TALLINN UNIVERSITY OF TECHNOLOGY

SCHOOL OF ENGINEERING

Department's title

ASSESSMENT OF THE MASS TRANSFER OF POLYAROMATIC SUBSTANCES IN THE CIRCULAR ECONOMY: APPLICATION TO CELLULOSIC AND PLASTIC MATERIALS USED FOR FOOD PACKAGING AND AGRICULTURE

Polüaromaatsete ainete massiülekande hindamine ringmajanduslikes rakendustes: toidupakendites ja põllumajanduses kasutatavad tselluloos- ja plastmaterjalid

BACHELOR THESIS/ MASTER THESIS

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Tallin 2023

AUTHOR'S DECLARATION

Hereby I declare that I have written this thesis independently.

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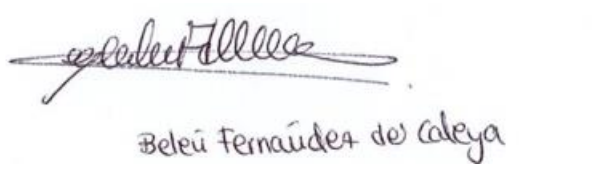

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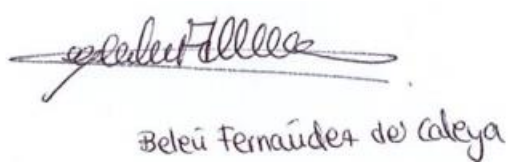

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TalTech Department`s title

THESIS TASK

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Study programme, BIOCEB (KVEM)

main speciality: Bioeconomy

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Consultants:

Thesis topic:

- Assessment of the mass transfer of polyaromatic substances in the circular economy: application to cellulosic and plastic materials used for food packaging and agriculture.
- Polüaromaatsete ainete massiülekande hindamine ringmajanduslikes rakendustes: toidupakendites ja põllumajanduses kasutatavad tselluloos- ja plastmaterjalid

Thesis main objectives:

1. Detection and localization of contaminants in food contact materials (FCM), along with quantification of their mass transfer.

2. Mitigation of health hazards through a comprehensive risk assessment of contaminant migration in recycled food packaging.

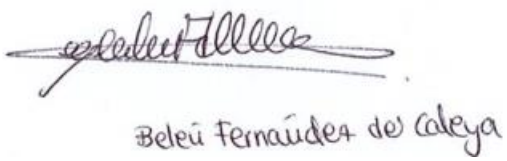
3. Implementation of preventive approaches within the supply chain or packaging design, in line with the framework Regulation 2023/2006/EC.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Evaluate the use of Raman Chemical Imaging as a tool to characterize the presence and spatial distribution of contaminants in selected FCM.	
2.	Employ sorption and diffusion techniques to measure and estimate apparent diffusion coefficients in the packaging materials. Develop an efficient method for the detection of contaminants in FCM.	
3.	Focus on the detection and evaluation of contaminants present in commercial food packaging that can be detected using the developed method.	

Language: english **Deadline for submission of thesis:** 12.06.2023

Student: Belén Fernández de Caleya 12.06.2023



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Although it is impossible to individually name everyone who contributed to this thesis, I extend my sincere appreciation to all those who played a part, whether directly or indirectly, in making this research a reality.

Thank you all.

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LIST OF ABBREVIATIONS

- BPA: bisphenol A.
- CaCO3: Calcium carbonate.
- CAGR: continue growing with an annual rate.
- CE: Circular Economy.
- CEF: EFSA Panel on food contact materials.
- CGR: Circular Gap Reporting.
- CO2: Carbon dioxide.
- DCM: Dichloromethane.
- DGCCRF: Direction Générale de la Concurrence, de la Consommation et de la Répression des Fraudes.
- DIPN: Diisopropyl napthalenes.
- DVS: Dynamic Vapor Sorption.
- EC: European Commission.
- EFSA: European Food Safety Authority
- EJ: Exajoules.
- EPA: Environmental Protection Agency.
- EU: European Union.
- FCCdb: Food Contact Chemicals Database.
- FCM: food contact materials.
- FLW: food losses and waste.
- FTIR: Fourier transform infrared.
- GC: gas chromatography.
- GDS: Global Distribution System
- GHG: greenhouse gasses.
- GMPs: good manufacturing practices.
- HPLC: high-performance liquid chromatography.
- INRAE: French National Institute for Agriculture, Food and Environment
- IR: infrared.
- MFA: material flow analysis.
- MFC: micro fibrillated cellulose.
- MRF: materials recovery facility for sorting.
- MS: mass spectrometry.
- NIR: near-infrared.
- NMR: nuclear magnetic resonance.
- OPP: 2-Phenylphenol.
- PAHs: Polycyclic aromatic hydrocarbons.
- PCR: post-consumer recycled.
- PFASs: per-and polyfluoroalkyl substances.
- PTFE: Polytetrafluoroethylene.
- PVC: polyvinyl chloride.
- SBR: styrene butadiene rubber.
- SDG: Sustainable Development Goals.
- TTC: Toxicological Threshold of Concern.
- US: United States.
- USD: United States dollar.
- UV: Ultraviolet.

ABSTRACT

The rise of a circular economy encouraged by consumers and comprehensive European policies opens an unregulated spread of contamination within recycled food contact materials (FCM). The presence of polycyclic aromatic hydrocarbons (PAHs) and mineral oils in packaging is of concern since the European Food Safety Authority (EFSA) highlighted their potential carcinogenic and genotoxic nature. In this context, actions must be taken to evaluate the risk of exposure and avoid a new sanitary crisis.

This work fits into two research projects carried out by Ph.D. students on evaluating the contamination of recycled food packaging, respectively with plastic and cellulosic materials. The main goals of this research were (1) to identify contaminants in food contact materials using chemical imaging, (2) assess the mass transfer of reference substances in plastic and paper materials to obtain experimental diffusivities, and (3) to implement a preventive approach that could help for the production of safer recycled food packaging.

Reference paper and board and plastic materials were used to develop the method intended to be later applied on commercial food packaging. Vibrational spectroscopy and Raman chemical imaging were employed to detect and localize contaminants in FCM. Diffusivities and sorption properties of reference materials were measured respectively by diffusion through several layers of material and by dynamic vapor sorption. The first findings show the potential of Raman imaging to characterize food packaging contamination. The understanding of highlighted heterogeneous distribution of substances in recycled materials, which comes from the properties of the matrix and of the contaminant, is a key challenge for describing mass transfer mechanisms in FCM. Experimental specific diffusivity values will help the development of a multiscale model of diffusion in FCM. Finally, the sorption properties of water on reference materials helped understanding the main characteristics of packaging materials to improve for the future production of safe recycled food packaging.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic compounds comprising two or more fused aromatic rings. Their exposure has been primarily associated with unintentional production through incomplete combustion or pyrolysis of organic matter during various industrial processes, including food processing and certain home cooking practices, such as grilling, smoking, toasting, roasting, and frying (Authority (EFSA), 2008; Sampaio et al., 2021). The mineral oil crisis has demonstrated that the sources are more considerable and include packaging materials, including recycled paper and cardboard (Chain (CONTAM), 2012). The exposure of European consumers to mineral oils and PAHs is currently under review by the European Food Safety Authority (EFSA), with the reasoning that PAHs with three or more rings should all be considered genotoxic and carcinogenic (*Public Consultation:*, n.d.). Molecules with two rings and phenolic compounds (bisphenols, ethoxylated or non-ethoxylated nonylphenols) are ubiquitous endocrine disruptors in food and the environment (European Commission. Directorate General for Environment., 2022; Kaleniecka & Zarzycki, 2019; Spataro et al., 2023).

The unregulated or unsupervised circular economy is likely to spread PAH-type contaminants uncontrollably. Studies by the SayFood Mixed Research Unit (P.-M. Nguyen et al., 2017, 2019) have shown that understanding PAH transfer mechanisms is insufficient, and their strong hydrophobicity and crystalline state do not prevent their transfers. They can be transferred without contact through an air film and cross aqueous environments (P.-M. Nguyen et al., 2016). This research led to establishing one of the most restrictive regulations in Europe for managing the risk of PAH transfer in France. The Food Contact Materials Sheet No. 4, dedicated to cellulosic materials (*Matériaux organiques à base de fibres végétales*, n.d.), mandates the industry to assess the risk of non-contact transfers from overpackaging into aqueous foods in 2019. The French anti-waste law No. 2020-105 goes further and imposes eliminating all mineral oils for all printing applications from 2025. These guidelines may be adopted on a European scale in the latest round of negotiation of the regulation on packaging and packaging waste (*Proposal Packaging and Packaging Waste*, 2023).

This work fits into this dynamic, particularly in the framework of two doctoral project proposals aimed at understanding and limiting the transfer of contaminants originating from recycled packaging materials, primarily through the addition of a corrective solution using functional barriers. The goal is to support the development of a new chemical imaging technique using vibrational spectroscopy resolved at the thickness scale of a packaging or even a cellulosic fiber to highlight transfer and study molecular mechanisms.

These methodological developments allow measuring and optimizing the technical solutions' performance. Two applications of materials containing PAHs are considered. In the first case, the PAHs are not intentionally added but are present in the recycling loop and support the National Agency for Research FoodSafeBioPack program (reference ANR-20-CE21-0009), which aims to develop "Safe recycled cellulosic materials as an alternative to plastic materials for food contact". In the second case, PAHs are intentionally added to modify the transmission spectrum of sunlight through the plastic of agricultural

greenhouses and thus increase agricultural yields. In both cases, the risk of PAH transfer exists and must be characterized and compared with acceptable thresholds for contamination and exposure scenarios. The study focuses on the transfer aspect.

The memoir is structured as follows. The second part presents a literature review on the practices used for food packaging, their circular use, and the risks associated with the upcycling of materials that would not be of food origin. The increased risks linked to using non-decontaminated or not recycled matter is particularly emphasized. Methods and best practices for assessing health safety are presented, as are new methods under development to characterize and reduce emerging risks. The specific objectives and the approach adopted in the project are offered in a third part. Part four details the equipment and methods used. The results are presented in the fifth part and discussed in a risk transfer evaluation logic. Conclusions and prospects are finally summarized in a final part.

2 LITERATURE REVIEW

2.1 From farm to fork and the bin: a review on the food production system in the EU

2.1.1 Overview of the impacts of food production

In recent times, there has been a significant shift in how we perceive the environment. What initially was considered as an unlimited resource with no cost, is now recognized as a precious and limited input that demands careful attention (Zaror, 1992). Consequently, there is a growing need to reduce the negative impact on the environment and prevent pollution.

The food industry is one of the world's largest industrial sectors and hence is a large user of energy (Roy et al., 2009) . This sector encompasses all the necessary steps to convert raw materials into finished food products. While being efficient in delivering a wide range of fresh and processed foods, it has its own environmental implications at every stage of the production process. Operating within a traditional linear economy, where there is no second life after consumption, it generates big amounts of waste that follow the "take, make, use and dispose" model. From production to processing, transportation, storage, distribution, and marketing, various quantities of waste can be identified, leading to untreated disposal problems and significant production challenges (Zaror, 1992). In order to develop a more sustainable food supply chain, it is necessary to know and define each of the steps of production (Table 1).

Considering and addressing these environmental hazards at each stage of the food supply chain is crucial for promoting sustainability, reducing waste, and mitigating the overall environmental impact of the food industry.

On the other hand, a Circular Economy (CE) promotes an earth-friendly economic development model. It focuses on closing loops in industrial systems, minimizing waste, and reducing raw material and energy inputs. This concept has gained significant importance in policymaking and has been increasingly implemented worldwide in production, consumption, and waste sectors (Seetharaman et al., 2022).

