≥ 99% (HPLC)	Sigma-Aldrich 42965-1G-F	36282-47-0	299.84
Trimethoprim ≥ 98% (HPLC)	Sigma-Aldrich T7883-5G	738-70-5	290.32
Venlafaxine hydrochloride (certified reference material; pharmaceutical secondary standard)	Supelco PHR1736-1G	99300-78-4	313.86

Table 4.2. Classification, chemical structure, CAS number, molecular weight, log K_{ow} , pK_a , and water solubility of selected organic micropollutants.

Organic micropollutants (OMPs)	Chemical Structure ^a	CAS number ^a	Molecular weight (g mol ⁻¹) ^a	log K_{ow}	pK_a	Water solubility (mg L ⁻¹) ⁱ
Pharmaceutical substances						
Antibiotic						
Florfenicol ^{**} $C_{12}H_{14}Cl_2FNO_4S$		73231-34-2	358.2	0.37 ^b	9.0 ^c	n/a (very poor)
Trimethoprim ² $C_{14}H_{18}N_4O_3$		738-70-5	290.32	0.91 ^a	7.12 ^a (at 20 °C)	400.0

Organic micropollutants (OMPs)	Chemical Structure ^a	CAS number ^a	Molecular weight (g mol ⁻¹) ^a	log <i>K</i> _{ow}	p <i>K</i> _a	Water solubility (mg L ⁻¹) ⁱ
<i>Anti-inflammatory and/or analgesic</i>						
Diclofenac ¹ C ₁₄ H ₁₁ Cl ₂ NO ₂		15307-86-5	296.1	4.51 ^a	4.15 ^a	2.37
Tramadol ^{**} C ₁₆ H ₂₅ NO ₂		27203-92-5	263.37	3.01 ^a	9.41 ^a 9.23 ^a (tertiary amine) 13.08 ^a (alcohol)	1151.2 (estimated)
<i>Antidepressant drug</i>						
Citalopram ^{**} C ₂₀ H ₂₁ FN ₂ O		59729-33-8	324.4	3.74 ^a 1.39 ^d (at 22 °C)	9.78 ^a	31.1 (estimated)
Venlafaxine ² C ₁₇ H ₂₇ NO ₂		93413-69-5	277.4	3.20 ^a	10.09 ^a (amine)	266.65 (estimated)

Organic micropollutants (OMPs)	Chemical Structure ^a	CAS number ^a	Molecular weight (g mol ⁻¹) ^a	log <i>K</i> _{ow}	p <i>K</i> _a	Water solubility (mg L ⁻¹) ⁱ
Pesticides						
Alachlor * <chem>C14H20ClNO2</chem>		15972-60-8	269.77	3.52 ^a	0.67 ^e (at 25 °C)	240.0
Clofibric acid ** <chem>C10H11ClO3</chem>		882-09-7	214.64	2.57 ^f	3.18 ^{f,g}	476.35 (estimated)
Diuron * <chem>C9H10Cl2N2O</chem>		330-54-1	233.09	2.68 ^a	3.7 ^h	42.0
Pentachlorophenol * <chem>C6HCl5O</chem> or <chem>C6Cl5OH</chem>		87-86-5	266.3	5.12 ^a	4.70 ^a	14.0

*Priority substances in the field of water policy (Directive 2013/39/EU);

¹Contaminants of emerging concern - 1st Watch List (EU Decision 2015/495);

²Contaminants of emerging concern - 3rd Watch List (EU Decision 2020/1161) and 4th Watch List (EU Decision 2022/1307);

**Other relevant contaminants of emerging concern;

n/a - not available.

Sources:

^a National Centre of Biotechnology, US (available at <https://pubchem.ncbi.nlm.nih.gov>).

^b Zong, H.; Ma, D.; Wang, J.; Hu, J. Research on Florfenicol Residue in Coastal Area of Dalian (Northern China) and Analysis of Functional Diversity of the Microbial Community in Marine Sediment. *Bull. Environ. Contam. Toxicol.* 2010, 84 (2), 245-249. <https://doi.org/10.1007/s00128-009-9923-1>.

^c Kye, H.; Oh, H.; Jung, Y.; Kwon, M.; Yoon, Y.; Kang, J.-W.; Hwang, T.-M. Oxidation of Florfenicol and Oxolinic Acid in Seawater by Ozonation. *Appl. Sci.* 2020, 10 (14), 4944. <https://doi.org/10.3390/app10144944>.

^d Kwon, J.-W.; Armbrust, K. L. Aqueous Solubility, n-Octanol-Water Partition Coefficient, and Sorption of Five Selective Serotonin Reuptake Inhibitors to Sediments and Soils. *Bull. Environ. Contam. Toxicol.* 2008, 81 (2), 128-135. <https://doi.org/10.1007/s00128-008-9401-1>.

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ⁱ ECOSAR application (version 2.0) - U.S. Environmental Protection Agency

4.2.3 Sorption batch experiments

Three types of sorption batch experiments were conducted to assess the MPP sorption capacities and affinity to OMPs: i) sorption kinetics of the 10 OMPs on virgin MPPs (LDPE, PET, or uPVC) in order to identify the necessary time to reach the equilibrium; ii) sorption experiments of the 10 OMPs (at the same concentration as that used in sorption kinetics) under a fixed time to assess the effect of MPP aging on sorption (virgin, ozone gas, RT1 or RT2 MPPs of LDPE, PET, or uPVC); and iii) equilibrium isotherms to understand the individual sorption of PCP on virgin or ozone gas aged MPPs of LDPE or PET.

4.2.3.1 Sorption kinetics

For the kinetics experiments, 250 mg of virgin MPPs (LDPE, PET, or uPVC) were weighted and added to each 50 mL ISO blue cap bottle (without the blue outlet ring), except for the control bottles. The load of MPPs (10 g L^{-1}) was selected for this study based on the work of Elizalde-Velázquez et al. (2020) and after preliminary experiments conducted with virgin MPPs, which results showed that lower loads of MPPs did not originate detectable changes in the OMP concentrations in solution. Aluminum foil was used to cover the bottles, avoiding the influence of light in the process. It was also placed between the glass bottle and the blue cap, thus avoiding that unwanted MPPs released from the polypropylene cap could contaminate the solution.

Regarding the OMPs, a solution was prepared (with $100 \mu\text{g L}^{-1}$ of each OMP) by dilution in Milli-Q ultrapure water ($\text{pH} = 6.7 - 6.8$) of the MIX10 working solution. An aliquot of the initial solution ($t = 0 \text{ h}$) was stored in triplicate in HPLC vials at -18°C . Then, 25 mL of this dilute solution (with 2% V/V methanol, pH ca. 5.8) was added to each bottle, including the control bottles (without MPPs). The bottles were placed in a VWR 18 L shaking water bath set to 25°C and 150 strokes per minute for the following time intervals: 2, 4, 8, 16, 24 and 30 h. Samples were run in triplicate, for each time interval.

All samples, including the controls, were vacuum filtered through 47 mm glass microfiber filters (pore size of $1.2 \mu\text{m}$, purchased from VWR) to remove the MPPs from suspension. For that, Normax (Portugal) glass filtration kits, 100 mL Kitasato glass flasks (Normax, Portugal), and a KNF Neuberger (Freiburg, Germany) N035.1.2AT.18 vacuum pump, were used. The filtered samples were stored in HPLC vials at -18°C .

4.2.3.2 Effect of microplastic particles aging on sorption

Another type of experiments was accomplished to analyze the influence of MPP aging on the sorption capacity of OMPs by each type of MPPs. The same procedure described in 4.2.3.1 was used, but all the samples (virgin and ozone or RT1 or RT2) were shaken for 24 h. The initial concentration of $100 \mu\text{g L}^{-1}$ of each OMP in the MIX10 solution was obtained by the same procedure described before.

As an additional step, the filtered MPPs obtained after the vacuum filtration step were stored in soda-lime glass Petri dishes, which were dried and kept in a desiccator, in the dark. These MPPs were used for phytotoxicity tests (Section 4.2.4).

For each polymer (LDPE, PET, or uPVC) and aging treatment (ozone, RT1 or RT2), a set of experiments was performed consisting of triplicate bottles of virgin MPPs + triplicate bottles of aged MPPs + a control bottle without the addition of MPPs, resulting in a total of 9 sets of experiments.

4.2.3.3 Equilibrium isotherms for pentachlorophenol (PCP)

PCP was selected to determine the equilibrium isotherms for virgin or ozone-aged MPPs of LDPE or PET. No isotherms were obtained for uPVC, since PCP had low sorption on the virgin or ozone-aged MPPs of this specific polymer (as described in 4.3.1.1). The weathered MPPs (RT1 and RT2) were not used to study the equilibrium isotherms of PCP because the recovered mass of MPPs from weathering was not sufficient.

The procedure was similar to that described in 4.2.3.1. Each set of experiments (triplicate bottles of virgin MPPs + triplicate bottles of ozone-aged MPPs + control bottle without MPPs) was carried out for 5 solutions with different initial concentrations of PCP ($t = 0$ h) of 50, 75, 100, 125 and $175 \mu\text{g L}^{-1}$ (with $\leq 3.5\%$ V/V methanol, pH ca. 5.9 - 6.2). The bottles were kept in the shaking bath for 24 h.

4.2.4 Phytotoxicity tests

Phytotoxicity tests were carried out to determine the effects of the OMP-sorbed MPPs, obtained as described in 4.2.3.2, on seed germination and early growth (root and shoots lengths) of two species of plants: *Lepidium sativum* (dicotyl garden cress) and *Sinapis alba* (dicotyl mustard). For that, Phytotoxkits (liquid samples) were purchased from Microbiotests Inc. (Kleimoer, Belgium). The Phytotoxkit (liquid samples) standard operating procedure (Microbiotests Inc.,

2016) (in accordance with ISO Standard 18763:2016) was thus slightly modified to simulate the presence of MPPs on the “contaminated soil”.

In summary, each test plate bottom was sequentially filled with the foam pad, the parafilm sheet and the white filter paper. Then, 20 mL of an OMPs solution (in the case of positive control plates) or 20 mL of Milli-Q ultrapure water were spread on the surface of the white filter, on the top of which a black filter was placed. Two solutions were used for the positive control plates: 100 $\mu\text{g L}^{-1}$ or 50 $\mu\text{g L}^{-1}$ of each of the 10 OMPs, by dilution in Milli-Q ultrapure water of the MIX10 working solution. The only modification to the standard procedure is that 2 mg of MPPs were added and spread on top of the black filter for selected plates. This load corresponds to 100 mg L^{-1} of MPPs, being within the range of exposure concentrations reported in the literature for studies with plants (Zhang et al., 2022). Afterwards, 10 seeds of one of the species were placed on top of the black filter. Finally, the cover was placed on the bottom part of the test plate and closed. All test plates were set in vertical positions in the cardboard holders and were incubated for 3 days at 25 °C (± 2 °C). Pictures of the test plates were taken at the end of the incubation period, with a smartphone placed at a fixed height and parallel to each plate set horizontally on a workbench.

For image analysis, the Image J software was used to measure the root and shoots lengths of the germinated seeds, following the procedure proposed in the Phytotoxkit (liquid samples) standard operating procedure (Microbiotests Inc., 2016).

A preliminary set of experiments was conducted to study the effects of the 100 $\mu\text{g L}^{-1}$ MIX10 solution and the effects of each of the three virgin MPPs on seed germination and early growth, with 5 types of test plates (each $n = 10$) being used for each plant species: negative control (without MPPs and OMPs); positive control (100 $\mu\text{g L}^{-1}$ of MIX10); and LDPE, PET, or uPVC virgin MPPs. LDPE was then selected among the three studied polymers since, as described in Section 4.3.1, it has an overall higher sorption capacity for the studied OMPs. For the test conducted to study OMP-sorbed LDPE MPPs, 11 types of test plates (each $n = 10$) were assayed (Fig. 4.1): 0) negative control (without MPPs and OMPs); 1) positive control 1 (100 $\mu\text{g L}^{-1}$ of MIX10); 2) positive control 2 (50 $\mu\text{g L}^{-1}$ of MIX10); 3) virgin MPPs; 7) virgin MPP+OMP (after sorption experiment); 4-6) ozone, RT1, or RT2 aged MPPs; 8-10) ozone, RT1, or RT2 aged MPP+OMP (after sorption experiment).

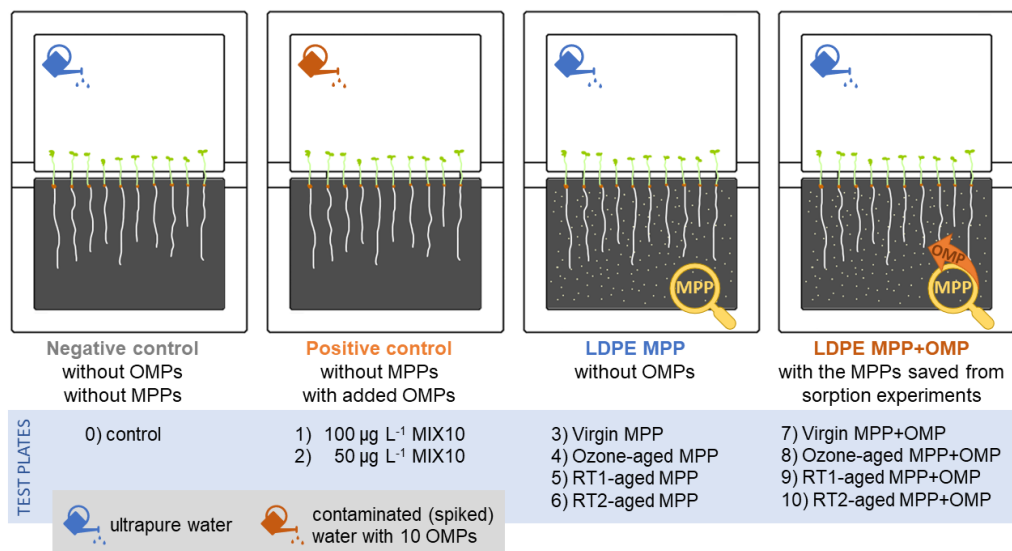


Fig. 4.1. Schematic of the test plates used for the LDPE phytotoxicity test.

In parallel, OMPs desorption was evaluated to account for the LDPE test, particularly for the test plates with OMP-sorbed MPPs. For that, 2 mg of MPP+OMP (virgin, ozone, RT1, or RT2 aged) and 20 mL of Milli-Q ultrapure water were added to 50 mL ISO blue cap bottles that were kept near the test plates for the duration of the experiment (3 days). The bottles were not shaken, and aluminum foil was used to cover the bottles and placed between the glass bottle and the blue cap.

4.2.5 Organic micropollutants quantification

An ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) analytical method was adopted to determine the concentration of the selected OMPs in the samples from the sorption batch experiments. The Shimadzu (Japan) UHPLC-MS/MS system used comprises a Nexera X2 UHPLC unit and a LCMS-8040 triple quadrupole mass spectrometer detector, with an electrospray ionization source operating in both positive and negative ionization modes. A Phenomenex (USA) Kinetex 1.7 µm XB-C18 100 Å (100 x 2.1 mm) column was used, with the respective pre-column, in the system with the oven temperature set at 40 °C. The mobile phase flow rate of 0.2 mL min⁻¹ was 50/50 (V/V) Milli-Q ultrapure water and HPLC gradient grade ethanol (LiChrosolv, Supelco, Germany), under isocratic mode. The injection volume was 20 µL. The quantification was performed using the transition between the precursor ion and the

most intense fragment by selected reaction monitoring. Detailed information on the UHPLC-MS/MS settings and analytical method (including the limits of detection and quantification) is described in Table 4.3 and Table 4.4. Shimadzu LC Solution Version 5.41SP1 software was used to convert raw data to each OMP concentration, based on the triplicate 10 points calibration curve (range 1-200 ppb) on Milli-Q ultrapure water.

Table 4.3. Method detection and quantification limits, respectively MDL and MQL, for each target analyte.

Analyte	MDL ($\mu\text{g L}^{-1}$)	MQL ($\mu\text{g L}^{-1}$)
Alachlor	0.014	0.046
Citalopram	0.170	0.516
Clofibric acid	0.031	0.090
Diclofenac	0.038	0.116
Diuron	0.017	0.055
Florfenicol	0.010	0.040
Pentachlorophenol	0.711	2.157
Tramadol	0.012	0.040
Trimethoprim	0.052	0.154
Venlafaxine	0.013	0.040

Table 4.4. Selected reaction monitoring (SRM) instrument parameters for tandem mass spectrometry analysis of target analytes. Capillary voltage, drying gas flow rate, nebulizing gas flow rate, desolvation and source temperature of the mass spectrometer were respectively 4.5 kV, 12.5 dm³ min⁻¹, 2.5 dm³ min⁻¹, 250 °C and 400 °C.

Analyte	ESI mode (NI or PI)	Precursor ion (m/z)	Quantification (SRM1)				Confirmation (SRM2)				Ion ratio
			Product ion	DP (V)	CE (V)	CXP (V)	Product ion	DP (V)	CE (V)	CXP (V)	
Alachlor	PI	270.15	238.15	-13.0	-13.0	-24.0	162.05	-13.0	-20.0	-15.0	1.91
Citalopram	PI	324.50	109.10	-24.0	-27.0	-19.0	262.20	-24.0	-20.0	-27.0	2.84
Clofibric acid	NI	213.10	127.00	10.0	13.0	13.0	85.00	10.0	11.0	30.0	4.96
Diclofenac	NI	293.90	250.10	21.0	11.0	17.0	214.05	21.0	20.0	23.0	22.47
Diuron	NI	231.10	186.00	11.0	17.0	19.0	150.00	11.0	23.0	28.0	4.40
Florfenicol	NI	356.00	336.05	13.0	10.0	24.0	185.10	13.0	18.0	20.0	1.39
Pentachlorophenol	NI	265.10	35.15	13.0	48.0	30.0	-	-	-	-	-
Tramadol	PI	264.00	57.00	-30.0	-25.0	-30.0	-	-	-	-	-
Trimethoprim	PI	290.80	230.00	-23.0	-24.0	-23.0	123.05	-23.0	-25.0	-21.0	1.46
Venlafaxine	PI	277.80	58.10	-30.0	-22.0	-22.0	260.15	-30.0	-12.0	-27.0	3.20

NI: negative ionization mode; PI: positive ionization mode; DP: declustering potential; CE: collision energy; CXP: collision cell exit potential.

4.2.6 Data analysis and statistics

The amount of OMPs sorbed per unit of mass of MPPs, q ($\mu\text{g g}^{-1}$) (q_e if sorption equilibrium is reached) was estimated using Eq. 4.1:

$$q = \frac{(C_{\text{control}} - C_{\text{sample}})}{m} V \quad \text{Eq. 4.1}$$

where, C_{control} is the concentration of each OMP ($\mu\text{g L}^{-1}$) in the control bottle liquid phase at a given time interval, C_{sample} is the concentration of each OMP ($\mu\text{g L}^{-1}$) in a sample bottle liquid phase (same as C_e if sorption equilibrium is attained), V (0.025 L) is the volume of the solution added to each bottle, and m is the mass (g) of MPPs added to the bottle. The concentration of OMPs in the control bottles liquid phase (C_{control}) was used instead of the initial concentration (C_0) to exclude any possible degradation or loss of the OMPs during the sorption experiment, e.g., due to the possibility of sorption to the ISO blue cap bottles, filtration system and/or the microfiber filters. Nevertheless, C_0 ($t = 0$ h) was used as a reference to ensure that the experiment was well conducted and to compare with C_{control} , as discussed in 4.3.1. Since samples were run in triplicates, the mean and respective standard deviation (SD) were calculated for all q results.

Two mathematical models were used to analyze the kinetics of the sorption reactions studied: pseudo-first-order model (PFO) and pseudo-second-order model (PSO) (Agbovi and Wilson, 2021; Ho and McKay, 1998; Lagergren, 1898). PFO model can be described by its non-linear form, as expressed in Eq. 4.2:

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{Eq. 4.2}$$

where, k_1 (h^{-1}) is the sorption rate constant of PFO and t (h) is the contact time between the sorbent and the sorbate.

PSO model was used as well in its non-linear form, as expressed in Eq. 4.3:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \text{Eq. 4.3}$$

where, k_2 ($\text{g } \mu\text{g}^{-1} \text{h}^{-1}$) is the sorption rate constant of PSO.

Three mathematical models were used to analyze the PCP equilibrium sorption isotherms: Langmuir, Freundlich, and linear (Agbovi and Wilson, 2021; Freundlich, 1907; Langmuir, 1916). The Langmuir model can be described by its non-linear form, as expressed in Eq. 4.4:

$$q_e = q_m \frac{K_l C_e}{1 + K_l C_e} \quad \text{Eq. 4.4}$$

where, K_l is the Langmuir sorption constant ($\text{L } \mu\text{g}^{-1}$), q_m is the maximum sorption capacity of the material ($\mu\text{g g}^{-1}$) and C_e is the concentration of the sorbate in the aqueous phase at equilibrium ($\mu\text{g L}^{-1}$).

The Freundlich model was applied in its non-linear form, as expressed in Eq. 4.5:

$$q_e = K_f C_e^{1/n} \quad \text{Eq. 4.5}$$

where, K_f is the Freundlich sorption constant ($(\mu\text{g g}^{-1})(\text{L } \mu\text{g}^{-1})^{1/n}$), and the surface heterogeneity is described by the exponential term $1/n$.

Finally, the linear model fitting was accomplished with a fixed intercept at zero and the slope being the equilibrium distribution coefficient K_d (L g^{-1}).

The PFO, PSO, Langmuir, Freundlich, and linear model fitting were achieved using the OriginPro 9 software. For all models, the quality of the fit was assessed by the Adjusted Coefficient of Determination (adj. R^2) and the Residual Sum of the Squares (RSS), as given by OriginPro 9.

The statistical analysis of the phytotoxicity results (Section 4.3.2) included the calculation of the average root and shoot lengths ($n \leq 10$, depending on the seed germination), and the respective SD. Additionally, the root and shoot lengths were compared for all the test plate results of each test using One-Way ANOVA and the post hoc Tukey test (OriginPro 9 software). The following assumptions were validated for the ANOVA model using the same software: independence, normality (normality tests e.g., Anderson-Darling test) and homogeneity (Levene's test).

The percentage effect of the different combinations tested of OMPs and/or MPPs on root and shoot growth was estimated by Eq. 4.6:

$$\%effect = \frac{a - b}{a} \times 100 \quad \text{Eq. 4.6}$$

where, a is the average root length or average shoot length in the negative control test plate, whereas b corresponds to the MPPs and/or OMPs test plates (Microbiotests Inc., 2016).

4.3 Results and Discussion

4.3.1 Evaluation of MPPs capacity to sorb organic micropollutants

In order to assess the MPPs capacity to sorb the selected OMPs, the sorption kinetics of the mixture of 10 OMPs were studied for each polymer, as well as the effect of MPP aging on sorption, and the equilibrium isotherms of the most sorbed OMP - PCP - on MPPs of LDPE or PET.

The sorption kinetics for virgin MPPs were evaluated to define an adequate contact time for further sorption experiments. These first experiments revealed that only alachlor on LDPE and PCP on the 3 polymers were discernibly sorbed under the conditions tested, when working with virgin MPPs (Table 4.5).

Table 4.5. Sorption kinetics: average organic micropollutants (mix 10) left in the filtered solution after 30 h of contact with microplastic particles ($C_0 = 100 \mu\text{g L}^{-1}$).

Organic micropollutant (OMP)	Sample (t = 30 h)	C ($\mu\text{g L}^{-1}$)					
		LDPE		PET		uPVC	
		Virgin (n = 3)	SD	Virgin (n = 3)	SD	Virgin (n = 3)	SD
Florfenicol	C _{control}	105.39	3.59	88.75	4.45	103.37	5.44
	C _{sample}	100.07	4.38	87.20	1.20	99.45	2.68
Trimethoprim	C _{control}	86.57	3.89	93.35	2.35	80.48	3.48
	C _{sample}	85.93	2.94	98.22	4.89	84.26	1.64
Diclofenac	C _{control}	109.25	1.51	121.82	0.31	104.99	0.98
	C _{sample}	110.62	2.58	115.83	4.24	102.68	1.94
Tramadol	C _{control}	98.03	1.10	96.65	0.37	103.88	0.94
	C _{sample}	97.03	2.74	96.88	3.51	103.07	2.05
Citalopram	C _{control}	58.83	2.64	65.73	0.57	71.72	0.99
	C _{sample}	64.18	5.13	69.60	1.62	75.12	3.41
Venlafaxine	C _{control}	92.70	1.95	97.56	0.67	99.81	2.69
	C _{sample}	90.16	4.40	96.96	4.14	100.38	3.84
Alachlor	C _{control}	100.66	3.67	93.58	0.49	125.45	4.71
	C _{sample}	89.65	1.38	92.15	3.16	125.86	3.70
Clofibric acid	C _{control}	116.86	5.89	121.23	8.32	82.36	1.54
	C _{sample}	115.76	1.84	125.47	6.66	84.67	2.34
Diuron	C _{control}	97.68	2.82	85.68	1.43	99.45	5.07
	C _{sample}	95.94	2.18	83.78	2.78	105.04	6.77
Pentachlorophenol	C _{control}	90.56	2.49	107.85	1.11	103.74	2.84
	C _{sample}	57.17	4.17	94.58	7.18	91.26	4.65

An apparent equilibrium was reached between 16 h and 24 h (Table 4.6, Fig. 4.2, and Fig. 4.3). Despite other studies reporting different timeframes to achieve equilibrium, such as Loncarski et al. (2020) for PCP adsorption on polyethylene and PET, it is known that the sorption rate is affected by multiple factors such as the characteristics of the MPPs. Therefore, 24 h was considered enough to reach equilibrium, under the conditions studied.

Table 4.6. Sorption kinetics: average retention of organic micropollutants (mix 10) on microplastic particles (q) through time ($C_0 = 100 \mu\text{g L}^{-1}$).

Organic micropollutant (OMP) ¹	t (h)	$q_t (\mu\text{g g}^{-1})$					
		LDPE		PET		uPVC	
		Virgin (n = 3)	SD	Virgin (n = 3)	SD	Virgin (n = 3)	SD
Alachlor	2	0.318	0.306	-	-	-	-
	4	0.766	0.143	-	-	-	-
	8	0.805	0.030	-	-	-	-
	16	1.178	0.075	-	-	-	-
	24	1.140	0.336	-	-	-	-
	30	1.099	0.140	-	-	-	-
Pentachlorophenol	2	1.241	0.272	0.260	0.294	0.228	0.112
	4	1.640	0.106	0.415	0.396	0.836	0.147
	8	1.965	0.168	1.043	0.484	1.096	0.237
	16	2.487	0.467	1.026	0.701	1.168	0.210
	24	3.437	0.255	1.524	0.573	1.287	0.299
	30	3.330	0.419	1.325	0.717	1.243	0.231

¹ The remaining OMPs studied are not included in this table, as no sorption was detected for the virgin polymers.

Table 4.7. Sorption Kinetics: estimated PFO and PSO parameters.

	PFO				PSO			
	$q_e (\mu\text{g g}^{-1})$	$k_1 (\text{h}^{-1})$	adj. R^2	RSS	$q_e (\mu\text{g g}^{-1})$	$k_2 (\text{g } \mu\text{g}^{-1} \text{h}^{-1})$	adj. R^2	RSS
LDPE-Alachlor	1.22 ± 0.13	0.14 ± 0.03	0.774	5.19	1.51 ± 0.24	0.10 ± 0.05	0.756	5.61
LDPE-Pentachlorophenol	3.22 ± 0.36	0.16 ± 0.04	0.796	10.0	3.94 ± 0.47	0.04 ± 0.02	0.876	6.09
PET-Pentachlorophenol	1.52 ± 0.21	0.10 ± 0.03	0.923	0.39	2.12 ± 0.45	0.04 ± 0.02	0.913	0.44
uPVC-Pentachlorophenol	1.29 ± 0.16	0.18 ± 0.05	0.867	3.79	1.63 ± 0.32	0.10 ± 0.07	0.830	4.85

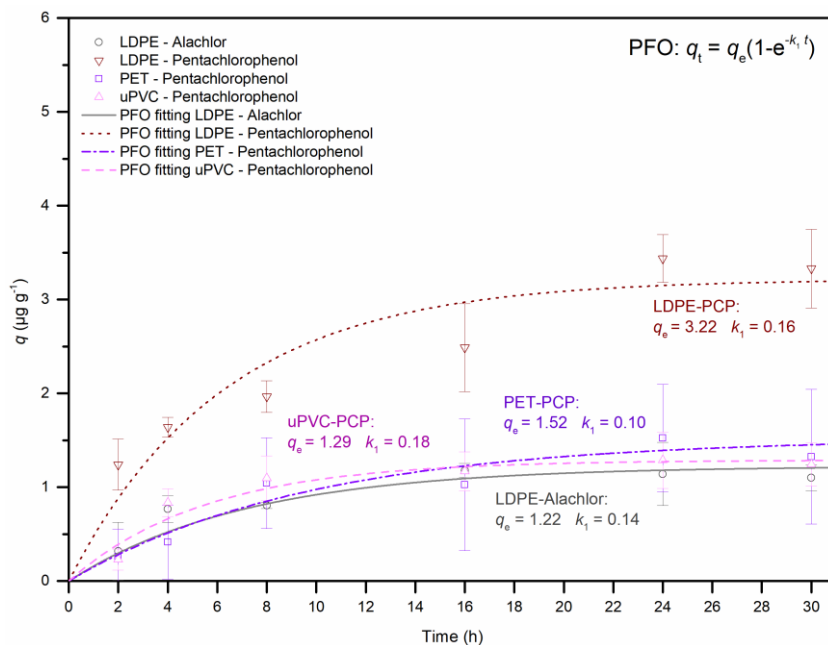


Fig. 4.2. Lagergren pseudo-first-order (PFO) kinetic model fitting for alachlor and/or pentachlorophenol (PCP) sorbed to LDPE, PET and uPVC (q_e in $\mu\text{g g}^{-1}$ and k_1 in h^{-1}).

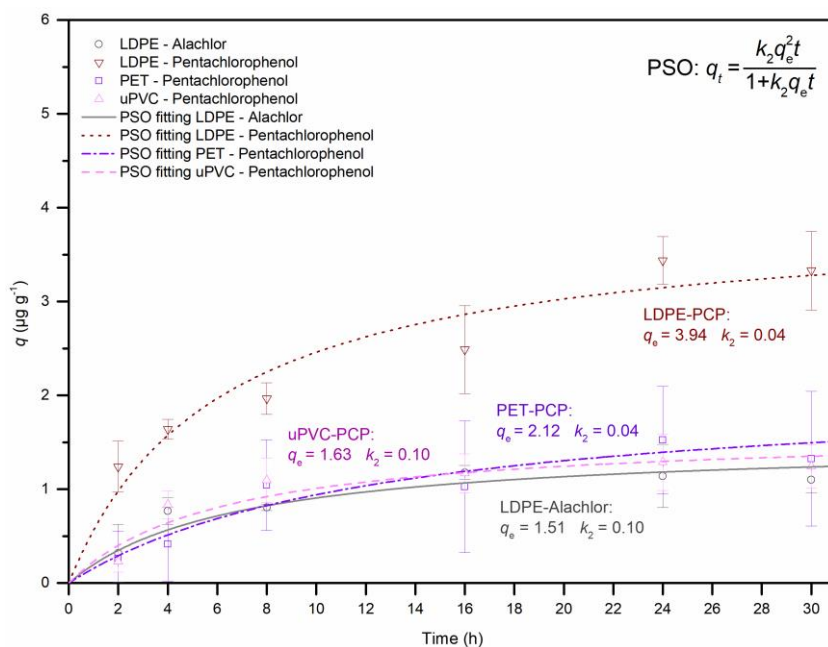


Fig. 4.3. Pseudo-second-order (PSO) kinetic model fitting for alachlor and/or pentachlorophenol (PCP) sorbed to LDPE, PET and uPVC (q_e in $\mu\text{g g}^{-1}$ and k_2 in $\text{g } \mu\text{g}^{-1} \text{h}^{-1}$).

Considering the adj. R^2 and RSS values (Table 4.7), the PFO model (Fig. 4.2) fitted better for the combination LDPE-alachlor, PET-PCP and uPVC-PCP, with the PSO model (Fig. 4.3) being more adequate to represent the sorption of PCP on LDPE over time. Taking into account that PCP is a relatively hydrophobic compound, it can explain why the PSO model fitted better for LDPE-PCP, since the interaction of hydrophobic compounds with the surface of hydrophobic microplastics is higher than when the sorbate is a more hydrophilic compound. One possible explanation for the PFO model fitting better for PET and uPVC is that the used MPPs of these two polymers have fewer active adsorption sites than those of LDPE. As alachlor is a hydrophilic to hydrophobic compound, it has a higher difficulty in sorbing on microplastics than PCP and is better represented by the PFO model, which is also associated to the external diffusion or the internal diffusion being the rate controlling steps (Wang and Guo, 2020a).

It should be noted that the concentration of the antidepressant citalopram in control samples (i.e., without MPPs in suspension) reached values of ca. $60 \mu\text{g L}^{-1}$ (C_0 ca. $100 \mu\text{g L}^{-1}$), suggesting that it could be potentially sorbed on other surfaces or degraded. For this reason, and as explained in Section 4.2.6, the sorption capacity was estimated based on the control sample concentration of each OMP instead of the initial concentration.

4.3.1.1 Effect of microplastic particles aging on sorption

4.3.1.1.1 Low-density polyethylene (LDPE)

LDPE sorption capacities were most impacted by aging (Fig. 4.4a) than those of PET (Fig. 4.4b) or uPVC (Fig. 4.4c). Additional data on these experiments can be found in Table 4.8.

In the particular case of LDPE (Fig. 4.4a), all the aging treatments studied led to changes in the sorption capacity of this polymer MPPs. Moreover, the rooftop weathering without and with rainwater (RT1 and RT2, respectively) led to a similar increase of the sorption capacity for most OMPs (different only for diclofenac, citalopram and clofibric acid), when compared with virgin LDPE, this increase being higher than that observed with the ozone treatment.

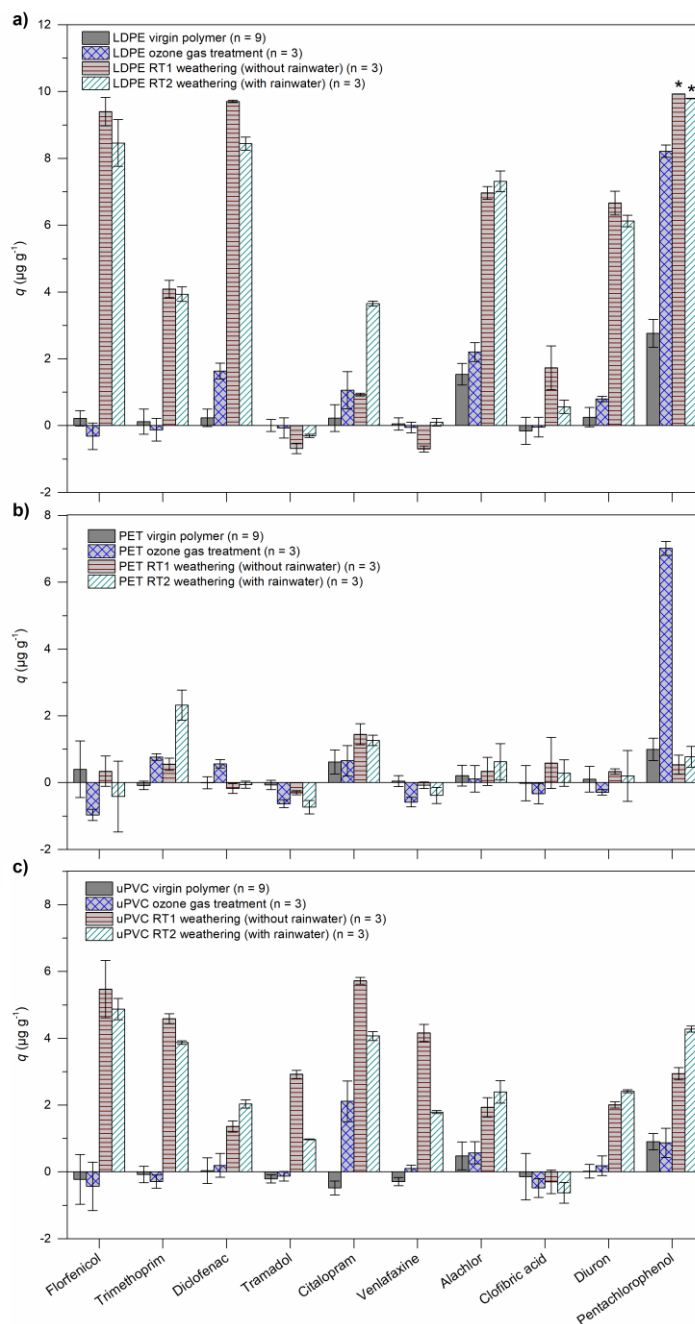


Fig. 4.4. OMPs sorbed per unit of mass of MPPs (virgin, aged by ozone treatment or rooftop weathering without – RT1 and with – RT2 rainwater), for a) low-density polyethylene (LDPE), b) poly(ethylene terephthalate) (PET) and c) unplasticized poly(vinyl chloride) (uPVC). * Pentachlorophenol concentration in solution after 24 h was below the method detection limit for LDPE RT1 and RT2 triplicated samples. Therefore, q was calculated admitting a null concentration for those samples.

Table 4.8. Average retention of organic micropollutants (mix 10) on microplastic particles (q) along 24 h ($C_0 = 100 \mu\text{g L}^{-1}$).

Micropollutant	$q (\mu\text{g g}^{-1})$											
	LDPE				PET				uPVC			
	Virgin (n = 9)	O ₃ gas (n = 3)	RT1 (n = 3)	RT2 (n = 3)	Virgin (n = 9)	O ₃ gas (n = 3)	RT1 (n = 3)	RT2 (n = 3)	Virgin (n = 9)	O ₃ gas (n = 3)	RT1 (n = 3)	RT2 (n = 3)
Florfenicol	0.22 ± 0.23	-0.32 ± 0.40	9.39 ± 0.42	8.46 ± 0.70	0.40 ± 0.84	-0.97 ± 0.17	0.34 ± 0.45	-0.42 ± 1.06	-0.23 ± 0.75	-0.43 ± 0.73	5.47 ± 0.86	4.87 ± 0.32
Trimethoprim	0.12 ± 0.38	-0.13 ± 0.34	4.09 ± 0.26	3.94 ± 0.22	-0.09 ± 0.13	0.77 ± 0.10	0.55 ± 0.19	2.32 ± 0.45	-0.08 ± 0.25	-0.29 ± 0.20	4.58 ± 0.15	3.87 ± 0.05
Diclofenac	0.23 ± 0.26	1.63 ± 0.24	9.70 ± 0.03	8.44 ± 0.19	-0.01 ± 0.18	0.56 ± 0.13	-0.18 ± 0.15	-0.06 ± 0.10	0.03 ± 0.39	0.19 ± 0.36	1.36 ± 0.17	2.03 ± 0.12
Tramadol	0.01 ± 0.18	-0.07 ± 0.30	-0.69 ± 0.16	-0.31 ± 0.05	-0.07 ± 0.14	-0.63 ± 0.12	-0.30 ± 0.06	-0.74 ± 0.20	-0.21 ± 0.12	-0.13 ± 0.14	2.92 ± 0.12	0.97 ± 0.01
Citalopram	0.22 ± 0.40	1.05 ± 0.56	0.93 ± 0.04	3.65 ± 0.08	0.62 ± 0.36	0.65 ± 0.46	1.44 ± 0.32	1.26 ± 0.16	-0.48 ± 0.21	2.11 ± 0.61	5.72 ± 0.10	4.07 ± 0.13
Venlafaxine	0.05 ± 0.19	-0.06 ± 0.16	-0.70 ± 0.09	0.10 ± 0.12	0.04 ± 0.16	-0.58 ± 0.14	-0.08 ± 0.10	-0.38 ± 0.24	-0.29 ± 0.12	0.10 ± 0.10	4.16 ± 0.26	1.79 ± 0.04
Alachlor	1.53 ± 0.32	2.20 ± 0.28	6.96 ± 0.19	7.31 ± 0.31	0.21 ± 0.31	0.11 ± 0.40	0.34 ± 0.42	0.62 ± 0.54	0.48 ± 0.42	0.57 ± 0.33	1.93 ± 0.29	2.39 ± 0.34
Clofibric acid	-0.16 ± 0.41	-0.05 ± 0.29	1.73 ± 0.65	0.56 ± 0.20	-0.02 ± 0.52	-0.33 ± 0.31	0.59 ± 0.77	0.28 ± 0.39	-0.14 ± 0.70	-0.48 ± 0.28	-0.30 ± 0.35	-0.63 ± 0.31
Diuron	0.25 ± 0.29	0.80 ± 0.08	6.66 ± 0.35	6.13 ± 0.17	0.10 ± 0.39	-0.30 ± 0.08	0.33 ± 0.08	0.20 ± 0.76	0.02 ± 0.21	0.18 ± 0.29	2.01 ± 0.09	2.41 ± 0.05
Pentachlorophenol	2.76 ± 0.42	8.21 ± 0.18	9.92* ± 0.01	9.79* ± 0.01	0.99 ± 0.34	7.01 ± 0.21	0.53 ± 0.29	0.77 ± 0.31	0.90 ± 0.25	0.87 ± 0.44	2.94 ± 0.18	4.28 ± 0.09

* Pentachlorophenol concentration in solution after 24 h was below the method detection limit for LDPE RT1 and RT2 triplicated samples. Therefore, q was calculated admitting a null concentration for those samples.

PCP and alachlor are the only two OMPs with significant sorption to the virgin LDPE, whereas the aged LDPE sorbed all other OMPs except tramadol and venlafaxine (ozone: PCP >>> alachlor ≥ diclofenac = citalopram = diuron; RT1: PCP ≥ diclofenac = florfenicol > alachlor = diuron > trimethoprim > clofibric acid = citalopram; RT2: PCP > florfenicol = diclofenac > alachlor > diuron > trimethoprim = citalopram). The two OMPs that showed no affinity to virgin or aged LDPE - tramadol and venlafaxine -, have high pK_a and similar $\log K_{ow}$. Although no universal rule (direct or indirect correlation) was found between pK_a or $\log K_{ow}$ and the affinity between the polymer and the OMPs, in most of the cases the sorption on LDPE (particularly for RT1 and RT2 samples) was higher when the $\log K_{ow}$ is higher. Furthermore, the OMPs with lower water solubility, such as diclofenac and PCP, were observed to have higher affinity to LDPE, especially after weathering.

In the previous chapter (Chapter 3), in which the MPPs were aged and characterized, several modifications were observed in the chemical structure of the LDPE MPPs after the aging treatments. That information can help to explain the increased sorption capacity of these aged MPPs, since the aging processes are known to increase the oxygen-containing functional groups on the plastics, affecting their surface hydrophobic properties and allowing additional interactions (Hüffer and Hofmann, 2016; G. Liu et al., 2019; Yu et al., 2020). The most substantial modification observed (assessed by ATR-FTIR - Attenuated Total Reflection - Fourier transform infrared spectroscopy) was the formation of carbonyl species ($C=O$), with the carbonyl absorbance peak intensity (and the Carbonyl Index estimated from it) being linked to the exposure time and the effectiveness of each aging treatment on each polymer. While the ozone gas aging treatment (1 h) was sufficient to detect an increase of the Carbonyl Index from 0.004 ± 0.001 (virgin) to 0.100 ± 0.002 , the weathering treatments significantly increased this index up to 0.243 ± 0.011 (13 weeks RT1) and 0.246 ± 0.006 (13 weeks RT2). Accordingly (Fig. 4.4a), RT1 and RT2 aged LDPE samples revealed similar sorption capacities, which are higher than those obtained with ozone-aging. Some other modifications detected after aging the LDPE MPPs (Chapter 3 - Section 3.3.1.1) were the formation of hydroxyl species (new absorption band at $3673\text{-}2960\text{ cm}^{-1}$ associated with O-H bonds) for RT1 and RT2 samples, and the increased intensity (or new absorption peaks) at $1468\text{-}717\text{ cm}^{-1}$ after the weathering treatments (to a lesser extent after the ozone gas treatment).

Pronounced modifications of the surface morphology (i.e., more and deeper cracks assessed by SEM - scanning electron microscopy), evidence of colonization by microorganisms (detected by SEM and validated by Raman microspectroscopy) and a higher increase in the degree of crystallinity (determined by XRD - X-ray diffraction) were observed after RT2 weathering, but not (microorganisms) or to a less degree (changes in the surface morphology and crystallinity) for RT1 weathering (Chapter 3 - Sections 3.3.2 and 3.3.3). Since the two weathering treatments

originated slightly different profiles only on the sorption capacities for diclofenac, citalopram and clofibric acid, this could suggest that the affinity and consequent sorption of most of the studied OMPs on LDPE MPPs were mainly governed by the surface chemical structure. The antidepressant drug citalopram was the only OMP that sorbed more on RT2 than on RT1 and, therefore, the identified differences observed between RT1 and RT2 samples might benefit the affinity of the LDPE MPPs to some specific compounds.

4.3.1.1.2 Poly(ethylene terephthalate) (PET)

Aged PET (Fig. 4.4b) showed a very distinct sorption behavior when compared to the other two polymers (Fig. 4.4a and c). Most of the studied OMPs showed very little to no affinity (particularly tramadol and venlafaxine) to either pristine or aged PET (Fig. 4.4b), but a clear exception was found for PCP which is markedly sorbed on PET aged by the ozone treatment. This result confirms that ozone can be an effective aging agent in inducing specific changes in the behavior of PET MPPs, as suggested in the previous chapter (Chapter 3). In fact, the increased sorption of PCP, from 0.99 ± 0.34 to $7.01 \pm 0.21 \mu\text{g g}^{-1}$ with the ozone-aged samples, may be linked to the widening of the 1714 cm^{-1} peak base, associated with the formation of carbonyl species as detected by ATR-FTIR analysis of PET MPPs aged by ozone (Chapter 3 - Section 3.3.1.2).

Another noteworthy result is the higher sorption of trimethoprim by the samples obtained in the RT2 weathering experiment (Fig. 4.4b), which may be related to a new absorption band at $3615\text{--}3115 \text{ cm}^{-1}$, associated with O-H bonds as observed in the previous chapter (Chapter 3 - Section 3.3.1.2). The formation of hydroxyl species and the increase of the trimethoprim compound sorption were also observed for weathering samples of LDPE (Fig. 4.4a) and uPVC (Fig. 4.4c). Thus, hydrogen bonds between the OH groups on these MPPs and the amine groups of trimethoprim may justify these results.

4.3.1.1.3 Unplasticized poly(vinyl chloride) (uPVC)

Both weathered (RT1 and RT2) uPVC samples have evident increased sorption capacities, but RT1-aged MPPs showed an overall higher sorption (Fig. 4.4c). Although low sorption was verified for both virgin (PCP > alachlor) and ozone-aged (citalopram $\geq$ PCP = alachlor) uPVC MPPs, the weathering treatments led to the sorption of almost all OMPs (RT1: citalopram = florfenicol = trimethoprim $\geq$ venlafaxine > PCP = tramadol = diuron = alachlor $\geq$ diclofenac; RT2: florfenicol = PCP = citalopram = trimethoprim > diuron = alachlor = diclofenac = venlafaxine $\geq$ tramadol). However, the sorption degree of most of OMPs (florfenicol, diclofenac, alachlor, clofibric acid, diuron, and PCP) was inferior to that observed for LDPE, and clofibric acid was not sorbed to uPVC.

Similarly to LDPE, no universal rule was found between pK_a or $\log K_{ow}$ and the affinity between uPVC and the OMPs. Still, there seems to be a different trend by which higher pK_a usually leads to higher sorption capacity on uPVC. This suggests that the OMPs molecular or cationic forms have a higher affinity for uPVC (at pH ca. 5.8, where the surface of uPVC is expected to be negatively charged) (Wu et al., 2019), indicating that electrostatic interactions may also be a relevant mechanism in the sorption process, as has been reported in the literature for PVC (Guo et al., 2019b, 2019a; Puckowski et al., 2021). Nevertheless, further experiments would be necessary to examine the effect of the solution pH and the interaction of each individual OMP studied with uPVC.

The increase of the carbonyl and polyene absorbance peaks intensity in the ATR-FTIR analysis previously reported (Chapter 3 - Section 3.3.1.3) for the weathered uPVC MPPs may be linked to the increased sorption capacity observed for these samples. Moreover, this assumption is further supported by the higher Carbonyl Index of RT1 samples (virgin: 0.73 ± 0.15 ; RT1: 4.82 ± 0.27 ; RT2: 3.37 ± 0.12) and the higher sorption capacity observed for several compounds on RT1-aged uPVC MPPs, with the main exceptions being diclofenac, alachlor, diuron and PCP. The low sorption capacity observed in the present study for ozone-aged MPPs is corroborated by the lack of major changes in uPVC after that aging treatment (Chapter 3). Therefore, similarly to aged LDPE, the Carbonyl Index can be a good indicator to estimate the global sorption capabilities of uPVC MPPs, although it is not valid for every single OMP.

4.3.1.1.4 Comparison to other reports in the literature

The sorption capacities obtained in the present study are overall much lower than those reported in the literature for the same polymers and OMPs already investigated, namely for: diclofenac with virgin and Fenton oxidized PET and high-density polyethylene (HDPE) (Munoz et al., 2021); PCP with virgin and extracted from personal care products LDPE and PET (Loncarski et al., 2020; Tubić et al., 2019); and trimethoprim (in freshwater or seawater matrices) with virgin polyethylene and PVC (Jia Li et al., 2018). Nevertheless, other studies showed more similar results, as that published by Elizalde-Velázquez et al. (2020), studying diclofenac sorption (diclofenac: $q_e < 0.08 \mu\text{g g}^{-1}$ for C_0 ca. 2.5 mg L^{-1}) on virgin ultra-high molecular weight polyethylene (UHMWPE) and average molecular weight polyethylene (AMWPE) (among other OMPs and polymers), using the same load of MPPs (10 g L^{-1}) of the present study. The study of diuron sorption on LDPE, PET and PVC obtained from plastic waste was demonstrated by Godoy et al. (2020) to be negligible, which agrees with that observed for virgin MPPs and all PET samples in this study, but not for the samples of weathered MPPs of LDPE and uPVC. The ambiguity between the sorption capacities reported in the literature can result from different methodologies followed and also depends on the MPPs used (e.g., particle size distribution).

4.3.1.2 Pentachlorophenol sorption on microplastic particles

The sorption behavior of PCP on both virgin and ozone-aged MPPs of LDPE (Fig. 4.4a) and PET (Fig. 4.4b) justified the selection of this OMP for further experiments aiming to study its sorption equilibrium isotherms on these types of MPP samples. The results show that for each polymer, the ozone-based aging greatly increased the sorption capacity (Fig. 4.5; Table 4.9).

From the three investigated mathematical models (Langmuir, Freundlich and linear), Langmuir fitted better for ozone-aged PET, while Freundlich was the best fitting for the other 3 datasets (Table 4.10). Thus, equilibrium PCP sorption on ozone-aged PET seems to be better represented by a monolayer homogeneous adsorption model than the virgin PET and virgin and ozone-aged LDPE. As reported previously, even though microplastics can have irregular shapes and non-uniform surfaces when analyzed under the microscope, the sorption can be represented by the Langmuir isotherm, by which there is macroscopic homogeneous adsorption (Wang and Guo, 2020b).

PCP had a higher affinity for LDPE than for PET under all the conditions tested but more discernibly for virgin MPPs, as respectively inferred in Fig. 4.4a and b, and supported by Fig. 4.5. The opposite behavior was described by Loncarski et al. (2020), i.e., PCP sorption isotherms for virgin MPPs of polyethylene and PET showed higher affinity of PCP to PET, and also higher sorption capacities of both polymers when compared with the results reported in this chapter.

Although it cannot be excluded the competition and synergistic effects among the 10 OMPs studied, the results of PCP sorption either when spiked individually or spiked simultaneously with other 9 OMPs are similar (Fig. 4.5), making these effects mostly negligible under the conditions tested. The use of sorbates at trace concentrations helps reducing these effects, while also allowing to perform the study in more environmentally relevant concentrations and with multiple analytes in solution.

More studies need to be developed in this field since this OMP is already targeted as a priority pollutant and considering that the realistic conditions in the environment favor the occurrence of aged MPPs.

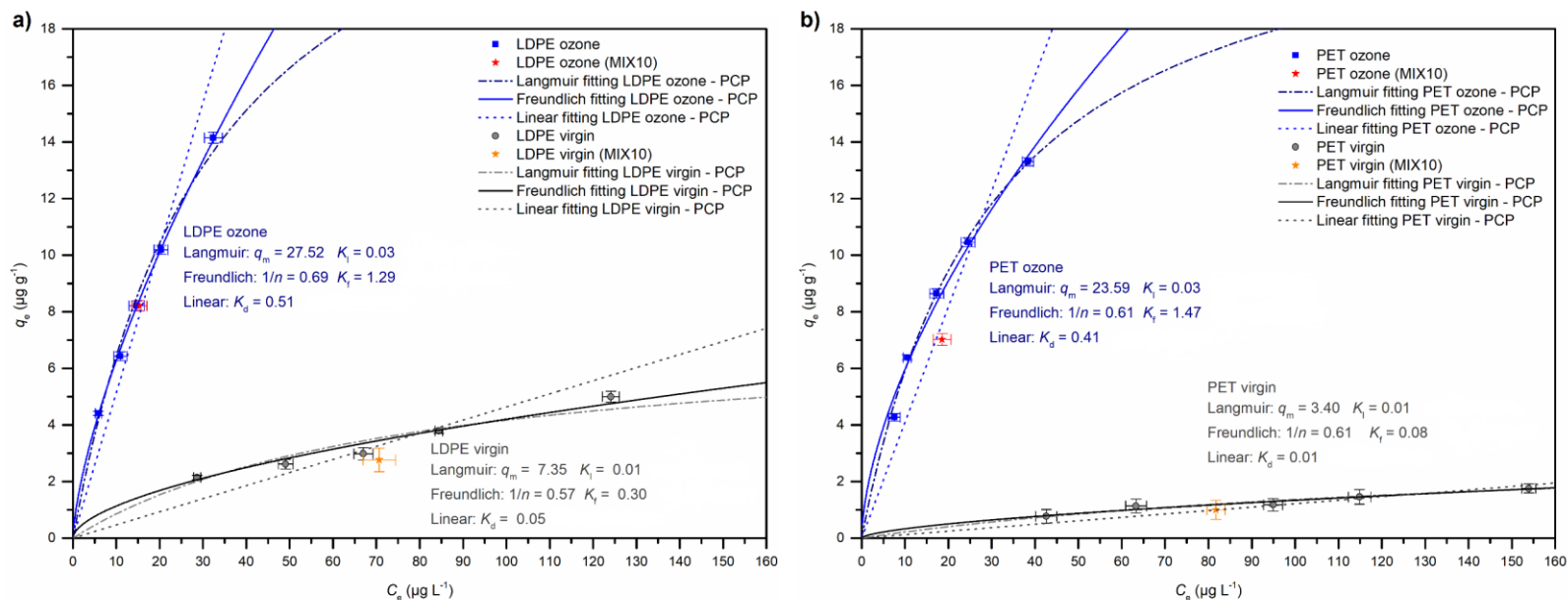


Fig. 4.5. Sorption equilibrium isotherms: pentachlorophenol (PCP) sorbed per unit of mass of MPP (virgin and aged by ozone treatment), for a) low-density polyethylene (LDPE), and b) poly(ethylene terephthalate) (PET). ★ represent the experimental data of PCP in Fig. 4.4a and Fig. 4.4b, i.e., the PCP sorption on (virgin or ozone aged) LDPE or PET when in solution with a total of 10 OMPs.

Table 4.9. Sorption equilibrium isotherms: average pentachlorophenol retention on microplastic particles (q) for different initial concentrations during 24 h.

Polymer	C_0 ($\mu\text{g L}^{-1}$)	Ozone				Virgin			
		C_e ($\mu\text{g L}^{-1}$)	SD	q_e ($\mu\text{g g}^{-1}$) ($n = 3$)	SD	C_e ($\mu\text{g L}^{-1}$)	SD	q_e ($\mu\text{g g}^{-1}$) ($n = 3$)	SD
LDPE	50	5.88	0.73	4.41	0.07	28.65	0.81	2.14	0.08
	75	10.92	1.53	6.43	0.16	49.08	1.72	2.62	0.17
	100	14.68	1.75	8.20	0.17	67.00	2.21	2.98	0.22
	125	20.33	1.61	10.19	0.16	84.41	0.85	3.79	0.09
	175	32.38	2.03	14.15	0.20	124.08	1.94	4.99	0.19
PET	50	7.55	1.34	4.27	0.13	42.60	2.42	0.77	0.24
	75	10.52	0.94	6.38	0.09	63.29	2.41	1.13	0.24
	100	17.28	1.63	8.64	0.16	94.93	2.21	1.18	0.22
	125	24.56	1.56	10.46	0.15	114.87	2.59	1.45	0.26
	175	38.38	1.31	13.30	0.14	153.91	1.61	1.76	0.16

Table 4.10. Sorption equilibrium isotherms: estimated Langmuir, Freundlich, and linear parameters.

MPPs	Langmuir				Freundlich				Linear (through the origin)		
	K_l ($\text{L } \mu\text{g}^{-1}$)	q_m ($\mu\text{g g}^{-1}$)	adj R^2	RSS	K_f ($(\mu\text{g g}^{-1})$ ($\text{L } \mu\text{g}^{-1})^{1/n}$)	$1/n$	adj R^2	RSS	$a = K_d$ (L g^{-1})	adj R^2	RSS
LDPE ozone	0.03 ± 0.01	27.52 ± 3.68	0.986	31.7	1.29 ± 0.05	0.69 ± 0.01	0.999	3.07	0.51 ± 0.05	0.958	577
LDPE virgin	0.01 ± 0.01	7.35 ± 1.33	0.934	15.4	0.30 ± 0.07	0.57 ± 0.05	0.972	6.58	0.05 ± 0.01	0.959	124
PET ozone	0.03 ± 0.01	23.59 ± 1.93	0.990	22.1	1.47 ± 0.21	0.61 ± 0.05	0.978	46.4	0.41 ± 0.04	0.945	1016
PET virgin	0.01 ± 0.01	3.40 ± 0.77	0.932	0.70	0.08 ± 0.03	0.61 ± 0.08	0.948	0.55	0.01 ± 0.01	0.977	3.92

4.3.2 Phytotoxicity of microplastic particles carrying organic micropollutants

MPPs have been identified as emerging pollutants in soil-plant systems, although there are still research gaps regarding the behavior and the extent of the effects of MPPs on these systems (Zhang et al., 2022). One of the identified sources of both soil MPPs and OMPs is the use of treated wastewater and biosolids in agriculture, since many OMPs are not efficiently removed during wastewater treatment (Chavoshani et al., 2020; Ng et al., 2018; Pérez-Reverón et al., 2022). Considering the observed sorption of some of the studied OMPs on MPPs in the previous section (4.3.1), it is worthy to investigate the MPPs being transported into soil-plant systems while carrying OMPs. Therefore, phytotoxicity tests were carried out with two species of plants: *Lepidium sativum* and *Sinapis alba*. The seed germination and the roots and shoots length mean and SD for each type of test plate and experiment are listed in Table 4.11. The results were compared and analyzed using the one-way ANOVA and post hoc Tukey test, and the percentage effect of the different combinations tested of OMPs and/or MPPs on root and shoot growth was estimated (Table 4.12).

For both species of plants, the seed germination does not show signs of being affected by any of the conditions tested, with only one seed of *Lepidium sativum* developing a root with less than 1 mm in length (ozone-aged LDPE). The species *Lepidium sativum* early growth was impacted when a solution containing at least 50 $\mu\text{g L}^{-1}$ of each of the 10 OMPs was used (roots = 40% effect; shoots = 32% effect), but no significant changes were observed when the seeds were exposed to virgin MPPs (LDPE, PET or uPVC) or virgin/aged LDPE with or without sorbed OMPs (roots $\leq 0\%$ effect; shoots $\leq 9\%$ effect). A study of MPPs acute toxicity (6 days) by Pignattelli et al. (2020) has shown that virgin polyethylene and PVC can negatively affect the germination rate and plant growth of *Lepidium sativum*, but this effect was not observed in this study.

On the other hand, *Sinapis alba* early root growth decreased when at least 50 $\mu\text{g L}^{-1}$ of each of the 10 OMPs was used (roots = 57% effect), but that concentration was not sufficient to originate significant changes in the shoots early growth (shoots = 9% effect). For that species, a higher concentration of the 10 selected OMPs is needed (such as 100 $\mu\text{g L}^{-1}$: roots = 70-79% effect; shoots = 35-39% effect) to lead to the decrease of the shoots early growth. Consequently, as expected, no significant changes were observed for the *Sinapis alba* shoots early growth when virgin MPPs or virgin/aged LDPE with or without sorbed OMPs were used (shoots $\leq 9\%$ effect). Overall, for both species, the roots early growth is more negatively affected by the presence of other substances than the shoots.

Table 4.11. Phytotoxicity tests results: preliminary and LDPE test.

Test	Plate	<i>Lepidium sativum</i>					<i>Sinapis alba</i>				
		Ger.	Length roots (mm)	SD	Length shoots (mm)	SD	Ger.	Length roots (mm)	SD	Length shoots (mm)	SD
i) preliminary	Negative control	10	78	5	28	5	10	61	8	26	2
	Positive control 1	10	27	4	16	2	10	18	2	16	3
	LDPE virgin MPP	10	82	6	29	5	10	57	3	26	3
	PET virgin MPP	10	79	4	28	3	10	59	6	27	4
	uPVC virgin MPP	10	80	6	26	4	10	59	4	26	6
ii) LDPE MPP+OMP	Negative control	10	69	5	30	2	10	77	5	19	3
	Positive control 1	10	18	4	14	2	10	16	4	13	4
	Positive control 2	10	42	3	20	1	10	33	6	18	4
	Virgin MPP	10	71	3	29	3	10	69	8	18	3
	Virgin MPP+OMP	10	74	3	31	3	10	69	6	19	3
	Ozone MPP	9	71	7	31	4	10	68	6	19	4
	Ozone MPP+OMP	10	73	5	31	3	10	68	8	19	2
	RT1 MPP	10	74	4	32	2	10	69	8	19	5
	RT1 MPP+OMP	10	70	6	31	3	10	65	5	18	1
	RT2 MPP	10	69	4	27	2	10	70	7	19	2
	RT2 MPP+OMP	10	71	3	30	5	10	65	7	18	2

Positive control 1 = 100 µg L⁻¹ of MIX10Positive control 2 = 50 µg L⁻¹ of MIX10

Table 4.12. Phytotoxicity tests: average percentage effect of the different combinations tested of OMPs and/or MPPs on root and shoot growth of two species of plants. The letters a (positive control 1), b (positive control 2), c (negative control) and d indicate that the difference of the means of the roots or shoots length between the plates from the same test is not significant at the 0.05 level.

Test	Plate	<i>Lepidium sativum</i>				<i>Sinapis alba</i>			
		Length roots (%)		Length shoots (%)		Length roots (%)		Length shoots (%)	
i) preliminary	100 $\mu\text{g L}^{-1}$ of MIX10	65	a	45	a	70	a	39	a
	LDPE virgin MPP	-5	c	-2	c	7	c	2	c
	PET virgin MPP	-1	c	1	c	3	c	-1	c
	uPVC virgin MPP	-3	c	6	c	2	c	3	c
ii) LDPE MPP+OMP	100 $\mu\text{g L}^{-1}$ of MIX10	75	a	54	a	79	a	35	a
	50 $\mu\text{g L}^{-1}$ of MIX10	40	b	32	b	57	b	9	c
	Virgin MPP	-2	c	3	c	10	cd	5	c
	Virgin MPP+OMP	-6	c	-3	c	10	cd	3	c
	Ozone MPP	-2	c	-2	c	11	cd	4	c
	Ozone MPP+OMP	-5	c	-2	c	11	cd	4	c
	RT1 MPP	-6	c	-5	c	10	cd	2	c
	RT1 MPP+OMP	-1	c	-3	c	16	d	6	c
	RT2 MPP	0	c	9	c	9	cd	1	c
	RT2 MPP+OMP	-2	c	-1	c	16	d	9	c

Contrary to what was observed with *Lepidium sativum*, *Sinapis alba* roots length results suggest that the presence of MPPs with OMPs may negatively affect the early growth of the species, specifically for the MPPs of LDPE that were aged by 13 weeks of weathering (roots = 16% effect). Nevertheless, these results show a very low decrease of the early growth of this species and, although significantly different (at a 0.05 level) from the negative control, are not significantly different from the other test plates with LDPE MPPs.

The desorption test (Table 4.13) carried out in parallel to the LDPE phytotoxicity test confirmed that the MPPs obtained from the sorption experiments are able to release some of the sorbed OMPs, although the concentration is overall below the method quantification limit when they are detected in solution. Additionally, this desorption test also allowed to confirm, once again, that the weathered LDPE samples (RT1 and RT2) have higher sorption capacities than virgin or ozone-aged LDPE, consequently leading to the higher desorption of OMPs (measured as larger peak areas in the chromatograms). However, the potential release of substances from the MPPs that result from the aging processes was not studied, and that could also contribute to the toxicity of the MPPs since the results are not significantly different between any virgin or aged LDPE MPPs and the correspondent OMP-sorbed MPPs.

Table 4.13. Phytotoxicity test: solution concentrations after desorption of each previously sorbed OMP (tramadol and venlafaxine were not sorbed on LDPE), during the desorption test for LDPE MPP+OMP.

Micropollutant	C ($\mu\text{g L}^{-1}$) LDPE			
	Virgin (n = 3)	O ₃ gas (n = 3)	RT1 (n = 3)	RT2 (n = 3)
Florfenicol	<MDL	<MDL	<MDL	<MDL
Trimethoprim	<MDL	<MDL	<MDL	<MQL
Diclofenac	<MDL	< 1	< 1	< 1
Citalopram	<MDL	<MDL	<MQL	<MQL
Alachlor	<MDL	<MDL	< 1	< 1
Clofibric acid	<MDL	<MDL	<MQL	<MQL
Diuron	<MDL	<MDL	<MQL	<MQL
Pentachlorophenol	<MDL	<MQL	<MQL	<MQL

MDL: Method detection limits

MQL: Method quantification limits

These results are compatible with the theory that MPPs can be transport vectors of other pollutants, such as the OMPs studied, with potential adverse effects to biota. However, considering the undetected (*Lepidium sativum*) or very low decrease (*Sinapis alba*) in the species early growth for the controlled conditions tested, the amount of OMPs necessary to negatively impact the early growth of these plants, and the amount of MPPs used and their low release of OMPs, it is unlikely that the combinations of MPPs and OMPs studied may cause major changes

to the dynamics of the early growth of *Lepidium sativum* or *Sinapis alba*. Nevertheless, since MPPs can transport OMPs, it cannot be yet excluded their potential adverse effects under specific scenarios, such as with more aged-advanced MPPs, under long-term chronic exposure, or in combination with other sources of OMPs (e.g., other particulate matter with sorbed pollutants). Additionally, other combinations with different OMPs and polymers, outside of those studied, may have more severe impacts.

Therefore, this shows that there is a need to study in more depth the impacts of MPPs on soil-plant systems, particularly after undergoing aging and interacting with co-occurring pollutants. These results should be beheld as a starting point to further understand this capability of MPPs and still leave the toxicity of the combinations studied on soil-plant systems as a possibility.

4.4 Conclusions

This study allowed to examine the potential of MPPs to be transport vectors for OMPs, demonstrating the major role of the aging degree of MPPs in the sorption process:

- Of the 3 polymers selected, LDPE sorption capacities were the most greatly increased by both ozone exposure and weathering. Likewise, uPVC sorption capacities increased, although mainly after weathering. For these two polymers (LDPE and uPVC), the Carbonyl Index can be a valuable indicator in a preliminary estimation of the global sorption capabilities of the aged MPPs in comparison to virgin ones. PET MPPs were the least affected by aging and, consequently, conserved their very low sorption capacities for almost all OMPs, with the interesting exceptions of PCP on ozone-aged MPPs and trimethoprim on RT2 weathered MPPs.
- Most of the OMPs selected had very low to no affinity to virgin MPPs. While PET kept very little affinity for almost all OMPs even after undergoing aging, few substances had no appreciable sorption on LDPE or uPVC after the aging treatments: LDPE - tramadol and venlafaxine, and uPVC - clofibric acid. PCP was the most sorbed OMP on LDPE and PET, for both virgin and aged MPPs, and thus further experiments were performed to study PCP sorption on LDPE or PET. This provided us with a more clear picture of the sorption of this pesticide on virgin or ozone-aged MPPs.

However, additional research is still needed to understand the sorption process of OMPs to aged MPPs in more complex matrices and to analyze the effect of ionic strength, pH, temperature, and organic matter in solution, as well as other particulate matter that can compete with MPPs (e.g., carbon-based nanomaterials). The undetected or very low decrease in the early growth of the plant species *Lepidium sativum* and *Sinapis alba*, under the conditions tested with LDPE MPPs, suggests that the studied combinations of OMPs and MPPs are unlikely to deeply affect the

early growth dynamics of these plants. Still, since MPPs can sorb and, consequently, transport OMPs, and aging can increase their sorption capacities, there is a need for further research on the toxicity of MPPs with sorbed pollutants on soil-plant systems.

Considering the importance of the MPPs aging degree in their sorption capacities, it is imperative that future studies on microplastics behavior and effects use aged samples, obtained from aging virgin samples in controlled conditions, to work with more environmentally relevant MPPs and to avoid underestimating the sorption capacities of the polymer under study. Nevertheless, virgin samples should also be included in each study, as that will help to compare results between different research projects and studies, since there is still no standard methodology for aging microplastics for this type of research. It should be considered that by working with aged MPPs obtained by controlled aging treatments, there will be a limitation on the number of experiments that can be performed based on the amount of MPPs recovered from those aging treatments. Thus, it is fundamental to develop protocols for aging microplastics specifically for sorption experiments and/or for assessing the effects on biota, allowing more collaborative efforts and faster and more efficient progress in this field of research.

5. Microplastics behavior and attenuation in a lab-scale DCMD system for desalination applications



In this chapter, the behavior of microplastic particles (MPPs) is explored in a lab-scale direct contact membrane distillation (DCMD) system used to produce drinking water from seawater, while also analyzing the impact of their presence on the water treatment process performance. Commercial MPPs of different polymers (LDPE, PET and uPVC) were first studied under temperature stress (TS) tests (using amber bottles) to mimic the exposure to the high temperatures commonly used in DCMD ($\sim 80\text{ }^{\circ}\text{C}$). These experiments lead to the selection of uPVC to test it under different loads and degrees of aging in the DCMD system. By analyzing the TS and DCMD MPPs samples by ATR-FTIR, UV-Visible spectroscopy and SEM, it was possible to conclude that minor aging is expected to occur in the three studied polymers in a DCMD system. However, uPVC can potentially undergo *pinking*, and less temperature-resistant polymers (such as LDPE) can suffer more substantial degradation, even potentially increasing membrane fouling during DCMD and, consequently, reducing the water recovery. High loads ($> 0.1\text{ g L}^{-1}$) of uPVC MPPs decreased the DCMD performance in terms of permeate flux, although no signs of inferior treated water quality were found in any studied scenario. The removal of MPPs in DCMD applications with seawater was analyzed by Raman microscopy, with all the results suggesting very high removal efficiencies ($\geq 99\%$).



5.1 Introduction

Even though the recognized importance of drinking water production from seawater and the need for the assessment of microplastics throughout water supply chains, there is a research gap concerning the microplastics behavior and removal during desalination processes, particularly when using membrane distillation processes (Section 1.1.5).

The research presented in this chapter constitutes one of the first assessments of microplastics behavior and removal during a membrane distillation treatment, at a lab-scale. The study was aimed at analyzing i) the behavior of microplastic particles (MPPs) in a direct contact membrane distillation (DCMD) system, regarding chemical and physical modifications of the particles and their distribution and fate inside the system, and ii) the potential influence of MPPs on the DCMD process, namely on the treated water production and quality. For that, temperature stress batch experiments (using amber bottles) were first conducted with three virgin polymers: LDPE - low-density polyethylene, PET - poly(ethylene terephthalate) and uPVC - unplasticized poly(vinyl chloride). Based on the results of these experiments, uPVC was selected to test the lab-scale DCMD system at two different MPPs loads and different aging degrees, in filtered seawater. The DCMD parameters, such as the vapor pressure gradient, membrane permeability, and the interval permeate flux, were followed during each experiment to infer the impact of the MPPs on the performance of the system. In parallel, the MPPs modifications were assessed by different characterization techniques at the end of the experiments, regarding the chemical structure, UV-visible absorption, and surface morphology. Finally, the treated water was analyzed for the presence of MPPs by Raman microscopy (μ Raman). This chapter also includes a section (5.2) dedicated to general considerations of the DCMD process, the lab-scale system used and previous experiments without microplastics, related to the PhD project.

5.2 DCMD: process and system configuration

Direct contact membrane distillation (DCMD) is one of the membrane distillation (MD) configurations available and the one selected for this work. Other configurations include air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). These configurations differ in how the vapor pressure gradient is maintained and the permeate vapor condensation method (Ashoor et al., 2016).

In DCMD, the retentate (feed stream) and the permeate (receiving stream) are in direct contact with a porous hydrophobic membrane and both can be in recirculation. Because the retentate temperature is increased to a pre-defined high temperature and the permeate is kept at a low temperature, a vapor pressure gradient is created between the two sides of the membrane. The

partial pressure at each side can be calculated by applying the Antoine equation (Eq. 5.1), where P^v is the water vapor pressure (mmHg) and T is the temperature (°C).

$$\log_{10} P^v = A - \left(\frac{B}{T + C} \right) \quad \text{Eq. 5.1}$$

The Antoine coefficients for water up to the normal boiling point (applicable temperature range region 1 - 100 °C) are the following: $A = 8.07131$; $B = 1730.63$; $C = 233.426$ - if T in °C and P in mmHg or torr (1 mmHg = 101.325/760 kPa) (*Perry's Chemical Engineer's Handbook 8th edition*, 2008).

The vapor pressure gradient is the driving force in membrane distillation, since the water vapor diffuses/flows from higher to lower vapor pressure across the membrane pores and condenses, leading to the production of a purified water flux from the retentate side of the membrane to the permeate side, while the particles and non-volatile undesired compounds are concentrated in the retentate side. Since the membrane is hydrophobic, it prevents the penetration of the aqueous solution into the pores due to the capillary force, which results in a vapor/liquid interface at each pore entrance (Nagy, 2019).

The vapor pressure gradient (ΔP) can be estimated by Eq. 5.2 (Zhang et al., 2010), which calculates the ΔP for counter-current flow, where $P_{P,IN}$, $P_{R,IN}$, $P_{P,OUT}$, and $P_{R,OUT}$ are the partial vapor pressures at the inlet (IN) and outlet (OUT) temperatures of the permeate (P) and retentate (R) side of the membrane cell.

$$\Delta P = \frac{(P_{R,IN} - P_{P,OUT}) - (P_{R,OUT} - P_{P,IN})}{\ln \left[\frac{(P_{R,IN} - P_{P,OUT})}{(P_{R,OUT} - P_{P,IN})} \right]} \quad \text{Eq. 5.2}$$

Apart from the ΔP , the other major factor that controls the mass transfer across the membrane pores is the transport mechanisms of the vapor molecules, which depend on the membrane's physical properties and on the free path of the vapor molecules (Nagy, 2019). Thus, the permeate flux J ($\text{kg m}^{-2} \text{h}^{-1}$) is given by Eq. 5.3 (Nagy, 2019), where ΔP is the vapor pressure gradient (kPa), and B is the membrane permeability ($\text{kg m}^{-2} \text{h}^{-1} \text{kPa}^{-1}$).

$$J = B \times \Delta P \quad \text{Eq. 5.3}$$

J can also be calculated by Eq. 5.4, where ΔW is the mass of the distillate (kg) produced in Δt , A is the effective area of the membrane (m^2) and Δt is the time interval (h).

$$J = \frac{\Delta W}{A \times \Delta t} \quad \text{Eq. 5.4}$$

The total flux can be estimated during the experiment by calculating ΔW and Δt always as the difference between the data at $t = n$ and $t = 0$. On the other hand, the interval flux, where ΔW

and Δt are the difference between the data at $t = n$ and $t = n-1$, is more relevant to analyze possible temperature instability and the flux decline through increased membrane fouling during the experiment.

As for heat transfer in the membrane interface, both in the retentate side and the permeate side, there is convective heat transfer in the boundary layer and heat transfer because of the mass transfer across the thermal boundary layer (the last one is frequently dismissed in the energy balance). Through the membrane there is conductive heat transfer (sensible heat) and heat transfer due to water vapor migration through the membrane pores (latent heat) (Ashoor et al., 2016). Under steady state conditions, the heat transfer flux can be expressed through an energy balance equation of the three regions (retentate, membrane and permeate), which can be used to calculate, using an iterative method, the membrane surface temperatures on feed and permeate sides in the DCMD module (Olatunji and Camacho, 2018).

5.2.1 DCMD lab-scale setup

A laboratory-scale DCMD system was previously installed at LSRE-LCM to conduct research related to desalination or wastewater treatment, as well as to test the performance of innovative membranes, e.g., carbon nanotubes blended membranes (Silva et al., 2015). The LSRE-LCM lab-scale system setup is represented in Fig. 5.1.

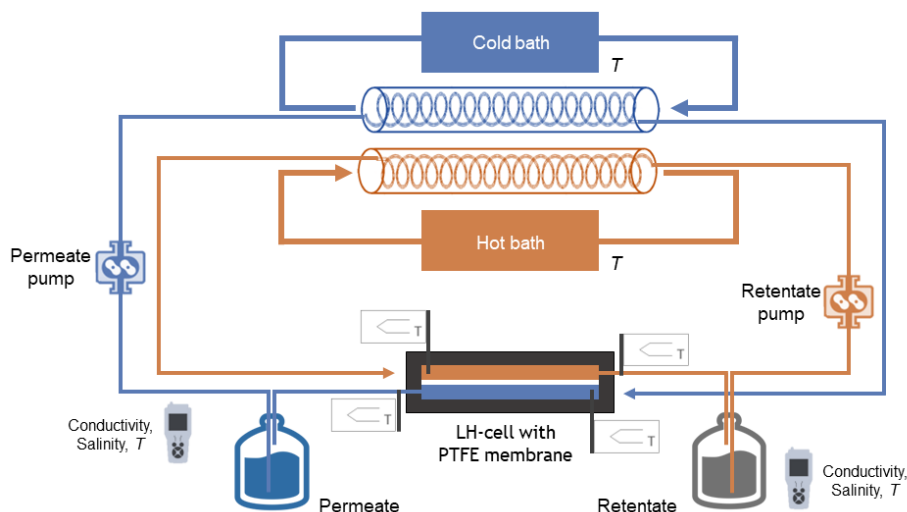


Fig. 5.1. Direct contact membrane distillation (DCMD) setup.

Different membrane module configurations are available at LSRE-LCM, which were already compared in works published by the research group (T. L. S. Silva et al., 2018). For the most recent research conducted, the LH-cell (a large cell with an H-like configuration and an effective membrane area of 70 cm²) has been the one selected because of the higher permeate quality obtained with this configuration when compared with another configuration referred to W-cell. The difference between these configurations is that the H-cell inlet streams enter the module parallel to the membrane, while the W-cell inlet streams enter the module perpendicular to the membrane.

Different commercial membranes or modified/prepared membranes were previously tested at the lab-scale DCMD system in studies by Morales-Torres et al. (2014) and Silva et al. (2015, 2018). Polytetrafluoroethylene (PTFE) hydrophobic membranes with 0.22 µm pore size and 150 µm thickness purchased from Merck Millipore Ltd (reference FGLP00010) are the commercial membranes selected for this PhD work, based on their good performance regarding the permeate flux obtained (T. L. S. Silva et al., 2018).

The main components of the DCMD system are listed in Table 5.1. Over the time of the PhD project, several modifications were made to the system (from 2018 to present), aiming to:

1. **Obtain higher efficiency in the water treatment process** (mainly due to less heat losses) **and increase the user safety** (in 2018): new more heat-resistant tubing material used for the hot bath water recirculation and connections between the retentate tubing and the heat exchanger, and new arrangement of the heat exchangers to make them both counter-current flow (Fig. 5.2).

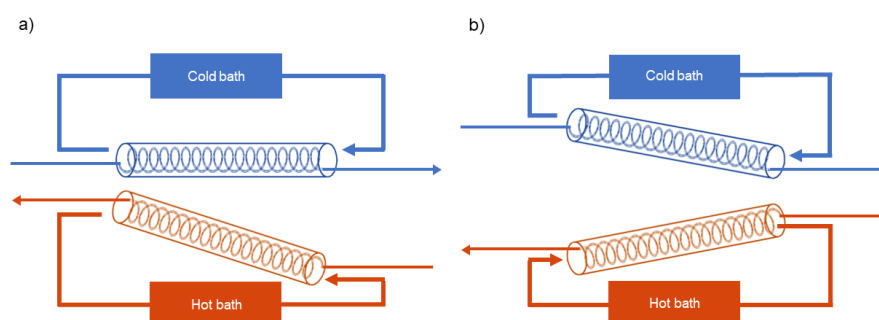


Fig. 5.2. Heat exchangers arrangement: a) until 2018, b) after.