The Circular Economy presents itself as a viable solution to address the pressing challenges of the 21st century, including biodiversity loss, climate change, resource depletion, water scarcity, population growth, and economic issues (Figure 1). By embracing the principles of circularity, such as minimizing the waste and reducing the environmental impact, the circular economy offers numerous benefits. These advantages include unlocking economic opportunities, redesigning products for longevity and recyclability, stabilizing the price volatility, and fostering job growth. The ultimate goal of the circular economy is to reshape global industrial systems, striving towards a zero-waste economy (*Food and the Circular Economy*, n.d.; Jeffries, 2018).

Table 1 - List of food production steps and their major environmental effects

Step	*Process*	*Source of impact*	*Environmental effects*	
1. Production	Source of the food. It will follow local and international guidelines to ensure quality and food safety.	Pesticides, fertilizers, and intensive farming practices.	Soil degradation, water pollution, and biodiversity loss.	a, b
2. Handling and Storage	Preparation and last-minute steps that food undergoes once the product has been harvested.	Improper handling and storage practices	Unnecessary resource depletion, increased greenhouse gas emissions, food spoilage and waste.	a, c
3. Processing and Packaging	Conversion of the food into an edible form converted into an edible form.	Use of packaging materials, improper disposal, and energy-intensive processing methods.	Waste (packaging and byproducts), plastic pollution, carbon emissions and energy consumption.	a, d, e
4.Distribution	Once the food is edible, it is transported and distributed to the necessary retail or supplier.	Use of transportation (inefficient transportation or long distances).	Carbon emissions, air pollution and climate change.	a, f
5. Retailing	From obtaining the food until its delivery.	Overstocking, improper storage, expiration of perishable products, and energy consumption.	Food waste and high energy consumption.	a
6. Consumption	Consumer purchases the product from the retailer	Consumer habits (food waste at the household level).	Contribution to greenhouse gas emissions in landfills and unnecessary resource consumption throughout the supply chain.	a, b, h

(a) Lewis, 2022; (b) Ritchie et al., 2022; (c) Burek & Nutter, 2020; (d) Santulli & Mastrolonardo, 2021; (e) Vitrac & Hayert, 2005, (f) Tassou et al., 2009; (g) Salas et al., 2021; (h)Notarnicola et al., 2017.

However, it is important to note that currently, only approximately 8.6% of the world's economy is classified as circular (*The World Is Now Only 8.6% Circular - CGR 2020 - Circularity Gap Reporting Initiative*, n.d.). This highlights the urgent need to accelerate the transition towards a circular economy. To achieve this, it is crucial to consider both immediate and long-term factors that impact the environment. To effectively accomplish this goal, it is essential to identify and address specific modules within the production process that contribute to contamination and understand their specific environmental effects (Jurgilevich et al., 2016). By targeting these areas, we can implement effective strategies and interventions to minimize environmental impact and accelerate the transition towards a truly circular economy.

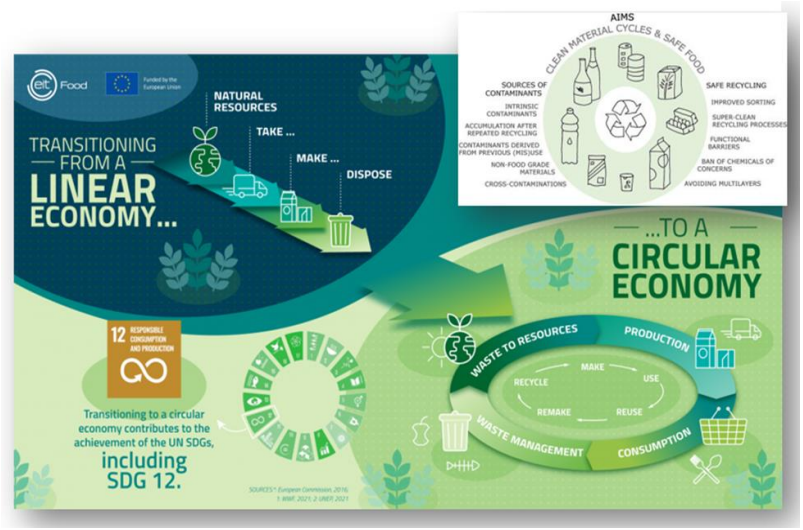


Figure 1 - Scheme of the transition of the linear economy of food production towards a circular model system (from Jurgilevich et al., 2016).

2.1.2 Material wastes of food production.

The primary focus of this study centers around analyzing and assessing the packaging module within the production process. The aim is to thoroughly examine packaging and identify strategies to effectively mitigate its impact on the environment.

The linear economy prevalent in the food industry is characterized by the generation of by-products, waste, and air emissions throughout the entire production chain. These emissions, including greenhouse gasses (GHG), contribute significantly to climate change and the degradation of ecosystems. Although the use of solid fuels has been on decline, the food industry continues to rely on other fossil fuel sources such as natural gas and petroleum (Ladha-Sabur et al., 2019). It is alarming to note that food production alone accounts for more than a quarter (26%) of global greenhouse gas emissions. Additionally, it utilized approximately half of the world's habitable land for agriculture and a high volume of 70% of global freshwater for irrigation (Ritchie et al., 2022). Moreover, the food sector consumes an estimated 200 EJ (exajoules) per year globally, with processing and distribution activities accounting for around 45% of this energy consumption (Ladha-Sabur et al., 2019).

These statistics highlight the urgent need to address the environmental impact of the food industry, particularly in terms of greenhouse gas emissions, land use, freshwater consumption, and overall energy efficiency.

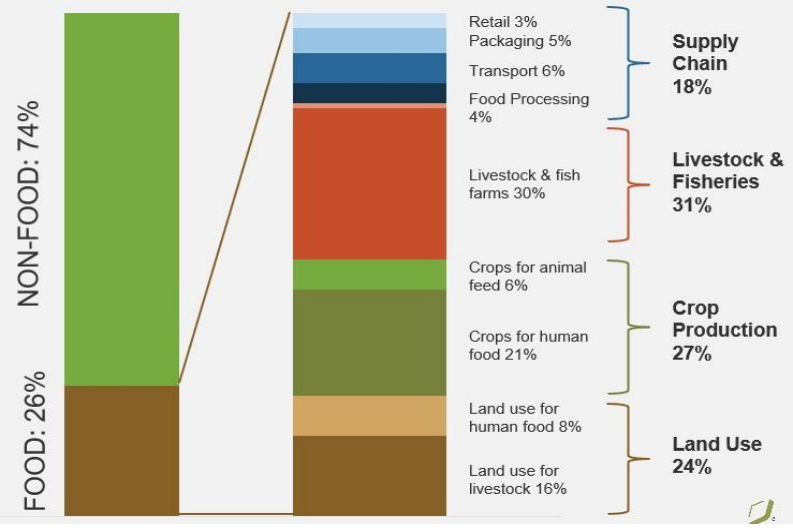


Figure 2-Global greenhouse gas emissions from food production in 2018 (from Ritchie et al., 2022).

As shown in Figure 2, 4,68% of global emissions of CO2 is coming from the supply chain of food, with 5% of it coming from packaging (Ritchie et al., 2022). Unfortunately, most food packaging is designed to be single use and not recycled. According to the US Environmental Protection Agency (EPA), food and food packaging materials make up almost half of municipal solid waste (US Environmental Protection Agency, 2019). Table 2 presented below shows the key impacts of food packaging on the environment (Kroyer, 1995; Marsh & Bugusu, 2007).

This is the reason why addressing the environmental impact of food packaging requires a multifaceted approach rather than a single solution. By considering the complete system, we can mitigate the environmental consequences of packaging and enhance the overall sustainability (Kroyer, 1995).

Table 2-Environmental impact of the food industry and the associated Sustainable Development Goals (SDG).

Environmental impact	*Source of impact*	*Effect*	*SDG*
Resource consumption	Production of packaging, transport	High consumption of water, energy and raw materials	
Waste generation	Packaging and food waste (landfills or incineration)	Bioaccumulation, GHG emissions, eutrophication, soil degradation, environment deterioration	
Greenhouse Gas emissions (GHG)	Transport, production, disposal, waste decomposition in landfills	Contribution to Climate Change and ozone depletion	

Single-Use plastics	Improper disposal	Contamination in the environment	
Recycling and waste management	Improper recycling infrastructure	Bioaccumulation, GHG emissions, eutrophication, soil degradation, environment deterioration, human health hazards	
Carbon footprint	Transport	Increase in greenhouse gas emissions	

The food industry's production process generates significant environmental impacts, including waste, pollution, and resource depletion. Transitioning towards a circular economy is essential to minimize these impacts and promote sustainability by reducing waste and resource consumption. Addressing specific areas such as food packaging is crucial to mitigate the environmental effects and move towards a zero-waste economy.

2.1.3 Chemical risks: A recurring source of crises

Generally, crises precede the implementation of regulations. Normally, when there is a significant concern about food safety due to the systemic contamination caused by one or multiple food packaging materials a crisis occurs. Only recently, Europe has started to recognize the potential crises caused by packaging materials, establishing the obligation of tracing all packaging components for organized recalls of packaged food products in the framework regulation 1935/2004/ (EC). This regulation states that materials in contact with food may not release constituents into food at levels that could endanger human health or bring changes in the composition, smell, or taste of the food. In addition, all packaging materials should be manufactured according to the principles of good manufacturing practices (GMPs) stated in Regulation (EC) 2023/2006.

Certain packaging materials used for food applications, such as plastics, ceramic and regenerated cellulose are covered by independent harmonized regulations at the european level. However, many other materials such as paper and board, rubber and silicone elastomers do not have any harmonized regulation yet (*European Framework Regulation (EC) 1935/2004 Solutions*, n.d.).

The initial concern started around thirty years ago, when Western governments showed great enthusiasm for the idea proposed and later developed by Jerome Nriagu and Clair Patterson (Nriagu, 1983; Patterson et al., 1987). This idea suggested that lead was the main reason for the collapse of the Roman civilization. However, while it is no longer considered as the main reason, lead poisoning from pottery has been recognized for centuries. In the 19th century, authorities diligently tacked all possible sources of lead. For instance, the French government ordered in 1879 the prohibition of tin and lead alloys for inner parts of materials used in food packaging(Vitrac & Hayert, 2005).

More recently, a major food safety incident occurred in the United States, when *Listeria monocytogenes*, a bacterium that can cause severe illness, particularly in pregnant women, the elderly, and individuals with weakened immune systems, was found in pre-packaged salads (Self et al., 2019). Its origin came from the insanitary state of the cleaning process of the packaging. Furthermore, bisphenol A (BPA) is a chemical commonly found in epoxy resin lining metal cans, and it has been associated with potential health risks like effects on the reproductive health, metabolism and the endocrine system (X. Wang et al., 2022). These examples highlight the need for ongoing vigilance and regulation to ensure the safety of food products.

2.1.4 How new laws are intended to curb wastes in the EU

The issues surrounding agri-food industry by-products and waste generation have prompted the European Union (EU) to achieve a zero-waste economy by 2025. This initiative has won the attention and interest of several researchers, regulators, customers, and stakeholders. The EU's Green Deal, introduced in 2019 by the European Commission, aims to transform the Climate Change Challenge and ecological transition into an opportunity for a new development model, putting the EU as a global leader (*Un Pacto Verde Europeo*, 2021). The Green Deal serves as a vital framework for expediting the transition to a CE.

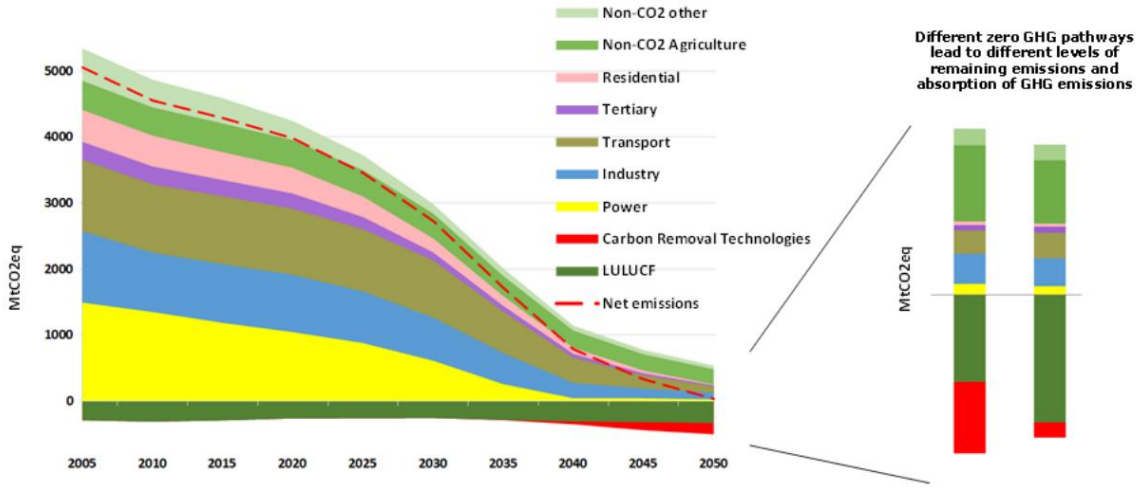


Figure 3-Greenhouse gas emissions under the scenario of global temperature increase of 1.5 ºC (from Amanatidis, 2020).

The European objective is to become the first climate-neutral continent by 2050 (Figure 3), fostering the competitiveness of European industries and ensuring a transition that is sustainable not only for the environment and the economy but also for society as a whole (European Environment Agency., 2013).

Consequently, discussions surrounding the Circular Economy (CE) have gained significant momentum within policy circles and rely in academic literature. Numerous researchers have undertaken studies on the theory and conceptualization of CE, the development of innovative models in the agri-food sector, definitions of food waste, strategies for the reduction of food losses and waste (FLW) along the agri-food

supply chain, and approaches for the valorization of food waste (Hamam et al., 2021). Additionally, scholars have explored emerging conversion tools, analyzed technological functionalities, and examined waste management practices.

Scholars have also evaluated the progress of CE strategies aimed at reducing the carbon footprint of the agri-food supply chain. Methodologies such as material flow analysis (MFA), which translates into increased energy savings, food waste recycling strategies, and cleaner production models, have been employed to assess both upstream and downstream impacts. The findings highlight the importance of implementing cleaner production models, increasing responsibility and awareness. It also indicated the necessity of appropriate policies and tools and a continuous application of an integrated preventive environmental strategy to mitigate all possible risks (Hamam et al., 2021).

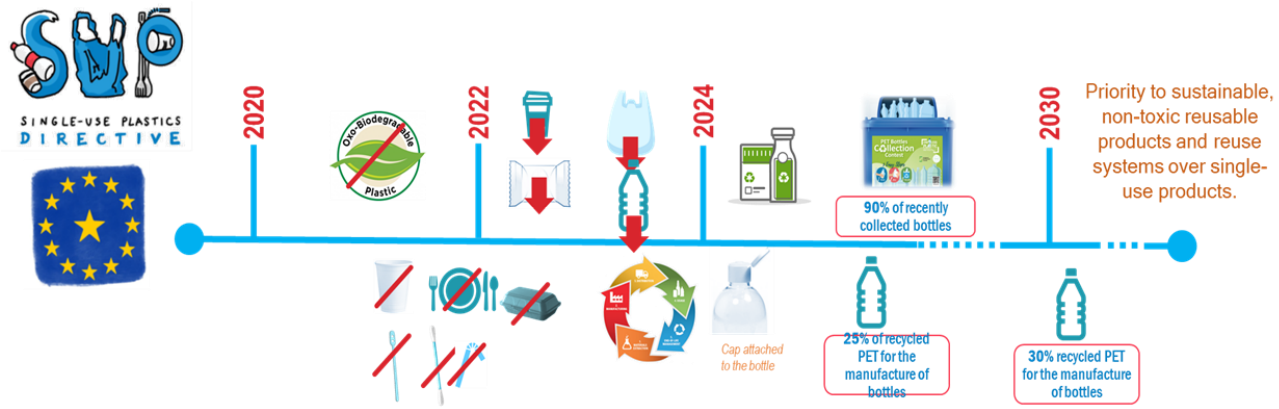


Figure 4-Main steps of the Single-Use Plastics EU Directive 2019/904 on the reduction of the impact of certain plastic products on the environment (from UMT SafeMat).

Europe has recognized the potential crises caused by food packaging materials and has implemented regulations to trace and recall FCM. However, while there are certain packaging materials under harmonized regulations, others lack them. It is important to highlight that because of past crises, the European Union's aim is to achieve the zero-waste economy and become climate-neutral by 2050 through the Circular Economy initiative, that involves reducing food losses and more efficient waste management.

2.2 Virgin vs recycled food packaging

Food meets many materials throughout its entire production process, from storage to preparation and eventual consumption. Food packaging is the enclosure of food designed to protect it from direct contamination or contact with physical, chemical, and biological sources (Cachon et al., 2019). This helps to prevent waste and ensure the quality of food throughout its shelf life. The term "Food Contact Materials" (FCMs) refers to all the materials used in packaging and containers (Food Contact Materials, n.d.), and is a crucial part of the modern food industry, where only a few foods are delivered to consumers unpackaged. Despite its key role in protection, food packaging can be considered superfluous at best, and accumulative

waste that threatens the environment and health at worst. However, packaging also serves secondary functions such as traceability, convenience, and tamper indication (Marsh & Bugusu, 2007).

Traceability allows the product to be tracked from its raw materials through the stages of production, processing, and distribution, which helps to improve supply management and quality. Convenience refers to the attractive visuals and barrier properties that attract consumers to purchase the product, helping manufacturers to sell their products (Minton & Bobroff, n.d.). Finally, tamper indication provides physical evidence of unauthorized access to the product, reducing the risk of manipulation or adulteration outside of a secure area (Marsh & Bugusu, 2007).

Packaging can be divided in three main types (Han et al., 2018);

a) *Primary packaging*, refers to the one in direct contact with the product itself and its purpose is to protect, preserve or inform the consumer. With regards to the influence of its composition, primary packaging is the most studied one since it is in direct contact with the food.

(b) *Secondary packaging* refers to the one whose main purpose is for branding display and logistical purposes.

c) *Tertiary packaging* facilitates protection, handling, and transportation.

In recent years, the global population has increased to approximately 8 billion due to advances in modern medicine and a decrease in global poverty, leading to a higher demand for food products that meet consumer expectations for quality and safety (Roser et al., 2013). Furthermore, pandemics like COVID-19, increased demand for ready-to-eat foods. In response to these demands, there has been an urge in the development of modern packaging technologies aimed at enhancing the quality and quantity of food packaging (Soltani Firouz et al., 2021). Furthermore, there is an expected growth in the number of foodservice suppliers who will enhance the market through digitalization of their operations. However, the growth of the food packaging industry may be hindered by the increasing emphasis on the use of recycled materials for packaging due to customers' awareness of climate change (*Food Packaging Market Size, Share & Growth Report, 2030*, n.d.)

According to the global food packaging market size in 2021 it reached the value of USD 346.5 billion and, in consonance with the global population's rise, it will continue growing with an annual rate (CAGR) of 5.5% from 2022 to 2030. In relation to the material properties, plastics offer a wide range of possibilities and thus are widely used in food packaging (Figure 5), being the leading materials in the segment with a revenue share of over 35% in 2021 (*Food Packaging Market Size, Share & Growth Report, 2030*, n.d.) But also other materials are used such as metals (aluminum, metalized and laminate films, tinplate), paper/ paperboard and glass. In countries with emerging economies and rise of population, such as China, Japan and India, it is expected to also have a big market size in food packaging. However, North America also reckons a considerable production of food packaging.

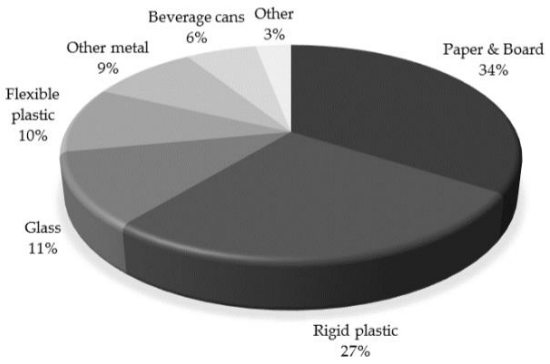


Figure 5-Market share of materials used for food packaging production (from Muller et al., 2017).

2.2.1 Plastic food packaging material

Plastics are organic polymers formed by a long chain of repeating units linked by condensation or addition reactions (Marsh & Bugusu, 2007). The molecular structure, molecular weight (Mw) and crystallinity degree will determine the properties of these plastics, such as their density, thermodynamics, and physical properties. It is possible to differentiate between two types according to their behavior when exposed to heat. Thermoplastics are remouldable, recyclable, and softer since they do not form any chemical bond when curing, and they return to their original condition under room temperature. Because of their properties, they are ideal for food packaging. Thermosets are strong and durable because of the formation of bonds under heat conditions, however they cannot be remolded (*Thermoplastics Properties, Types, Uses, Advantages and Disadvantages | Science Online*, 2017).

In comparison with other packaging materials like paper, plastics can range from fluid and moldable to strong and durable. However, the main disadvantage according to their properties is permeability to light, gasses, and low molecular weight compounds (Marsh & Bugusu, 2007). Finally, with regards to the barrier properties, plastic packages are more permeable than other materials such as glass, and it is directly relying on their resistance to sorption and diffusion of substances through the material.

Plastic food packaging can be categorized into polyolefins (e.g., polyethylene and polypropylene), copolymers of ethylene (e.g., ethylene-vinyl acetate and ethylene-vinyl alcohol), substituted olefins (e.g., polyvinyl chloride and polystyrene), polyesters (e.g., polyethylene terephthalate), and polyamides (e.g., nylon 6 and MXD6). Each category has distinct properties that make them suitable for various food packaging applications.

The global market for plastic packaging, which includes beverages, food, pharmaceuticals, and household care, was valued at USD 355.0 billion in 2021. It is projected to have a compound annual growth rate (CAGR) of 4,2% from 2022 to 2030. Plastic has been widely adopted as an ideal material for food packaging due to its flexibility, rigidity, and printability, and with the world's increasing population, its demand is expected to continue growing. In 2021, plastic held a dominant market share of 51,5% in the

food packaging industry, and this trend is expected to persist in the future (*Global Plastic Packaging Market Size & Share Report, 2030*, n.d.).

2.2.2 Paper and board food packaging material

Pulp is a plant-derived material used to produce paper and similar products. It is considered environmentally friendly and suitable for packaging applications. However, raw paper alone has limitations in terms of barrier properties, heat and strength. To overcome these limitations, post-manufacturing treatments like coating, lamination, shaping, and embossing are commonly used (Deshwal et al., 2019; Oloyede & Lignou, 2021;Santulli & Mastrolonardo, 2021).

The initial step in paper production is pulping, which involves separating wood fibers through mechanical, chemical, or thermal treatments. This crucial step eliminates lignin, as it lacks the ability to form fibers, resulting in cellulose and hemicellulose, which determine the properties of the paper. The resulting solution containing cellulose and hemicellulose fibers is known as pulp. Subsequently, bleaching treatments are applied to improve the whiteness of both chemical and mechanical pulp. The beating treatment follows, increasing the fiber surface area and enhancing water holding capacity while facilitating the formation of new bonds among the fibers, producing more uniformous pores (Bajpai, 2021). Finally, the refining process focuses on enhancing the physical properties of the final paper sheet. Additional treatments such as calendering, lamination, impregnating, and saturating may be employed to achieve specific functional requirements for the end product (Deshwal et al., 2019).