2. **Use the DCMD system for other projects** (in 2019-2020): Four T-type ball valves were installed at the inlet and outlet of the circulating baths in order to be able to use the same circulating baths in the updated DCMD system and in a new DCMD system (with

the same design as the updated version of the old DCMD system) that was installed to be used with wastewaters, mainly olive mill wastewater (VERPRAZ project, NORTE-01-0247-FEDER-39789), and avoid possible contaminations. This new system also shares the temperature readers, peristaltic pumps, and precision balance but none of the tubing and probes, and not the LH-cell. During this period, the DCMD system changed location in the Chemical Engineering department to another laboratory, requiring a new arrangement for the peristaltic pumps.

3. **Maintenance and repair** (in 2018-present): all the PFA, pumps, and silicone tubing and connections were replaced after 2018 experiments and a new cold circulating bath was installed due to malfunction of the previous one. The coil condensers and other glass components were cleaned with a nitric acid solution. A new LH-cell membrane module was made due to the accumulated damage the previous one suffered. One of the peristaltic pumps was repaired. Periodically, the silicone tubing and connections are replaced due to their limited durability.
4. **Automatize the data acquisition**: new temperature and conductivity readers that can be connected to a computer were acquired and installed. For future works, a new procedure for data collection with the DCMD system is going to be developed since some of the data can be recorded using a data acquisition board.

Table 5.1. Main components of the DCMD system.

Function	2018 experiments (old DCMD system)	2020-2022 experiments (updated DCMD system)
Membrane	Commercial membrane of PTFE (Merck Millipore Ltd, ref. FGLP00010)	
Membrane module	LH-cell (new module was made in 2019)	
Permeate reservoir	1) 1 L or 2 L plastic (HDPE) bottles Or 2) 25 L HDPE jerrycan Or 3) 10 L ISO blue cap bottle	1) 1 L ISO blue cap bottles Or 2) 5 L ISO blue cap bottle
Retentate reservoir	1) 1 L graduated glass cylinder Or 2) 25 L HDPE jerrycan	1) 1 L graduated glass cylinder Or 2) 10 L ISO blue cap bottle
Circulating baths	Cold: MX 7L R-20, VWR Hot: MX06S, VWR	Cold: AD15R-30-V12V, VWR Hot: MX06S, VWR
Permeate and retentate recirculating flow pumps	Two FH100 Thermo Scientific reversible peristaltic tubing pumps	
Heat exchange	Two heat exchangers: coil condensers	
Tubing	• PFA 6.35x9.52 mm (retentate inlet) • Swagelok PFA 1/4 and 1/8 tubing • Silicone 5x8 mm and 6x9 mm tubing • Thermo Scientific general-purpose tubing of norprene size 16 (pumps) • Buran N 6x11.3 mm (retentate connections to the heat exchangers) • Baths: cold - silicone 7x13 mm; hot: silicone 7x13 mm in 2018, and buran N (synthetic rubber) 6x11.3 mm after	
Experiment time measurement	VWR digital timer	
Permeate-bottle mass measurement	Radwag WLC 2/A2 precision balance (maximum of 2 kg)	
Temperature measurement	VWR total-range digital thermometers with a total of four type-K probes: two at the permeate and retentate cell inlets and two at the cell outlets (2018: 620-2006, after: 620-2049)	
Conductivity, salinity, and temperature record	Two VWR CO310 portable instruments	Two VWR CO310M portable instruments

5.2.2 Data analysis

The DCMD lab-scale system allows the manual data collection of the experiment time, the circulating baths temperatures, permeate and retentate cell inlet and outlet temperatures, permeate-bottle mass (if the precision balance is used), permeate and retentate conductivity, salinity, and temperature, and retentate volume (if the graduated glass cylinder is used). The data details are listed in Table 5.2.

Table 5.2. Data collected for each DCMD experiment and corresponding applicability.

Data collected (every 10 or 30 min)	Equipment used	Applicability
Experiment time (min)	Digital timer	Permeate interval flux (Eq. 5.4)
Permeate and retentate rotations per minute (set at the beginning of each experiment)	Reversible peristaltic tubing pumps	Flow rates through pump calibration curves; Operating parameter
Circulating baths temperatures (°C)	Hot and cold circulating baths with advanced programmable temperature controllers	Operating parameter
Permeate and retentate cell inlet and outlet temperatures (°C)	Digital thermometers with type-K probes	Result; Permeate water density (thermodynamic tables); Partial vapor pressure (Eq. 5.1) and ΔP calculation (Eq. 5.2)
Permeate-bottle mass (g)	Precision balance	Permeate interval flux (Eq. 5.4) and water recovery calculation
Permeate and retentate conductivity ($\mu\text{S cm}^{-1}$ or mS cm^{-1}), temperature (°C), and salinity (ppt, parts per thousand)	CO310(M) portable instruments	Result (25 °C compensated and uncompensated conductivity, and salinity), rejection

With the permeate flux and ΔP results, the membrane permeability (B) can be calculated through Eq. 5.3. The flux decline (%) can be determined with reference to a selected or average permeate interval flux obtained after ΔP stabilizes. For this, during the time interval when the DCMD system is displaying stable ΔP and permeate interval flux, the average ΔP , permeate interval flux, and membrane permeability can be calculated with the data collected for that Δt .

While the portable conductivity meter used only directly measures the uncompensated conductivity and the temperature, those results can be used to calculate the compensated conductivity, salinity, and Total Dissolved Solids (TDS).

The compensated conductivity was calculated by the model expressed by Eq. 5.5, where EC_{25} is the compensated conductivity ($\mu\text{S cm}^{-1}$ or mS cm^{-1}), EC is the measured (uncompensated) conductivity ($\mu\text{S cm}^{-1}$ or mS cm^{-1}), a is the temperature compensation factor ($^{\circ}\text{C}^{-1}$), and T is the measured temperature ($^{\circ}\text{C}$) (Hayashi, 2004). The temperature compensation factor selected was $0.0191\text{ }^{\circ}\text{C}^{-1}$ (Bridgewater et al., 2012).

$$EC_{25} = \frac{EC}{1 + a \times (T - 25)} \quad \text{Eq. 5.5}$$

Salinity can be determined indirectly after determining the conductivity and temperature of the water sample, using the 2520B standard method (Bridgewater et al., 2012). The portable conductivity meter used has an algorithm that applies that method, so no additional calculations are needed.

TDS can be determined by multiplying the conductivity by a TDS factor. However, this parameter was not used in this work, since the TDS-EC relationship was not determined in the laboratory for the water samples under study.

The water recovery (%) is a parameter that measures the percentage of distilled water produced from the water feed, while the rejection parameter (%) allows for measuring the membrane impermeability for TDS, salt, or other undesired compounds in the water.

A Microsoft Excel template was created to organize all the data collected during each experiment and calculate the ΔP , permeate flux (total and interval), permeability, flux decline, water recovery, and rejection. After each experiment, the results expected are the tables and/or diagrams with the evolution through the experiment time of: i) permeate and retentate cell inlet and outlet temperatures; ii) ΔP and permeate flux; iii) flux decline; iv) permeate and retentate compensated conductivity; v) permeate and retentate salinity; vi) water recovery and rejection.

5.2.3 Operating parameters

The lab-scale DCMD system can be operated with different feed streams (in the retentate side) and receiving streams (in the permeate side), different membranes and membrane modules can be used, each circulating bath can be set within a temperature range, and the peristaltic pumps can be operated to create a range of flow rates. Because of this, before other parameters might be studied, the relationships between the permeate interval flux and the water vapor pressure gradient (ΔP), or between the permeate interval flux and the retentate and permeate flow rates, should be established. To achieve that, short experiments of 1.5 h (at least 1 h with stable ΔP) can be performed by fixing one of the variables and changing the other for a range of values. For each flow rate (same flow rate operation for both pumps) and for each ΔP (generally achieved

by keeping the cold bath temperature at 17.0 °C and changing the hot bath temperature) at least two experiments (duplicates) need to be completed before model fitting to the data. The permeate flux is expected to be a linear function of ΔP (Eq. 5.3) and to increase for higher flow rates until it approaches a plateau (Gryta, 2012).

In order to test the system and have reference values of the permeate interval flux, experiments were first performed with distilled water (DW) as both feed and receiving stream. The initial volumes were $V_{P,0} = 300$ mL (2018: 1 L HDPE bottle, 2021: 1 L ISO blue cap bottle) and $V_{R,0} = 1000$ mL (1 L graduated glass cylinder). In 2018, the permeate flux was calculated while testing in duplicates six hot bath temperatures (45.0, 55.0, 70.0, 78.0, 90.0 and 99.5 °C, with flow rates of 500 mL min⁻¹ and $T_{\text{COLD}} = 17.0$ °C) and six flow rates (100, 200, 300, 400, 500, 600 mL min⁻¹, with $T_{\text{HOT}} = 90.0$ °C and $T_{\text{COLD}} = 17.0$ °C). In 2021, the permeate flux was calculated while testing in triplicates five hot bath temperatures (55.0, 70.0, 80.0, 90.0 and 98.0 °C, with flow rates of 500 mL min⁻¹ and $T_{\text{COLD}} = 17.0$ °C) and seven flow rates (100, 200, 300, 400, 500, 600, 700 mL min⁻¹, with $T_{\text{HOT}} = 90.0$ °C and $T_{\text{COLD}} = 17.0$ °C). The main results of those experiments were organized in Fig. 5.3 and Fig. 5.4.

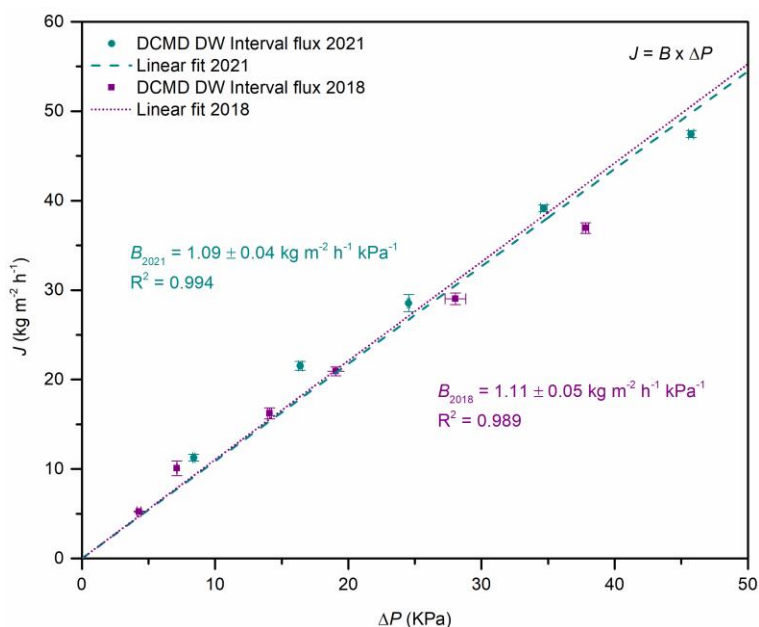


Fig. 5.3. Permeate interval flux as a function of the vapor pressure gradient, when using distilled water (DW) as both receiving and feed stream ($Q = 500$ mL min⁻¹).

As demonstrated by Fig. 5.3, the membrane permeability obtained when using 2018 or 2021 data is the same. This was expected since the PTFE commercial membrane used is the same. However,

the range of ΔP obtained for the two sets of experiments is discernibly different (2018: 4.3 - 37.8 kPa; 2021: 8.4 - 45.7 kPa), particularly considering the hot bath temperature settings used (2018: 45.0, 55.0, 70.0, 78.0, 90.0 and 99.5 °C; 2021: 55.0, 70.0, 80.0, 90.0 and 98.0 °C). After the updates to the system (described in 5.2.1), for the same hot bath temperature setting, the retentate reached higher temperatures and, therefore, contributed to a higher ΔP and consequently a higher permeate interval flux (Table 5.3). This improvement in the system operation can be explained by the combined effect of the improved heat exchange (particularly for the retentate) after the new arrangement of the heat exchangers, the reduction in the heat losses with the selection of a different material for the hot circulating bath tubing (which also contributed to the user safety), and the new tubing and cleaning of the system glass components.

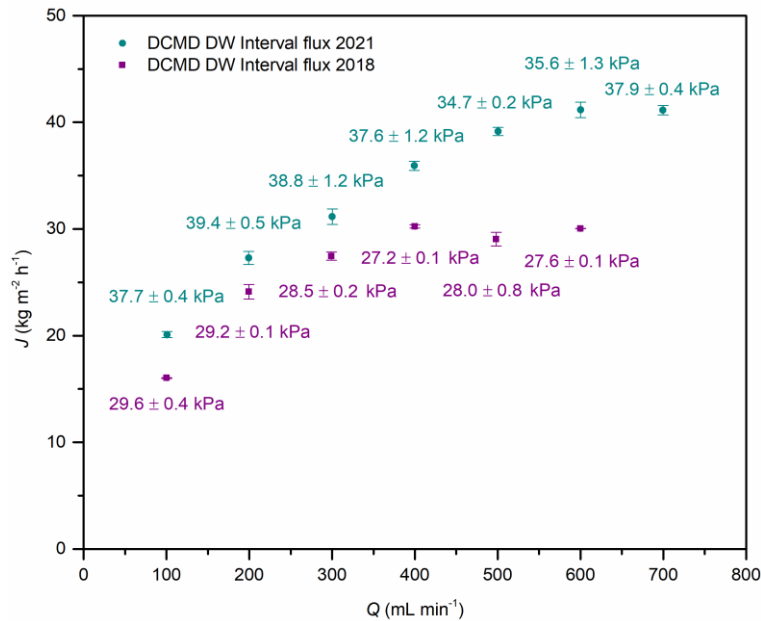


Fig. 5.4. Permeate interval flux as a function of the permeate and retentate flow rates in recirculation ($Q_P = Q_R$), when using distilled water (DW) as both receiving and feed stream ($T_{\text{COLD}} = 17$ °C; $T_{\text{HOT}} = 90$ °C).

Conversely, the relationship between the permeate interval flux and the pump's flow rates changed significantly from 2018 to 2021, as shown in Fig. 5.4 and Table 5.4. The higher ΔP achieved due to the update of the system is the main cause of this change. Additionally, since the update, the peristaltic pumps calibration curves changed as well, allowing to reach the same flow rate for a lower setting of rotations per minute, probably due to the reduction in the head losses achieved with the use of new tubing and cleaning of the heat exchangers.

Table 5.3. Operating parameters: Influence of the hot bath setting temperature (500 mL min⁻¹ and $T_{\text{COLD}} = 17.0$ °C).

Set of data	$T_{\text{hot bath}}$ (°C)	Average T (°C)				Stable ΔP (kPa)	Stable J (kg m ⁻² h ⁻¹)
		P_{in}	R_{in}	P_{out}	R_{out}		
2018	45.0	18.8	38.9	20.5	36.8	4.3 ± 0.1	5.2 ± 0.1
	55.0	19.5	46.4	22.0	43.6	7.1 ± 0.1	10.1 ± 0.8
	70.0	22.7	58.2	24.3	54.8	14.1 ± 0.2	16.2 ± 0.6
	78.0	21.4	64.4	25.8	59.9	19.1 ± 0.2	20.9 ± 0.5
	90.0	22.7	72.9	28.0	67.1	28.0 ± 0.8	29.0 ± 0.6
	99.5	24.0	80.2	30.4	73.1	37.8 ± 0.2	36.9 ± 0.6
2021	55.0	20.6	49.2	22.9	46.3	8.4 ± 0.1	11.3 ± 0.4
	70.0	22.4	61.6	26.0	57.3	16.4 ± 0.1	21.5 ± 0.5
	80.0	23.8	70.1	28.4	64.9	24.5 ± 0.1	28.6 ± 1.0
	90.0	25.1	78.2	31.0	71.7	34.7 ± 0.2	39.1 ± 0.4
	98.0	26.3	85.0	33.3	77.6	45.7 ± 0.2	47.4 ± 0.4

 Table 5.4. Operating parameters: Influence of the pump's flow rates setting ($T_{\text{HOT}} = 90.0$ °C and $T_{\text{COLD}} = 17.0$ °C).

Set of data	$Q_P = Q_R$ (mL min ⁻¹)	Average T (°C)				Stable ΔP (kPa)	Stable J (kg m ⁻² h ⁻¹)
		P_{in}	R_{in}	P_{out}	R_{out}		
2018	100	17.9	79.0	33.0	63.0	29.6 ± 0.4	16.0 ± 0.1
	200	19.8	76.2	30.5	65.4	29.2 ± 0.1	24.1 ± 0.7
	299	21.2	74.6	29.4	66.2	28.5 ± 0.2	27.4 ± 0.4
	400	22.3	72.9	29.1	66.1	27.2 ± 0.1	30.2 ± 0.2
	498	22.7	72.9	28.0	67.1	28.0 ± 0.8	29.0 ± 0.6
	600	23.0	72.4	27.7	67.1	27.6 ± 0.1	30.0 ± 0.1
2021	101	18.2	86.0	36.4	66.9	37.7 ± 0.4	20.1 ± 0.3
	199	20.1	84.1	32.7	70.8	39.4 ± 0.5	27.3 ± 0.6
	300	21.7	82.2	31.2	72.1	38.8 ± 1.2	31.1 ± 0.7
	399	23.1	80.8	31.0	72.3	37.6 ± 1.2	35.9 ± 0.4
	500	25.1	78.2	31.0	71.7	34.7 ± 0.2	39.1 ± 0.4
	600	24.8	78.8	30.7	72.2	35.6 ± 1.3	41.2 ± 0.7
	700	25.3	80.0	30.2	73.7	37.9 ± 0.4	41.1 ± 0.4

These first experiments were used to establish the operating parameters for the experiments that followed. In 2021, the hot bath temperature was set to 90 °C, since it allows a good permeate flux while ensuring the safety of the user and equipment, and a reduction of the energy consumption compared to higher temperature settings. Previously, in 2018, it was set to 99.5 °C, but it was too close to the boiling point of water and, therefore, it was necessary to add more water during long duration experiments due to evaporation. Although the update granted better results when increasing the pumps flow rates from 500 mL min⁻¹ to 600 mL min⁻¹, it was decided to keep the 2018 setting of 500 mL min⁻¹ to protect the equipment, reduce the energy consumption and conduct all experiments under the same pumps flow rates setting.

5.2.4 Long duration experiments in 2018 and lessons learned

In 2018, after studying the DCMD system operating parameters (5.2.3), three long duration experiments were conducted with the system: i) SW50 - 50 h experiment with unfiltered seawater (SW) as feed water, ii) SW24 - 24 h experiment with SW, and iii) PW24 - 24 h experiment with purified water (PW). For these experiments, the initial volume of the receiving stream was PW instead of DW. The SW was collected as described in Section 5.3.3, but it was not filtered, and the water sampling in Leça da Palmeira beach was performed on the same day as each DCMD experiment began. Due to the limitations encountered during these experiments, it was found necessary to update the system, as described in Section 5.2.1. A summary of experimental conditions of the tests conducted is listed in Table 5.5. A summary of the main results is listed in Table 5.6, Table 5.7 and Table 5.8.

Table 5.5. DCMD experimental conditions and tests of the 2018 long duration experiments.

Experimental conditions and tests	SW50	SW24	PW24
Time (h)	50	24	24
$Q_P = Q_R$ (mL min ⁻¹)	500	500	500
T cold bath (°C)	17.0	17.0	17.0
T hot bath (°C)	99.5	99.5	99.5
Feed water	25 L SW (25 L HDPE jerrycan)	25 L SW (25 L HDPE jerrycan)	25 L PW (25 L HDPE jerrycan)
Receiving stream	1.3 L PW (1 L or 2 L HDPE bottles during data collection + 25 L HDPE jerrycan for the night and storage)	1.3 L sterilized PW (10 L ISO blue cap bottle)	1.3 L PW (10 L ISO blue cap bottle)
Permeate flux study	yes	no	no
Microbiologic study	no	yes	no
OMPs quantification	no	yes	yes

The SW50 experiment was conducted with the goal to i) determine the stable ΔP and stable permeate interval flux when using SW as feed water, and ii) determine an adequate experimental time, during which there was no flux decline due to membrane fouling.

As depicted in Fig. 5.5, when using 25 L of SW as feed water, the system takes ca. 5 h to achieve the stable ΔP . A stable ΔP of 28.5 ± 0.4 kPa is maintained for the duration of the second day of data collection (16 - 29 h), during which an average permeate interval flux of 30.1 ± 0.4 kg m⁻² h⁻¹ is conserved. However, during the second night, membrane fouling reaches a point that leads to the flux decline: to 24.3 kg m⁻² h⁻¹ (flux decline = 19%) at $t = 40$ h, and 11.9 kg m⁻² h⁻¹ at $t = 50$ h (flux decline = 61%).

After the second night, an increase in the ΔP from 26.6 ± 0.2 kPa ($t = 40$ -41 h) to 31.0 ± 0.1 kPa ($t = 49$ -50 h) is observed (Fig. 5.5). This was caused in part due to the increase of the retentate temperature in the container (from 59.3 ± 0.4 °C during the second day to 62.7 °C at $t = 50$ h) since there is less volume in recirculation, and by the decrease of the permeate temperature after exchanging for the 25 L container for the night. Additionally, there was probably a drop in the room temperature (there was no significant variation of the recirculating baths temperatures) during the second night which contributed to lower the permeate and retentate temperatures (retentate temperature in the container of 58.4 °C at $t = 40$ h).

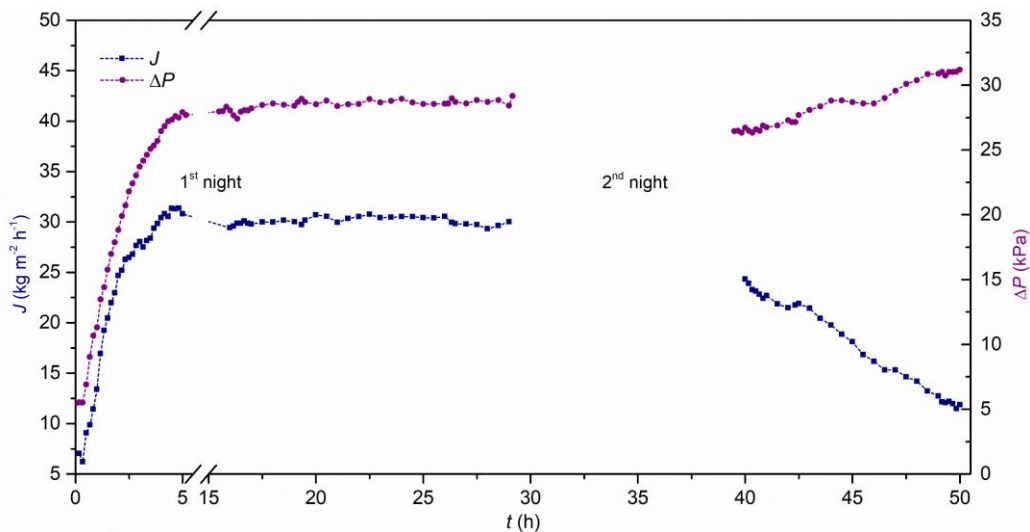


Fig. 5.5. Vapor pressure gradient and permeate interval flux through time for the SW 50 h experiment conducted in 2018.

Table 5.6. 2018 DCMD experiments: average (after 5 h) temperatures at the LH-cell.

Experiment	Average T (°C)			
	P_{in}	R_{in}	P_{out}	R_{out}
SW50 (50 h)	23.1 ± 0.1	73.3 ± 0.2	28.9 ± 0.4	67.8 ± 0.2
SW50 (first 24 h)	23.1 ± 0.1	73.2 ± 0.3	29.0 ± 0.3	67.7 ± 0.3
SW24 (5 - 9.5 h)	22.9 ± 0.2	70.6 ± 0.3	28.3 ± 0.3	65.1 ± 0.3
PW24 (18 - 24 h)	22.6 ± 0.1	72.8 ± 0.4	27.9 ± 0.2	67.3 ± 0.4

Table 5.7. 2018 DCMD experiments: average (after 5 h) vapor pressure gradient, permeate interval flux and membrane permeability, and flux decline and water recovery at the end of the experiment.

Experiment	Stable ΔP (kPa)	Stable J ($\text{kg m}^{-2} \text{h}^{-1}$)	Stable B (kg $\text{m}^{-2} \text{h}^{-1} \text{kPa}^{-1}$)	Flux decline (%)	Water recovery (%)
SW50 (50 h)	28.5 ± 0.4	30.1 ± 0.4	1.06 ± 0.02	61	39
SW50 (first 24 h)	28.4 ± 0.4	30.1 ± 0.4	1.06 ± 0.01	0	20
SW24	25.0 ± 0.4	-	-	-	18
PW24	28.0 ± 0.5	-	-	-	19

Table 5.8. 2018 DCMD experiments: Compensated conductivity and salinity at the beginning and end of the experiment, and salt rejection at the end of the experiment.

Experiment	EC_{25} (P: $\mu\text{S cm}^{-1}$; R: mS cm^{-1})				Salinity (ppt)				Salt rejection (%)
	P_i	P_f^{**}	R_i	R_f	P_i	P_f	R_i	R_f	
SW50 (50 h)	2.1	0.0	49.5	81.5	0.0	0.0	32.4	54.8	100
SW50 (first 24 h)	2.1	0.0	49.5	64.8	0.0	0.0	32.4	42.3	100
SW24	3.3	0.8	52.8	64.3	0.0	0.0	34.8	41.9	100
PW24	2.3	0.0	8.5*	12.6*	-	-	-	-	-

* For the PW24 experiment, since the feed water is purified water, the conductivity units are $\mu\text{S cm}^{-1}$.

** Reading of the water conductivity of the last permeate bottle produced and not of all volume produced.

Even though membrane fouling (as evident in Fig. 5.6a) and flux decline (Fig. 5.5) occurred during this experiment, the salt rejection was kept at 100%, with no signs of contamination of the permeate water quality, as assessed by the measurement of the conductivity and salinity (Table 5.8).

The permeability with SW at stable ΔP was estimated to be $1.06 \pm 0.02 \text{ kg m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ (Table 5.7), being similar to the one determined with distilled water in Section 5.2.3 ($1.11 \pm 0.05 \text{ kg m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$). Due to membrane fouling, the permeability decreased during the SW50 experiment to $0.91 \text{ kg m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ at $t = 40 \text{ h}$ and to $0.38 \text{ kg m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ at $t = 50 \text{ h}$. Comparing the SW50 stable ΔP obtained ($28.5 \pm 0.4 \text{ kPa}$) with the one in the previous section with DW for the same operation conditions ($\Delta P = 37.8 \pm 0.2 \text{ kPa}$, $J = 36.9 \pm 0.6 \text{ kg m}^{-2} \text{ h}^{-1}$), it shows the high impact of increasing the volume of the feed water from 1 L to 25 L in the operation of the system. A larger volume is more challenging to heat (because more energy is needed) and to minimize the heat losses (due to the necessity to use a bigger retentate container), leading to a lower stable ΔP . While the permeate interval flux (Table 5.7) was expected to be lower for the SW50 experiment because of the smaller ΔP , it was higher than anticipated, particularly considering that a smaller membrane permeability is likely to occur with seawater, due to e.g., suspended solids, when compared to distilled water.

Based on the SW50 experiment results, it was deemed sufficient to conduct the next experiments for only 24 h, maintaining all the other experimental conditions. The SW24 experiment was performed with the goal of assessing the efficiency of the DCMD system to remove organic micropollutants (OMPs) and microorganisms from the seawater. During this second experiment, the hot circulating bath malfunctioned at some point during the night period of the experiment (9.5 - 20.5 h; results not shown). Because of this, the retentate temperature decreased ca. 11°C at the cell inlet and was only back to normal (Table 5.6) at $t = 22.5 \text{ h}$, leading to a lower water recovery than expected (Table 5.7) because of the decrease of the ΔP to 14.8 kPa . Nevertheless, admitting the same membrane permeabilities as the previous experiment, the stable ΔP obtained for the experiment period of 5 to 9.5 h ($25.0 \pm 0.4 \text{ kPa}$) is probably undervalued since the water recovery estimated from it would be 17% at $t = 24 \text{ h}$ ($26.5 \text{ kg m}^{-2} \text{ h}^{-1}$ at stable conditions) without considering the hot bath malfunction or flux decline due to fouling. This result is below expected considering the SW50 results and the measured permeate volume at $t = 24 \text{ h}$ (Table 5.7). Despite the identified problems, the permeate water quality was as expected when assessed with the DCMD instruments (Table 5.8). Membrane fouling occurred as observed in Fig. 5.6b, although the results do not suggest that, as consequence, the flux declined.

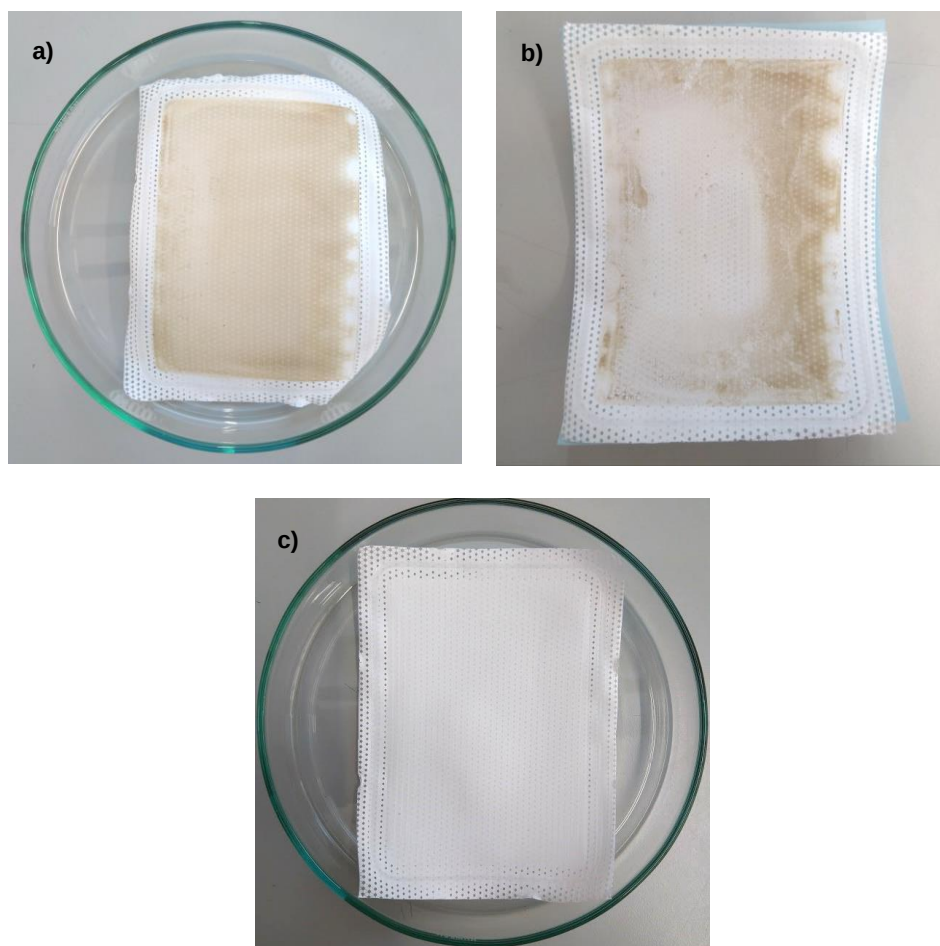


Fig. 5.6. PTFE membranes (retentate side) used at the end of the experiments:
a) SW50, b) SW24, and c) PW24.

The PW24 experiment was conducted with the goal to test the DCMD system contamination with organic micropollutants (OMPs). Similarly to the previous experiment, the hot circulating bath malfunctioned during the night period of the experiment (6 - 17 h; results not shown), affecting the retentate temperature and, consequently, the ΔP and the water recovery. An average ΔP of 28.0 ± 0.5 kPa was obtained for the 18 - 24 h period. The water recovery estimated from it results in 20% at $t = 24$ h, when admitting the same membrane permeabilities of the DW 2018 operating parameters study ($1.11 \text{ kg m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) for the period of 5 - 24 h ($31.1 \text{ kg m}^{-2} \text{ h}^{-1}$ at stable conditions) and of the SW50 for the beginning of the experiment (until $t = 5$ h), and without considering the hot bath malfunction. Therefore, the average ΔP calculated is probably close to the stable ΔP expected for this experiment, considering the decreased permeate flux during the

hot circulating bath malfunction. Moreover, as also expected, no sign of membrane fouling was observed (Fig. 5.6c).

Regarding the microbiologic study done with the SW24 experiment, it was concluded that the DCMD system was very difficult to keep in the necessary sterile conditions to correctly analyze the microbiologic contamination of the distilled water produced from the seawater, because there are several components that could not be sterilized. This study was performed using the membrane filtration technique to isolate and enumerate the colonies of microorganisms, with the analysis of the total microbial content (total heterotrophic colony count at 22 °C and 37 °C), enterococci, and *Escherichia coli* (microbiologic quality standards for drinking water set by Directive 98/83/EC) (The Council of the European Union, 1998). This analysis followed the recommendations of the WHO guidelines for detection and enumeration of faecal indicator organisms in water intended for human consumption (World Health Organization, 2017) and the methods for microbiological parameters listed in EU Directive 2015/1787 (European Commission, 2015c) in effect at the time of the experiment. The following samples were analyzed: i) at $t = 0$ h: SW, sterilized PW (negative control); ii) at $t = 24$ h: SW (positive control), retentate, sterilized PW (negative control 2), permeate; iii) at $t = 24$ h + 3 days (regrowth): sterilized PW (negative control 3), and permeate. *Escherichia coli* colonies were only detected (CFU/100 mL > 0) in the SW-0h and SW-24h samples, while enterococci colonies were only detected in the SW-0h sample. Therefore, the treated water obtained is in conformity with the EU legal recommendations for drinking water regarding enterococci and *Escherichia coli* parameters. On another hand, total heterotrophic colonies (both at 22 °C and 37 °C) were detected in the following samples: SW-0h, SW-24h, retentate-24h, permeate-24h and permeate-regrowth. The number of total heterotrophic colonies in the permeate (24 h and regrowth) was much higher than the count in the SW and retentate samples. It should be noted that the retentate high temperature and salinity create harsher conditions for bacterial development, which could explain why it had a lower total colony count when compared to the seawater at $t = 0$ h and to the permeate at $t = 24$ h. The contamination of the permeate samples could have occurred due to lack of impermeability of the membrane for some microorganisms or due to contamination of the DCMD system. In both cases, it is recommended that a disinfection step is taken after or integrated with the DCMD treatment.

Regarding the OMPs quantification, the SW24 and PW24 experiments allowed to conclude that the DCMD system was contaminated with some organic pollutants that were used before in other studies (T. L. S. Silva et al., 2018; Vinoth Kumar et al., 2020) that also used the same system. The quantification was performed by pre-concentration of the sample by solid-phase extraction (SPE) using Waters Oasis HLB cartridges, followed by ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS). The methods used were previously developed at the LSRE-LCM laboratories and allowed to analyze 32 substances

(including pesticides, pharmaceutical substances, and PFOS), and 10 deuterated substances as internal standards. The only substance studied that was quantified and for which there was no indication of being a system or analysis contamination was perfluorooctane sulfonate (PFOS), with $11.5 \pm 0.8 \text{ ng L}^{-1}$ in the SW24 seawater at $t = 0 \text{ h}$ and $22.1 \pm 1.5 \text{ ng L}^{-1}$ at $t = 24 \text{ h}$ in the SW24 retentate (method quantification limit of 1.89 ng L^{-1}). PFOS was below the method detection limit (0.62 ng L^{-1}) for SW24 permeate at $t = 24 \text{ h}$ and for all PW24 samples: PW, permeate at $t = 24 \text{ h}$ and retentate at $t = 24 \text{ h}$. These results suggest a very high membrane efficiency to remove this substance under the conditions tested. Considering that the DCMD system has several components made of plastic, particularly the tubing, and that the substances under study could accumulate in the system between treatments, no further studies were performed to investigate the efficiency of the DCMD system to remove OMPs during the present PhD studies. Nevertheless, this was one of the reasons why all the tubing of the DCMD system was replaced after these 3 experiments, as previously described in Section 5.2.1.

The 2018 DCMD experiments were decisive in understanding the system limitations and in identifying the necessary upgrades and repairs. After updating and testing the system as described in Sections 5.2.1 and 5.2.3, and in sequence of the two previous chapters, the 2022 experiments with the DCMD system focused on studying the behavior and attenuation of MPPs in the system.

5.3 Material and methods

5.3.1 Microplastic particles (MPPs)

Virgin MPPs of LDPE (average particle diameter of $509 \pm 221 \text{ }\mu\text{m}$), PET ($161 \pm 79 \text{ }\mu\text{m}$) and uPVC ($159 \pm 43 \text{ }\mu\text{m}$) were purchased in powder form from Goodfellow (UK) at the beginning of this PhD work. The main characteristics of these MPPs, regarding the physical and chemical properties and interaction with certain organic substances, are described in the two previous chapters (Sections 3.2.1, 3.3 and 4.3.1).

5.3.2 Organic micropollutants (OMPs)

The same OMPs selected for the study presented in the previous chapter were used again here: alachlor, citalopram, clofibric acid, diclofenac, diuron, florfenicol, pentachlorophenol (PCP), tramadol, trimethoprim, and venlafaxine. More details on these organic substances can be found in Section 4.2.2.

5.3.3 Seawater (SW)

Seawater samples were collected at *Leça da Palmeira* beach, in Matosinhos, north of Portugal (Fig. 5.7). The sampling site was selected since former studies with the DCMD unit at LSRE-LCM laboratories used seawater collected there for desalination studies (T. L. S. Silva et al., 2018). While ideally the seawater should be collected in the sea and not at the beach (a desalination plant seawater intake can be at distances of a couple hundred meters to a few kilometers from the coastline and usually below the sea surface), the available sampling equipment led to that adjustment. To ensure sample collection reproducibility, the APA/SNIRH bathing water monitorization station PTCK3P - *Leça da Palmeira* (EPSG:3857 coordinates: 41.190833, - 8.706944) was selected (APA, 2022a). This water monitorization station is periodically used to collect water samples to analyze microbiological parameters (total and fecal coliforms, enterococci, *Escherichia coli*, salmonella, and *Streptococcus*), phenolic compounds, surfactants, turbidity, pH, and oil and grease (APA, 2022b).

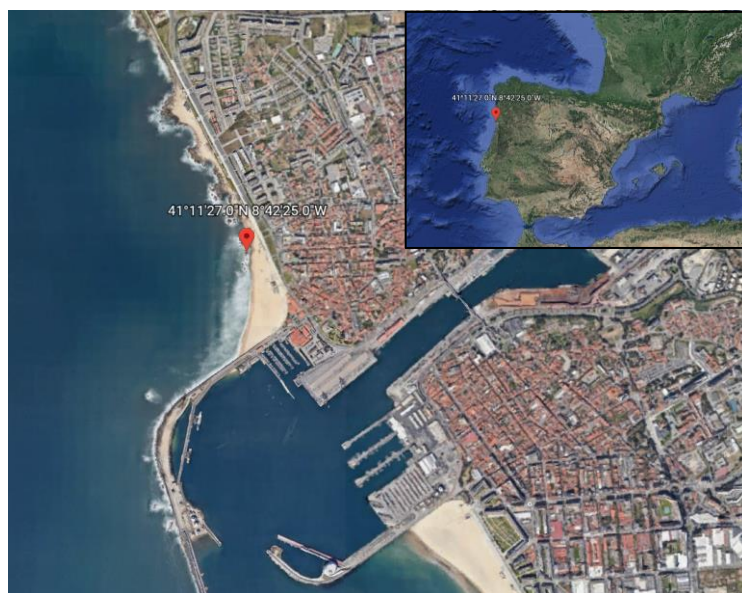


Fig. 5.7. Seawater sampling location (*Leça da Palmeira* beach, Matosinhos, Portugal).

Source: Google Earth – 25/10/2018 picture.

Leça da Palmeira beach (Fig. 5.8) is characterized as an Atlantic Ocean urban beach with an extensive sand strip and rocky clusters. The potential sources of contamination at the beach include two water courses (Sardoal stream and *Leça* river), a wastewater treatment plant (WWTP), Leixões harbor (fishing and cargo and passenger ships docking) and other anthropogenic

activities. Therefore, the risk of short-term (for less than 72 h) pollution episodes occurrence is low but may occur due to excessive surface flow of the tributaries during rainfall situations (leads to entrainment of the microbiological load), untreated clandestine discharges in the rainwater drainage system, sewer network overload or operation problems with the WWTP, or nearby vessels. The APA assessment of the potentially pathogenic organisms' proliferation risk indicated that the risk is moderated for macroalgae (with historical occurrence of blooms, that resulted in carpets of brown or green algae in water and/or sand) and low (there is no record of previous occurrences) for cyanobacteria and phytoplankton (APA, 2022a).



Fig. 5.8. Photograph taken on the 18th of October 2022 sampling.

US-EPA “dipping using sample container” method of surface water sampling was selected to collect the seawater samples. This method involves collecting the sample directly into the container, without disturbing the bottom sediment (US-EPA, 2021). Bottles with a capacity of 5 L were employed for this procedure. Each open bottle was plunged straight down to a depth of 15 to 30 cm below the water surface, moved horizontally to the surface while tipped slightly to let trapped air escape, and removed in a vertical position. Approximately 2.5 cm of headspace was left in each sample container.

The seawater samples collected were preserved in cold (-18 °C) until two days before treatment in the DCMD system. Then, the samples were vacuum filtered through 47 mm glass microfiber filters (pore size 1.2 µm, purchased from VWR) to remove suspended particles (including microplastics). The pH of the seawater was analyzed before (SW) and after filtration (FSW) using a Consort (Belgium) C6010 instrument: $\text{pH}_{\text{SW}} = 8.27$ and $\text{pH}_{\text{FSW}} = 8.11$ (for the samples used for the DCMD experiments).

5.3.4 Temperature stress (TS) batch experiments (in amber bottles)

Two sets of experiments were performed to mimic the possible plastic aging by temperature when MPPs are in suspension in the retentate during a DCMD treatment, using: i) Milli-Q ultrapure water (TS-UPW); and ii) filtered seawater (TS-FSW).

For that, 2 g of virgin MPPs of LDPE, PET or uPVC and 600 mL of ultrapure water (UPW) or filtered seawater (FSW) were added to each 1 L amber bottle, closed with aluminum foil instead of the plastic cap, thus resulting in six different experiments: LDPE/PET/uPVC TS-UPW and LDPE/PET/uPVC TS-FSW. The bottles were placed inside a paraffin bath for 24 h, which was heated continuously for the duration of the experiment to keep the ultrapure water or seawater at ca. 80 °C. The contents of the bottles and the paraffin baths were continuously stirred (850 rpm) with magnetic stirring bars with polytetrafluoroethylene (PTFE) encasement.

After 24 h, the bottles were removed from the paraffin bath and were let to cool down at room temperature. Finally, the contents of the bottles were vacuum filtered through 47 mm glass microfiber filters (pore size 1.2 µm, purchased from VWR) to separate the MPPs from the liquid phase. For that, Normax (Portugal) glass filtration kits, 1000 mL Kitasato glass flasks (LINEX, Portugal), and a VCP 80 vacuum pump (VWR) were used. The filters with the MPPs collected were stored inside soda-lime glass Petri dishes and dried in a desiccator in the dark.

In addition, another experiment (TS-OMP) was performed to test the stability of the 10 OMPs under the temperatures achieved during a treatment in the DCMD system. For that, the same procedure was followed but without using MPPs, and with a solution with the 10 OMPs (with 100 µg L⁻¹ of each OMP) instead of ultrapure water or seawater. The solution (with 2% V/V methanol) was prepared by dilution in Milli-Q ultrapure water of a MIX10 working solution, following the same procedure described in Sections 4.2.2 and 4.2.3. After cooling down, triplicate samples of the solution were stored in HPLC vials at -18 °C.

The pH of the ultrapure water, filtered seawater or OMP solution was analyzed at $t = 0$ h (before adding the MPPs) and $t = 24$ h (after filtration or after cooling down in the case of the OMP solution) using a Consort (Belgium) C6010 instrument (Table 5.9).

Table 5.9. Temperature stress batch experiments (amber bottles).

Solution	Polymer	T (°C)	pH $t = 0$ h	pH $t = 24$ h
Ultrapure water (UPW)	LDPE	80.4	6.91	6.49
	PET	80.1		6.89
	uPVC	81.7		7.04
Filtered seawater (FSW)	LDPE	79.8	7.90	8.39
	PET	78.4		8.43
	uPVC	78.3		8.21
10 OMPs	-	79.0	5.76	7.11

5.3.5 Direct contact membrane distillation (DCMD) experiments

In order to study the behavior of MPPs in the DCMD system and test the efficiency of the treatment in their removal, five experiments were conducted:

1. **MD-PW-C** - Control experiment with purified water (PW) as feed and distilled water (DW) as receiving stream, without MPPs, during 24 h;
2. **MD-FSW-C** - Control experiment with filtered seawater (FSW) as feed, without MPPs during 8 h;
3. **MD-FSW-TS** - 8h experiment with FSW spiked with 0.1 g L^{-1} of TS-FSW-aged uPVC (obtained as described in Section 5.3.4 by aging uPVC at a given temperature in FSW);
4. **MD-FSW-V** - 8 h experiment with FSW spiked with 0.2 g L^{-1} of virgin uPVC;
5. **MD-FSW-R** - 8 h experiment with FSW spiked with 0.1 g L^{-1} of uPVC recovered (R) from the previous experiment (i.e., MD-FSW-V-aged uPVC).

For this, the updated DCMD system, detailed in Section 5.2.1, was used (Fig. 5.9). As reservoirs, two 1 L ISO blue cap bottles were used with the precision balance to recover and measure the permeate, and one 10 L ISO blue cap bottle was used for the retentate. Since the precision balance maximum weight is 2 kg, the two 1 L bottles were necessary, changing the bottle (without stopping the system) when the bottle in use started to reach its volume limit. After exchanging the permeate container, the permeate produced was stored in a 5 L ISO blue cap bottle, leaving ca. 0.3 L inside the 1 L bottle for the next bottle exchange. Additionally, the same 5 L ISO blue cap bottle was used for the MD-PW-C experiment during the night period.

The initial volumes of permeate in each bottle were 300 mL of distilled water (DW), while a volume of 10000 mL of PW or FSW was used as feed water. The PW was obtained by reverse osmosis of tap water using a Panice (Italy) system with 5 stages of filtration: prefiltration with two sediment filters (5 μ and 1 μ) and one activated carbon filter, 50 gpd reverse osmosis membrane, and one activated carbon postfilter. All the FSW used for these experiments was collected on the same day (18th October 2022). Aluminum foil was used to close the bottles instead of the cap, except for the uncapped permeate bottle being used with the precision balance. For each experiment, a new PTFE membrane was cut and installed in the LH-cell.

As explained in Section 5.2.3, the operating parameters were set to the following values:

- Hot bath temperature: 90 °C (making the retentate being at ca. 80 °C at the LH-cell inlet);
- Cold bath temperature: 17 °C (making the permeate being at ca. 25 °C at the LH-cell inlet);
- Peristaltic pumps flow rates: 500 mL min⁻¹.

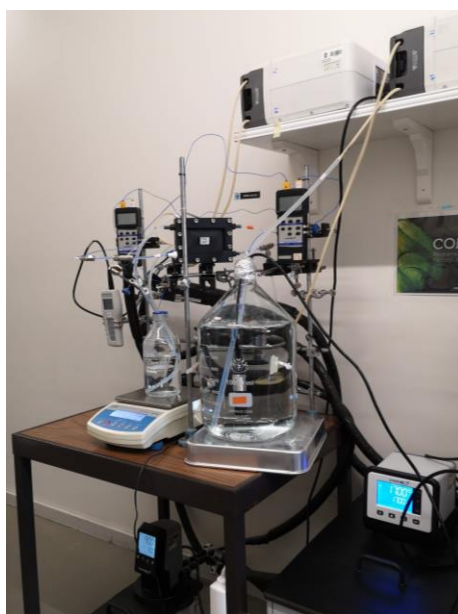


Fig. 5.9. Updated DCMD system (2022) dedicated to seawater treatment.

All the experiments followed the same main procedure, with the load of MPPs (0.0, 0.1 or 0.2 g L⁻¹ of uPVC), sample type of uPVC (virgin, TS-FSW-aged or MD-FSW-V-aged), and feed stream (PW or FSW) being the parameters under study. The experiment time (8 h for FSW or 24 h for PW) was selected by considering the feed initial volume (10 L) and that it was not desirable to reach a salinity concentration in the retentate that would increase the membrane fouling rate and lead to flux decline.

Before each experiment, the permeate and retentate tubing was cleaned by recirculating distilled water in the system without the LH-cell installed. At the beginning of each experiment ($t = 0$ h), the recirculating temperature baths were at the desired temperature setting and the timer was set when the precision balance reading stabilized or started to increase (permeate-bottle mass at $t = 0$ h), after starting the two peristaltic pumps simultaneously (ca. 0.1 L of DW fill the permeate tubing). During each experiment, the permeate-bottle mass, baths temperatures, cell temperatures, conductivity, and salinity were registered at exactly every 10 min, or 30 min if the permeate interval flux was constant over time.

At the end of each experiment, the peristaltic pumps were immediately reversed after recording the last data point in order to collect the permeate and retentate in the tubing. After removing the permeate and retentate containers and LH-cell, the system was cleaned with: 1) distilled water; 2) solution of hydrogen peroxide to avoid biofilm formation inside the tubing; and 3) distilled water until low conductivity is achieved. The membranes were stored in soda-lime Petri dishes and the LH-cell was cleaned with water and compressed air.

For the experiments with MPPs (MD-FSW-TS, MD-FSW-V, and MD-FSW-R), both the retentate and permeate were vacuum filtered through two 47 mm glass microfiber filters (pore size 1.2 μm , purchased from VWR), following the same procedure as in Section 5.3.4. The retentate was filtered with the goal of collecting the MPPs to characterize them and identify potential modifications. The first 1 L of distilled water used to clean the retentate tubing was filtered as well with the same filter, and the MPPs were washed with distilled water to remove most of the seawater salts. The permeate was filtered to enable the analysis of the presence of MPPs in the treated water. The retentate and permeate filters were weighted before filtration and after drying in the desiccator. The volume of filtered permeate was measured using 1 L graduated glass cylinder to compare with and validate the permeate flux calculations.

5.3.6 Characterization of MPP samples and Raman microscopy analyses

The MPPs samples were characterized before and after the batch experiments used to simulate aging by temperature (Section 5.3.4), and before and after the DCMD experiments (Section 5.3.5).

Considering the relevant data provided by Fourier transform infrared (FTIR) spectroscopy with an Attenuated Total Reflection (ATR) sampling technique in Chapter 3, this technique was selected again for the work presented in this chapter. More detailed information on the ATR-FTIR spectroscopy analysis can be found in Section 3.2.4.1. In addition to the analysis of the MPPs samples with this technique, FSW salts were also analyzed. For that, FSW was left in the laboratory oven at 80 °C until all the water evaporated and the salt crystallized.

Since uPVC MPPs changed coloration, the optical absorbance of uPVC samples was measured by UV-Visible spectroscopy using a JASCO V-560 spectrophotometer (JASCO, Japan). The baseline correction was performed with barium sulfate (Sigma-Aldrich, CAS: 7727-43-7, purity 98%). Each measurement was performed with a 0.5 nm resolution of the 200-800 nm region.

Scanning Electron Microscopy (SEM) analyses were performed for some uPVC MPPs samples (i.e., virgin, MD-FSW-TS-aged and MD-FSW-R-aged) using the same methodology as described in Section 3.2.4.3.

The 47 mm glass microfiber filters (pore size 1.2 μm , purchased from VWR), used to vacuum filtrate the permeate after the MPPs experiments with the DCMD system, were analyzed for the presence of MPPs. No pre-treatment step (density separation or digestion) of the water samples was performed since low levels of particles or organic matter were anticipated for the treated water. Raman microscopy (μRaman) measurements were made using a WITec alpha300 R confocal Raman microscope (WITec, Germany) that uses a WITec UHTS 300 VIS spectrometer (600 lines/mm grating) coupled with a FI CCD detector (spectral resolution of 0.8 $\text{cm}^{-1}/\text{pixel}$, 1650x200 pixels, -60 $^{\circ}\text{C}$). Two randomly selected areas per filter (one at the center and the other at the edge of the filter) were selected at a magnification of 50x. Then, the spectra were recorded using 10 mW of laser power and the 532 nm excitation wavelength, with 5 accumulations and an integration time of 1 s per spectrum. An aliquot of virgin uPVC and one unused filter were analyzed to add those spectra to the system library as reference. The data processing was achieved with the Project FIVE and WITec ParticleScout software.

5.3.7 Organic micropollutants quantification

The concentration in solution of the OMPs was determined by an ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) analytical method, as previously described in Section 4.2.5.

5.3.8 Data analysis

Whenever possible, the average and respective standard deviation were calculated for the experimental data, as was the case for the OMPs concentrations in solution during the TS-OMP experiment. The DCMD data analysis was conducted as previously described in Section 5.2.2, with Microsoft Excel being used to obtain those calculations. The graphical representation of the results was performed with the OriginPro 9 software.

5.4 Results and Discussion

The temperature stress (TS) batch experiments with MPPs in amber bottles, carried out before the DCMD experiments, allowed to study the individual effect of exposing the MPPs to a temperature stress when in suspension in water, with thermal degradation and hydrolysis being the main mechanisms at play. Based on the results of those experiments with three polymers, uPVC was selected to study the behavior of MPPs in a lab-scale DCMD system.

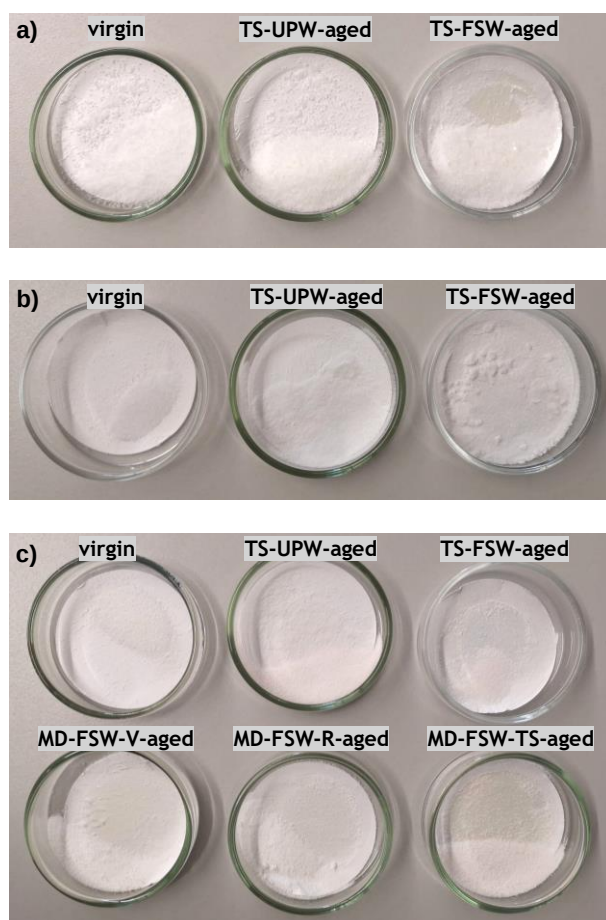


Fig. 5.10. Photographs of the MPPs of a) LDPE, b) PET, and c) uPVC, after the TS and/or DCMD experiments.

5.4.1 LDPE and PET under temperature stress (in amber bottles)

Very fast fouling of the membranes was observed during the vacuum-filtration of the LDPE samples, particularly for the LDPE MPPs aged at ca. 80 °C in filtered seawater (TS-FSW-aged samples). A film was deposited on the filter (Fig. 5.10a), consisting mainly of seawater salts (primarily NaCl) and LDPE, according to the ATR-FTIR analysis for the TS-FSW-aged sample (Fig. 5.11), which might be the cause for the filter fouling. For the LDPE MPPs aged at ca. 80 °C in ultrapure water (TS-UPW-aged samples), a change in the electric conductivity of the water sample was detected, increasing from 5.31 $\mu\text{S cm}^{-1}$ to 12.84 $\mu\text{S cm}^{-1}$, which was a higher increase than what was observed for PET (7.98 $\mu\text{S cm}^{-1}$) and uPVC (6.94 $\mu\text{S cm}^{-1}$). The combination of these two results can be evidence of the release of substances from LDPE MPPs to the water due to the degradation of the polymer.

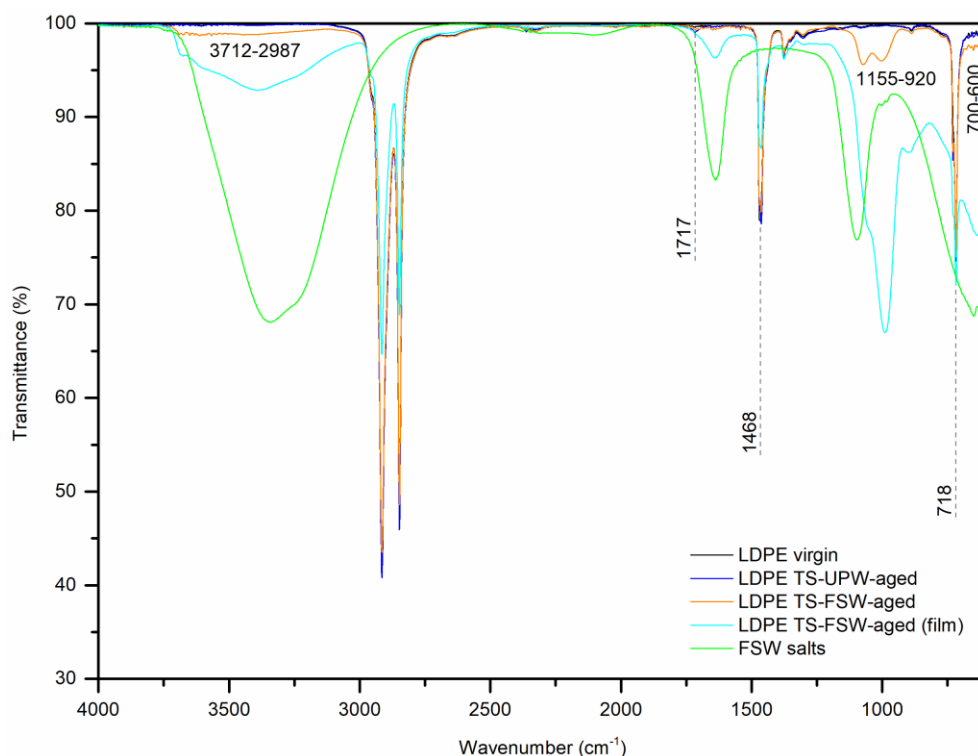


Fig. 5.11. ATR-FTIR spectra for low-density polyethylene (LDPE) before and after the temperature stress (TS) batch experiments and for the FSW salts.

The ATR-FTIR spectra of the LDPE samples (Fig. 5.11) show very few modifications of the LDPE chemical structure, with most of the new absorption bands resulting from interference of the FSW salts. Indeed, the LDPE TS-UPW-aged sample only has some minor modifications with a very

small increase of the C=O absorption at 1717 cm^{-1} (carbonyl species), and distortion of the LDPE medium intensity characteristic absorption peaks at 1468 cm^{-1} (CH_2 bending deformation) and at 718 cm^{-1} (CH_2 rocking deformation). The LDPE TS-FSW-aged sample has the same modifications identified for the LDPE TS-UPW-aged sample, with the additional increase of the absorption intensity at the bands $3712\text{--}2987\text{ cm}^{-1}$, $1155\text{--}920\text{ cm}^{-1}$, and $700\text{--}600\text{ cm}^{-1}$, which can be related to the presence of FSW salts.

From visual observation of the PET samples, no signs of polymer degradation were identified, although salt crystals were observed mixed with the PET MPPs on the TS-FSW-aged sample (Fig. 5.10b). The ATR-FTIR analysis (Fig. 5.12) did not allow to identify any modification in the chemical structure of the polymer for the TS-UPW-aged sample. For the TS-FSW-aged sample, there was an increase in the absorption intensity at $3761\text{--}2980\text{ cm}^{-1}$ band, the band near 972 cm^{-1} (O- CH_2 stretching of ethylene glycol segment in PET) (Donelli et al., 2010; Holland and Hay, 2002) and the $700\text{--}600\text{ cm}^{-1}$ band. While these can be interferences from the FSW salts, the band near 972 cm^{-1} has been used before by Cobbs and Burton (1953) to follow the crystallization of PET on heating, since it is one of the crystallinity-sensitive bands of that polymer (Bahl et al., 1974).

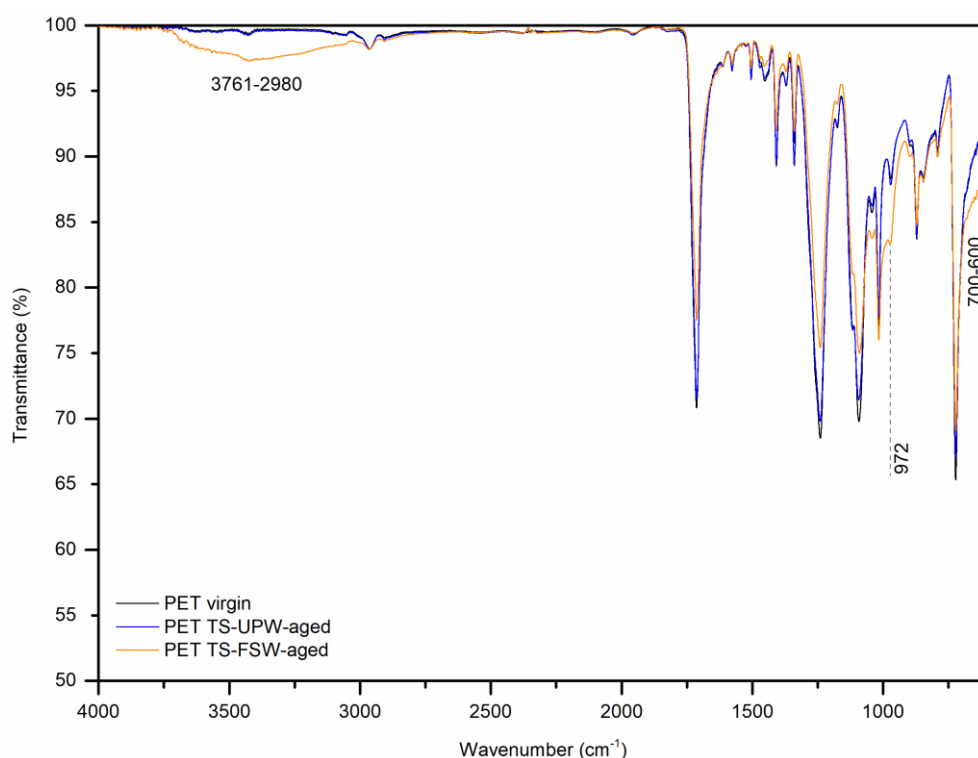


Fig. 5.12. ATR-FTIR spectra for poly(ethylene) terephthalate (PET) before and after the temperature stress (TS) batch experiments.

5.4.2 uPVC under temperature stress (in amber bottles) and behavior in a lab-scale DCMD system

Visual observation of the uPVC samples revealed that after the temperature stress batch experiments, both the TS-UPW-aged and TS-FSW-aged samples acquired a pinkish coloration (Fig. 5.10c). This change in coloration was analyzed in more detail by UV-Visible spectroscopy. The results (Fig. 5.13) of the two aged samples show increased absorption for visible wavelengths (380-750 nm), with maximum absorption at 443 nm. The lower absorption of these samples in the red region (620-750 nm) of the visible spectrum results in a higher emission in that wavelength, giving the samples their pinkish coloration. These results are in agreement with what was previously observed by De Campos and Martins Franchetti (2005) after thermally treating PVC (1 h at 130 °C). This discoloration of PVC has been previously described in the literature as *pinking*, with short chain conjugated polyenes being identified as the most likely functional groups responsible for the development of the pink color (Edge et al., 2010; Lemaire et al., 2003, 2000; Schiller et al., 2018).

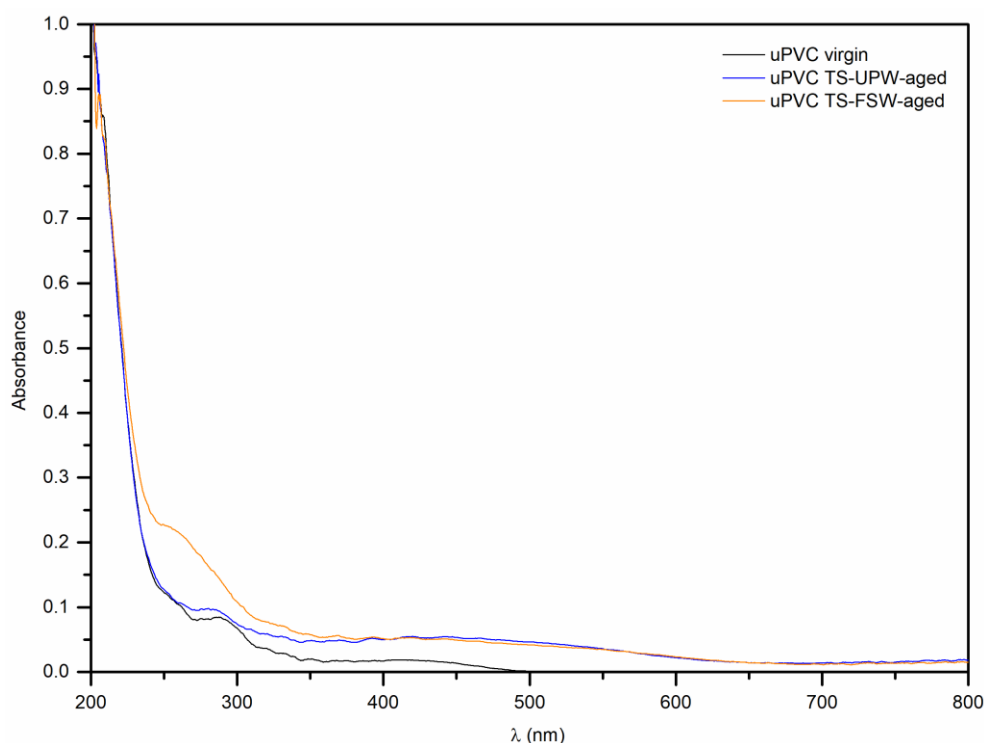


Fig. 5.13. UV-VIS spectra for unplasticized poly(vinyl chloride) (uPVC) before and after the temperature stress (TS) batch experiments.

In the present study, the *pinking* was the result of thermal degradation of the surface of the MPPs in conditions of reduced light and high moisture, and under temperatures of ca. 80 °C, being observed for the TS-UPW-aged, TS-FSW-aged, and MD-FSW-TS-aged samples of uPVC. It should be noted that while the temperature of the retentate reached values of ca. 80 °C at the entrance of the LH-cell during the DCMD experiments, most of the volume stayed at lower average (after 4 h) temperatures inside the retentate container (as recorded by the conductivity meter): MD-PW-C (24 h) = 69.1 ± 0.3 °C, MD-PW-C (first 6.5 h) = 69.2 ± 0.1 °C, MD-FSW-C = 70.2 ± 0.2 °C, MD-FSW-V = 70.7 ± 0.1 °C, MD-FSW-R = 70.2 ± 0.2 °C, MD-FSW-TS = 69.8 ± 0.4 °C.

For both aged samples, there was increased absorption in the UV region of the spectrum (Fig. 5.13); however, much more distinctly with the TS-FSW-aged sample. The most substantial difference between the two samples was detected for 250-300 nm, due to the increase of the absorption of short-wave UV (UV-C) and middle-wave UV (UV-B). This suggests that this increase in the absorption in the UV region is mostly due to the seawater constituents.

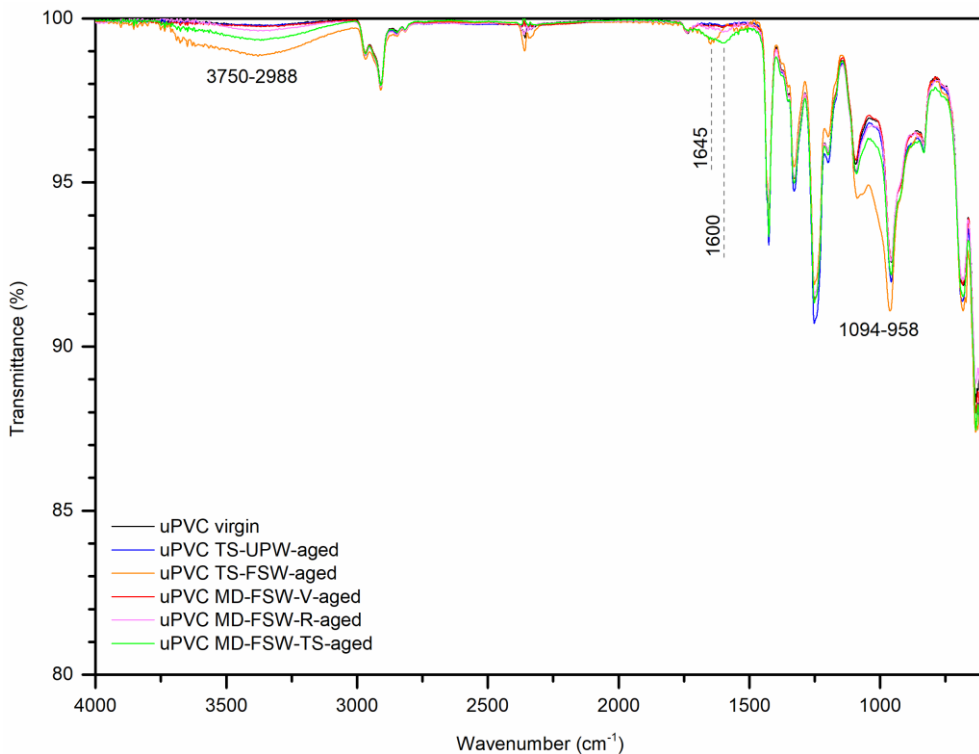


Fig. 5.14. ATR-FTIR spectra for unplasticized poly(vinyl chloride) (uPVC) before and after the temperature stress (TS) batch experiments and the DCMD experiments.

ATR-FTIR measurements were performed for uPVC samples after the temperature stress batch experiments but also after the DCMD treatments. This polymer was selected for the experiments in the lab-scale DCMD system since the temperature stress batch experiments showed that thermal degradation occurred for uPVC but, contrary to what was observed for LDPE, there was a lesser risk of membrane fouling due to the polymer degradation. The ATR-FTIR results (Fig. 5.14) show the increase of the absorption intensity at the $3750\text{--}2988\text{ cm}^{-1}$ band for the TS-FSW-aged sample, after the DCMD treatment with the TS-FSW-aged sample (MD-FSW-TS-aged) and after two DCMD treatments of the virgin uPVC (MD-FSW-R-aged). Since the TS-FSW-aged sample was not rinsed with distilled water, while the DCMD samples were rinsed, and the band intensity is much higher for the TS-FSW-aged sample and decreased for the same sample after the DCMD treatment (MD-FSW-TS, Fig. 5.14), this suggests that the increase at this band is mostly due to the presence of FSW salts. Similarly, there was increased absorption at the $1094\text{--}958\text{ cm}^{-1}$ band for the MD-FSW-TS-aged sample, and particularly for the TS-FSW-aged sample. This is expected to be another FSW salts interference.

The increased absorption at 1645 cm^{-1} observed for the TS-FSW-aged uPVC sample is expected to be the interference of the FSW salts, since their analysis revealed an absorption band with a maximum at 1638 cm^{-1} . However, for the MD-FSW-TS-aged and MD-FSW-R-aged samples there was increased absorption for the $1718\text{--}1450\text{ cm}^{-1}$ band, with a maximum at 1600 cm^{-1} . The increased absorption in this region can be due to the formation of conjugated polyenes sequences (--CH=CH--) in the polymer chains, suggesting that the DCMD treatment was effective in modifying the chemical structure of uPVC in those two experiments. No modifications of the chemical structure were identified for TS-UPW-aged and MD-FSW-V-aged uPVC samples. Therefore, no correlation between the *pinking* of the TS-UPW-aged, TS-FSW-aged and MD-FSW-TS-aged samples (Fig. 5.10c) and the polyene group (MD-FSW-TS-aged and MD-FSW-R-aged samples) could be reached. This lack of correlation can be due to a different ratio/amount of formed and oxidized polyenes during the experiments and their lengths (Andrady, 2003) since the TS and DCMD experiments were conducted under different light and dissolved oxygen conditions.

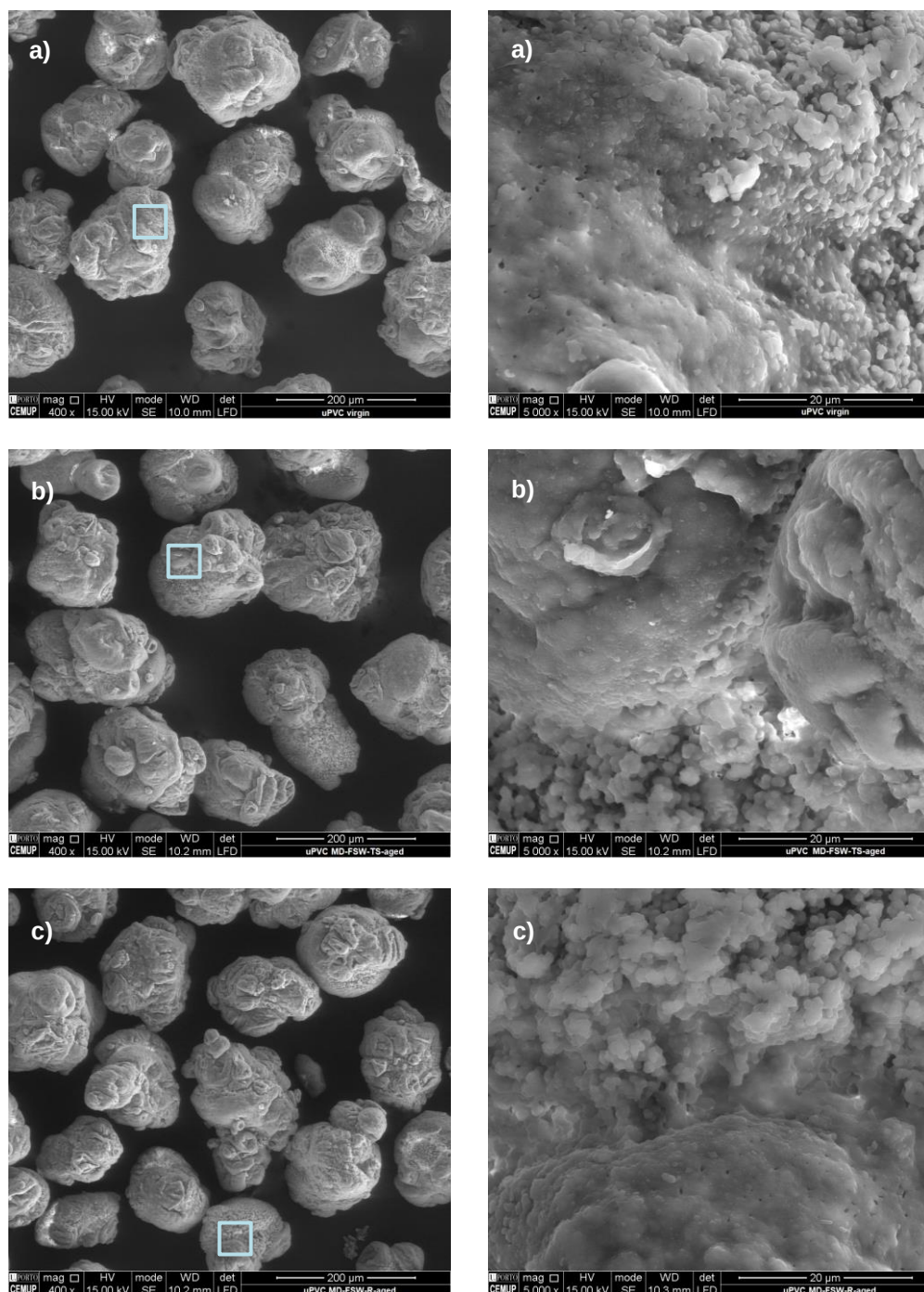


Fig. 5.15. SEM images (at 400x and 5000x) of uPVC samples:
a) virgin, b) MD-FSW-TS-aged, and c) MD-FSW-R-aged.

The SEM analysis of uPVC samples after the MD-FSW-TS and MD-FSW-R treatments did not allow to identify any relevant surface or size modification in comparison with the virgin uPVC (Fig. 5.15). This was expected considering that no modification was detected for uPVC in Chapter 3 (Section 3.3.2) after more aggressive treatments, and the previously observed surface heterogeneity of the uPVC particles acquired (Appendix D). The surface morphology of the uPVC MPPs used for this study is composed of two main morphologies (Fig. 5.16): i) areas with irregular but smoother surfaces, and ii) areas with more uniform but very rough surfaces (granular). In both areas, small pores can be observed (Fig. 5.15).

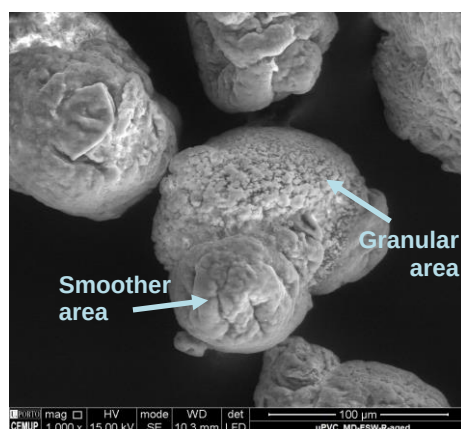


Fig. 5.16. Surface morphology of an uPVC MPP (MD-FSW-R-aged).

Regarding the physical behavior (i.e., mobility and fate) of the uPVC MPPs during the DCMD treatments, the presence of MPPs was detected inside the LH-cell, on the retentate side (Fig. 5.17a). This confirms that at least some MPPs were able to recirculate with the retentate in the DCMD system. However, since the retentate container was not agitated, most of the MPPs stayed sedimented on the bottom of the retentate container and only a portion in suspension (Fig. 5.17b). This constitutes one of the limitations of these experiments conducted with MPPs, because the MPP mechanical aging was reduced (main mechanism of degradation was the thermal stress), and because the potential impact on the DCMD system operation was also reduced.

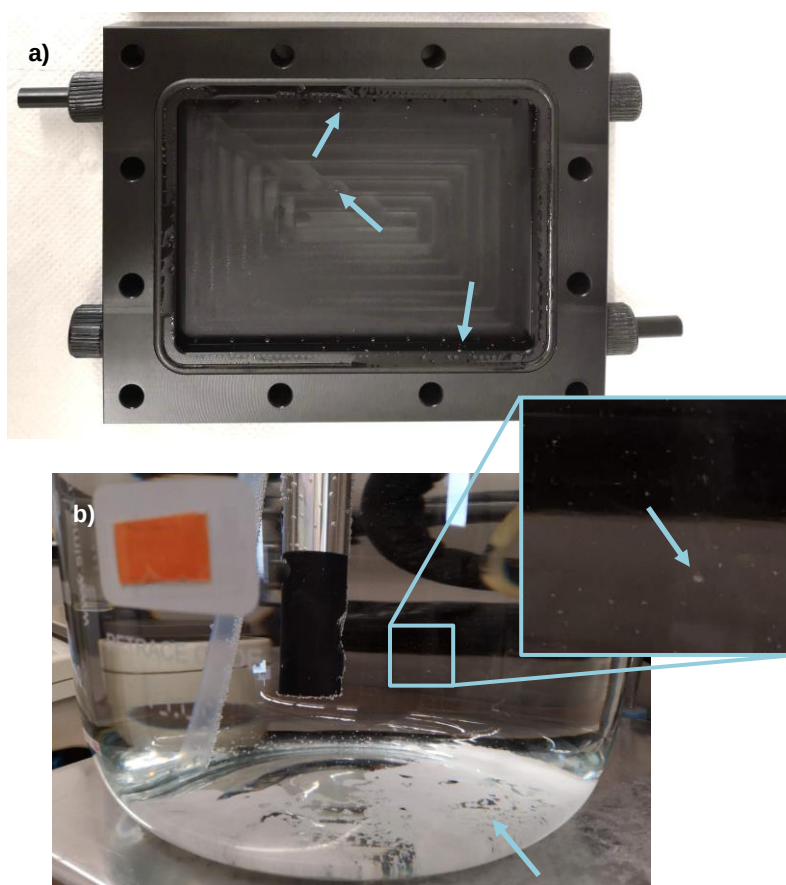


Fig. 5.17. MPPs distribution and fate in the DCMD system: a) inside the retentate side of the LH-cell, and b) in suspension or sedimented in the retentate container.