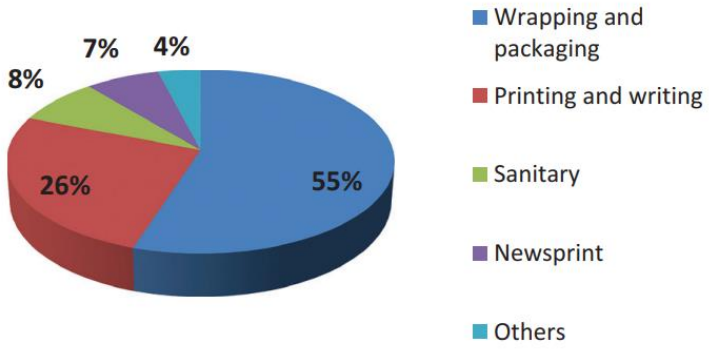


Figure 6-Global consumption of paper materials by end-use (from Chauhan & Meena, 2021).

The paper-based sector has experienced significant global growth, with a Compound Annual Growth Rate (CAGR) of 6.4% in 2021, driven in large part by growing consumer interest in eco-friendly packaging options. In fact, paper and paperboard production now accounts for 34% of the global packaging market (Figure 5). In 2000, approximately 47% of all paper and board produced was used for packaging applications (Deshwal et al., 2019). This trend towards paper-based packaging reflects a growing awareness

of the environmental impact of traditional plastic packaging, and a desire among consumers to choose more sustainable options.

Paper-based packaging can be categorized into several types, including kraft paper, greaseproof paper, parchment paper, bleached paper, glassine paper, and others. Among these types, kraft paper emerged as the dominant player in the market (Figure 6), holding the largest market size in 2020 (Deshwal et al., 2019). Furthermore, statistical data based on the consumption patterns of major markets revealed that the Asia Pacific region led the global food contact paper market in 2020 and is expected to maintain its dominance until 2028 (Food contact market, n.d.).

Table 3-Comparison of the main characteristics between paper and plastic packaging (after Deshwal et al., 2019).

Aspect	*Paper packaging*	*Plastic packaging*
Cost	Relatively affordable	Generally cheaper to produce
Material properties	Less resistant to moisture	Permeable to light, gasses, and low molecular weight compounds
	More rigid and prone to tearing	Range from fluid and moldable to strong and durable
Sustainability	Renewable and biodegradable	Non-biodegradable, but can be recycled in many cases
Barrier properties	Less effective barrier against gasses and liquids	Can provide effective barrier properties
Weight	heavier	Lightweight
Recyclability	Recyclable, by the rates can vary	Can be recycled, but the recycling infrastructure varies
Environmental impact	Generally considered more environmentally friendly in terms of disposal and biodegradability	Can have a significant environmental impact depending on disposal and recycling practices

2.2.3 Recycled Packaging material

The rapid spread of information has made the public increasingly aware of the packaging waste crisis and its impact on the planet. As a result, many countries are now enacting realistic policies to reduce its production, consumption, and waste. Some of these policies focus on improving the waste management of packaging materials, including their collection, treatment, and disposal. This process encompasses all the measures taken before a substance or product becomes waste, and it can be implemented at every level of the supply chain. By implementing these policies, we can work towards mitigating the effects of waste on the environment and promoting a sustainable future.

The execution of waste reduction plans is currently limited by the lack of reduction targets in national prevention plans and confusion with recycling. While recycling is an important aspect of waste management, it refers to recovery operations that transform waste materials into the same or different products. However, due to delayed awareness of environmental deterioration caused by human activities, an immense amount of waste has already been produced. Therefore, waste prevention targets should have a strong focus on recycling, as reducing waste at the source alone cannot effectively address the issue of existing waste.

2.2.3.1 Recycled plastic food packaging material.

For recycled plastics to be used in food contact applications, the recycling process must be demonstrated to efficiently remove all contaminants from the input plastic, as mandated by the European Commission Regulation 2022/1616. This new directive replaces Regulation (EU) No 282/2008 and introduces a mechanism to control the decontamination of plastics, reducing the risk to human health while not affecting food properties (Welle, 2023). Therefore, it is necessary to ensure that the dietary exposure to any potential unknown contaminants via migration into food is below the risk level to human health. According to the EFSA Panel on food contact materials (CEF), the dietary exposure should not exceed 0.0025 µg/kg body weight/day for a person weighing 60 kg (EFSA Panel on food contact materials (CEF), 2011). As shown in Figure 7, recycling process typically involves six main steps: (1) collection of post-consumer materials, (2) sorting and categorizing them based on parameters such as color, thickness, and intended use, (3) washing to remove impurities, (4) shredding into smaller pieces to eliminate remaining impurities, (5) identifying the pieces by class and quality, and (6) melting and crushing the shredded plastic to produce a new usable product (Siddique et al., 2008).

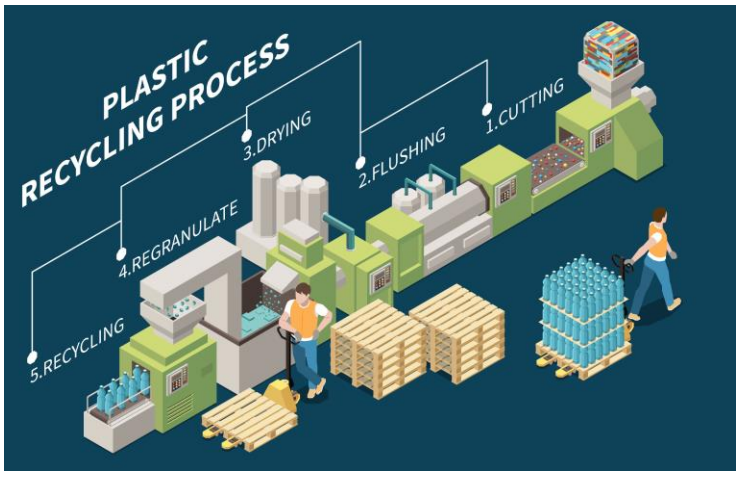


Figure 7-Main steps of the recycling process of plastic materials (Plastics Recycling in Four Simple Steps, 2023).

However, there are risks associated with the use of recycled plastic materials, particularly with regards to contaminants migrating into food from various sources. These sources include the possible misuse of the

plastic after food consumption, contact with non-food products (cosmetics, hygiene products, or household cleaners), and chemicals from multi-layered materials (such as PVC, polyolefins, or glues) and the chemicals used in the recycling process (like detergents and alkalis) (EFSA Panel on food contact materials (CEF), 2011). Moreover, degradation products that arise during the recycling process due to various conditions also pose a risk.

It is worth noting that the lack of public knowledge on recycling can lead to the combination of different types of plastic during manufacturing, increasing the risk of contamination, and raising the cost and time required for recycling. Therefore, ensuring the quality of the input, improving the efficiency of decontamination, and optimizing the final use of the recycled plastic are all crucial steps in risk assessment and must be improved (EFSA, 2012).

2.2.3.2 Recycled paper and board food packaging material

Recycling paper involves the reutilization of recovered paper through appropriate processing to create new paper or other paper-based products (Ervasti et al., 2015). This recycling process not only reduces waste generated from paper production and the carbon footprint but also extends the lifespan of raw materials like wood, fibers, and biomass, which can be utilized for other purposes. However, it is important to acknowledge that certain additives and laminating procedures used in paper packaging can pose severe health hazards. In comparison with plastics, paper recycling lacks a decontamination step and does not have an obligation for closed-loop recycling (Biant et al., 2023).

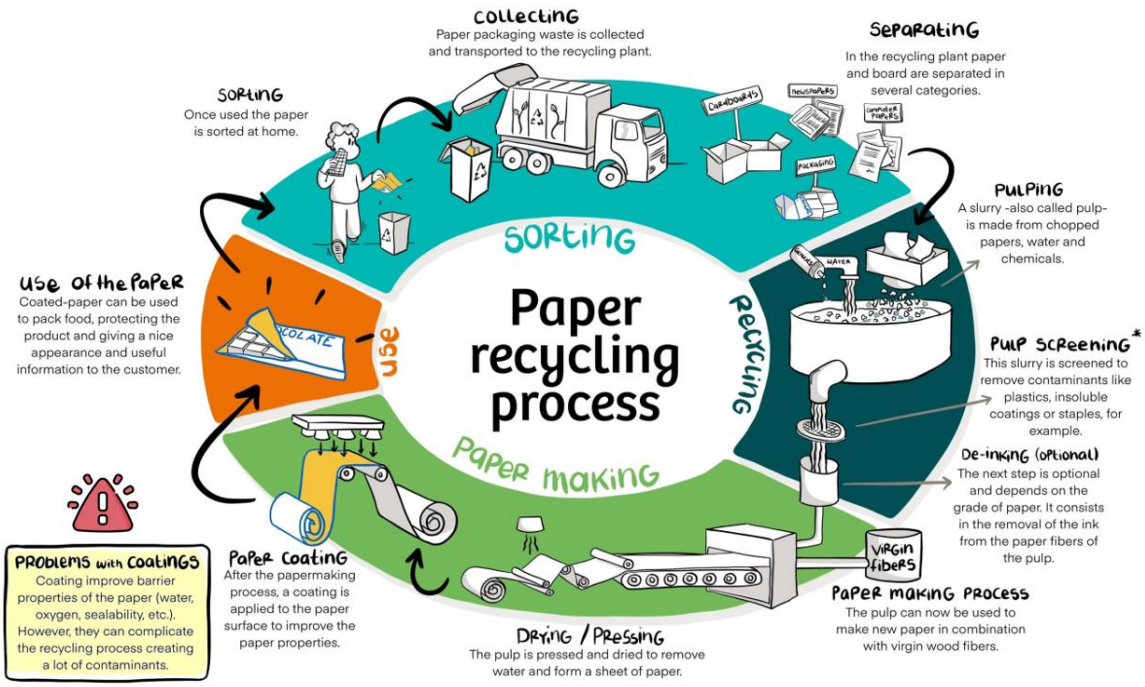


Figure 8-Main steps of the recycling process of paper materials (Lactips, 2023).

The recycling process can be divided into several steps to ensure the effective reuse of paper, as it is shown in Figure 8. Initially, discarded paper is collected and designated for recycling facilities. Once placed in the appropriate recycling bin, it is transported to a materials recovery facility for sorting (MRF). At this place, the paper is meticulously measured and sorted into distinct categories, for different processing methods. After thorough sorting and contamination checks, the paper is compacted into bales and sent to a paper mill, marking the true commencement of the recycling process. To break down the paper further into separate paper fibers, substantial quantities of water and chemicals are added. This process produces a mushy mixture called pulp, which serves as the raw material for the production of recycled paper. Once significant contaminants are removed, the pulp undergoes a flotation process, in order to eliminate dyes and inks. This process is called de-inking and it represents the final stage in the recycling process.

Moreover, recycled paperboard used for food packaging has been found to contain more than 250 health-threatening chemicals, with recycled pulp showing higher levels of contaminants than non-recycled pulp. These contaminants primarily include mineral oils, bisphenols, phthalates, isomers of diisopropyl naphthalene (DIPN), photoinitiators, inorganic elements, 2-Phenylphenol (OPP), Phenanthrene, and PFASs (*Recycled Content in Food Packaging & Toxic Chemical Exposure*, n.d.).

Nevertheless, despite this significant drawback, there is potential for improving recycled packaging by implementing measures to control contaminant migration, leading to the development of promising materials with minimal environmental impact.

Food packaging is important for the protection and preservation of food, as well as serving secondary functions like traceability, convenience, and tamper indication. Plastic and paper are two commonly used materials, with plastic dominating the market due to its flexibility and printability. However, there is an increasing demand for recycled packaging materials due to environmental concerns. It is important to mention that the recycling processes, for both materials, needs to improve or completely develop (in the case of paper) an efficient decontamination step in order to ensure no hazards to human health.

2.3 Safety Assessment

2.3.1 Definition

Safety assessment refers to the systematic evaluation of potential risks associated with a particular product, activity or process to ensure its safety for human health, the environment, or other relevant criteria (Kritzinger, 2006a). It often follows a structured and scientific approach, utilizing methods such as:

- Hazard identification
- Risk Assessment
- Risk Management
- Risk Decision and Communication

Safe assessment is a dynamic and ongoing process, as new information or scientific advancements may require the re-evaluation and updating of previous assessments. It plays a crucial role in various fields, including food and drug safety, environmental risk assessment, occupational health and safety, and product development, to ensure that potential risks are identified and minimized to protect individuals (Kritzinger, 2006b; P. Wang, 2017)

2.3.2 Safety Management

Hazard identification refers to recognizing potential hazards that could cause harm to human health, the environment or property. It involves systematically identifying the inherent properties or characteristics of a substance activity, or situation that have the potential to cause adverse effects. This information is crucial for conducting a comprehensive risk assessment.

Risk assessment is defined as the process of evaluating the likelihood and potential consequences of the identified hazards. It involves analysis of available data and information to estimate the level of risk associated with a particular hazard. Risk assessment considers facts like the severity, the nature, the level, and the duration of the hazard.

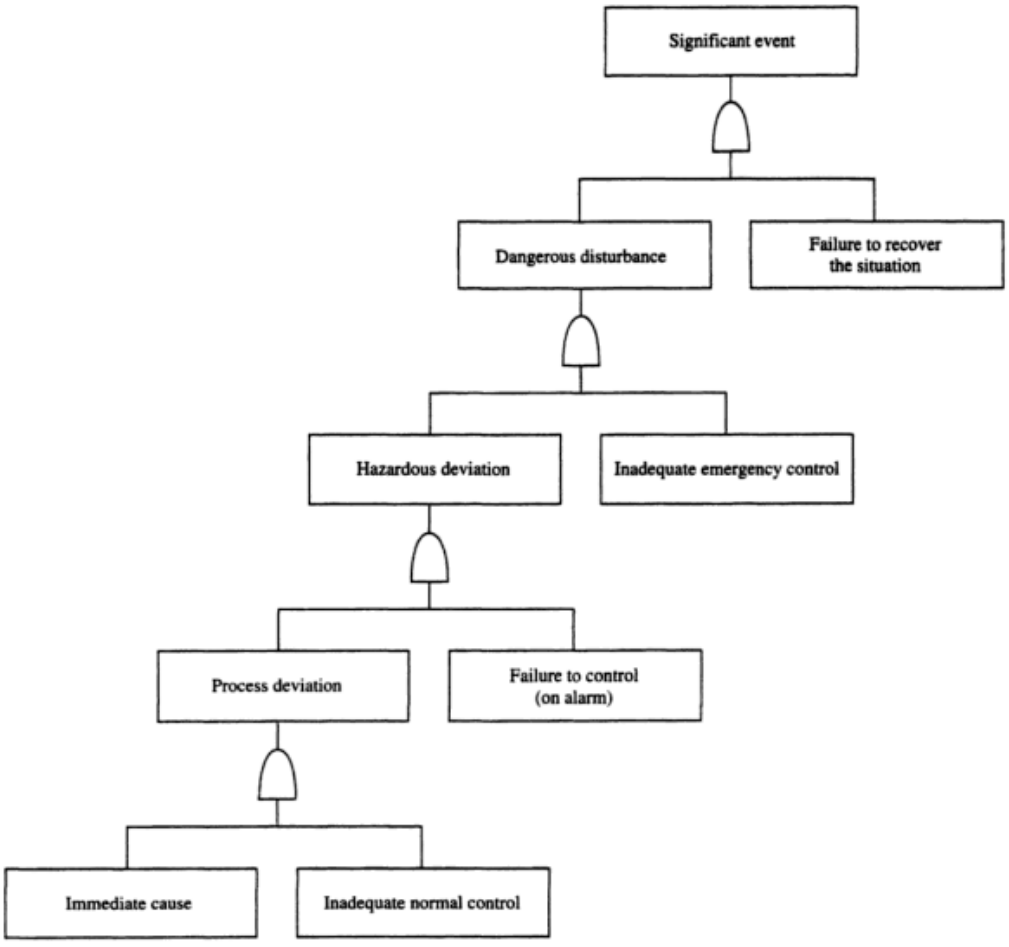


Figure 9- Fault tree representation of the general incident scenario (from Wells, 1997).

2.3.3 Risk assessment of food packaging contamination

The EU framework regulations EC 1935/2004 and EC 2023/2006 establish general requirements for all food contact materials and promote good manufacturing practices, respectively. The protection of consumers from hazardous chemicals is ensured by the inertia principle, which regulates the migration of substances from packaging to foodstuffs. The European regulation (EC) 10/2011 specifies a positive list of substances than can be present in recycled plastic materials intended for food contact, while a negative list of substances only exists for paper and board materials in French and German recommendations. The inhomogeneity of such rules is a proof that there is a need for additional regulations regarding recycled materials (Ball, 2016; Schäfer, 2014).

The migration of chemicals from packaging materials into the food they contain is commonly referred to as migration, which becomes a concern when the levels of these chemicals in food reach unacceptable concentrations, as defined by the toxicological threshold of concern (TTC). The contamination resulting from migration involves the cross-mass transfer of various substances originating from different sources (Douziech et al., 2020).

The range of chemicals that can migrate from different components of packaging is extensive. Around 1,500 evaluated compounds are authorized for use in food packaging within the European Union, but there are still potentially hazardous and uncontrolled compounds. Furthermore, the complexity of the migration process increases with the inclusion of additional packaging components as well as variations in contact conditions and temperatures. However, despite its complexity, all these exchanges can be explained from a thermodynamic perspective. Thermodynamics, in this context, focuses on achieving equilibrium at the interface between the phases and components involved, disregarding the time required for migration to occur (Vitrac & Hayert, 2005).

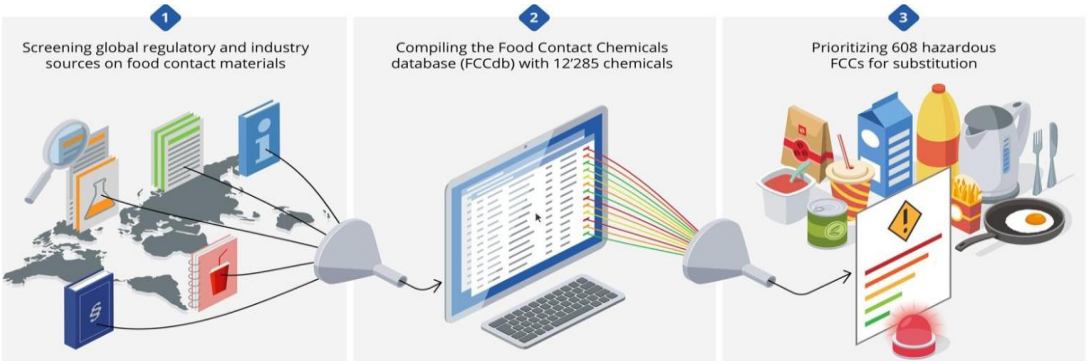


Figure 10-Schematic representation of safe FCM production procedure. (1) Screening of global regulatory sources of FCM. (2) FCCdb list of 12.285 substances potentially used in the production of FCM. (3) Substitution of hazardous substances to other ones for FCM production (from Groh et al., 2021).

When it comes to recycled FCM, it is crucial to acknowledge their diverse composition and consider their complete history (Figure 10). Understanding the potential migration of hazardous contaminants necessitates examining the various sources from which these materials originate, since each of them introduces a unique

set of potential contaminants. Therefore, conducting a comprehensive assessment of the entire lifecycle of these materials becomes necessary to accurately evaluate the migration risk (Vitrac & Hayert, 2005).

Complying with European restrictions poses significant challenges when relying on traditional migration tests that involve the use of food-simulating liquids like water, edible oils, and other solutions. These tests are not only time-consuming and expensive but also generate hazardous laboratory waste. By utilizing acceptable thresholds, migration modeling offers a cost-effective approach to assess non-evaluated and non-intentionally added substances. This expansion of predictive tools and approaches has a global impact, not only enabling the evaluation of contributions to FCM, but also facilitating the implementation of preventive measures throughout the supply chain to mitigate the risk of unintended interactions with food packaging (Vitrac & Hayert, 2005).

The regulation (CE) 10/2011, as previously mentioned, provides guidelines for migration assessment, allowing the utilization of "generally recognized diffusion models (based on data)" to estimate migration levels and reduce the need for extensive experimentation. These models are based on Fick's diffusion equation and rely on two important parameters: the diffusion coefficient (D) and the partition coefficient (KPL) (Martinez-Lopez et al., 2014). In order to properly estimate the migration of molecules from a packaging material to food, several properties of the transfer, listed in Table 4, must be measured.

Table 4-List of properties evaluated during the risk assessment of migration of molecules from packaging to food.

List of properties	*Meaning*	*Unit*	*Method of measurement*
D	Diffusion coefficient	$m^2.s^{-1}$	Transfer of molecules through several layers of materials (Roe test)
$K_{F/P}$	Partition coefficient	/	Ratio of concentrations in food and packaging at the macroscopic equilibrium [a]
C_p^0	Initial concentration of substance in the packaging	$mg.kg^{-1}$	Extraction and chromatographic analysis (GC-MS)
Fo	Fourier number	/	Dimensionless time of diffusion, inferred from concentration profiles of Roe test [a,b]
$L_{P/F}$	Dilution ratio between food and packaging	/	Usually, the length of packaging layer over the length of food layer [a]
v^*	Dimensionless migration kinetics	/	Ratio of concentration in food over the concentration in food at equilibrium [a,c]

(a) Zhu et al., 2019.

(b) $Fo = \frac{D_p t}{l_p^2}$.

(c) $v* = min[\frac{2\sqrt{Fo}}{\sqrt{\pi}}; 1 - \frac{2}{\pi^2} exp(-\frac{\pi^2}{4} Fo)]$ *(Crank, 1975)*

Chemical risk assessments are important for ensuring consumer safety. To assess the risk of negative health effects from chemical exposure, it is crucial to have information about the levels of chemicals migrating

from FCM. Migration modeling is a tool used for regulatory testing that tends to overestimate actual migration models. Different mathematical approaches have been developed to model chemical migration from FCM, with specific models designed for different packaging materials. Deterministic models are commonly used for plastic packaging, which mathematically describe the underlying physicochemical mechanisms of migration, often governed by a diffusion process described by Fick's law. These models assume a homogeneous initial distribution of the chemical, zero initial concentration in the food, and no resistance for transfer between the FCM and the food. For paper and board packaging materials, chemical migration is studied through mathematical modeling due to the materials' inherent heterogeneity and porosity, which pose challenges for modeling purposes (Amanatidis, 2020).

2.4 Possible technological response to accelerate the adoption of the circular economy.

2.4.1 New sensors: Chemical Imaging

2.4.1.1 Vibrational spectroscopy

The growing demand for product quality improvement and production rationalization across various industries has resulted in a significant increase in the application of vibrational spectroscopic techniques such as Raman, infrared (IR), and near-infrared (NIR) spectroscopy. This trend has led to the gradual substitution of time-consuming traditional analytical techniques like gas chromatography (GC), high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR), and mass spectrometry (MS), as well as nonspecific control procedures, with more specific and environmentally compatible tools offered by vibrational spectroscopy. It is based on the energy transitions associated with the absorption or emission of electromagnetic radiation. It involves the study of molecular vibrations, including stretching and bending vibrations, which provide valuable information about the chemical and physical properties of molecules. Raman spectroscopy and infrared spectroscopy are widely used for this purpose, offering complementary insights, and facilitating molecule identification in samples and polymers (Chang et al., 2023).