5.4.3 OMPs under temperature stress (in amber bottle)

Finally, one temperature stress (TS) batch experiment (in amber bottle) was conducted to analyze the potential degradation of 10 OMPs due to the temperature, since previous experiments (Section 5.2.4) demonstrated that it was not feasible, at this point, to conduct studies with trace concentrations of organic pollutants in the DCMD system due to contamination left between experiments. The results (Table 5.10) show only a very small but appreciable decrease in the concentration of florfenicol, alachlor and diuron. Therefore, the OMPs studied are mostly stable under the temperatures achieved during a DCMD treatment and, consequently, the MPPs in suspension in the retentate can interact with them and potentially sorbed them during that process, or afterwards when the retentate is cooling down to room temperature.

Table 5.10. Temperature stress batch experiment: OMPs.

Organic micropollutant (OMP)	Sample	C ($\mu\text{g L}^{-1}$) (n = 3)	SD	ΔC ($\mu\text{g L}^{-1}$)
Florfenicol	t = 0 h	117.6	4.6	16.1
	t = 24 h	101.5	5.4	
Trimethoprim	t = 0 h	88.5	2.2	2.4
	t = 24 h	86.0	2.5	
Diclofenac	t = 0 h	107.3	1.8	< 0
	t = 24 h	107.4	5.8	
Tramadol	t = 0 h	112.1	0.9	< 0
	t = 24 h	113.8	1.2	
Citalopram	t = 0 h	129.9	4.0	1.2
	t = 24 h	128.7	2.6	
Venlafaxine	t = 0 h	112.8	2.0	< 0
	t = 24 h	115.6	1.2	
Alachlor	t = 0 h	127.3	0.7	4.8
	t = 24 h	122.5	1.8	
Clofibric acid	t = 0 h	106.3	4.4	4.7
	t = 24 h	101.6	6.1	
Diuron	t = 0 h	122.7	0.7	9.5
	t = 24 h	113.1	2.1	
Pentachlorophenol	t = 0 h	100.1	2.4	< 0
	t = 24 h	111.7	4.9	

As discussed in the previous chapter (4.3.1), the sorption capacity for OMPs is deeply influenced by the MPP aging degree. Therefore, for a retentate with an initial concentration of $100 \mu\text{g L}^{-1}$, it can be predicted at least some sorption of alachlor and/or pentachlorophenol to the polymers studied. However, depending on the matrix and the final concentration of the OMPs at the end of the treatment, the sorption equilibrium is expected to shift. Further experiments would be needed to study this interaction in a DCMD system.

5.4.4 Influence of uPVC MPPs on the DCMD process

The MD-PW-C experiment was carried out for 24 h with the main goal of testing the system with the combination of operating parameters and volume of feed selected for this study (5.3.5), while also enabling the estimation of the maximum distilled water production under those conditions.

The MD-PW-C stable conditions were reached after ca. 3 h of operation and no flux decline was observed (Fig. 5.18). An average ΔP of 35.7 ± 0.4 kPa and permeate interval flux of 38.9 ± 0.3 kg m⁻² h⁻¹ were maintained for $t = 4$ -6.5 h and $t = 15.5$ -24 h of operation, corresponding to a permeability of 1.09 ± 0.02 kg m⁻² h⁻¹ kPa⁻¹. Based on the difference between the measurement of the total volume of permeate produced and the volume of permeate produced during the data collection, the volume produced during the night was estimated and, from that, resulted the estimated average permeate interval flux of 39.1 kg m⁻² h⁻¹ for the night period ($t = 6.5$ -15.5 h). These results ($t = 4$ -24 h) are aligned with the 2021 data in Section 5.2.3. Moreover, the water recovery reached 65% at $t = 24$ h, with no signs of membrane fouling and a good permeate water quality (Table 5.12 and Table 5.13).

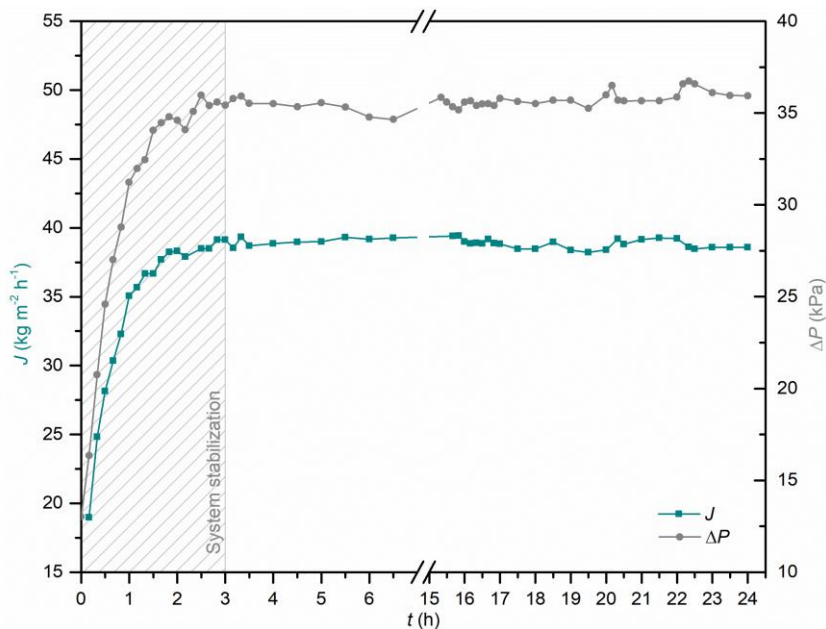


Fig. 5.18. Vapor pressure gradient and permeate interval flux through time for the MD-PW-C experiment from 2022.

Table 5.11. 2022 DCMD experiments: average (after 4 h) temperatures at the LH-cell.

Experiment	Average T ($^{\circ}\text{C}$)			
	P_{in}	R_{in}	P_{out}	R_{out}
MD-PW-C (24 h)	24.8 ± 0.2	78.7 ± 0.2	30.6 ± 0.3	72.4 ± 0.4
MD-PW-C (first 6.5 h)	25.0 ± 0.1	78.6 ± 0.1	30.8 ± 0.1	71.9 ± 0.4
MD-FSW-C	23.6 ± 0.1	78.6 ± 0.1	28.3 ± 0.1	73.5 ± 0.1
MD-FSW-V	23.0 ± 0.1	79.2 ± 0.1	27.2 ± 0.1	74.6 ± 0.1
MD-FSW-R	23.5 ± 0.1	78.6 ± 0.1	28.0 ± 0.1	73.4 ± 0.1
MD-FSW-TS	23.3 ± 0.1	78.5 ± 0.2	27.9 ± 0.1	73.5 ± 0.2

Table 5.12. 2022 DCMD experiments: average (after 4 h) vapor pressure gradient, permeate interval flux and membrane permeability, and water recovery at the end of the experiment.

Experiment	MPPs (g L^{-1})	Stable ΔP (kPa)	Stable J ($\text{kg m}^{-2} \text{h}^{-1}$)	Stable B ($\text{kg m}^{-2} \text{h}^{-1} \text{kPa}^{-1}$)	Water recovery (%)
MD-PW-C (24 h)	-	35.7 ± 0.4	38.9 ± 0.3	1.09 ± 0.02	65
MD-PW-C (first 6.5 h)	-	35.2 ± 0.4	39.1 ± 0.2	1.11 ± 0.01	17
MD-FSW-C	-	36.8 ± 0.1	32.8 ± 0.3	0.89 ± 0.01	18
MD-FSW-V	0.2	38.5 ± 0.1	28.7 ± 0.3	0.75 ± 0.01	16
MD-FSW-R	0.1	36.8 ± 0.2	31.2 ± 0.3	0.85 ± 0.01	17
MD-FSW-TS	0.1	36.9 ± 0.3	31.9 ± 0.3	0.87 ± 0.01	17

Table 5.13. 2022 DCMD experiments: Compensated conductivity and salinity at the beginning and end of the experiment, and salt rejection at the end of the experiment.

Experiment	EC_{25} (P : $\mu\text{S cm}^{-1}$; R : mS cm^{-1})				Salinity (ppt)				Salt rejection (%)
	P_i	P_f^{**}	R_i	R_f	P_i	P_f	R_i	R_f	
MD-PW-C (24 h)	2.3	1.5	4.9*	15.4*	-	-	-	-	-
MD-PW-C (first 6.5 h)	2.3	1.9	4.9*	6.9*	-	-	-	-	-
MD-FSW-C	5.4	10.6	52.8	65.3	0.0	0.0	34.9	42.1	100
MD-FSW-V	3.6	3.9	52.1	62.9	0.0	0.0	34.3	40.3	100
MD-FSW-R	3.7	4.8	50.1	61.4	0.0	0.0	32.9	39.3	100
MD-FSW-TS	3.9	10.6	50.5	60.9	0.0	0.0	33.1	38.9	100

* For the MD-PW-C experiment, since the feed water is purified water, the conductivity units are $\mu\text{S cm}^{-1}$.

** Reading of the water conductivity of the last permeate bottle produced and not of all volume produced.

The previous experiment with PW was carried out for 24 h, while those that followed with FSW as feed were carried out for only 8 h. This decrease in the experiment time was necessary since it was observed a decrease in the permeate water quality after 15-16 h of operation when only 10 L of FSW are used under the conditions tested. A total of four experiments (MD-FSW) were conducted with seawater to study potential changes in the performance of the DCMD system when MPPs are in suspension in seawater.

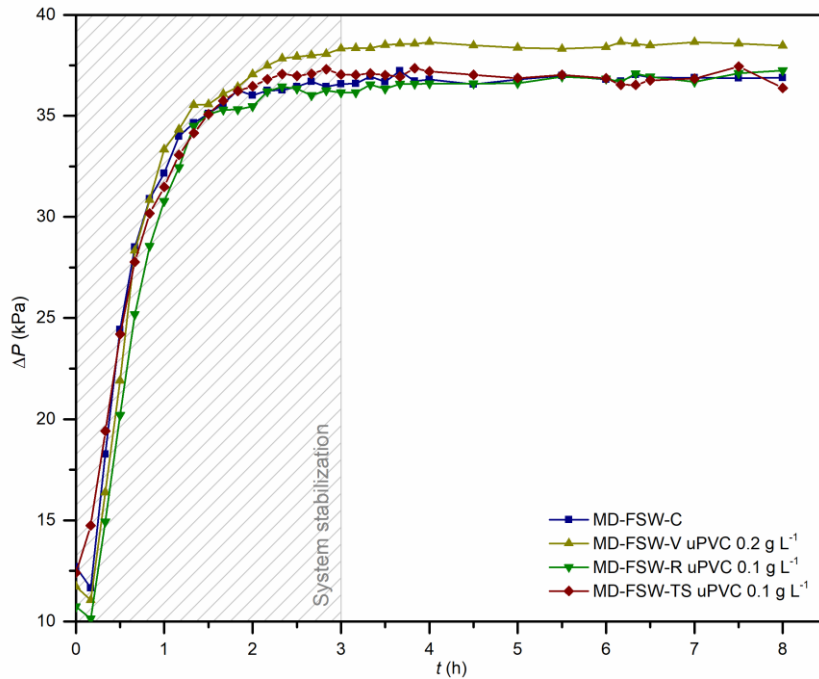


Fig. 5.19. Vapor pressure gradient through time for the 8 h MD-FSW experiments.

As represented in Fig. 5.19, the control experiment with FSW (MD-FSW-C) and the two experiments with 0.1 g L^{-1} of MPPs (MD-FSW-R and MD-FSW-TS) have the same stable ΔP (ca. 37 kPa), while the experiment with the higher MPP load of 0.2 g L^{-1} (MD-FSW-V) achieved a higher stable ΔP of $38.5 \pm 0.1 \text{ kPa}$. This could have happened due to slight variations in the heat transfer (e.g., in the heat exchangers) and/or in the heat losses during the MD-FSW-V experiment compared to the other three (Table 5.11). Still, since uPVC has a smaller specific heat capacity ($1000 - 1500 \text{ J K}^{-1} \text{ kg}^{-1}$, according to the supplier) than FSW, the specific heat capacity of the mixture is lower than that of FSW, leading to less energy being needed to change the temperature of the mixture. However, the first hypothesis is more likely since the mass of MPPs (1 or 2 g) is negligible in the FSW-MPPs mixture. Nevertheless, it was observed that DCMD

experiments with FSW consistently reached higher ΔP than those of DW or PW, which could also be explained by the lower specific heat capacity of FSW when compared with DW/PW.

As expected, the stable permeate interval flux results of the four experiments (Fig. 5.20) are below the one obtained for the MD-PW-C experiment (Fig. 5.18). The following trend was observed: MD-PW-C > MD-FSW-C > MD-FSW-TS $\geq$ MD-FSW-R > MD-FSW-V. Therefore, these results suggest that the presence of MPPs in suspension might influence the membrane permeability and, consequently, the permeate interval flux, with higher MPPs loads decreasing the flux (Table 5.12). This is particularly evident for the experiment with the highest MPPs load (MD-FSW-V), since it is the one with the highest stable ΔP and lowest stable J , leading to the lowest stable B of $0.75 \pm 0.01 \text{ kg m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$. As a result, that is also the experiment with the lowest water recovery (Table 5.12), with none of the experiments showing signs of flux decline. Under the conditions studied, the uPVC MPP aging degree (MD-FSW-R and MD-FSW-TS experiments) played a less important role than the MPPs load on the permeate flux (Table 5.12).

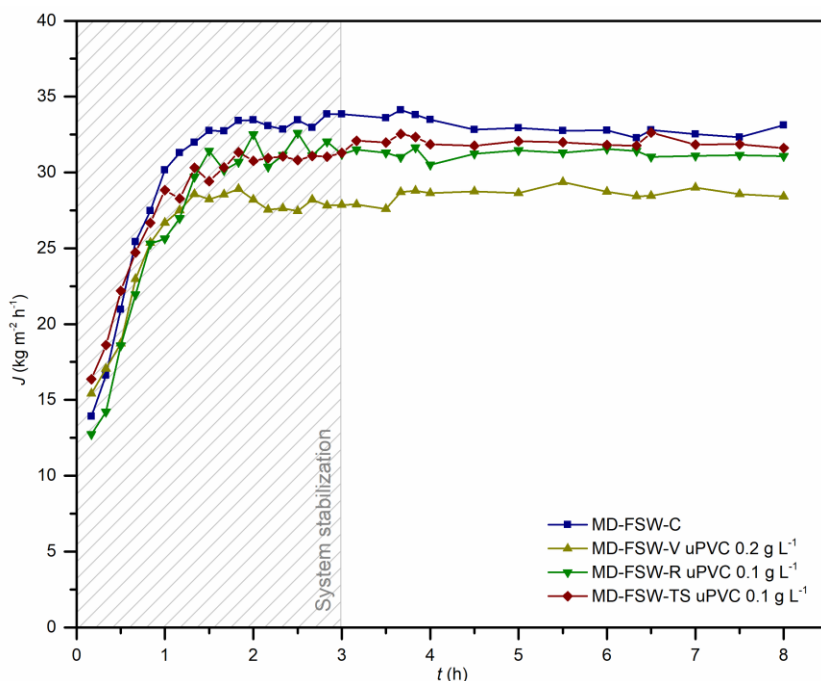


Fig. 5.20. Permeate interval flux through time for the 8 h MD-FSW experiments.

As listed in Table 5.13, all experiments produced a permeate with good water quality concerning conductivity and salinity. Therefore, there are no signs of contamination of the permeate or

decrease in the salt rejection efficiency. It should be noted that a disinfection step (e.g., UV) would be advisable to ensure that the water produced fulfills all requirements regarding the microbiologic parameters as set by the EU Drinking Water Directive (The European Parliament and the Council of the European Union, 2020a).

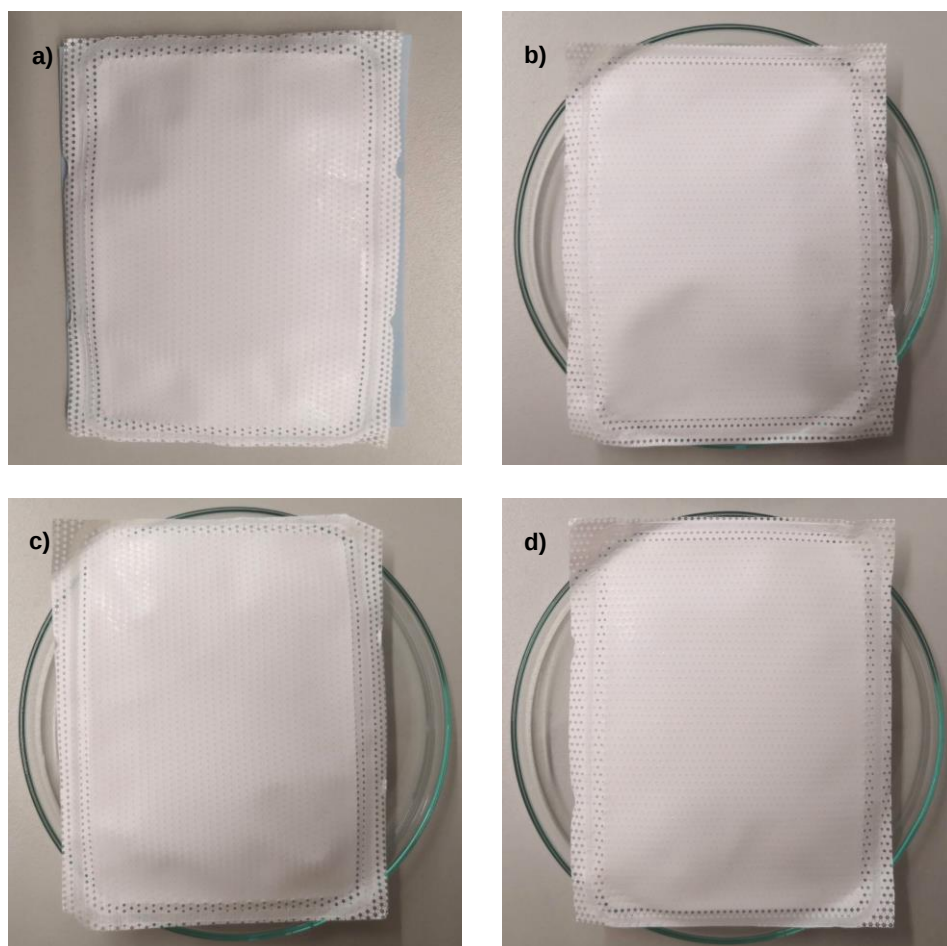


Fig. 5.21. PTFE membranes (retentate side) at the end of the experiments (i.e., used membranes):
a) MD-FSW-C, b) MD-FSW-TS, c) MD-FSW-V, and d) MD-FSW-R.

Membrane fouling was minor and did not affect the permeate flux. In all MD-FSW type experiments, it was similarly detected the presence of small salt crystals on the membrane retentate side (Fig. 5.21). It should be noted that the vacuum filtration pre-treatment of the SW samples decreased the fouling of the membranes significantly, since the suspended solids (e.g., sediment) were removed.

5.4.5 DCMD performance in removing MPPs

Although the primary goal of this work was not to test the efficiency of the DCMD system in keeping the MPPs from the permeate, the treated water produced in each of the three experiments with MPPs was vacuum filtrated and the filters were analyzed for the presence of MPPs by μ Raman. Before that, an unused glass filter and a sample of virgin uPVC were analyzed to be used as reference (Fig. 5.22).

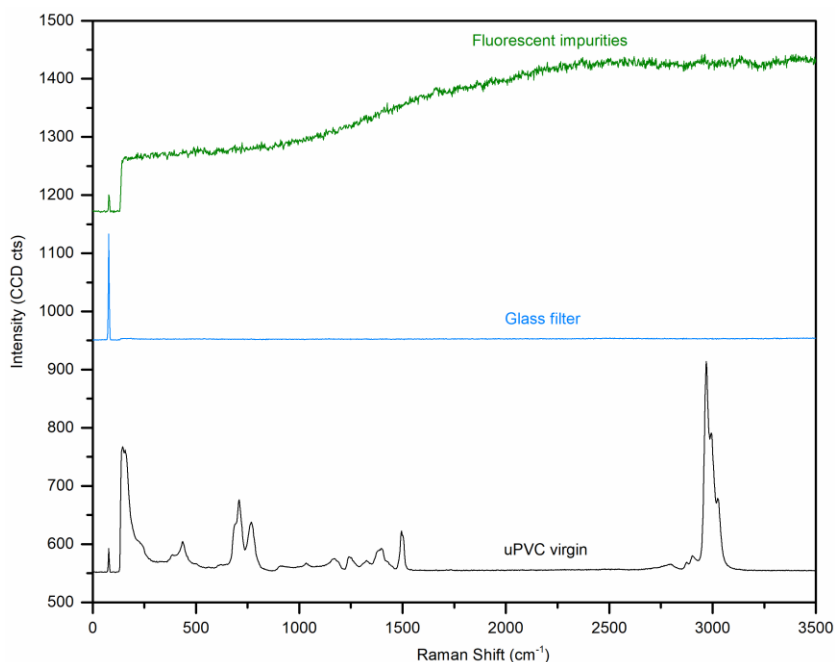


Fig. 5.22. μ Raman spectra of reference materials used in the particle count.

Table 5.14. Number of particles identified using WITec ParticleScout software.

Area scanned	Permeate volume (mL)	Total	Glass filter	Fluorescent impurities	Others
a) MD-FSW-V - center	2150	204	128	75	1
b) MD-FSW-V - border		45	32	13	0
c) MD-FSW-R - center	2290	40	31	9	0
d) MD-FSW-R - border		12	9	2	1
e) MD-FSW-TS - center	2320	50	48	2	0
f) MD-FSW-TS - border		47	38	8	1

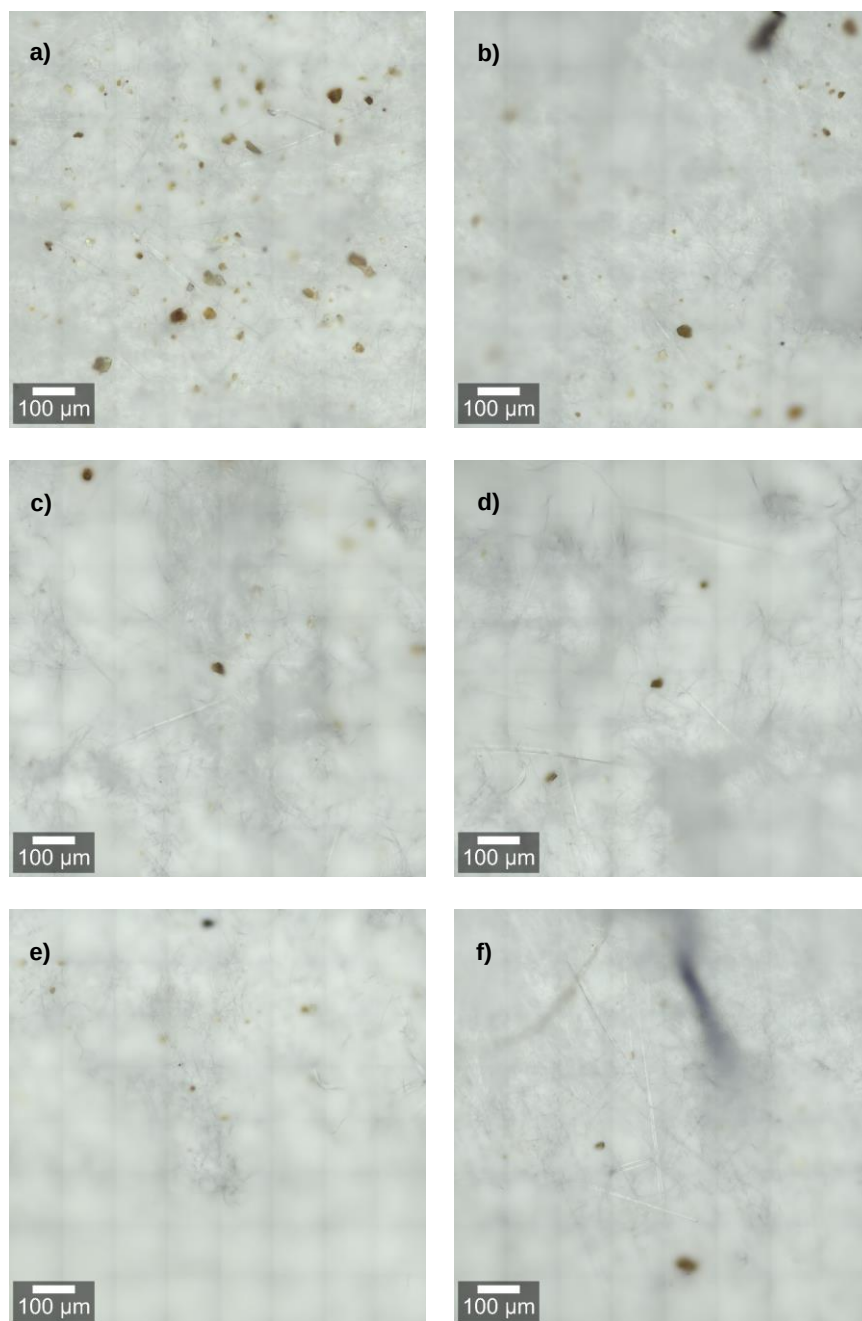


Fig. 5.23. Areas of the filters scanned with WITec ParticleScout:

- a) MD-FSW-V -aged center, b) MD-FSW-V -aged border, c) MD-FSW-R-aged center, d) MD-FSW-R-aged border, e) MD-FSW-TS-aged center, f) MD-FSW-TS-aged border.

Almost all the particles quantified using the WITec ParticleScout (Table 5.14 and Fig. 5.23) were identified as irregularities of the glass filter or as fluorescent impurities. Still, the Raman spectrum of one particle in each filter indicated the presence of other particles in the treated water. Of those three particles (Fig. 5.24), only the one in the MD-FSW-V filter could potentially be identified as uPVC. That particle is purple and has a 2.2 μm length, 1.7 μm width and a circularity of 0.811. Therefore, it is highly unlikely that this particle is one of the uPVC added MPPs and most probably is a contamination. The particle in the MD-FSW-R filter has a length of 7.0 μm and a width of 0.7 μm , suggesting that it is a fiber. The biggest unidentified particle was on MD-FSW-TS filter and has a 46.6 μm length and 34.2 μm width, with no match to the reference spectra of uPVC. In light of these observations, it is recommended that future research should include the pre-treatment of the permeate, with a digestion step, to remove organic matter and have a faster analysis of each filter. Similarly, the glass fiber filters used should be substituted by others with smoother surfaces.

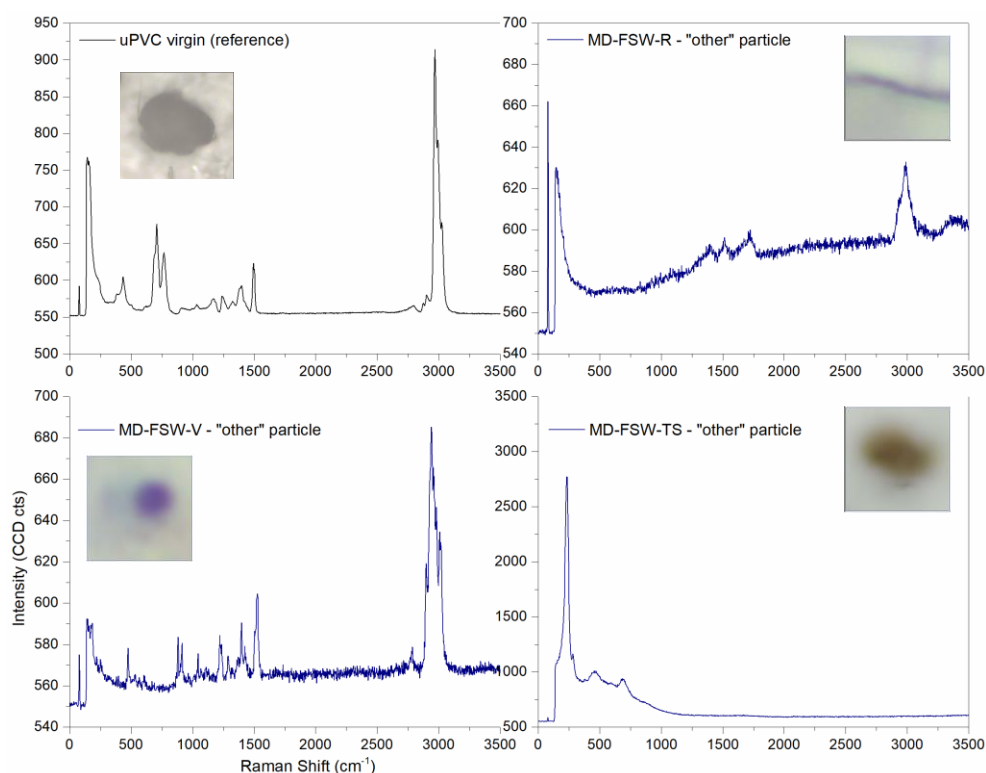


Fig. 5.24. μ Raman spectra and images of the unidentified particles.

The mass of the dried filters, used to vacuum filtrate the treated water, was practically unchanged ($\Delta m \leq 0.0003 \pm 0.0001$ g). The mass of MPPs recovered from the experiments was higher than 99.3%, as assessed by weighting the filters used to vacuum filtrate the retentate. Taking this into account and the lack of evidence of the spiked MPPs on the treated water filters, the DCMD system has a very high efficiency ($\geq 99\%$) in removing MPPs from water. This result was expected and is in line with what has been observed when membrane technologies are used to remove MPPs from water (Yaranal et al., 2021).

5.5 Conclusions

The research presented allowed to study the behavior and influence of MPPs in a lab-scale DCMD system, while being used for a desalination process. Therefore, this study constitutes one of the first on this specific topic, namely regarding the analysis of MPPs for DCMD applications.

Concerning the behavior of the MPPs in a DCMD system, due to the relatively high temperatures that the retentate can reach, the treatment can potentially lead to the degradation of the polymers and the release of substances and/or smaller particles into the water. This can be problematic since the quality of the retentate water is further decreased during the treatment, whereas membrane fouling (and consequently flux decline) can occur faster. Of the three polymers studied, only LDPE results from the temperature stress test suggest that this polymer could potentially create this problem. However, other more temperature-sensitive polymers, such as temperature-responsive polymers, could pose some additional challenges to a desalination process using a DCMD system. In parallel, PET showed very slight modifications after the temperature stress treatment and uPVC MPPs underwent *pinking*. These results lead to the selection of uPVC to conduct the studies with the DCMD system.

The majority of uPVC MPPs sedimented in the retentate container since it was not agitated. Still, MPPs were found at the LH-cell (retentate side) at the end of the experiment, suggesting that, even at this lab-scale, MPPs can be in recirculation in a DCMD system. Nevertheless, this limited the MPP mechanical aging, and thermal degradation and hydrolysis were the main degradation mechanisms that could increase the aging degree of MPPs during these experiments. Since very few modifications were identified for a longer period than what is expected for a desalination treatment, it is anticipated that the aging of MPPs can be negligible but grow mainly dependent on the resistance of the polymers to higher temperatures. Further studies would be necessary to investigate the behavior of polymers with lower densities and that would more easily stay in suspension.

Regarding the potential influence of MPPs on the DCMD process, the results indicate that higher MPPs loads ($> 0.1 \text{ g L}^{-1}$) might have some influence on the membrane permeability and, consequently, on the permeate interval flux and water recovery. However, the tested MPPs loads are much higher than those usually found in the environment. Even so, the quality of the water produced has not decreased in any studied scenario with MPPs. Therefore, the presence of MPPs that are relatively resistant to temperature is expected to have minimal interference with the normal working of a desalination unit based on a DCMD system.

Finally, no signs were found of the added uPVC MPPs in the treated water produced (permeate), as assessed by μ Raman. All the results suggest a very high efficiency ($\geq 99\%$) in removing MPPs from water when using a DCMD system. Thus, DCMD is an alternative to other technologies, such as reverse osmosis, to obtain MPPs-free drinking water from seawater. Since the retentate is going to have a higher load of MPPs compared to the raw seawater, it is advised that the retentate is treated before being returned to the sea.

6. Conclusions and future work

6.1 Main conclusions and findings

Plastic pollution is undeniably one of the biggest environmental challenges that humankind faces in the XXI century, due to the high dependence on plastic products, their fragmentation into microplastics and nanoplastics through wear and tear, leaching of plastic-related chemicals into the environment, inadequate waste management, and the persistence and accumulation of plastics of all sizes in the environment. In the context of the rise of the microplastic pollution research field, this PhD work focused on providing better knowledge of microplastics behavior in the environmental compartments, particularly concerning the plastic aging and interaction with co-occurring contaminants, and delivering one of the first studies on microplastics behavior and attenuation in drinking water production from seawater sources by using a membrane distillation technology. The main conclusions obtained are encapsulated below, exploring the main findings presented by the previous chapters of this thesis.

Due to the high complexity of microplastic pollution and in order to organize the current knowledge on microplastics in the environmental compartments, a DPSIR analysis was conducted. Consequently, the driving forces, pressures, states, impacts and responses of the microplastic pollution were reviewed. This literature review at the beginning of the PhD project allowed to identify that the study of microplastics in aquatic environments, particularly coastal and marine ecosystems, was at a much more developed state than other environments, leading to the selection of the urban environment as the focus of the next chapters. Additionally, it was concluded that there was a lack of studies on microplastics impacts on plants, which led to the implementation of phytotoxicity studies in subsequent research in the scope of the PhD project. The DPSIR analysis was particularly directed at reviewing the current downstream and upstream responses to the microplastic pollution, what enabled to identify that there was a knowledge gap regarding the efficiency of existing treatment technologies in eliminating microplastics, particularly for drinking water production, which was decisive in selecting this topic as part of the experimental component of the PhD project.

While several studies were identified on the degradation mechanisms and pathways of plastics during their designed lifetime, there was a knowledge gap on the aging of plastics in the environment at their end-of-life. This led to the selection of three polymers (LDPE, PET and uPVC) and different treatments (ozone for 1 h, UV-C for 96 h, solar radiation for 120 h, and natural weathering conditions in an urban rooftop for 3 months) that can contribute for their aging in urban environments, with the goal to assess their modifications regarding the chemical structure, surface morphology and crystallinity. The aging treatments selected affected the

microplastics differently depending on the polymer: LDPE was aged by all treatments but mostly by ozone and rooftop weathering, PET was hypothesized to have been slightly aged by ozone and rooftop weathering, while uPVC was more affected by the UV-C treatments, followed by rooftop weathering. The aging agents studied were confirmed to cause modifications to the three polymers, particularly regarding their chemical structure. For LDPE and uPVC, this led to the calculation of the Carbonyl Index as a metric for the oxidation of the polymers and enabled the quantification of some of the changes in the chemical structure through time. However, some samples of LDPE microplastics that had similar Carbonyl Indices showed different degrees of aging concerning the surface morphology. That can be explained by the surface of the particle being oxidized, contributing to the formation of cracks (which can provide preferential areas for foreign substances and organisms to lodge) and the consequent gradual disintegration of the particle, with removal/degradation of some of the oxidized material at the surface and, because of that, a stabilization of the Carbonyl Index value. This led to the conclusion that, even though the Carbonyl Index is a good metric, it should not be used alone when assessing the aging of microplastics, with the study of the surface morphology and crystallinity providing complementary and important information. Overall, LDPE was shown to be more susceptible to aging than uPVC, while PET was the most resistant to the aging conditions tested, leading to the conclusion that PET microplastics in the environment are going to be closer to their pristine properties than LDPE and uPVC microplastics under the same conditions.

Following these findings and in response to the insufficient research pertaining to the role of the aging of microplastics on their sorption capacities, the previously obtained LDPE, PET and uPVC samples of ozone-aged (ozone gas) or weathered (with and without rainwater) microplastics were used for sorption batch experiments with ten organic micropollutants (alachlor, citalopram, clofibric acid, diclofenac, diuron, florfenicol, pentachlorophenol, tramadol, trimethoprim, and venlafaxine). These experiments allowed to examine the potential of microplastics to be transport vectors for the selected pollutants and demonstrated that the aging degree can play a major role in the sorption process. LDPE sorption capacities increased the most after ozone exposure or weathering, while uPVC sorption capacities increased mainly after weathering. PET microplastics, as predicted, conserved their low sorption capacities for almost all micropollutants, since they were least affected by aging. The increased sorption of pentachlorophenol on ozone-aged and trimethoprim on weathered (with rainwater) microplastics of PET confirmed that those were effective in introducing modifications to that polymer. While most micropollutants had very low to no affinity to virgin microplastics and that was maintained for most substances with PET after aging, that was not the case with LDPE and uPVC. For those polymers, there was an increased affinity from only one or two substances being sorbed to virgin microplastics up to nine substances being sorbed to the aged microplastics. Pentachlorophenol was identified as the most sorbed substance on LDPE and PET, leading to further studies on the

sorption of this pesticide on virgin or ozone-aged microplastics. Another relevant finding of this study was the possibility to link the identified modifications of the aged microplastics to the increase of the sorption capacities, particularly for LDPE. For this polymer, it was observed that the affinity and consequent sorption of most of the studied micropollutants on LDPE microplastics were mainly governed by the surface chemical structure, making the Carbonyl Index also a relevant metric to help predict the sorption of substances by aged microplastics in the environment. Finally, phytotoxicity tests with two plants (*Lepidium sativum* and *Sinapis alba*) showed that the studied combinations of microplastics and micropollutants are unlikely to deeply affect the early growth dynamics of these plants.

The last part of the PhD work presented the opportunity to follow up the previous studies into a more applied scenario of drinking water production from seawater and to test microplastics behavior and attenuation when using the DCMD technology. First, temperature stress tests, in amber bottles, were conducted and revealed that, since DCMD exposes the retentate with the microplastics in suspension to higher temperatures, this could lead to the aging of some polymers depending on their resistance to temperature. Therefore, of the three selected polymers, LDPE could potentially create some problems during the use of the technology, while PET showed very few modifications after the temperature stress treatment and uPVC underwent *pinking*. Taking this into account, uPVC was selected for the experiments with a lab-scale DCMD system, which was updated during the PhD project. During the treatments of filtered seawater with added microplastics of uPVC, it was observed that most of the particles sedimented in the retentate container since it was not agitated. However, microplastics were found at the membrane module on the retentate side, at the end of the experiment, leading to the conclusion that the microplastics were able to recirculate in the system. The assessment of the aging of the microplastics after the DCMD treatments revealed that the aging of MPPs can be negligible for certain polymers, although dependent on the resistance of the polymers to the higher temperatures employed. In parallel, the potential influence of the presence of microplastics in the well-functioning of a DCMD system was studied and disclosed that only higher loads of uPVC particles ($> 0.1 \text{ g L}^{-1}$) might have some influence on the membrane permeability, which is unlikely to occur in full-scale applications due to the lower environmental loads of MPPs. Consequently, it is predicted that the presence of microplastics that are relatively resistant to temperature would have minimal interference with the normal functioning of a DCMD system. Lastly, the presence of the added microplastics of uPVC to the feed stream was analyzed in the treated water produced, suggesting a very high efficiency ($\geq 99\%$) in removing MPPs from water when using a DCMD system.

Thus, the PhD work presented with this thesis achieved the objectives identified in Section 1.2, providing new insights on the behavior and attenuation of microplastics in the environmental compartments.

6.2 Future work

During the PhD project, several research questions were identified that were not tackled but should be addressed in the future in order to expand the current knowledge on this topic. These include:

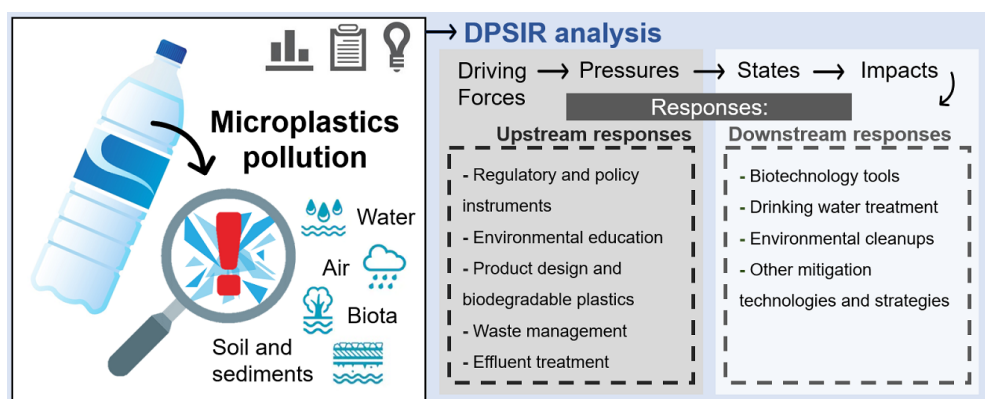
- The study of the aging of (micro)plastics, by a combination of abiotic and biotic mechanisms, in other environments and specific scenarios, such as those of food processing or hospital settings, enabling to determine the degradation, mobility and fate of microplastics in those environments and providing the necessary information to do risk assessments and create mitigation measures;
- Explore the role of polymer additives, such as stabilizers, plasticizers, lubricants and flame retardants, on the behavior of microplastics in the environment, particularly regarding the protection of the polymer from aging stressors, but also their potential leaching;
- Additional research on the sorption process of co-occurring pollutants (under environmental relevant concentrations) on aged microplastics in more complex matrices, analyzing the effect of ionic strength, pH, temperature, and organic matter in solution, as well as other particulate matter that can compete with microplastics;
- Analyze the role of the microplastics colonization by microorganisms in the behavior of microplastics, particularly regarding the potential to be transport vectors for other contaminants;
- Further research on the toxicity of microplastics with sorbed pollutants on soil-plant systems;
- The development of protocols for aging microplastics specifically for sorption experiments and/or for assessing the effects on biota, allowing more collaborative efforts and faster and more efficient progress in this field of research;
- Further studies on microplastics behavior during desalination treatments with environmentally relevant concentrations of a mixture of microplastics (different polymers studied together) and co-occurring pollutants.

Dissemination of results

Journal article with peer-review:

REVIEW: Miranda, M. N., Silva, A. M. T., & Pereira, M. F. R. (2020). Microplastics in the environment: A DPSIR analysis with focus on the responses. *Science of The Total Environment*, 718, 134968. <https://doi.org/10.1016/j.scitotenv.2019.134968>

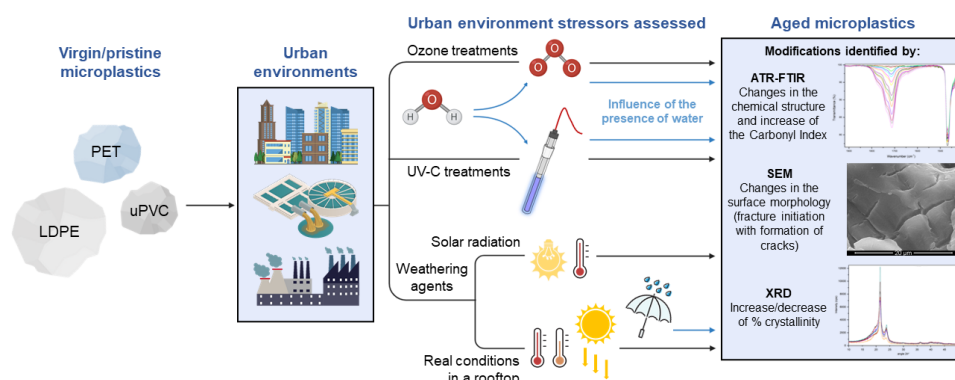
Graphical abstract:



Abstract: This review organizes key information about microplastic pollution through a DPSIR (driving forces, pressures, states, impacts and responses) analysis, namely the current knowledge on the sources of microplastics in the environment, the abundance, mobility and fate of microplastics distributed across the different environmental compartments, as well as their socio-economic and environmental impacts. The available or developing upstream and downstream responses to the microplastic pollution are also reviewed as part of the DPSIR analysis. These include the regulatory and policy instruments, environmental education campaigns, product design, the development of biodegradable plastics, environmental cleanups, waste management, drinking water and wastewater treatment plants, and other treatment technologies and processes. Whenever possible, the current trends and discerning gaps in the research conducted so far by the scientific community are identified, giving some clues to what is going to be the future research on this topic and into new lines of research.

ARTICLE: Miranda, M. N., Sampaio, M. J., Tavares, P. B., Silva, A. M. T., & Pereira, M. F. R. (2021). Aging assessment of microplastics (LDPE, PET and uPVC) under urban environment stressors. *Science of The Total Environment*, 796, 148914. <https://doi.org/10.1016/j.scitotenv.2021.148914>

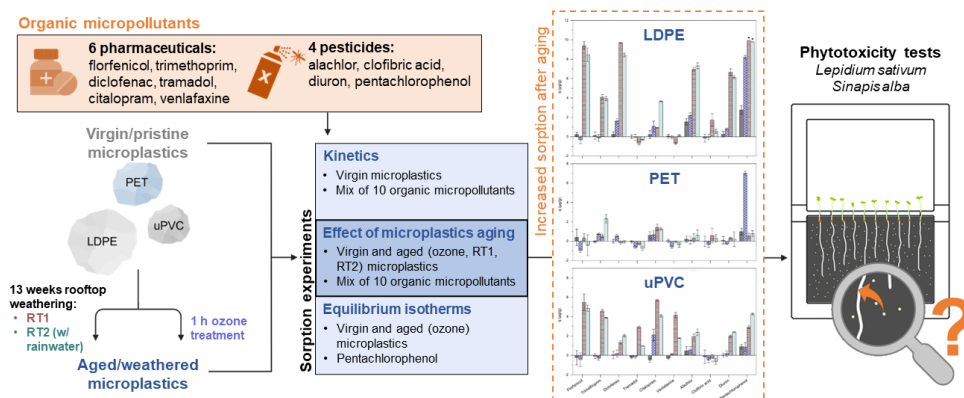
Graphical abstract:



Abstract: The changes in the chemical structure, surface morphology and crystallinity are reported for three different polymers (LDPE, PET and uPVC) in microplastic form, after being artificially exposed to different aging agents that can affect microplastics in urban environments: ozone, UV-C, and solar radiation. In parallel to the laboratory experiments, the microplastics were exposed to real weathering conditions for three-months in a building rooftop located in the city of Porto (Portugal). By analysing the (virgin and aged) microplastic samples periodically through ATR-FTIR spectroscopy and estimating the Carbonyl Index, it was possible to sketch the aging degree evolution through time and identify the most aggressive agents for each polymer regarding the changes in their chemical structure. SEM and XRD measurements allowed to complement the ATR-FTIR results, giving a more complete picture of the effects of each treatment on each polymer and suggesting that ATR-FTIR measurements are not sufficient to correctly evaluate the aging degree of microplastics. The changes observed in the microplastic particles studied support the theory that microplastics in the environment undergo aging and change their characteristics through time, potentially affecting their behavior and intensifying their impacts.

ARTICLE: Miranda, M. N., Ribeiro, A. R. L., Silva, A. M. T., & Pereira, M. F. R. (2022). Can aged microplastics be transport vectors for organic micropollutants? - Sorption and phytotoxicity tests. *Science of The Total Environment*, 850, 158073. <https://doi.org/10.1016/j.scitotenv.2022.158073>

Graphical abstract:



Abstract: Microplastics have been investigated over the last decade as potential transport vectors for other pollutants. However, the specific role of plastic aging, in which plastics change their characteristics over time when exposed to environmental agents, has been overlooked. Therefore, sorption experiments were herein conducted using virgin and aged (by ozone treatment or rooftop weathering) microplastic particles of LDPE - low-density polyethylene, PET - poly(ethylene terephthalate), or uPVC - unplasticized poly(vinyl chloride). The organic micropollutants (OMPs) selected as sorbates comprise a diversified group of priority substances and contaminants of emerging concern, including pharmaceutical substances (florfenicol, trimethoprim, diclofenac, tramadol, citalopram, venlafaxine) and pesticides (alachlor, clofibrilic acid, diuron, pentachlorophenol), analyzed at trace concentrations (each $\leq 100 \mu\text{g L}^{-1}$). Sorption kinetics and equilibrium isotherms were obtained, as well as the confirmation that the aging degree of microplastics plays a major role in their sorption capacities. The results show an increased sorption of several OMPs on aged microplastics when compared to pristine samples, i.e., the sorption capacity increasing from one or two sorbed substances (maximum $3 \mu\text{g g}^{-1}$ per sorbate) up to nine after aging (maximum $10 \mu\text{g g}^{-1}$ per sorbate). The extent of sorption depends on the OMP, polymer and the effectiveness of the aging treatment. The modifications (e.g., in the chemical structure) between virgin and aged microplastics were linked to the increased sorption capacity of certain OMPs, allowing to better understand the different affinities observed. Additionally, phytotoxicity tests were performed to evaluate the mobility of the OMPs sorbed on the microplastics and the potential effects (on germination and early growth) of the combo on two species of plants (*Lepidium sativum* and *Sinapis alba*). These tests suggest low or

no phytotoxicity effect under the conditions tested but indicate a need for further research on the behavior of microplastics on soil-plant systems.

ARTICLE: Miranda, M. N., Fernandes, A. R. T., Silva, A. M. T., & Pereira, M. F. R. (xxxx). Behavior and removal of microplastics during desalination in a lab-scale direct contact membrane distillation system. (Submitted)

Conference paper:

Miranda, M. N.; Silva, A.M.T.; Pereira, M.F.R.. "Evaluation of the role of plastic aging on the sorption of pesticides and pharmaceutical substances on microplastics". Paper presented in μ MED 2022 - 3rd International Conference on Microplastic Pollution in the Mediterranean Sea, Naples, 2022. (Submitted)

Conference abstracts:

1. Miranda, M. N.; Ribeiro, Ana Rita Lado; Silva, A.M.T.; Pereira, M.F.R.. "Influence of microplastic (LDPE, PET and uPVC) aging on the sorption of ten organic contaminants in water". MICRO 2022 International Conference - Online Atlas Edition: Plastic Pollution from MACRO to nano, 2022.
2. Miranda, M. N.; Silva, A.M.T.; Pereira, M.F.R.. "Evaluation of the role of plastic aging on the sorption of pesticides and pharmaceutical substances on microplastics". μ MED 2022 - 3rd International Conference on Microplastic Pollution in the Mediterranean Sea, Naples, 2022.
3. Miranda, M. N.; Silva, A.M.T.; Pereira, M.F.R.. "Assessment of urban environment aged microplastics as potential carriers of micropollutants to soil-plant systems". 8th EuChemS Chemistry Congress, Lisbon, 2022.
4. Miranda, M. N.; Sampaio, M. J.; Silva, A.M.T.; Pereira, M.F.R.. "Effect of simulated treatments and weathering processes on the aging of land-based microplastics". MICRO 2020 International Conference - Fate and Impacts of Microplastics: Knowledge and responsibilities, Lanzarote, 2021.

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Appendices

Appendix A – Full agreement of the co-authors on the inclusion of the manuscripts



Co-authors authorization regarding the full agreement of the inclusion of the manuscripts in the present thesis

M. Fernando R. Pereira, Full Professor at the Faculty of Engineering of the University of Porto (FEUP), and Adrián M. T. Silva, Associate Professor at FEUP, hereby authorize the PhD student Mariana Nogueira Miranda, from the FEUP Doctoral Program in Chemical and Biological Engineering, to include the following publication in her doctoral thesis entitled “Behavior and attenuation of microplastics in environmental compartments”:

Miranda, M. N., Silva, A. M. T., & Pereira, M. F. R. (2020). Microplastics in the environment: A DPSIR analysis with focus on the responses. *Science of The Total Environment*, 718, 134968. <https://doi.org/10.1016/j.scitotenv.2019.134968>

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Co-authors authorization regarding the full agreement of the inclusion of the manuscripts in the present thesis

M. Fernando R. Pereira, Full Professor at the Faculty of Engineering of the University of Porto (FEUP), Adrián M. T. Silva, Associate Professor at FEUP, Maria J. Sampaio, researcher at LSRE-LCM, and Pedro B. Tavares, Associated Professor at University of Trás-os-Montes and Alto Douro (UTAD), hereby authorize the PhD student Mariana Nogueira Miranda, from the FEUP Doctoral Program in Chemical and Biological Engineering, to include the following publication in her doctoral thesis entitled "Behavior and attenuation of microplastics in environmental compartments":

Miranda, M. N.; Sampaio, M. J.; Tavares, P. B.; Silva, A.M.T.; Pereira, M.F.R.. "Aging assessment of microplastics (LDPE, PET and uPVC) under urban environment stressors". *Science of The Total Environment* 796 (2021): 148914. <http://dx.doi.org/10.1016/j.scitotenv.2021.148914>.

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Co-authors authorization regarding the full agreement of the inclusion of the manuscripts in the present thesis

M. Fernando R. Pereira, Full Professor at the Faculty of Engineering of the University of Porto (FEUP), Adrián M. T. Silva, Associate Professor at FEUP, and Ana R. Lado Ribeiro, researcher at LSRE-LCM, hereby authorize the PhD student Mariana Nogueira Miranda, from the FEUP Doctoral Program in Chemical and Biological Engineering, to include the following publication in her doctoral thesis entitled "Behavior and attenuation of microplastics in environmental compartments":

Miranda, M. N.; Ribeiro, Ana Rita Lado; Silva, A.M.T.; Pereira, M.F.R.. "Can aged microplastics be transport vectors for organic micropollutants? - Sorption and phytotoxicity tests". *Science of The Total Environment* 850 (2022): 158073.
<http://dx.doi.org/10.1016/j.scitotenv.2022.158073>.

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Appendix B – EU Watch List

2015 EU Watch List substances, as published by Decision (EU) 2015/495:

Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC

Name of substance/group of substances	CAS number ⁽¹⁾	EU number ⁽²⁾	Indicative analytical method ⁽³⁾ ⁽⁴⁾ ⁽⁵⁾	Maximum acceptable method detection limit (ng/l)
17-Alpha-ethinylestradiol (EE2)	57-63-6	200-342-2	Large-volume SPE — LC-MS-MS	0,035
17-Beta-estradiol (E2), Estrone (E1)	50-28-2, 53-16-7	200-023-8	SPE — LC-MS-MS	0,4
Diclofenac	15307-86-5	239-348-5	SPE — LC-MS-MS	10
2,6-Ditert-butyl-4-methylphenol	128-37-0	204-881-4	SPE — GC-MS	3 160
2-Ethylhexyl 4-methoxycinnamate	5466-77-3	226-775-7	SPE — LC-MS-MS or GC-MS	6 000
Macrolide antibiotics ⁽⁶⁾			SPE — LC-MS-MS	90
Methiocarb	2032-65-7	217-991-2	SPE — LC-MS-MS or GC-MS	10
Neonicotinoids ⁽⁷⁾			SPE — LC-MS-MS	9
Oxadiazon	19666-30-9	243-215-7	LLE/SPE — GC-MS	88
Tri-allate	2303-17-5	218-962-7	LLE/SPE — GC-MS or LC-MS-MS	670

⁽¹⁾ Chemical Abstracts Service.

⁽²⁾ European Union number — not available for all substances.

⁽³⁾ To ensure comparability of results from different Member States, all substances shall be monitored in whole water samples.

⁽⁴⁾ Extraction methods:

LLE — liquid liquid extraction,

SPE — solid-phase extraction.

Analytical methods:

GC-MS — Gas chromatography-mass spectrometry,

LC-MS-MS — Liquid chromatography (tandem) triple quadrupole mass spectrometry.

⁽⁵⁾ For monitoring 2-Ethylhexyl 4-methoxycinnamate in suspended particulate matter (SPM) or in sediment (size < 63 µm), the following analytical method is indicated: SLE (solid liquid extraction) — GC-MS, with a maximum detection limit of 0,2 mg/kg.

⁽⁶⁾ Erythromycin (CAS number 114-07-8, EU number 204-040-1), Clarithromycin (CAS number 81103-11-9), Azithromycin (CAS number 83905-01-5, EU number 617-500-5).

⁽⁷⁾ Imidacloprid (CAS number 105827-78-9/138261-41-3, EU number 428-040-8), Thiacloprid (CAS number 111988-49-9), Thiamethoxam (CAS number 153719-23-4, EU number 428-650-4), Clothianidin (CAS number 210880-92-5, EU number 433-460-1), Acetamiprid (CAS number 135410-20-7/160430-64-8).

2018 update on the EU Watch List substances, as published by Decision (EU) 2018/840:

Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC

Name of substance/group of substances	CAS number ⁽¹⁾	EU number ⁽²⁾	Indicative analytical method ⁽³⁾ ⁽⁴⁾	Maximum acceptable method detection limit (ng/l)
17-Alpha-ethinylestradiol (EE2)	57-63-6	200-342-2	Large-volume SPE - LC-MS-MS	0,035
17-Beta-estradiol (E2), Estrone (E1)	50-28-2, 53-16-7	200-023-8	SPE - LC-MS-MS	0,4
Macrolide antibiotics ⁽⁵⁾			SPE - LC-MS-MS	19
Methiocarb	2032-65-7	217-991-2	SPE - LC-MS-MS or GC-MS	2
Neonicotinoids ⁽⁶⁾			SPE - LC-MS-MS	8,3
Metaflumizone	139968-49-3	604-167-6	LLE - LC-MS-MS or SPE - LC-MS-MS	65
Amoxicillin	26787-78-0	248-003-8	SPE - LC-MS-MS	78
Ciprofloxacin	85721-33-1	617-751-0	SPE - LC-MS-MS	89

⁽¹⁾ Chemical Abstracts Service

⁽²⁾ European Union number – not available for all substances

⁽³⁾ To ensure comparability of results from different Member States, all substances shall be monitored in whole water samples.

⁽⁴⁾ Extraction methods:

LLE — liquid liquid extraction

SPE — solid-phase extraction

Analytical methods:

GC-MS — Gas chromatography-mass spectrometry

LC-MS-MS — Liquid chromatography (tandem) triple quadrupole mass spectrometry

⁽⁵⁾ Erythromycin (CAS number 114-07-8, EU number 204-040-1), Clarithromycin (CAS number 81103-11-9), Azithromycin (CAS number 83905-01-5, EU number 617-500-5)

⁽⁶⁾ Imidacloprid (CAS number 105827-78-9/ 138261-41-3, EU number 428-040-8), Thiacloprid (CAS number 111988-49-9), Thiamethoxam (CAS number 153719-23-4, EU number 428-650-4), Clothianidin (CAS number 210880-92-5, EU number 433-460-1), Acetamiprid (CAS number 135410-20-7/160430-64-8)

2020 update on the EU Watch List substances, as published by Decision (EU) 2020/1161:

Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC

Name of substance/group of substances	CAS number ⁽¹⁾	EU number ⁽²⁾	Indicative analytical method ⁽³⁾	Maximum acceptable method detection limit (ng/l)
Metaflumizone	139968-49-3	604-167-6	LLE-LC-MS-MS or SPE-LC-MS-MS	65
Amoxicillin	26787-78-0	248-003-8	SPE-LC-MS-MS	78
Ciprofloxacin	85721-33-1	617-751-0	SPE-LC-MS-MS	89
Sulfamethoxazole ⁽⁴⁾	723-46-6	211-963-3	SPE-LC-MS-MS	100
Trimethoprim ⁽⁵⁾	738-70-5	212-006-2	SPE-LC-MS-MS	100
Venlafaxine and O-desmethylvenlafaxine ⁽⁶⁾	93413-69-5 93413-62-8	618-944-2 700-516-2	SPE-LC-MS-MS	6
<i>Azole compounds</i> ⁽⁷⁾			SPE-LC-MS-MS	
Clotrimazole	23593-75-1	245-764-8		20
Fluconazole	86386-73-4	627-806-0		250
Imazalil	35554-44-0	252-615-0		800
Ipconazole	125225-28-7	603-038-1		44
Metconazole	125116-23-6	603-031-3		29
Miconazole	22916-47-8	245-324-5		200
Penconazole	66246-88-6	266-275-6		1 700
Prochloraz	67747-09-5	266-994-5		161
Tebuconazole	107534-96-3	403-640-2		240
Tetraconazole	112281-77-3	407-760-6		1 900
Dimoxystrobin	149961-52-4	604-712-8	SPE-LC-MS-MS	32
Famoxadone	131807-57-3	603-520-1	SPE-LC-MS-MS	8,5

⁽¹⁾ Chemical Abstracts Service.

⁽²⁾ European Union number.

⁽³⁾ To ensure comparability of results from different Member States, all substances shall be monitored in whole water samples.

⁽⁴⁾ Extraction methods:

LLE – liquid liquid extraction

SPE – solid-phase extraction

Analytical methods:

LC-MS-MS – Liquid chromatography (tandem) triple quadrupole mass spectrometry.

⁽⁵⁾ Sulfamethoxazole and trimethoprim shall be analysed together in the same samples but reported as individual concentrations.

⁽⁶⁾ Venlafaxine and O-desmethylvenlafaxine shall be analysed together in the same samples but reported as individual concentrations.

⁽⁷⁾ The azole compounds shall be analysed together in the same samples but reported as individual concentrations.

2022 update on the EU Watch List substances, as published by Decision (EU) 2022/1307:

Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC

Name of substance/group of substances	CAS number ⁽¹⁾	EU number ⁽²⁾	Indicative analytical method ⁽³⁾ ⁽⁴⁾	Maximum acceptable method detection or quantification limit (ng/l)
Sulfamethoxazole ⁽⁵⁾	723-46-6	211-963-3	SPE-LC-MS-MS	100 ⁽¹¹⁾
Trimethoprim ⁽⁵⁾	738-70-5	212-006-2	SPE-LC-MS-MS	100 ⁽¹¹⁾
Venlafaxine and O-desmethylvenlafaxine ⁽⁶⁾	93413-69-5 93413-62-8	618-944-2 700-516-2	SPE-LC-MS-MS	6 ⁽¹¹⁾
<i>Azole compounds ⁽⁷⁾</i>			SPE-LC-MS-MS	
Clotrimazole	23593-75-1	245-764-8		20 ⁽¹¹⁾
Fluconazole	86386-73-4	627-806-0		250 ⁽¹¹⁾
Imazalil	35554-44-0	252-615-0		800 ⁽¹¹⁾
Ipconazole	125225-28-7	603-038-1		44 ⁽¹¹⁾
Metconazole	125116-23-6	603-031-3		29 ⁽¹¹⁾
Miconazole	22916-47-8	245-324-5		200 ⁽¹¹⁾
Penconazole	66246-88-6	266-275-6		1 700 ⁽¹¹⁾
Prochloraz	67747-09-5	266-994-5		161 ⁽¹¹⁾
Tebuconazole	107534-96-3	403-640-2		240 ⁽¹¹⁾
Tetraconazole	112281-77-3	407-760-6		1 900 ⁽¹¹⁾
Dimoxystrobin Azoxystrobin ⁽⁸⁾	149961-52-4 131860-33-8	604-712-8 603-524-3	SPE-LC-MS-MS	32 ⁽¹¹⁾ 200 ⁽¹²⁾
Famoxadone	131807-57-3	603-520-1	SPE-LC-MS-MS	8,5 ⁽¹¹⁾
Diflufenican	83164-33-4	617-446-2	SPE-LC-MS-MS	10 ⁽¹²⁾
Fipronil	120068-37-3	424-610-5	SPE-HPLC-MS-MS	0,77 ⁽¹²⁾
Clindamycin	18323-44-9	242-209-1	SPE-LC-MS-MS	44 ⁽¹²⁾
Ofloxacin	82419-36-1	680-263-1	SPE-UPLC-MS-MS	26 ⁽¹²⁾
Metformin and Guanyurea ⁽⁹⁾	657-24-9 141-83-3	211-517-8 205-504-6	SPE-LC-MS-MS	156 000 ⁽¹²⁾ 100 000 ⁽¹²⁾
<i>Sunscreen agents ⁽¹⁰⁾</i>				
Butyl methoxydibenzoyl-methane	70356-09-1	274-581-6	SPE-LC-MS-MS/ESI	3 000 ⁽¹²⁾
Octocrylene	6197-30-4	228-250-8		266 ⁽¹²⁾
Benzophenone-3	131-57-7	205-031-5		670 ⁽¹²⁾

(¹) Chemical Abstracts Service

(²) European Union number – not available for all substances

(³) To ensure comparability of results from different Member States, all substances shall be monitored in whole water samples.

(⁴)

Extraction methods:

SPE – solid-phase extraction

Analytical methods:

HPLC-MS-MS – High-performance liquid chromatography (tandem) triple quadrupole mass spectrometry

LC-MS-MS – Liquid chromatography (tandem) triple quadrupole mass spectrometry

LC-MS-MS/ESI – Liquid chromatography (tandem) triple quadrupole mass spectrometry with positive electrospray ionisation

UPLC-MS-MS – Ultra-performance liquid chromatography (tandem) triple quadrupole mass spectrometry

(¹) Sulfamethoxazole and trimethoprim, although not grouped, shall be analysed together in the same samples but reported as individual concentrations.

(²) Venlafaxine and O-desmethylvenlafaxine shall be analysed together in the same samples but reported as individual concentrations.

(³) The azole compounds shall be analysed together in the same samples but reported as individual concentrations.

(⁴) Dimoxystrobin and azoxystrobin shall be analysed together in the same samples but reported as individual concentrations.

(⁵) Metformin and guanylurea shall be analysed together in the same samples but reported as individual concentrations.

(⁶) The sunscreen agents shall be analysed together in the same samples but reported as individual concentrations.

(¹) Maximum acceptable detection limit

(²) Maximum acceptable quantification limit

Appendix C – ATR-FTIR spectra

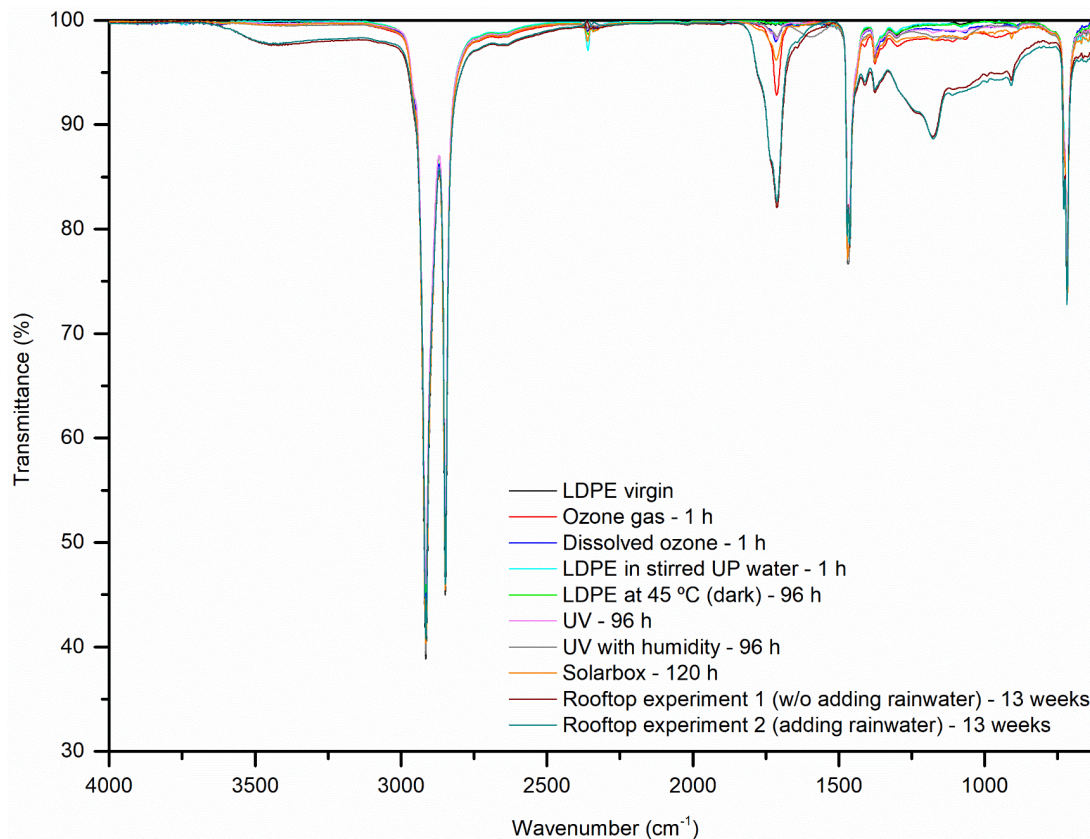


Fig. A1. ATR-FTIR complete set of spectra for LDPE.

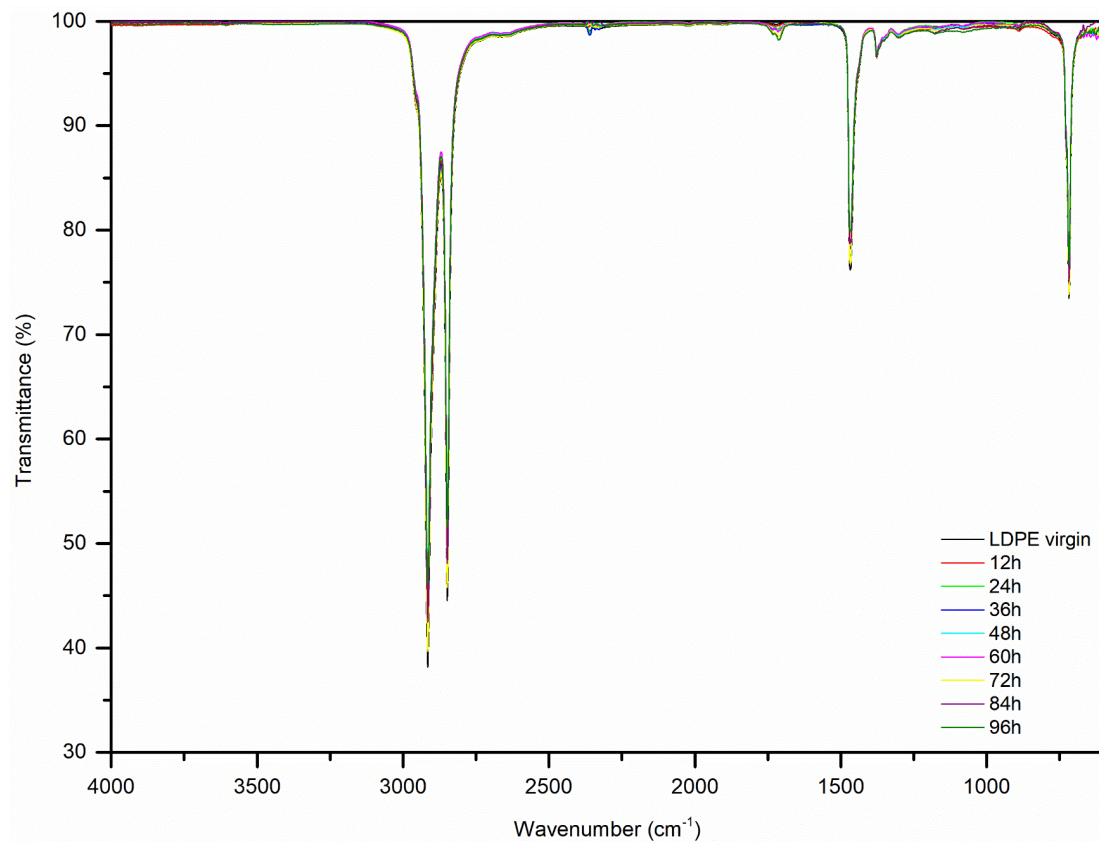


Fig. A2. ATR-FTIR spectra for LDPE: UV-C.

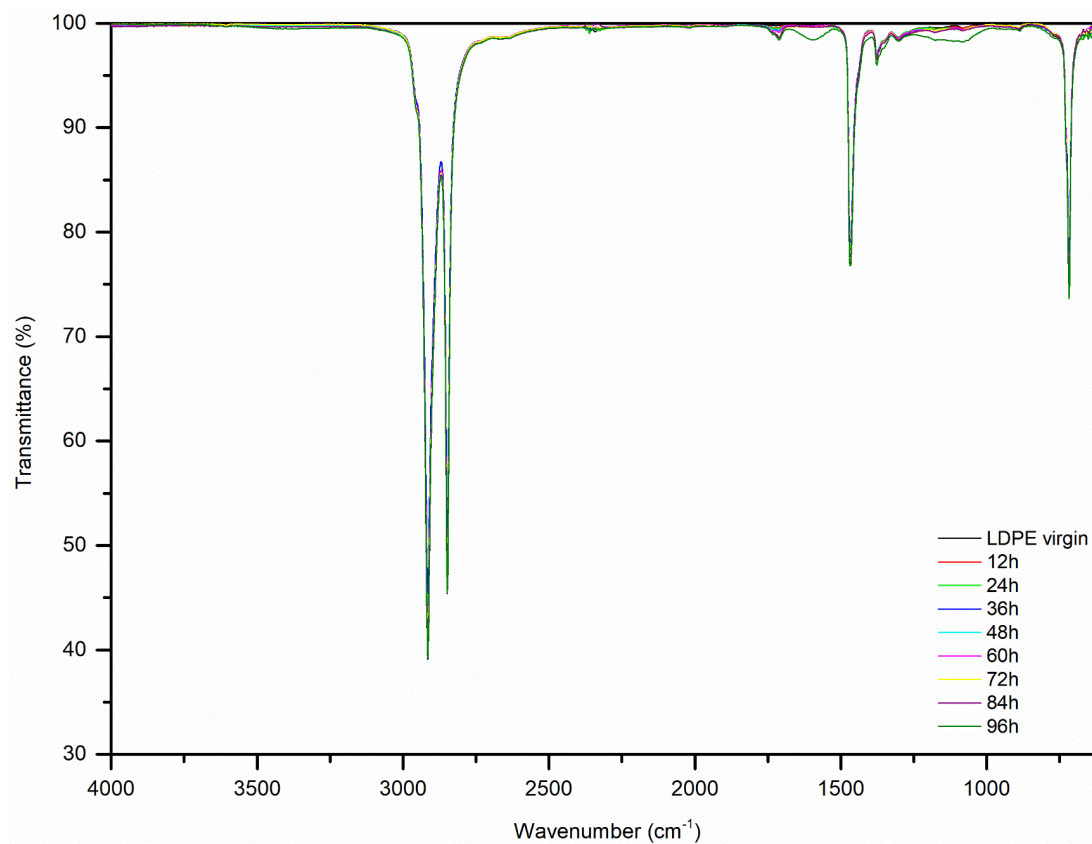


Fig. A3. ATR-FTIR spectra for LDPE: UV-C with humidity.

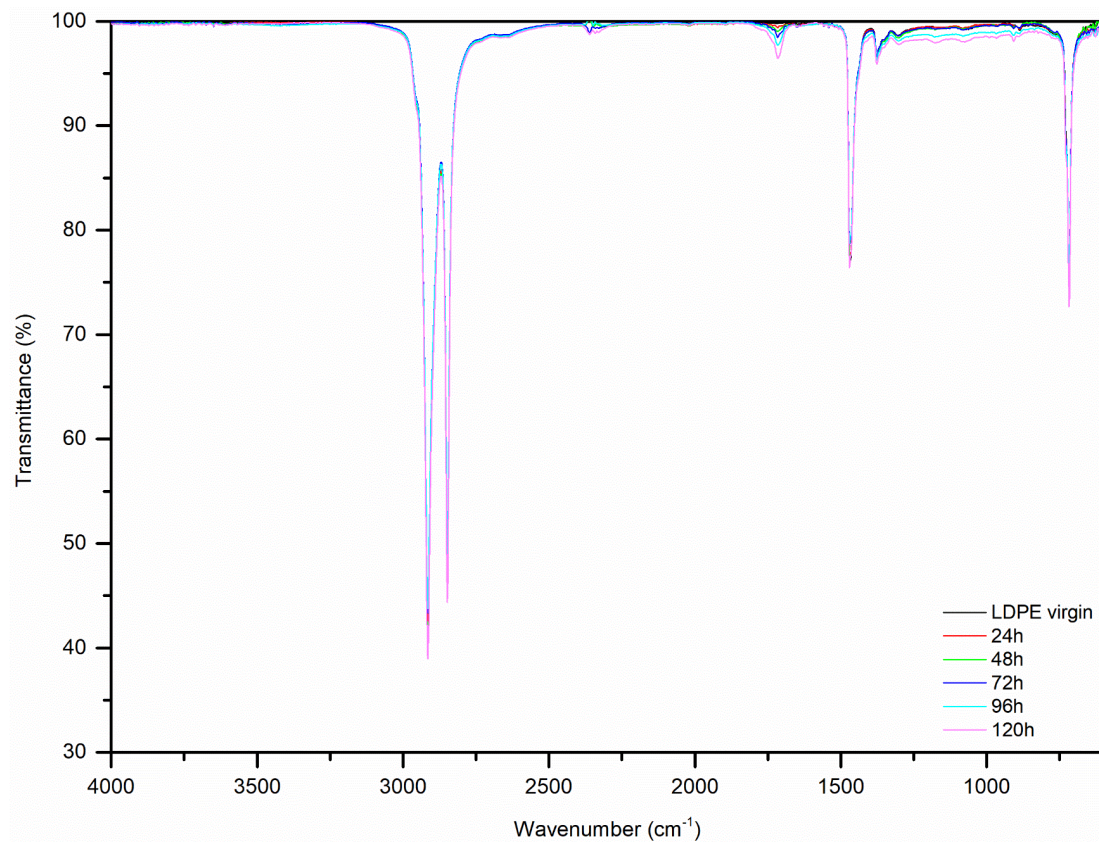


Fig. A4. ATR-FTIR spectra for LDPE: Solarbox.

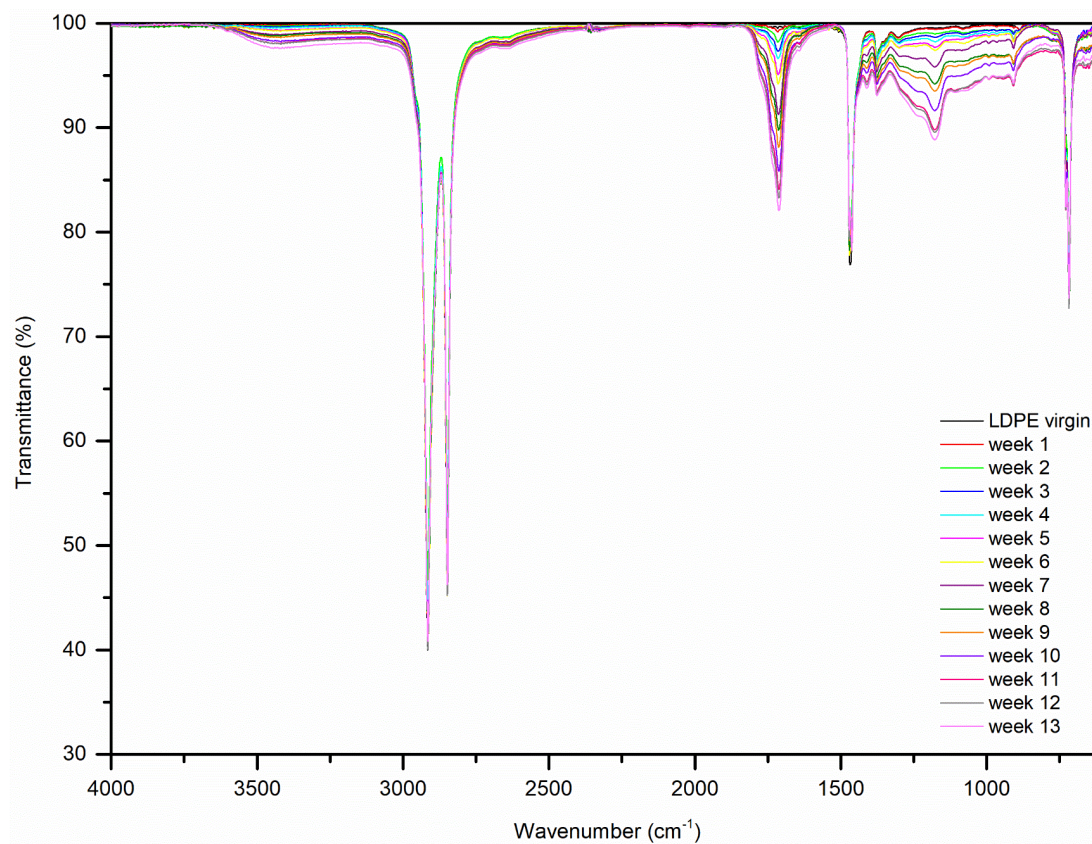


Fig. A5. ATR-FTIR spectra for LDPE: Rooftop experiment 1.