Synthetic polymers, such as the ones used for packaging have become an integral part of our daily lives. This report aims to demonstrate the crucial role that vibrational spectroscopic techniques play as characterization and control tools throughout the entire life cycle of polymeric products (Singh et al., 2014).

2.4.1.2 Raman spectroscopy

Non-destructive spectroscopy techniques are widely considered the optimal choice for process monitoring (Scotter, 1997). Among these techniques, Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy are particularly notable for their effectiveness in detailed material analysis. Raman spectroscopy, developed in the first half of the 20th century by Nobel laureates Chandrasekhara Venkata Raman and Grigorij Samuilovĭc Landsberg (Raman, 1953), provides comprehensive vibrational information about molecules and offers several practical advantages over infrared spectroscopy.

Equation 1-Raman shift

$$Raman\ \ shift[cm^{-1}] = \frac{10^7}{\lambda_{ex}[nm]} - \frac{10^7}{\lambda[nm]} \qquad (1)$$

While infrared spectroscopy has long been recognized as a valuable and non-invasive tool for compound analysis, Raman spectroscopy surpasses it in terms of vibrational data (Table 5).

Table 5-List of advantages and disadvantages of Raman spectroscopy compared to IR spectroscopy (Orlando et al., 2021; Scotter, 1997).

Raman spectroscopy		IR spectroscopy	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**
Detail vibrational data	Limited sensitivity for some compounds	Wide applicability to various sample types	Water interference affects signal quality
Minimal interference from water	Inefficient detection of low-frequency vibrations	Well-established and widely used technique	Limited sensitivity for certain compounds
Simple optical setup in the visible spectrum	May require longer acquisition times	Good for qualitative and quantitative analysis	Handling challenges with certain materials
Versatile sample preparation with glass/ quartz cells	Limited applicability to intractable polymers, singles crystals, and aqueous solutions	Well-developed databases for compound identification	Difficulty in distinguishing similar functional groups
Can measure both Stokes and anti-Stikes scattering	Requires higher laser power for certain measurements	Suitable for non-destructive analysis	Limited information on molecular symmetry
Independent of incident radiation wavelength for Raman shifts	Less efficient for analysing samples with strong IR absorption	Provides complementary information to Raman spectroscopy	Limited spectral range for certain instruments

Electromagnetic radiation interacts with matter through absorption, transmittance, and scattering. Absorption occurs when photons match the energy gap between electronic energy levels, while scattering occurs when photons interact with a crystal lattice or molecule, causing changes in polarization (Figure 13). Scattering can be elastic (Rayleigh) or inelastic (Raman) depending on whether the energy of the scattered photon matches the incoming photon. In Raman scattering, the energy difference between the incoming and outgoing photons is known as the Raman shift (equation 1). Importantly, the magnitude of Raman shifts is independent of the wavelength of the incident radiation (Bumbrah & Sharma, 2015; P. Larkin, 2017)

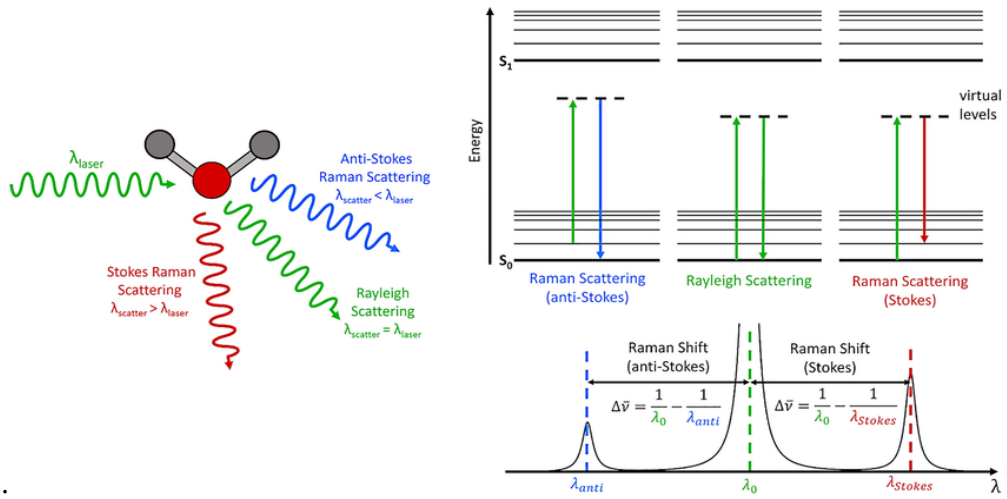


Figure 11-Jablonski energy diagram representing the energy transitions involved during light absorption and emission (Dey, 2022).

Raman spectroscopy relies on the detection of inelastic scattering, which occurs due to the frequency difference between incident radiation and vibrating molecules. However, Raman scattering is weaker than Rayleigh scattering (only 1 in 10^8 scattered photons) , and specialized equipment is needed to remove the stronger Rayleigh component (Bumbrah & Sharma, 2015)

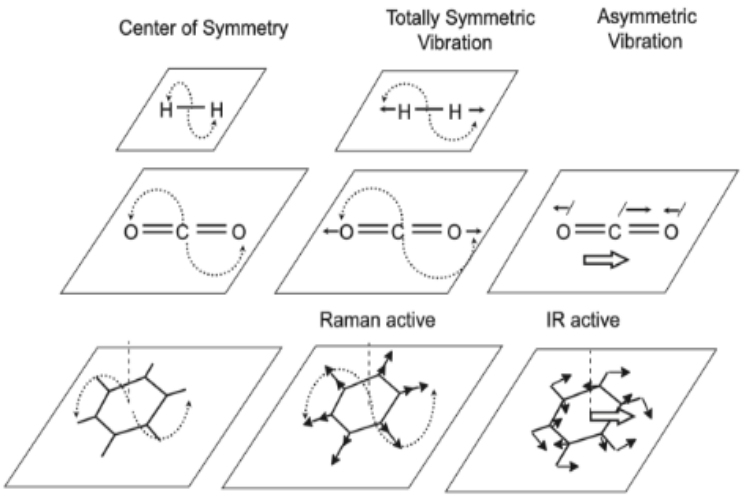


Figure 12-Center of symmetry, Raman and IR active symmetric stretching vibrations of H2, CO2, and benzene molecules (P. J. Larkin, 2018; Zi et al., 1996).

2.4.1.3 Chemical Imaging: overview

Chemical Imaging is the process of generating a visual representation of component distribution by simultaneously measuring spectra and spatial time information. This technique allows for the spatially resolved recording of chemical and physical properties of a sample. Chemical imaging combines various vibrational spectroscopy techniques, including mid-infrared, Raman, and fluorescence, with microscopy to identify and locate chemicals within materials without the need for solvent extraction or dilution (Biant et

al., 2023). By collecting spectral information for each surface location (pixel) in an x-y axis, the data can be transformed into a two-dimensional image representing the surface area (Qin et al., 2016).

Over the past decade, chemical imaging has made significant advancements and has become a valuable tool in various fields. In the context of risk analysis for food contact materials (FCM), it can be utilized to track the migration of potentially carcinogenic molecules from recycled paper or plastic packaging materials into food products (Kamruzzaman, 2021). By employing vibrational spectroscopic techniques that rely on light-matter interactions, chemical imaging enables the acquisition of spectral information and the creation of real-time images depicting a sample's chemical structure and component distribution.

2.4.2 Responsible Food Packaging design

As mentioned earlier, the utilization of post-consumer recycled (PCR) packaging is steadily growing. However, there are specific variables that pose challenges for their application. These include potential contamination resulting from unintended consumer usage, cross-contamination from other packaging materials, and from the recycling process itself, which can ultimately impact human health and safety. Additional limitations include difficulties in processing materials with different compositions, such as multilayer films, as well as concerns regarding polymer degradation and stability after multiple recycling cycles (Sanfins Cecon et al., 2021). To address these issues, further research is necessary to develop solutions.

One potential solution to prevent the migration of contaminants is the implementation of functional barriers (Figure 16). Functional barriers are multilayer structures designed to hinder or prolong the release of chemicals from food contact materials into the food itself (Feigenbaum et al., 2005). These barriers are intended for direct contact with food and should not introduce substances that affect the properties of the food or pose potential risks to human health. However, a notable drawback of these materials is that the resulting packaging, including the functional barrier, is no longer biodegradable, posing a recycling challenge (Johansson, 2011).

Novel strategies for enhancing functional barriers are currently being explored. In recent years, the growing environmental concerns have led to an increased emphasis on the use of recycled plastics and paper in food packaging. This trend has underscored the need for effective functional barriers to prevent contaminants from migrating into food. Future trends in the food packaging industry include a greater use of biobased polymers, increased utilization of nanotechnology to improve performance, and a rise in the adoption of active or intelligent packaging (Johansson, 2011).

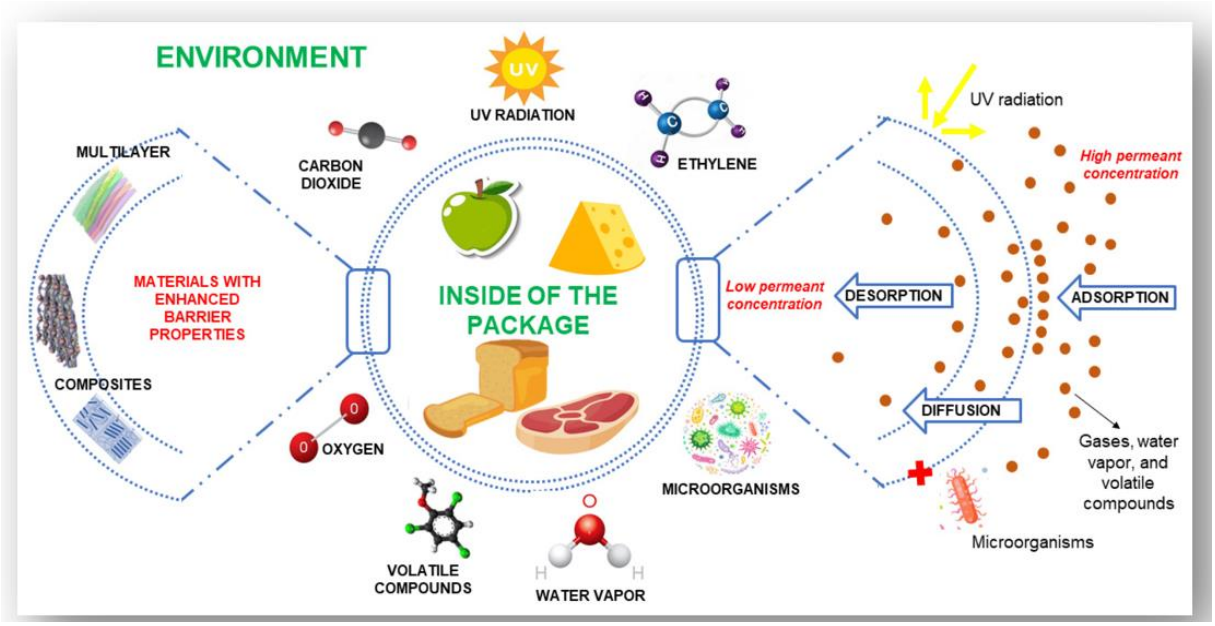


Figure 13-Barrier function of food packaging and hazardous agents for food safety present in the environment, along with some examples of enhanced barrier materials technologies (Versino et al., 2023).

Vibrational spectroscopy techniques such as Raman are increasingly used across industries to improve product quality and streamline production processes. They offer specific and environmentally friendly alternatives to traditional methods of analysis. Chemical imaging combines these techniques with microscopy to visualize the real-time distribution of components in a sample. This type of imaging can be used in analyzing the migration of contaminants in post-consumer recycled packaging materials and study the efficiency of functional barriers.

3 GOALS AND APPROACHES

3.1 General goals

This research project fits in today's overall context of overconsumption, waste management and new circular economy comprehensive policies. In order to include the envisaged technological responses in the food packaging assessment loop, several existing or new methodologies need to be developed at the lab scale. The project has identified the following key goals:

1. Detection and localization of contaminants in food contact materials (FCM), along with quantification of their mass transfer.
2. Mitigation of health hazards through a comprehensive risk assessment of contaminant migration in recycled food packaging.
3. Implementation of preventive approaches within the supply chain or packaging design, in line with the framework Regulation 2023/2006/EC.

To achieve these overarching goals, the project has outlined specific objectives that need to be accomplished:

- Evaluate the use of Raman Chemical Imaging as a tool to characterize the presence and spatial distribution of contaminants in selected FCM.
- Employ sorption and diffusion techniques to measure and estimate apparent diffusion coefficients in the packaging materials.
- Develop an efficient method for the detection of contaminants in FCM.
- Focus on the detection and evaluation of contaminants present in commercial food packaging that can be detected using the developed method.

By addressing these objectives, the project aims to enhance the understanding of contaminant migration in food packaging, improve detection methods, and contribute to the development of preventive measures for safer food contact materials.

3.2 Overview of experimental approaches

To achieve the three main goals of the study, the experimental strategy is divided into two major blocks, as it is shown in the following Figure 17.

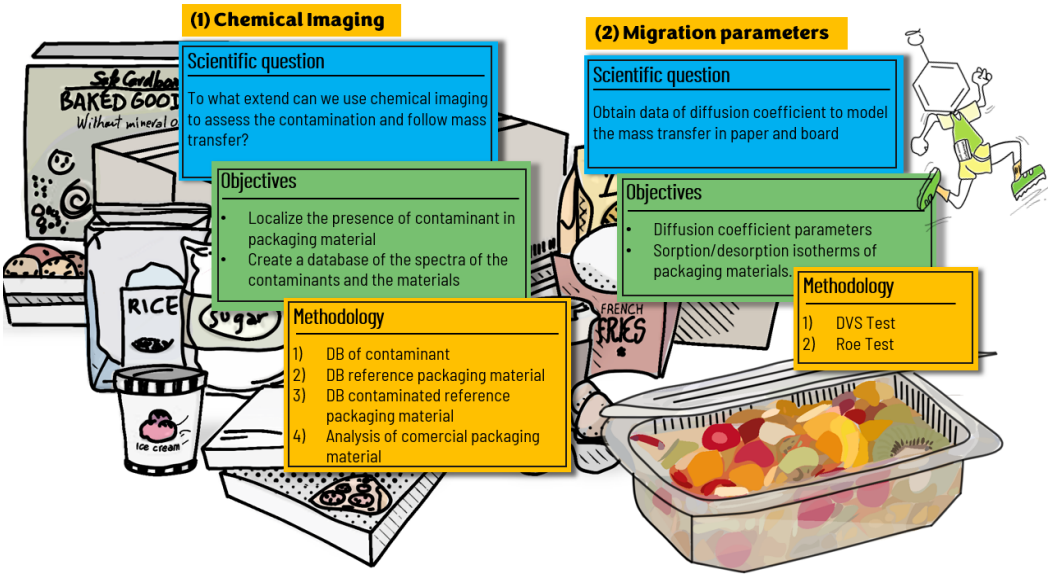


Figure 14-Objectives and methodologies of the two main experimental blocks of the project.

3.2.1 Vibrational spectroscopy and chemical imaging

The first block involves the study of the application of vibrational spectroscopy as a tool to characterize the presence and location of contaminants in recycled packaging. The objective is to be able to develop a method by the use of Raman spectroscopy, to quantify mass transfer in these types of packaging. The methodology followed can be described below, in Table 6, following the flow of scientific questions that need to be solved in order to achieve our goal.

Table 6-Workflow of scientific questions, methodologies and objectives involved in the project.

Scientific question	*Secondary questions*	*Methodology*	*Objectives*
Can we detect our molecules of interest with Raman spectroscopy?	• What is the nature of our contaminants? • Which are the Raman spectra of our contaminants? • What are the optimal parameters to obtain the best spectra?	1) Raman spectra of contaminant	Database of spectra of pure molecules
Can we detect our molecules of interest in the packaging material with Raman spectroscopy?	• Which method of contamination do we use for each material and contaminant? • How can we use Raman to detect the contaminant in the material?	2) Raman spectra of packaging material	Detection of molecules in a matrix (recycled plastic, paper, and board)
Is it possible to characterize the diffusion coefficient of the molecules of interest in the recycled packaging using Raman?	• Which type of transfer do we want to assess? • Which is the time of diffusion of each contaminant for each material? • How can we extract the diffusion coefficient from a Raman measurement?	3) Raman spectra of contaminated packaging material	Characterization of the diffusion of the molecules in the recycled plastic, paper and board materials

The detection of molecules and their distribution in a matrix will be assessed using chemical imaging, as can be seen in the example of recycled kraft paper contaminated by aromatic compounds, in Figure 15 (Biant et al., 2023).

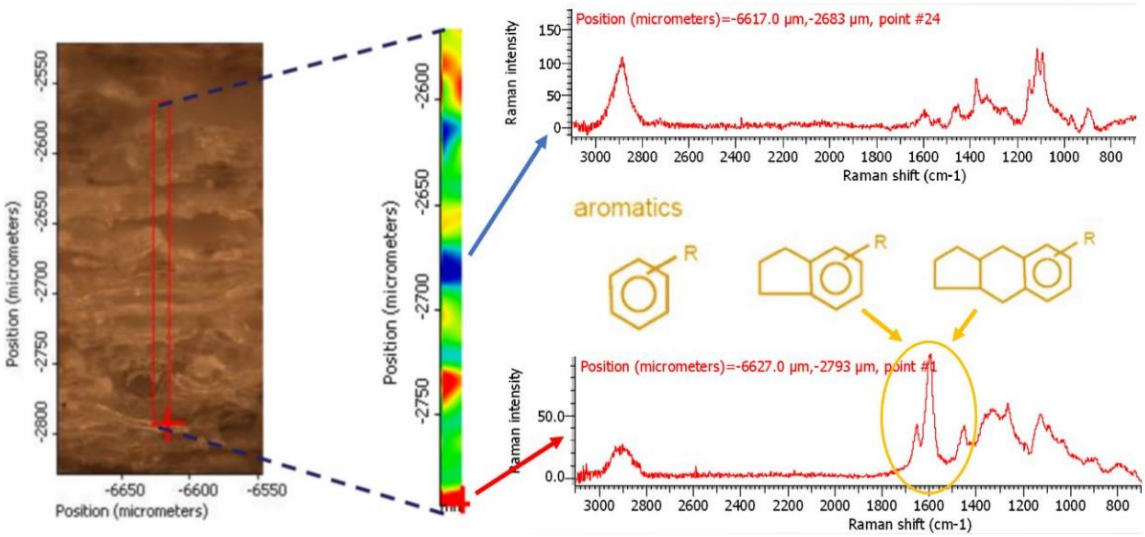


Figure 15-Distribution of aromatic compounds along the cross-section of a recycled kraft paper sample (from Biant et al., 2023).

The contribution of Raman in this report is significant in several aspects. Firstly, it plays an important role in the detection and identification of molecules of interest in recycled packaging. Secondly, it helps assess the diffusion behavior of each contaminant in different materials. This in general will enable deeper understanding of the mass transfer processes in recycled packaging materials.

3.2.2 Diffusion profiles using Roe test.

The second main block involves the use of two complementary techniques used to determine the diffusivities of the molecules of interest. These parameters will later be useful for the modelization of mass transfer in recycled food contact materials. The two techniques used are the Roe test and the DVS test. Both are carried out in parallel to provide complete information.

For the **Roe test,** a calibration curve is initially made using UV spectroscopy for each family of molecules in a determined solvent. Later, the test is performed with the molecule of each family that showed the best curve, and different types of packaging material. This method is able to measure the apparent diffusion coefficient in polymers for values between 10^{-11} to 10^{-18} $m^2.s^{-1}$, which are calculated from the accumulation or losses of the compound in each layer at different times while being compared to theoretical values. These theoretical values are coming from dimensionless abacuses (Figure 12), numerical models or analytical equations. From a single experiment at different times of migration, it is possible to calculate the

dimensionless parameter of the Fourier's number (F_0). With these values, it is possible to calculate D for different polymers at different experimental times. The major advantages of this method, against other solid-contact methods, are that it avoids chemical affinity limitations and additional mass transfer resistances. Moreover, it provides several advantages such as keeping the symmetry of diffusion from the two sources, providing a concentration profile that can easily be compared to dimensionless profiles and the ability to calculate a broad accurate range of D under similar contact conditions.

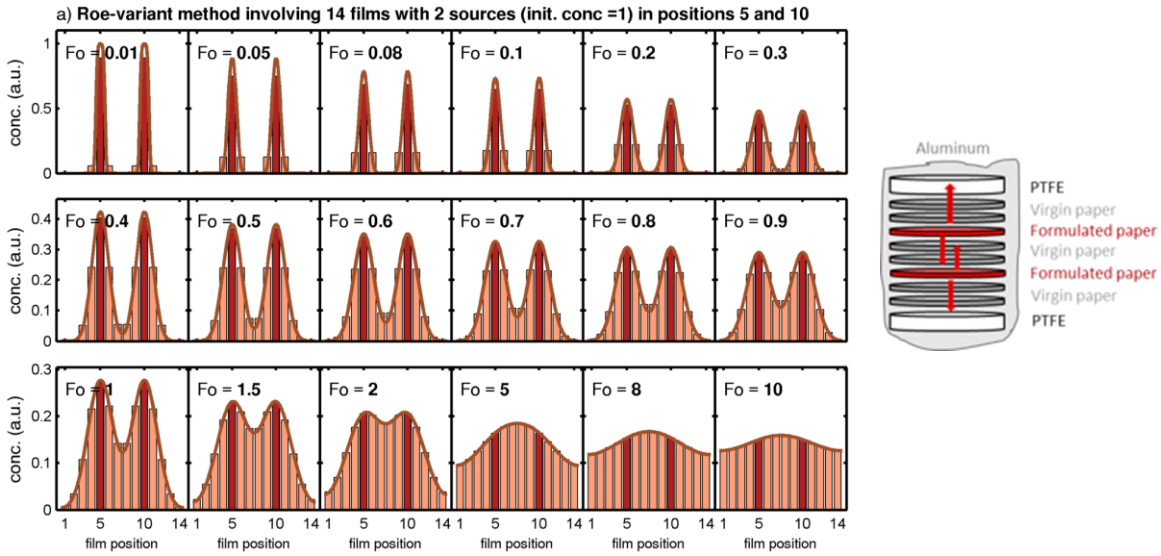


Figure 16-(left) Abacuses of concentration profiles measured during the Roe-variant method involving 14 films with 2 sources (initial concentration=1) in positions 5 and 10. (Right) Schematic representation of a Roe-type test involving 8 films with 2 sources.

Its main limitation is the high dilution induced by the dispersion of a small amount of substance in a large volume of polymer. This dilution problem can be solved by inserting two sources of contaminated polymer instead of just one. Furthermore, ROE's method requires a minimum of 2 days and the high dilution because of the dispersion of a small volume of the compound in a bigger volume of the polymer. To avoid this, the method was adapted by using two sources in order to reduce the dispersion of the sample in the plastic/paper.