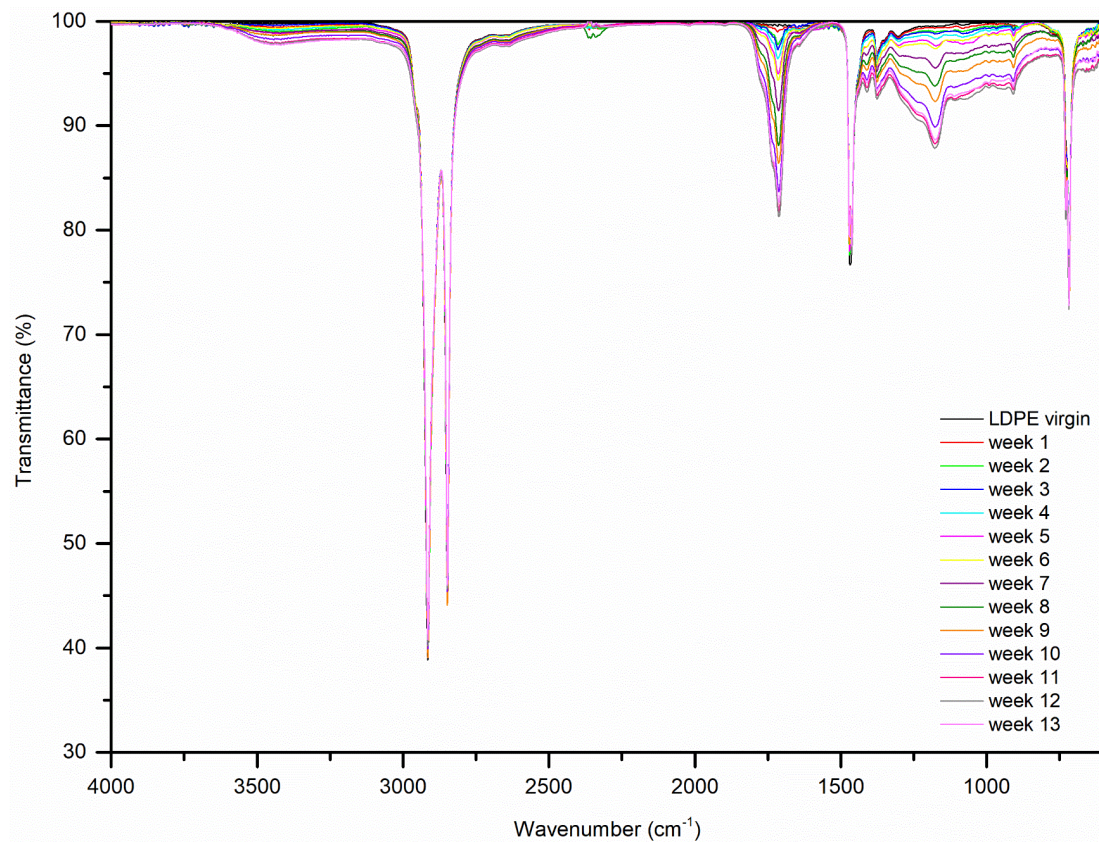


Fig. A6. ATR-FTIR spectra for LDPE: Rooftop experiment 2 (with rainwater).

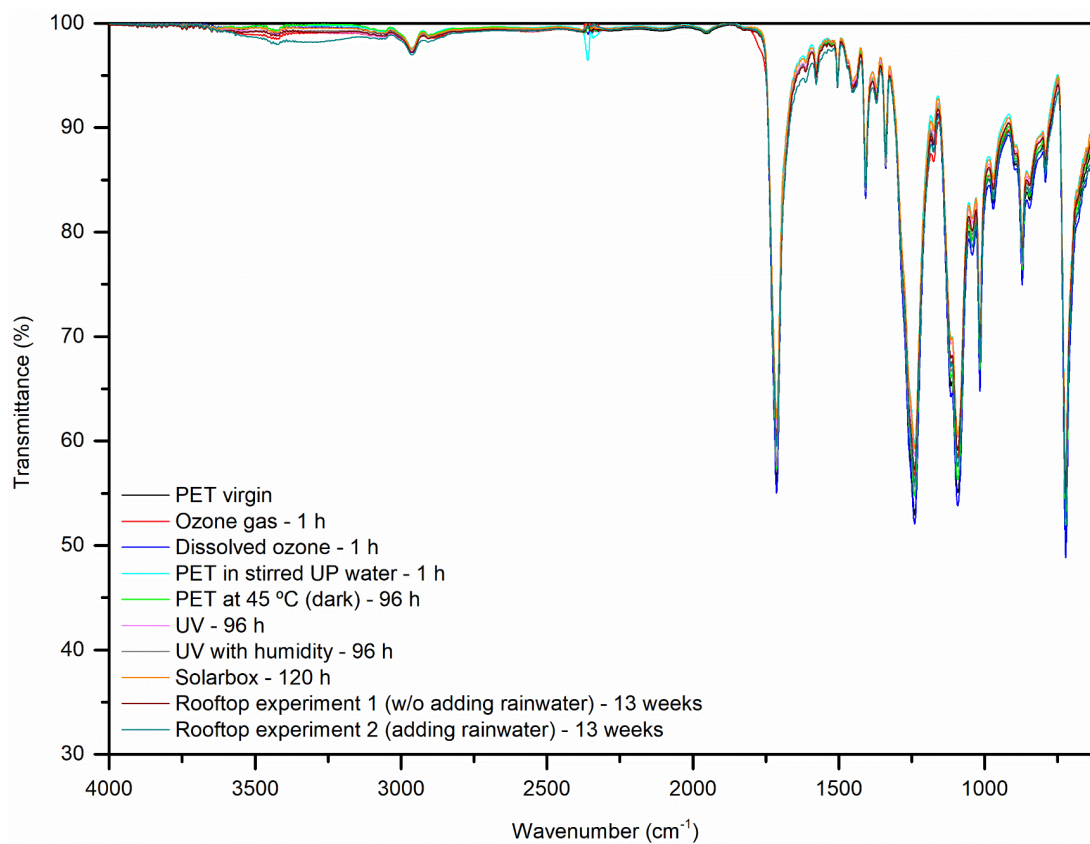


Fig. A7. ATR-FTIR complete set of spectra for PET.

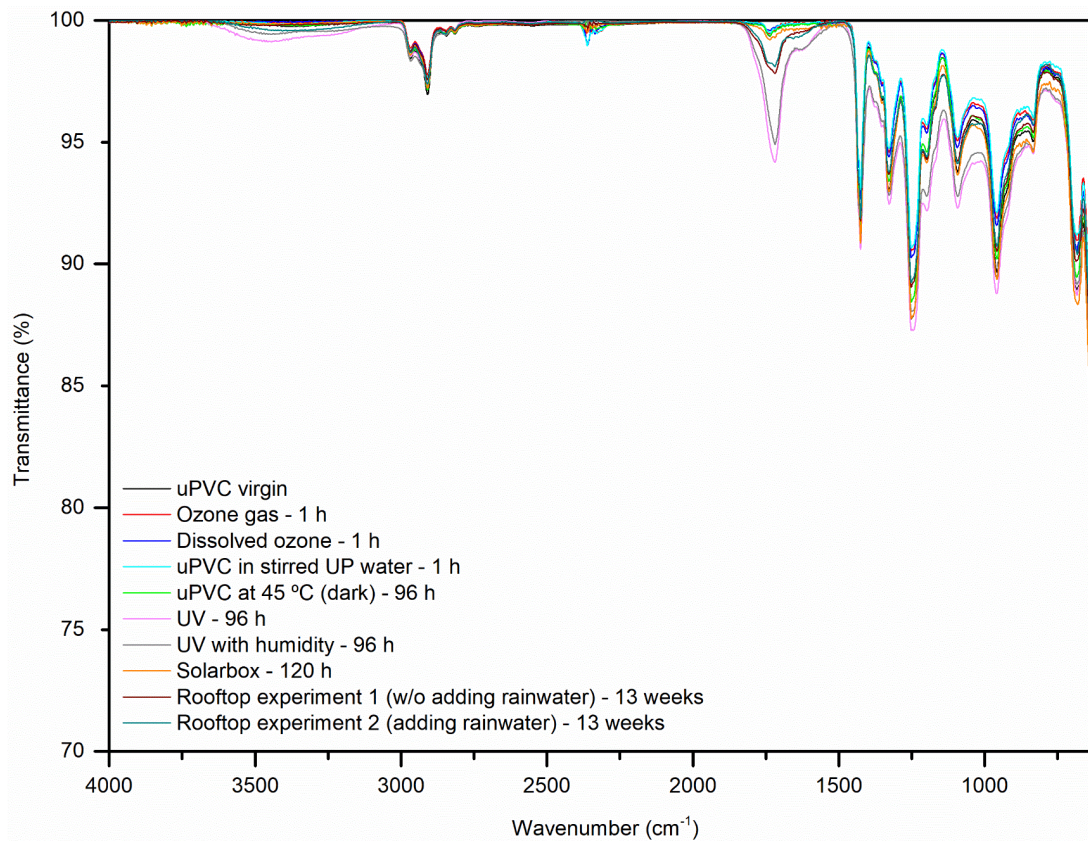


Fig. A8. ATR-FTIR complete set of spectra for uPVC.

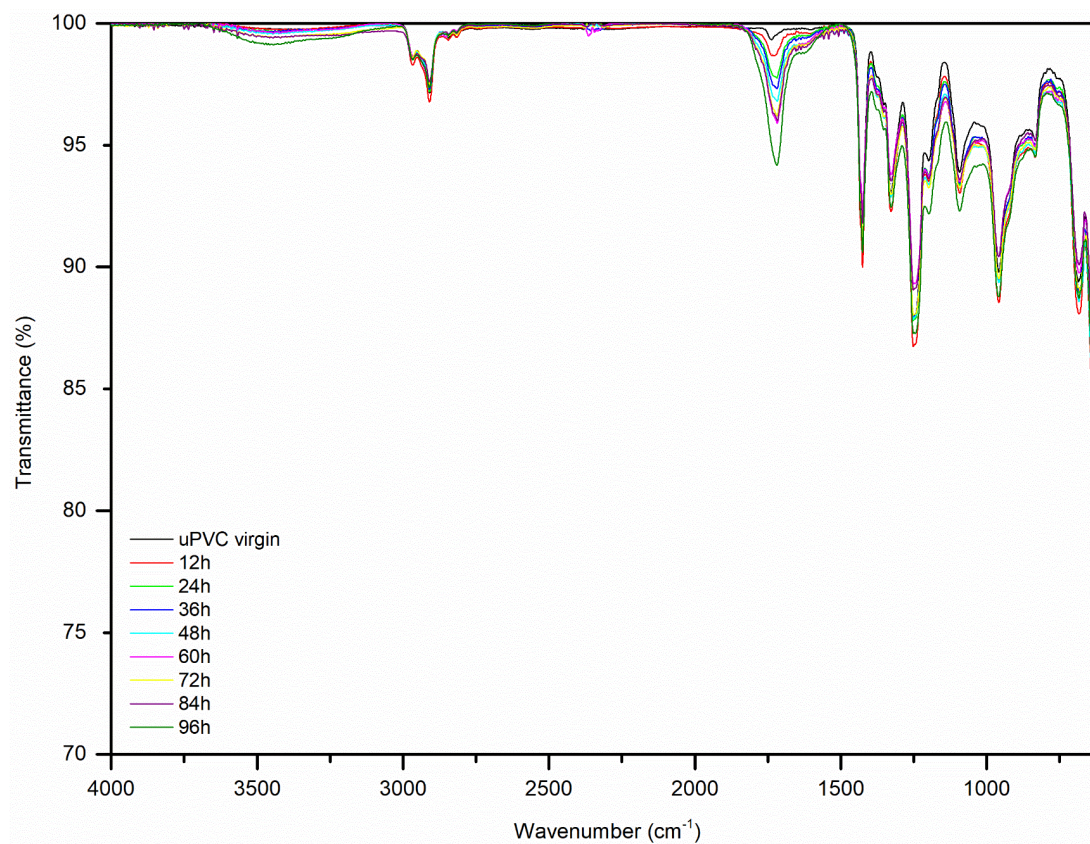


Fig. A9. ATR-FTIR spectra for uPVC: UV-C.

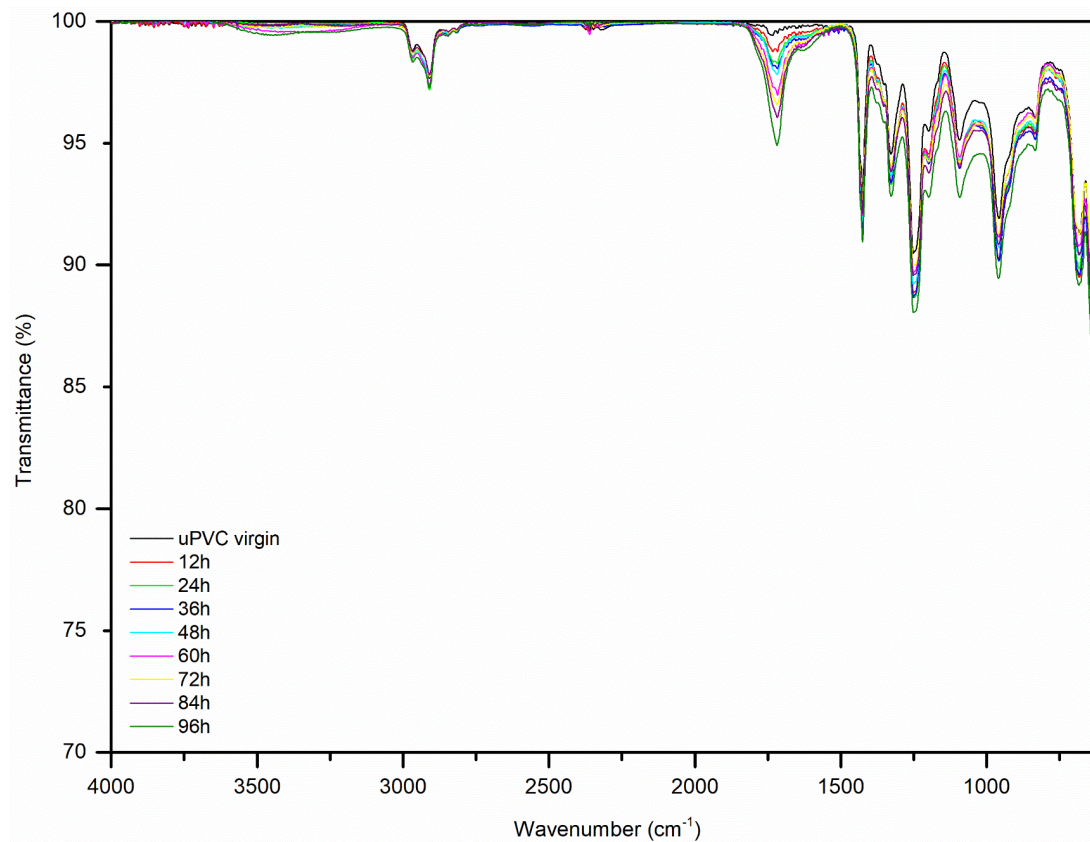


Fig. A10. ATR-FTIR spectra for uPVC: UV-C with humidity.

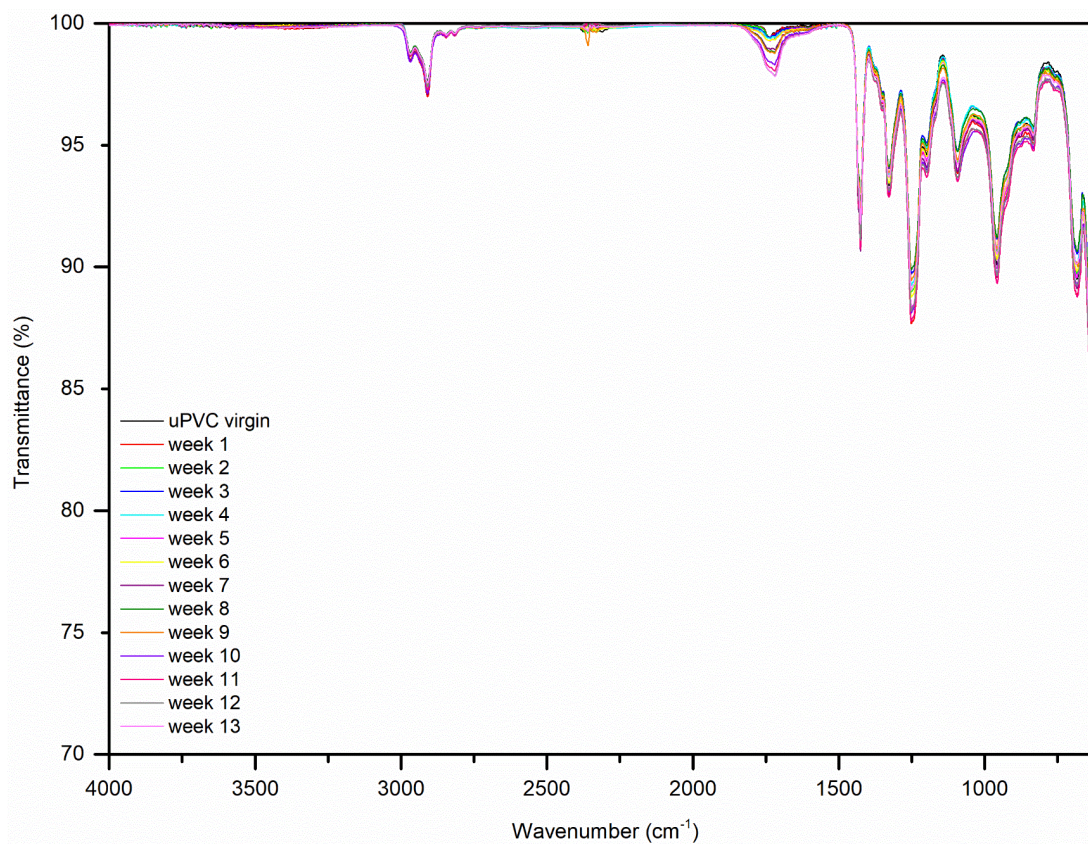


Fig. A11.ATR-FTIR spectra for uPVC: Rooftop experiment 1.

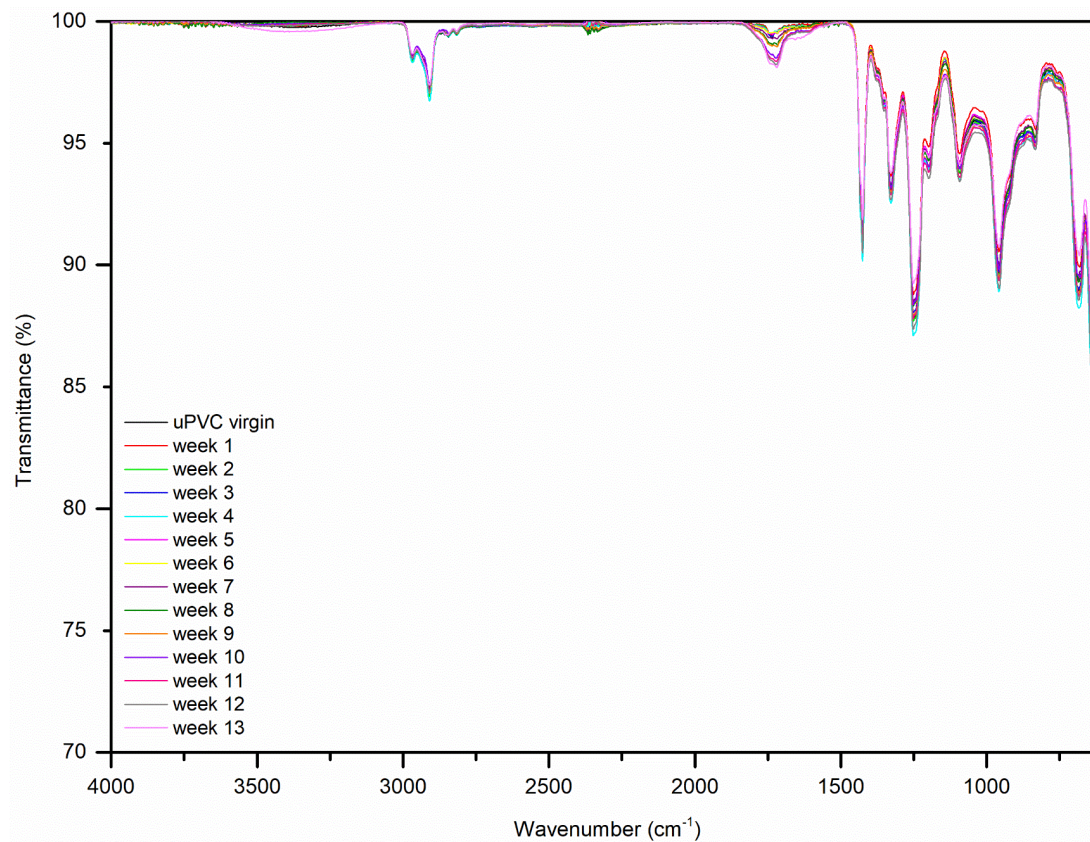


Fig. A12. ATR-FTIR spectra for uPVC: Rooftop experiment 2 (with rainwater).

Appendix D – SEM images

SEM images: LDPE

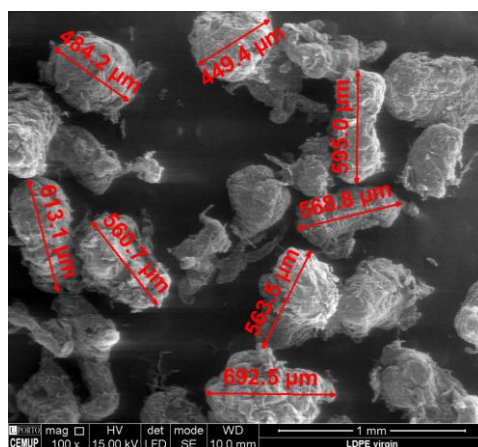
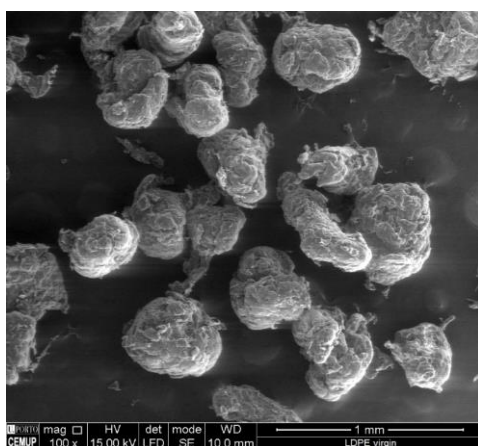
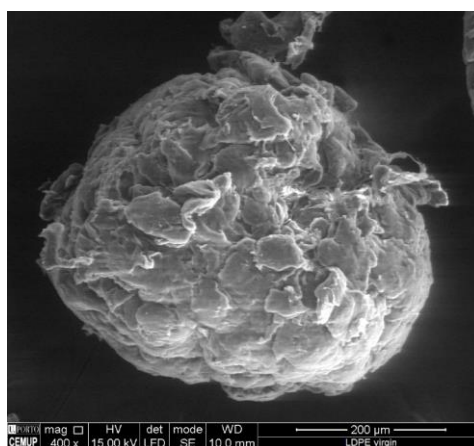


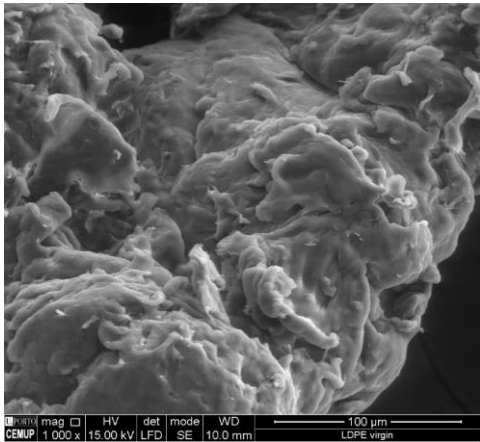
Fig. A13. SEM image of virgin LDPE.



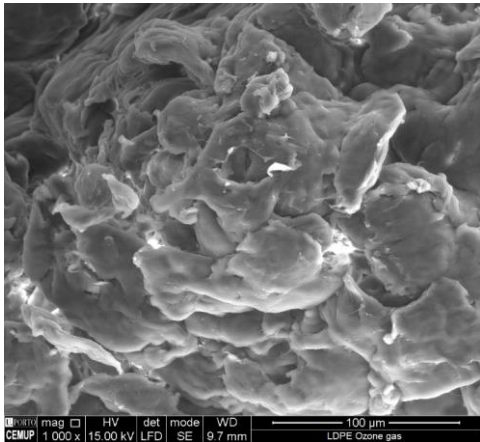
LDPE virgin



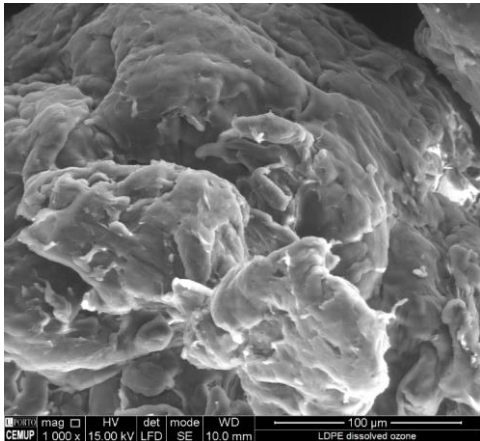
LDPE virgin



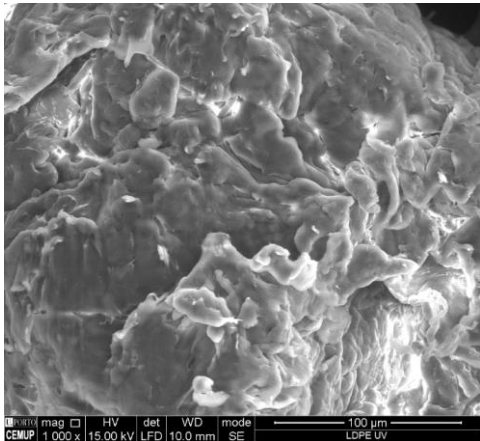
LDPE virgin



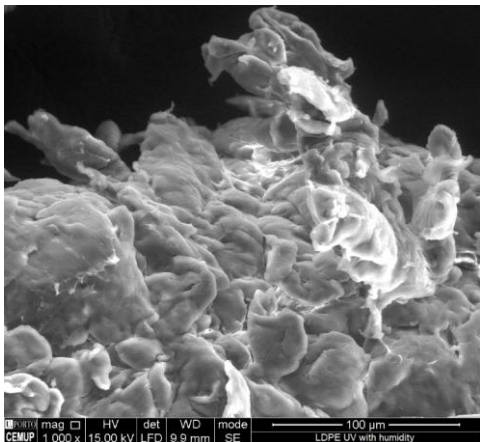
LDPE ozone gas (1 h)



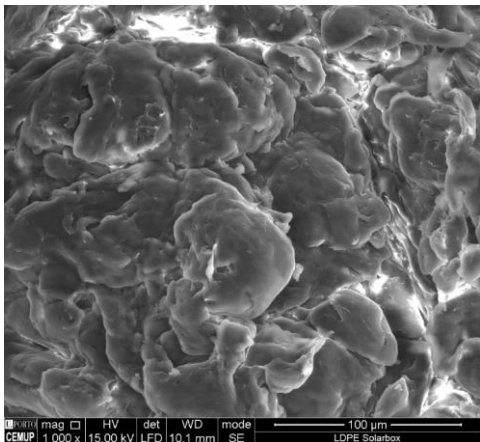
LDPE dissolved ozone (1 h)



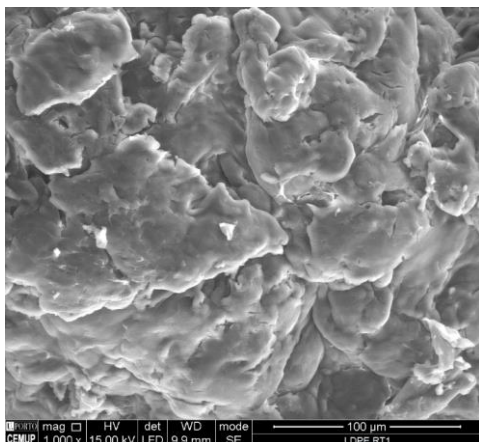
LDPE UV-C (96 h)



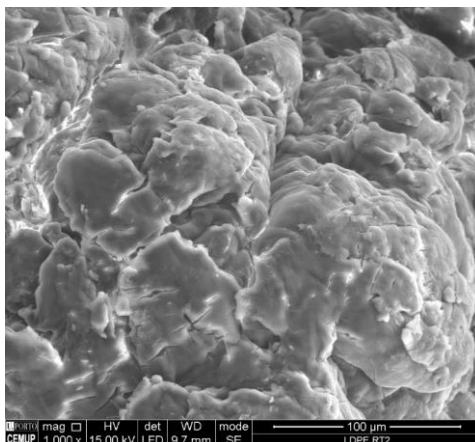
LDPE UV-C with humidity (96 h)



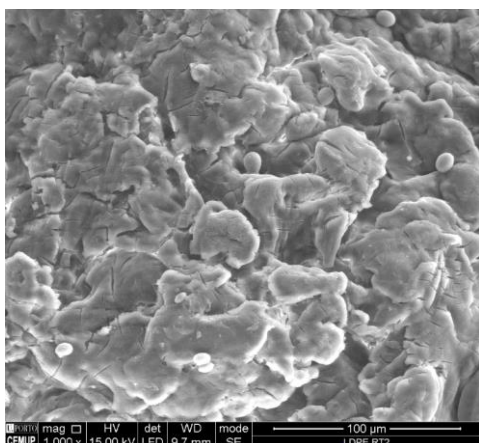
LDPE Solarbox (120 h)



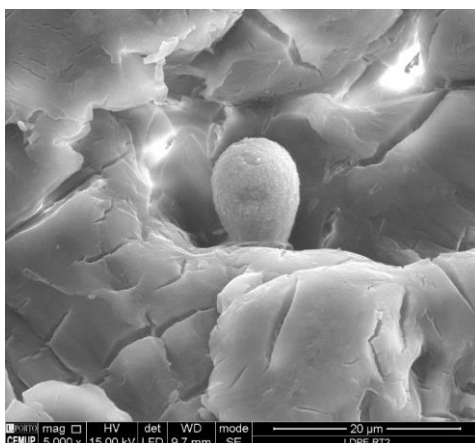
LDPE RT1 (13 weeks)



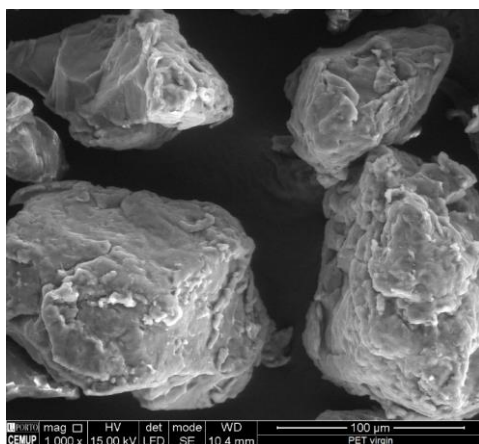
LDPE RT2 (13 weeks)



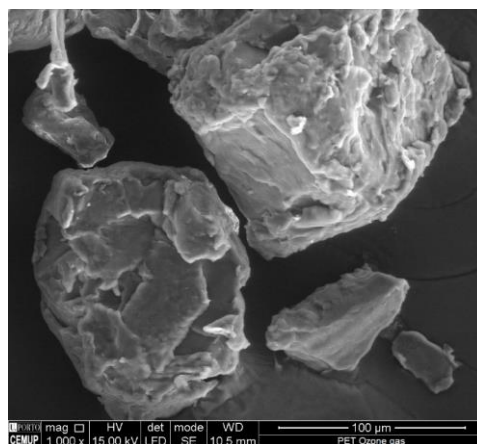
LDPE RT2 (13 weeks)



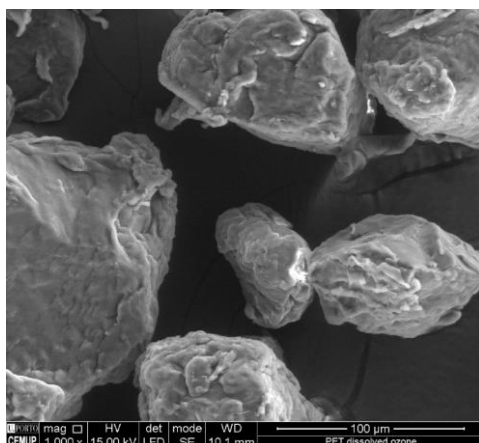
LDPE RT2 (detail) (13 weeks)



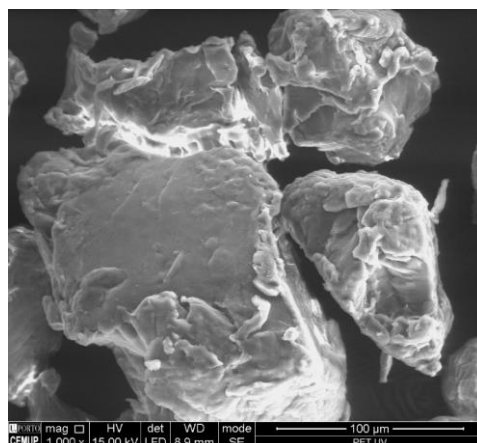
PET virgin



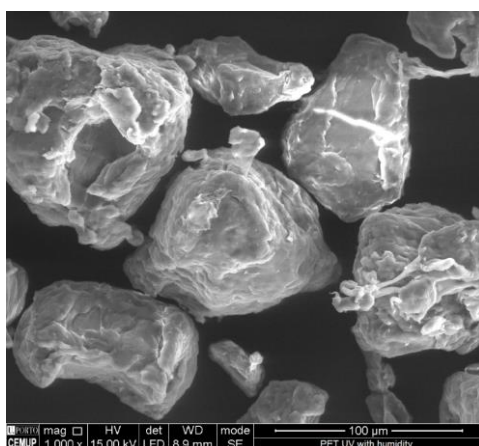
PET ozone gas (1 h)



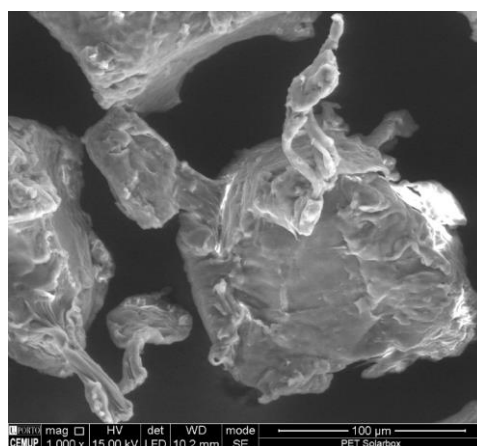
PET dissolved ozone (1h)



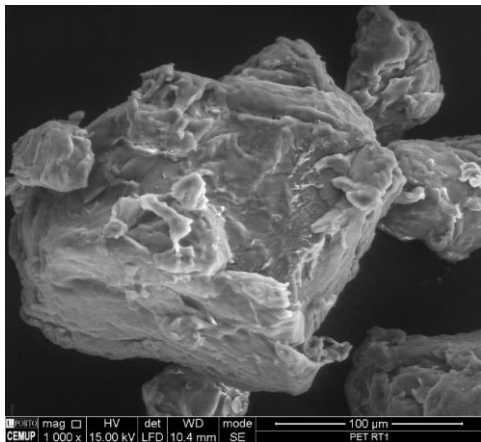
PET UV-C (96 h)



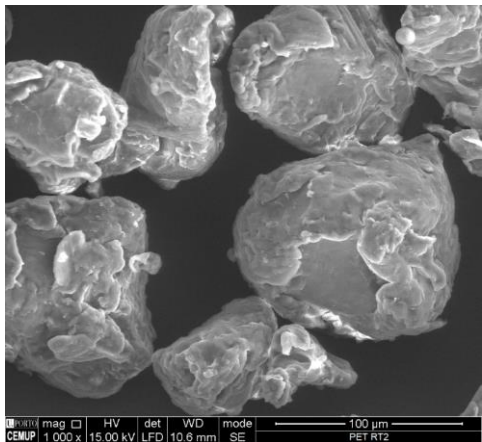
PET UV-C with humidity (96 h)



PET Solarbox (120 h)



PET RT1 (13 weeks)



PET RT2 (13 weeks)

SEM images: uPVC

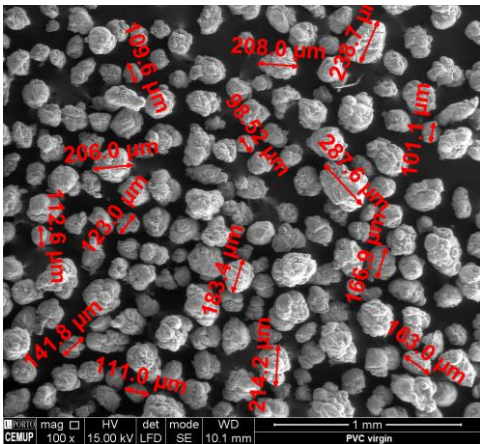
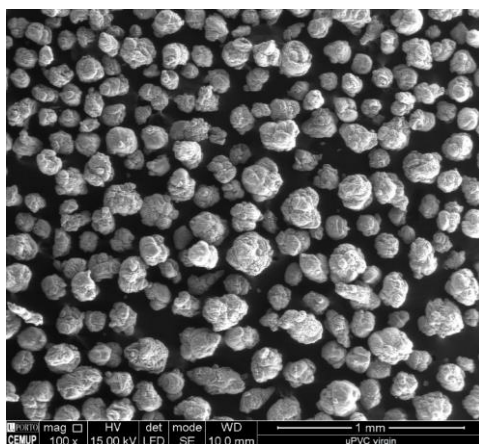
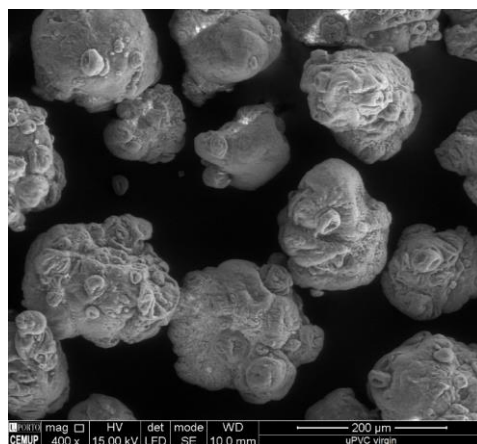


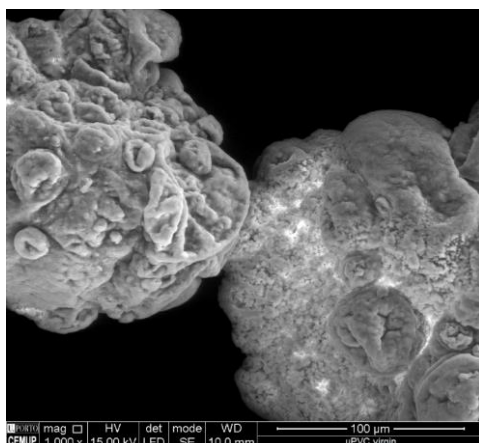
Fig. A15. SEM image of virgin uPVC.



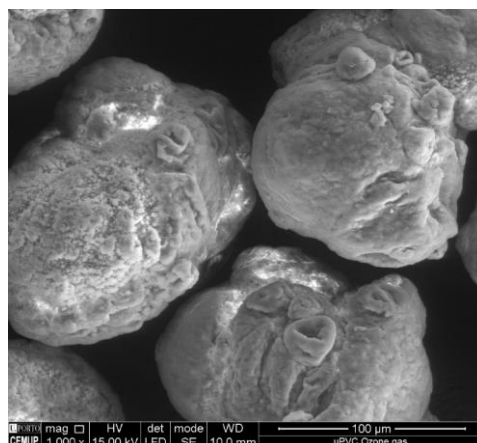
uPVC virgin



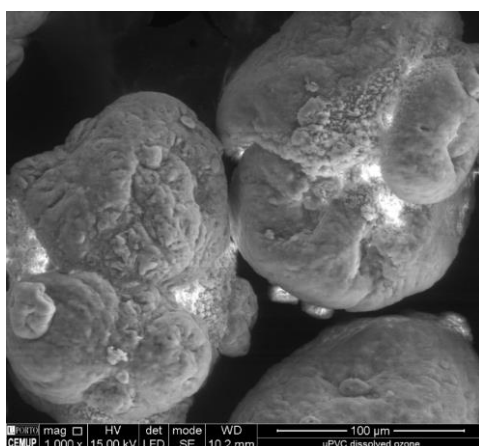
uPVC virgin



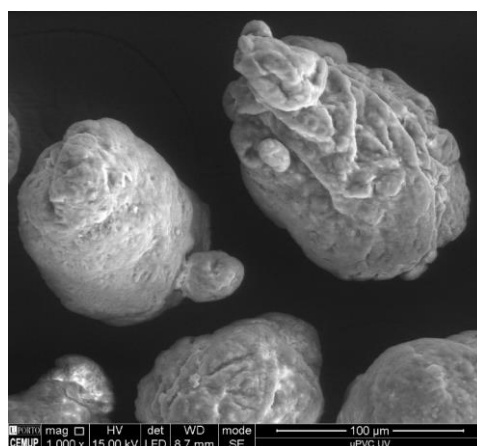
uPVC virgin



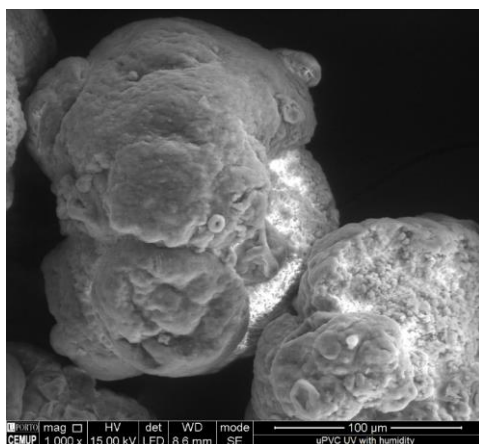
uPVC Ozone gas (1 h)



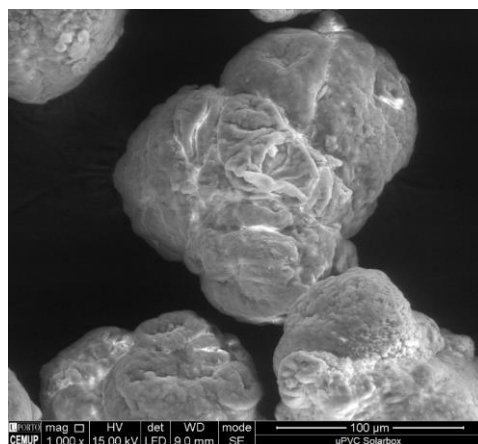
uPVC dissolved ozone (1 h)



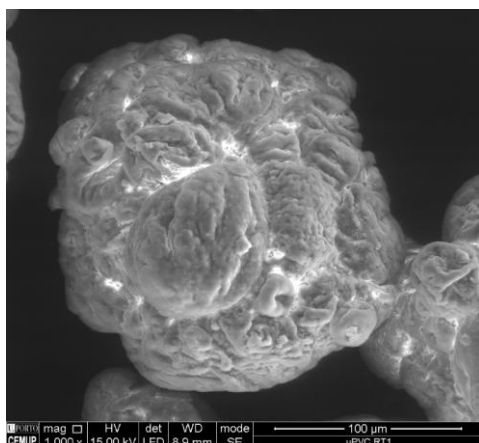
uPVC UV-C (96 h)



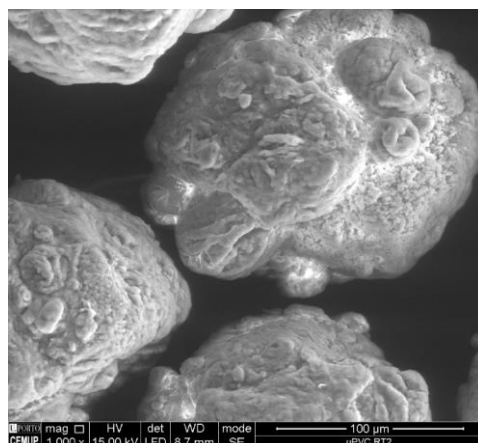
uPVC UV-C with humidity (96 h)



uPVC Solarbox (120 h)



uPVC RT1 (13 weeks)



uPVC RT2 (13 weeks)

Appendix E – XRD diffractograms

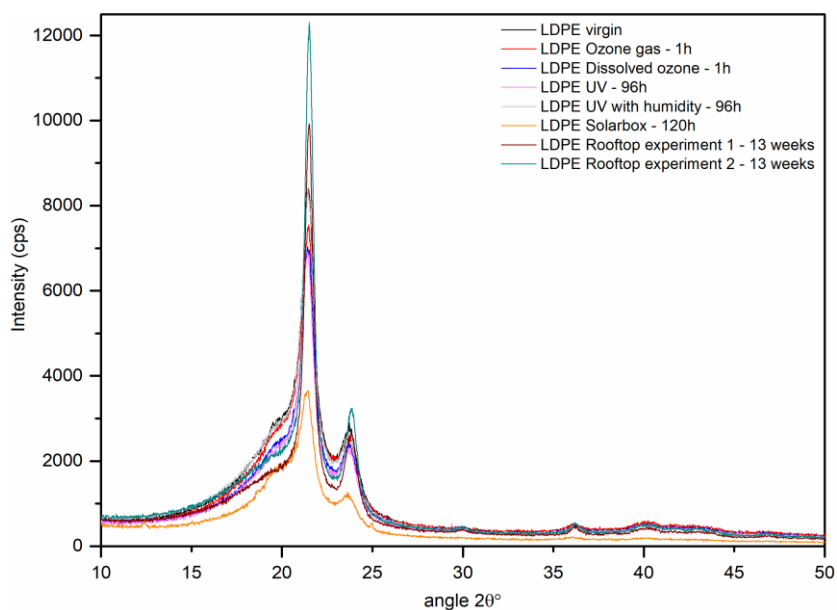


Fig. A16. XRD complete set of diffractograms for LDPE.

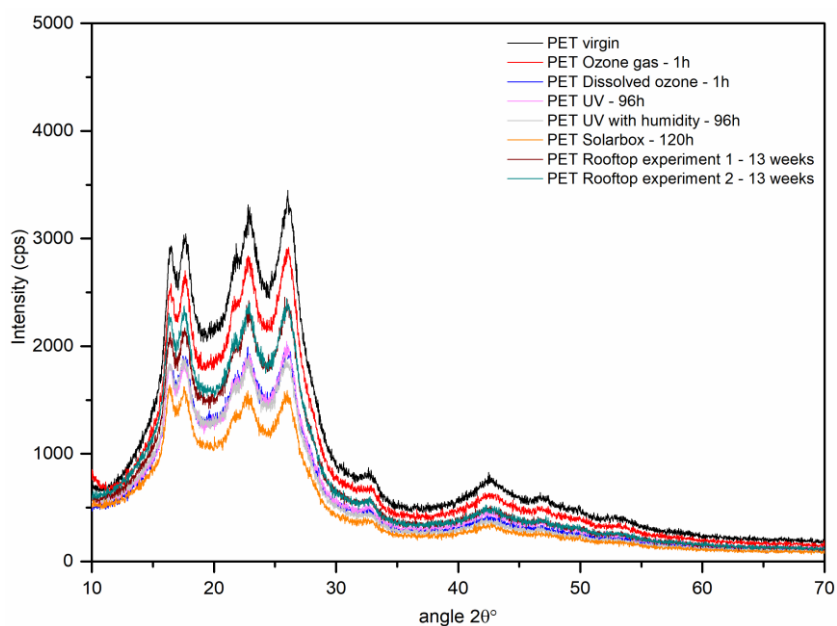


Fig. A17. XRD complete set of diffractograms for PET.

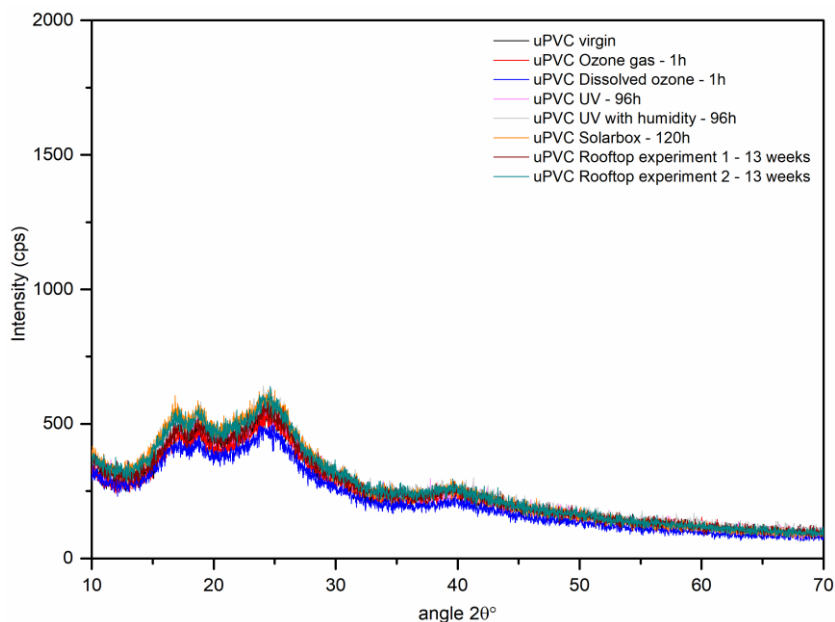
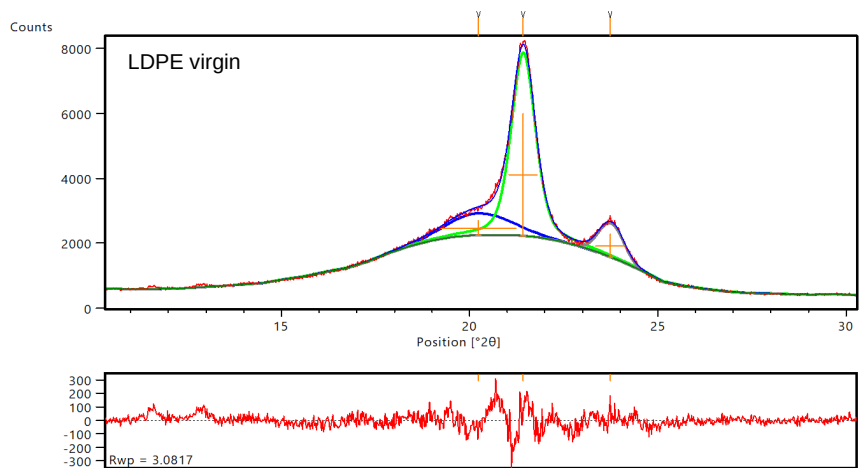
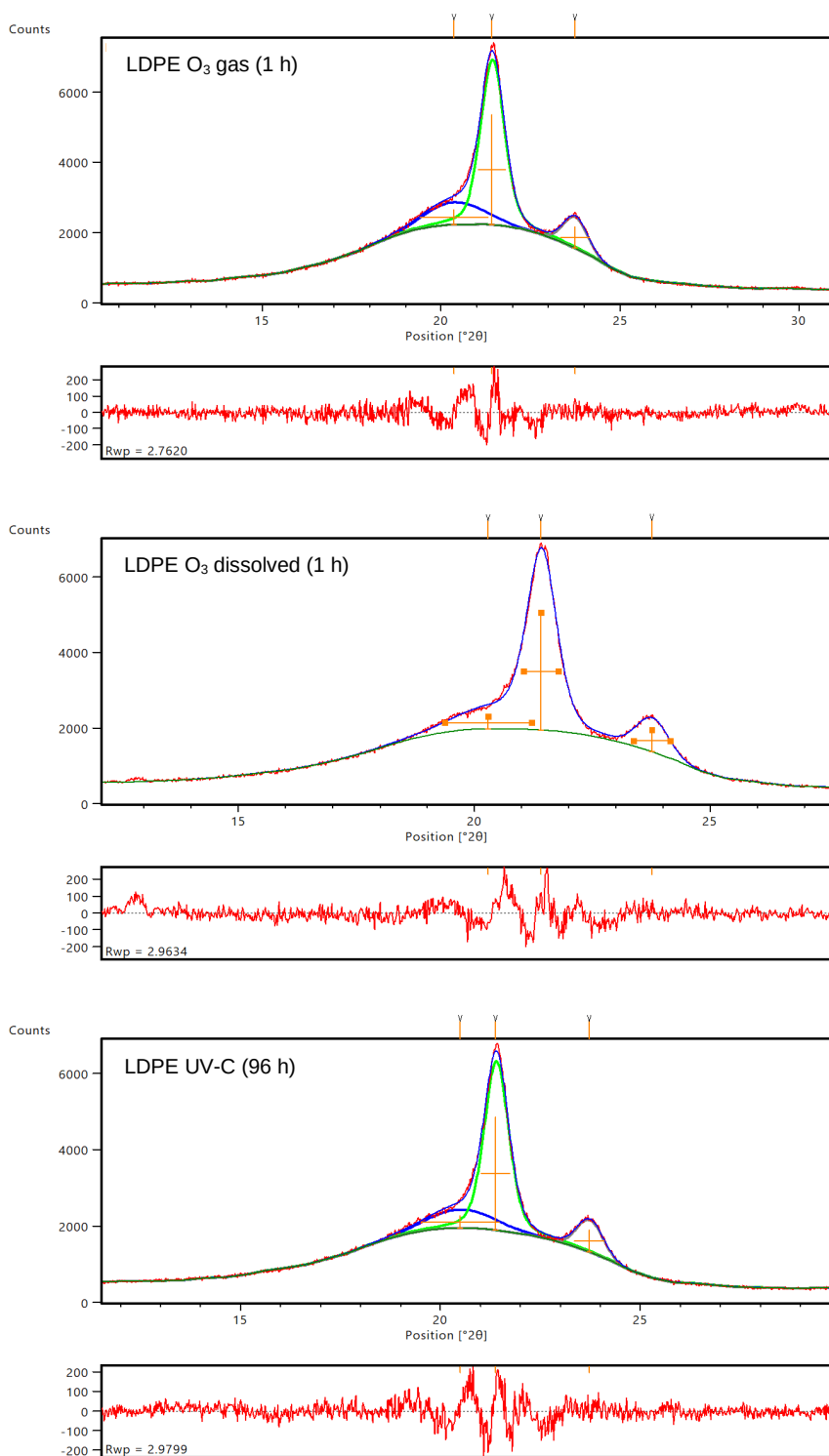


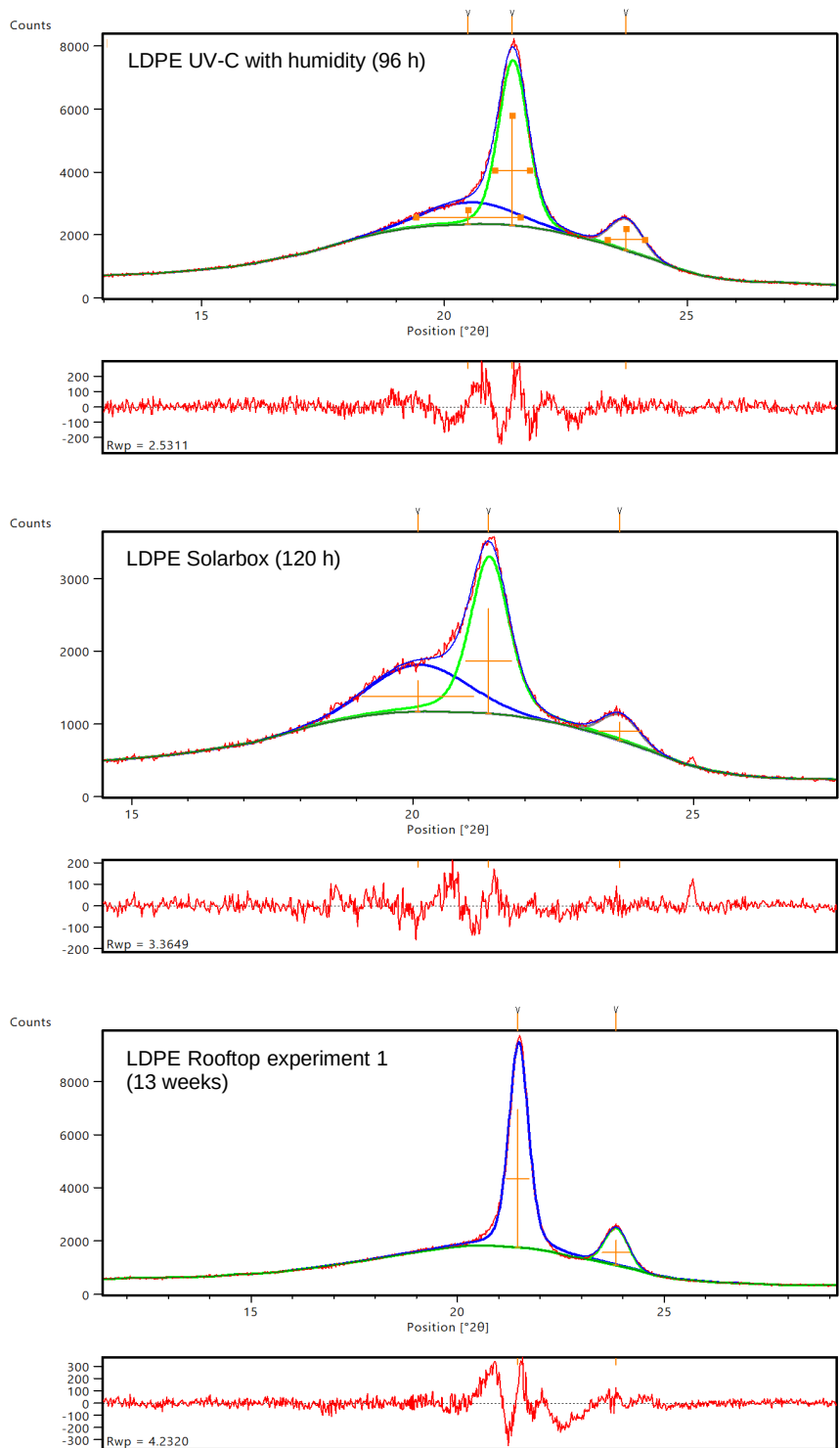
Fig. A18. XRD complete set of diffractograms for uPVC.

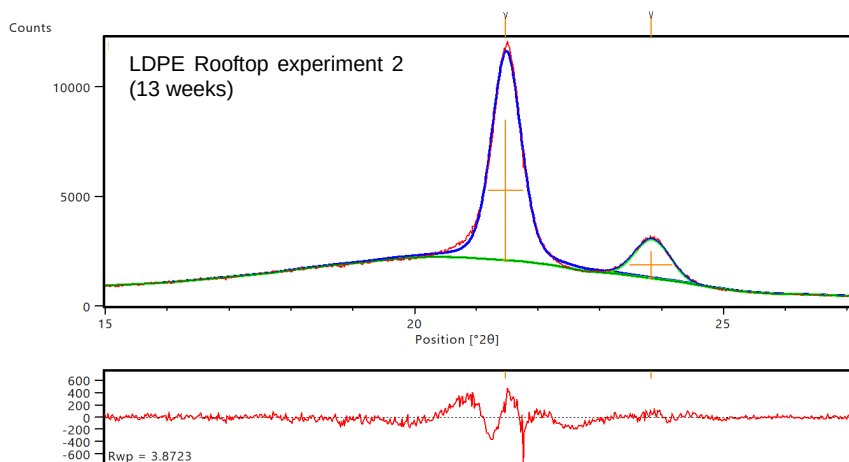
LDPE crystalline peaks

Baseline: Bending factor = 39, Granularity = 19



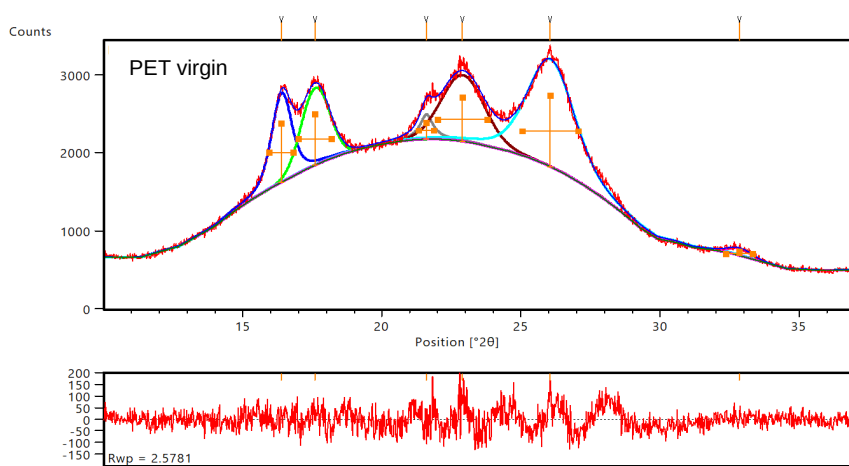


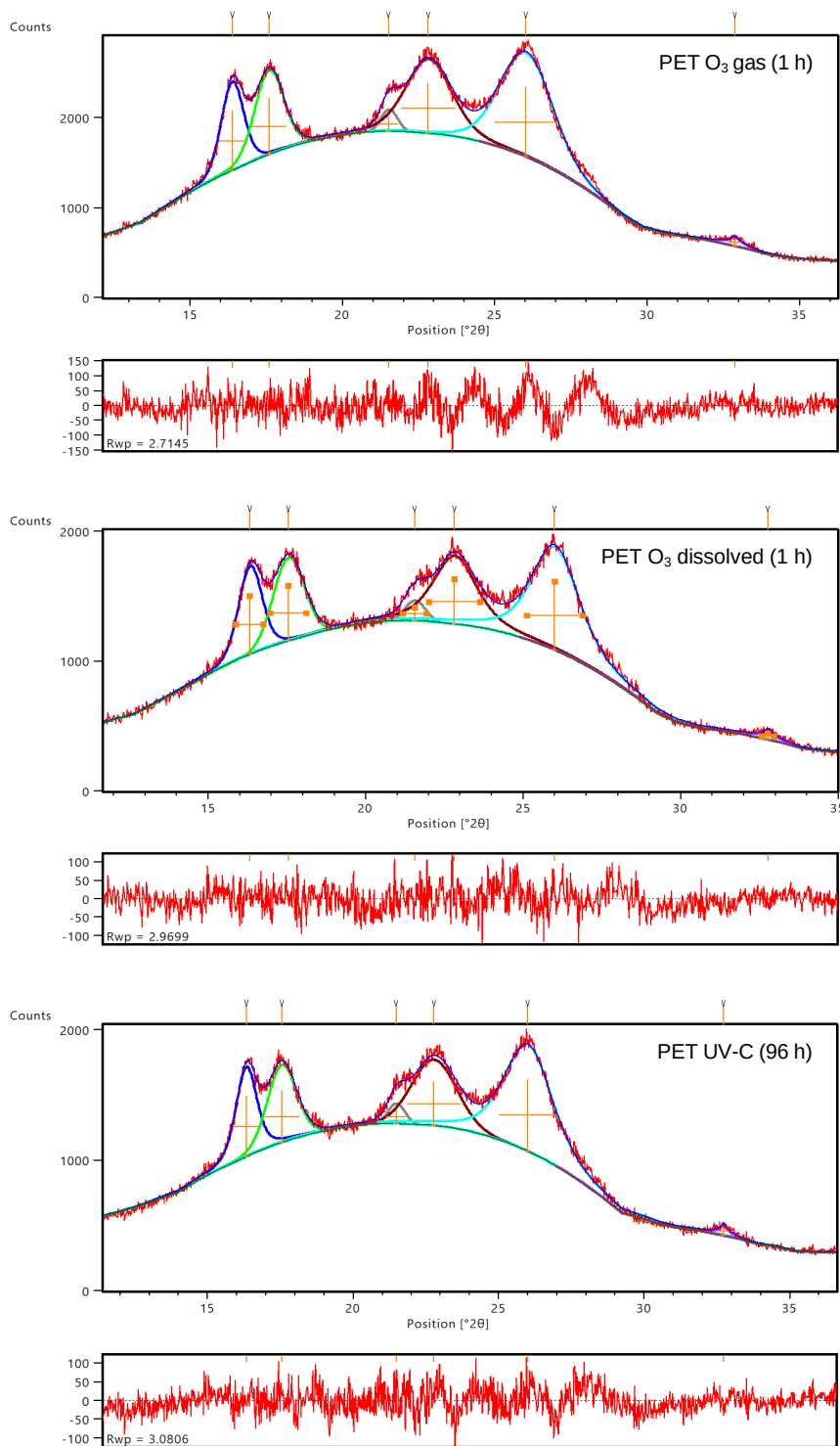


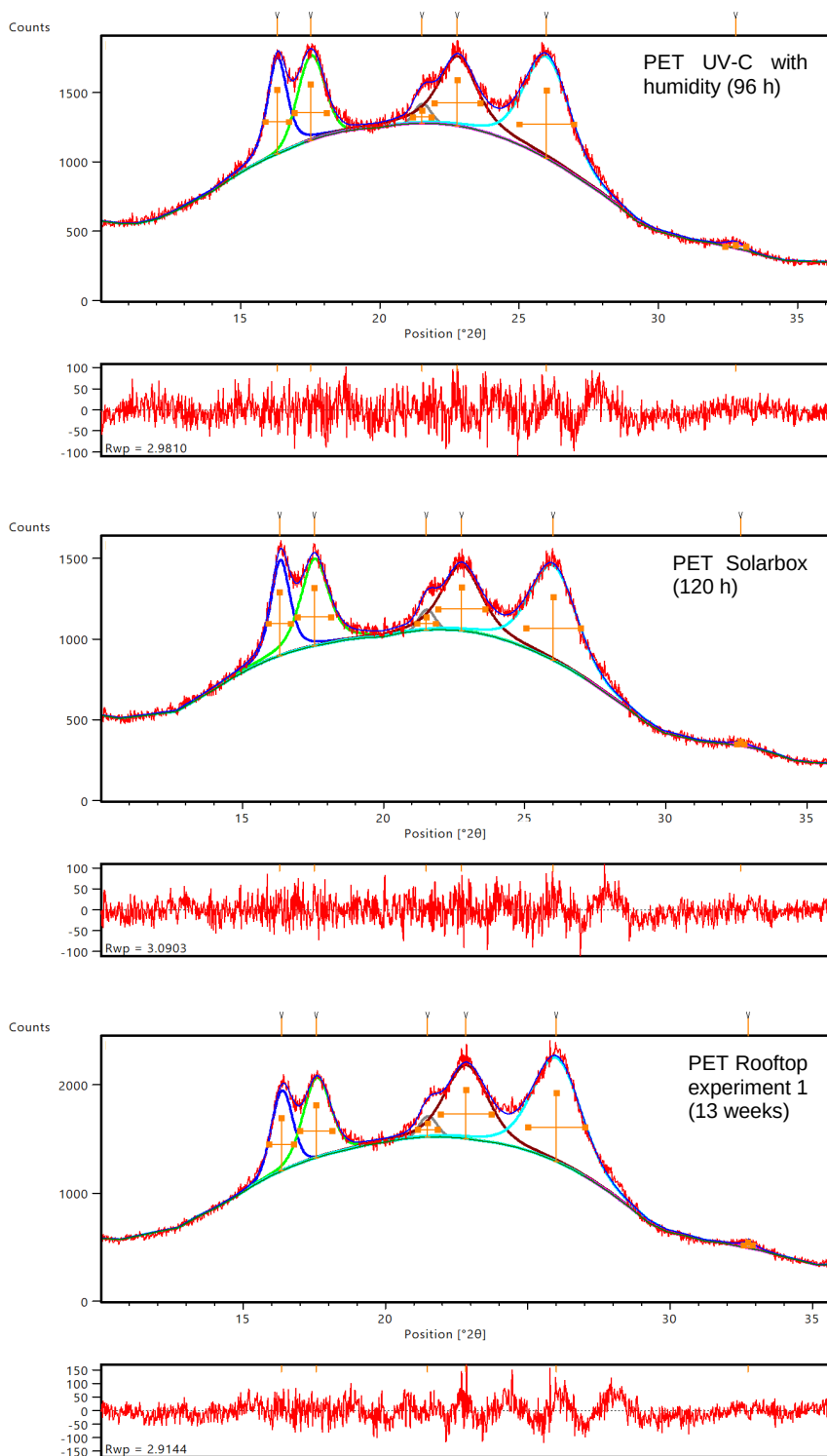


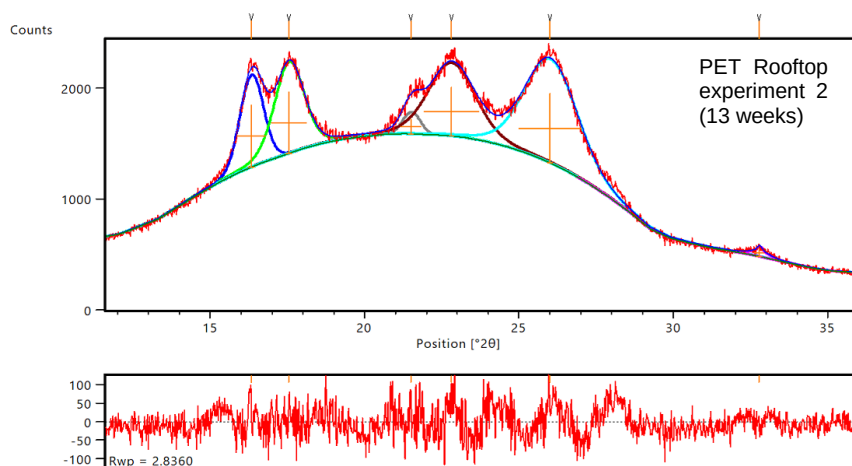
PET crystalline peaks

Baseline: Bending factor = 35, Granularity = 25



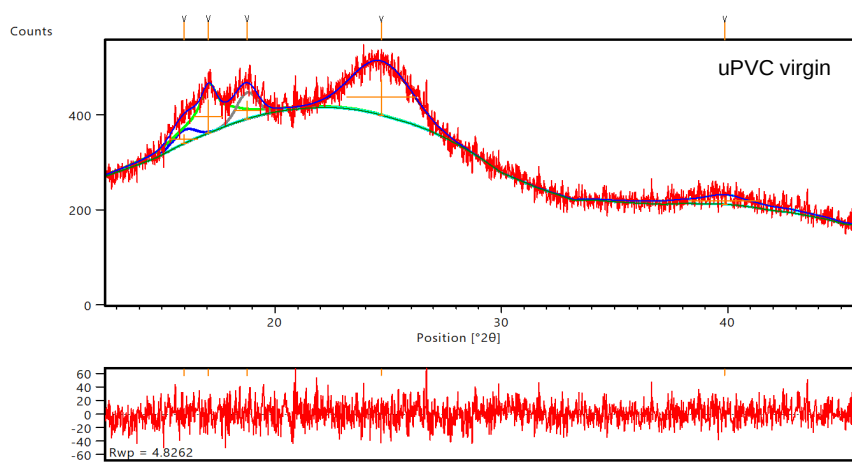


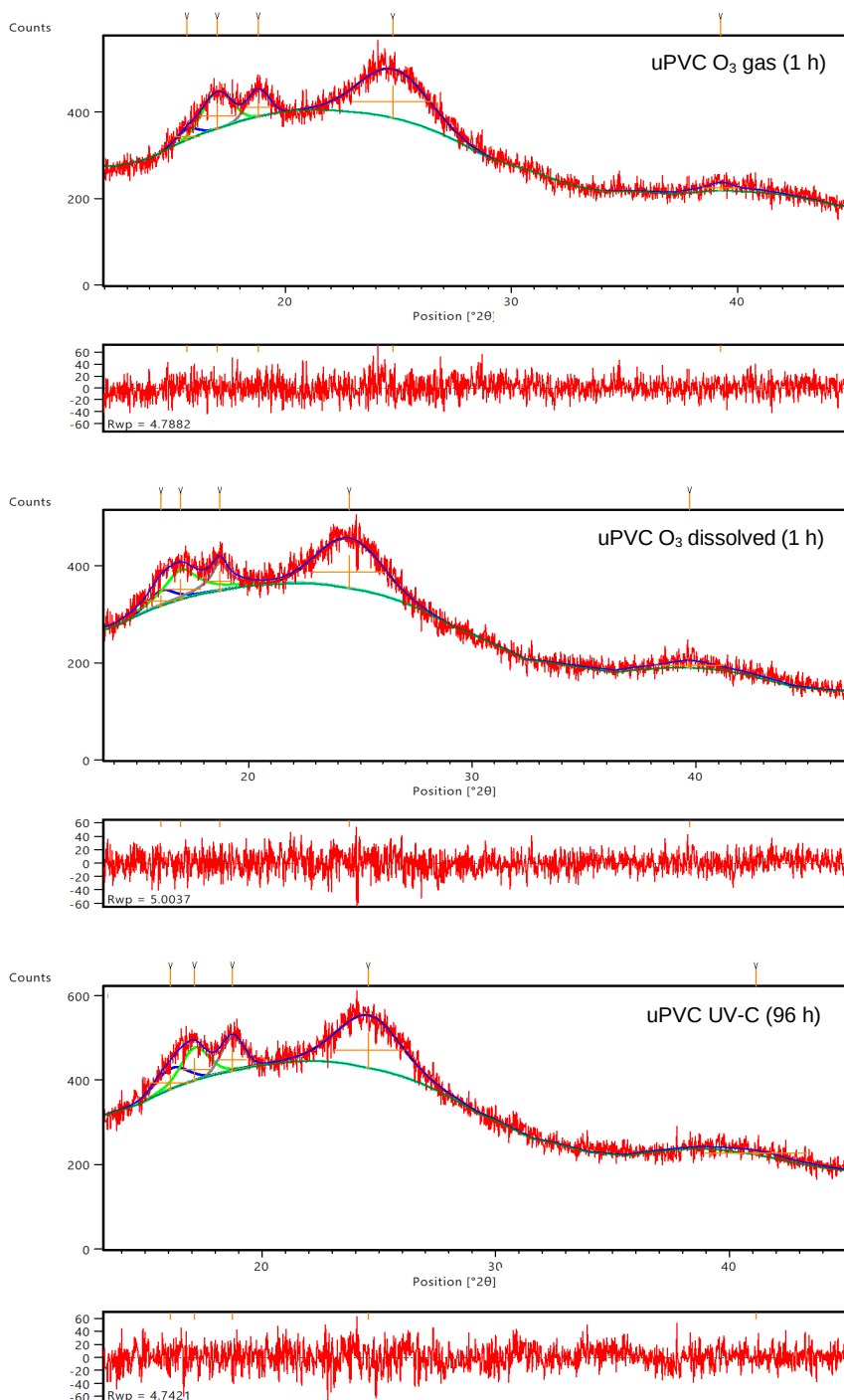


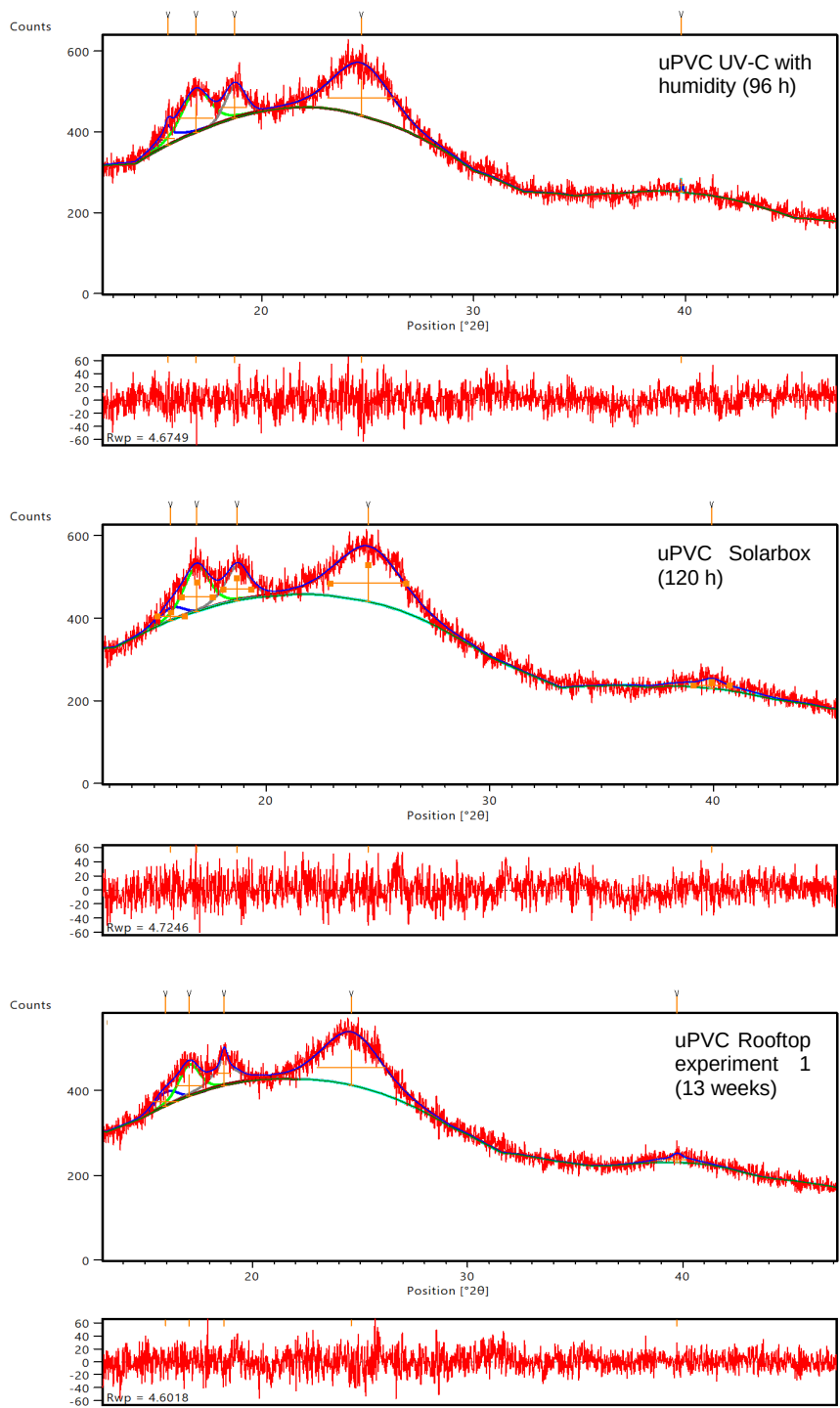


uPVC crystalline peaks

Baseline: Bending factor = 33, Granularity = 30







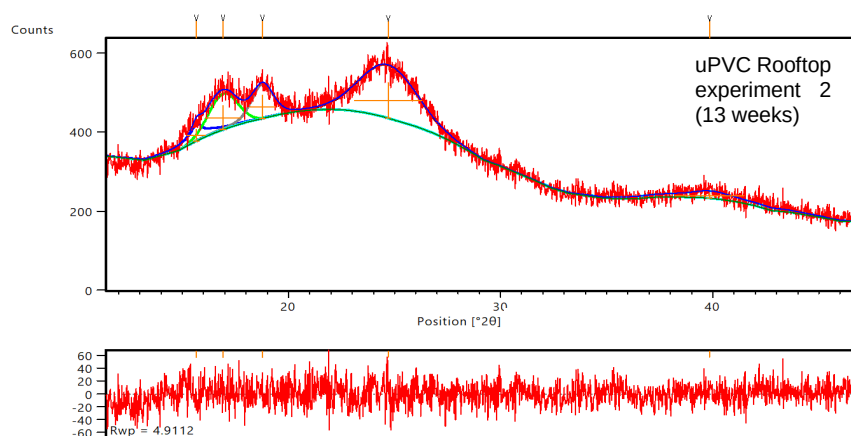


Table A1. LDPE, PET and uPVC crystalline peaks areas sum and amorphous area.

	LDPE			PET			uPVC		
	ϕ_c	ϕ_a	R_{wp} (%)	ϕ_c	ϕ_a	R_{wp} (%)	ϕ_c	ϕ_a	R_{wp} (%)
Virgin	4895.3	9366.3	3.08	5391.9	13158.4	2.58	563.7	1346.3	4.83
O ₃ gas (1 h)	4369.6	8858.3	2.76	4653.6	10760.6	2.71	487.6	1521.7	4.79
O ₃ dissolved (1 h)	4057.2	7327.8	2.96	3203.3	7268.7	2.97	528.5	1029.4	5.00
UV-C (96 h)	3777.5	7262.3	2.98	3243.2	7064.9	3.08	571.5	1706.1	4.74
UV-C with humidity (96 h)	4626.9	9820.3	2.53	3085.2	6787.8	2.98	570.5	1688.5	4.67
Solarbox (120 h)	2568.7	4014.0	3.36	2609.6	5406.1	3.09	662.7	1545.8	4.72
Rooftop experiment 1 (13 weeks)	4270.8	6323.4	4.23	3904.8	8960.3	2.91	525.6	1609.5	4.60
Rooftop experiment 2 (13 weeks)	5271.5	7249.2	3.87	3849.7	9648.2	2.84	639.1	1750.8	4.91

ϕ_c : sum of crystalline peaks areas

ϕ_a : amorphous area

R_{wp} : weighted profile residual of the Rietveld refinement