The experimental setup developed during this work will help acquiring diffusivities that are important values to feed migration models and understanding kinetics of contamination through packaging materials. This method, initially used for plastic films, will be adapted to cellulosic materials, and will provide important information about the key structural properties of a fibrous material to know for describing mass transfer mechanisms.

3.2.3 Dynamic vapor sorption of volatile substances

The sorption properties of volatile molecules on solid materials are important for their storage, stability, processing, and performance. Factors like thermodynamic compatibility, structure, and morphology influence the transfer of water mass between the polymer and the environment. The diffusion coefficient of water in several packaging materials is initially measured by sorption and desorption of water vapor.

Later, we will analyze the diffusion coefficient of the packaging materials once it is contaminated with organic volatile contaminants, such as toluene. The microbalance device used to measure the DVS is presented in Figure 11. It uses a vector gas carrying a known amount of substance (controlled by its partial pressure in the gas) over a sample on a sensitive microbalance, which detects slight changes in the mass.

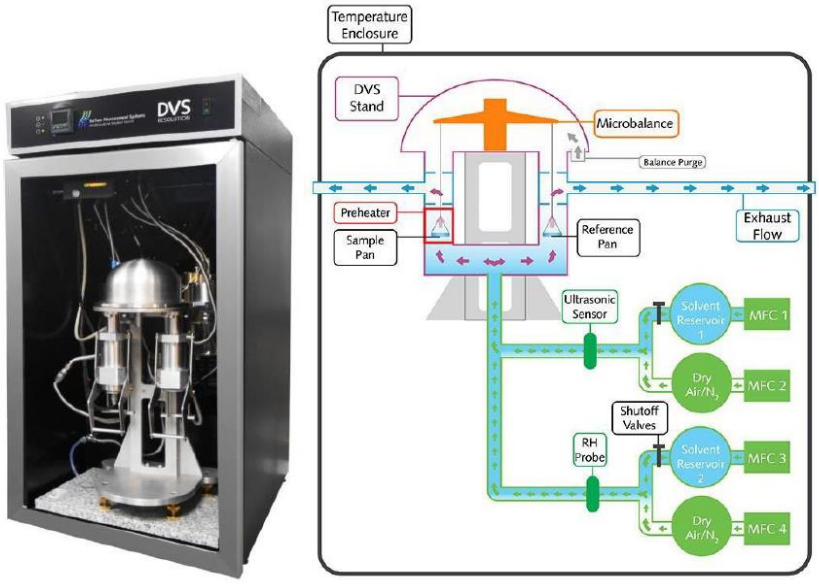


Figure 17-(left) DVS experimental device. (Right) Schematic description of the DVS equipment operation

Moisture sorption isotherms provide information about the relationship between the water uptake (or moisture) of the matrix and the relative humidity of the environment. These isotherms allow for estimating the moisture content of the matrix under specific relative humidity and temperature conditions. Mathematical models can be used to represent the equilibrium moisture adsorption and desorption of materials at different environmental conditions.

While moisture isotherm data is available for many materials, there is relatively limited data for paper-based materials. Paper and paperboard materials, due to their high porosity, readily absorb moisture in high-humidity environments. Understanding the shape of the moisture sorption isotherm provides insights into the physical and chemical structure of the material. This knowledge can be valuable in selecting appropriate packaging materials for different purposes, including reducing contaminant migration in the specific case of this project.

4 MATERIALS AND METHODS

4.1 Materials

4.1.1 Packaging materials

While the primary emphasis of this study is on the analysis of recycled plastic and paper packaging, only the paper and board materials have been examined this far. Consequently, the research exclusively mentions the analysis conducted on these materials. Two categories of recycled paper FCM were used, namely reference and commercial materials, as presented in Table 7.

Table 7-List of reference materials and commercial packaging evaluated in the project and their main properties.

Types	Reference paper and board packaging			Commercial paper and board packaging		
	Blotting paper	Gerstar paper GDS	Cup Forma	Rice packaging	Chocolate cake packaging	Pet food packaging
Properties	100% cotton, plain	Softwood + hardwood. One-sided coat	Bleached board (3 layers)	Recycled	Not recycled	Recycled

4.1.2 Contaminants

The selection of contaminants was made based on various parameters, as it is shown in Table 8, including (1) molecular family, (2) density, (3) boiling and melting temperature, (4) their physical state, (5) tolerable daily intakes, (6) human health concern, and (7) high quality Raman spectra.

Table 8-Molecules analyzed for the risk assessment of recycled plastic and paper FCM.

Molecule	CAS Number	Family	Density (g/ml)	Mw (g/mol)	Melting Temperature (°C)	Boiling temperature (°C)	Physical state
Benzophenone	119-61-9	Cyclic ketone	1,11	182,21	48	305	Crystal
4,4'-Bis (dimethylamino) benzophenone	90-94-8	Cyclic ketone	1,021	324,50	89	470	Crystal
Acetophenone	98-86-2	Cyclic ketone	1,028	120,14	19	202	Crystal/ liquid
Methyl acetate	79-20-9	Ester	0,934	74,10	-98	56	Liquid
Phenyl acetate	122-79-2	Ester	1,073	136,10	-30	196	Liquid
Toluene	108-88-3	Oligophenyls	0,871	92,138	-95	110,6	Liquid
p-Terphenyl	92-94-4	Oligophenyls	1,23	230,30	212	389	Crystal
Dibutyl phthalate (DBP)	84-74-2	Phthalate	1,043	278,348	-35	340	liquid
Butyl benzyl phthalate (BBP)	85-68-7	Phthalate	1,1	312,370	-35	370	liquid
Di-isodecyl phthalate (DDP)	26761-40-0	Phthalate	0,965	446,66	-50	370	liquid
BHT	128-37-0	Phenol	1,048	220,35	69-73	265	Crystal
Nonanal	124-19-6	Linear aldehyde	0,827	142,24	-19,3	195	Liquid
DBP	84-74-2	Phthalate	1,043	278,34	-35	340	Liquid
DEGDB	120-55-8	Benzoate	1,175	314,33	24	235	Liquid
Benzophenone	119-61-9	Cyclic ketone	1,11	182,22	47-51	305	Crystal
p-Terphenyl	92-94-4	Oligophenyls	1,23	230,3	212	389	Crystal

The selected contaminants for:

- Paper and board packaging come from the list of molecules in Food Contact Materials Sheet No.4 from the French DGCCRF (Competition, Consumer Affairs and Fraud Prevention General Directorate).
- Plastic packaging comes from the European regulation (CE) 10/2011 of the European Commission.

4.2 Methods

4.2.1 Concentration in extracts: UV spectroscopy

Ultraviolet (UV) spectroscopy measurements were performed in both blocks of the experimental strategy (Table 9). The absorbance reading obtained from the device can be correlated with concentration values, making UV spectroscopy a valuable tool for quantifying contaminants in a solution. For each contaminant utilized in the Roe test, a calibration curve was generated beforehand. While multiple calibration curves were obtained, this report will focus on showing the most significant ones.

Table 9-Protocol of experiments carried out with the UV spectroscopy and their objectives.

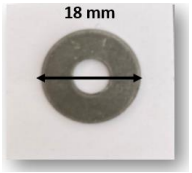
Protocol	Recycled paper packaging samples	Recycled plastic packaging samples	Objective
Calibration curve	Quartz cuvettes Contaminants Blank: solution DCM: Ethanol (3:1)	Quartz cuvettes Contaminants: Blank: solution DCM: Ethanol (3:1)	Plot calibration curve to determine the concentration of contaminants of interest.
Roe test	Quartz cuvettes Reference sample Blank: solution DCM: Ethanol (3:1) or Ethanol (96%)	Quartz cuvettes Reference sample Blank: solution DCM: Ethanol (3:1) or Ethanol (96%)	Quantify the amount of contaminant in the films of the test.

4.2.2 Determination of diffusivities

To study the diffusion coefficient of molecules in paper or plastic by solid contact, a Roe-type method was followed. The materials required are described in the following Table 10.

Table 10-List of materials and products used for the Roe experiments.

Material	Requirements
Polymer material	Pieces of paper or plastic in a circular shape (3 x 3 cm) Metal support (18 mm diameter)
Compound of interest	Pure concentration
Glass lens	In order to let the samples dry.



PTFE (Teflon) circles	To avoid the mass transfer of the contaminant outside the test.
Aluminum foil	Protect from the heat
Metal/ copper support	Maintains the stack of films in contact in order to allow the migration of the contaminant through the different layers

The procedure is described in the following lines:

- *Day 1: Formulation of the sources*. Three films (two sources and one reference) of polymer will be impregnated overnight in a solution with the desired compound's diffusion coefficient we want to measure.
- *Day 2: Assembling the films in a stack*. Remove only two films from the solution and let them dry. Create a stack of eight, eleven or fourteen films and introduce the two dried sources in a symmetrical position (for example position 5 and 10 for a stack of fourteen films). This stack will be placed between wood cylinders, inside a copper cylinder and tightened with a clamp. All of the stacks should be wrapped with aluminum foil and introduced in an oven, during the selected temperature *T* and period of time *t*.
- *Day 2+N: Extraction of the substance from the films*. After *t* hours or days in the oven, prepare one bottle containing 4mL and an extraction solvent, DCM: Ethanol (3:1) for each film of the stack and the reference sample.
- *Day 2+N+1: Concentration profile.* After one night in the shaker, the absorbance of each solvent of extraction is measured by UV spectroscopy. The concentration of the substance in each bottle is inferred from a comparison with a previously plotted calibration curve.

-

4.2.3 Sorption isotherms of recycled packaging material for water and solute

The experiments involving the Dynamic Vapor Sorption (DVS) are currently ongoing. For now, the absorption of water on blotting, CupForma and Gerstar paper has been measured. The analysis on films of microfibrillated cellulose (MFC) and bilayer materials has also been performed (Figure 18).

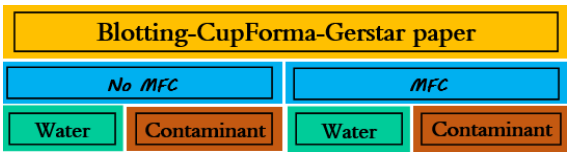


Figure 18-Schematic representation of the different combinations (materials and volatile molecules) evaluated with the DVS microbalance.

The device used in the experiment consists of a temperature-controlled enclosure containing a microbalance and ultrasound probe control boxes. The enclosure is connected to an inert gas supply (nitrogen). The

measurement cell, located on the left, is used for the sample, while the reference cell on the right remains empty. To perform a measurement a method needs to be created. This involves specifying parameters such as start and stop partial pressures, duration, incubator temperature, preheater temperature, and cycle type (half, full, or multiple). After creating the method, it can be registered, and a post-method can be configured to reduce nitrogen consumption. To launch the method, the corresponding tank (A for the solvent or B for water) is opened in the *instrument control* tab. The method is loaded, the sample name is entered, and baskets/hooks are placed in both cells. The balance is tared, and after stabilization, the sample is loaded into the measuring cell. The chamber then should be closed, and the N_2 flow rate is adjusted. The method is then run, and after the corresponding time, the results will be saved. The progress of the measurement can be tracked in the *Method tab*, while the *System live data* tab provides real-time information on mass, partial pressures, and temperature.

The main data extracted from the measurement are the partial pressure of water over time (usually from 0% to 100% for sorption then back to 0% for desorption, by steps of 10% partial pressure) and the mass variation of the sample during these steps. The sample mass increases and decreases with the water partial pressure and reaches a plateau value at the end of each step. The isotherms (of sorption and desorption) are then plotted using the mass uptake value at the plateau of each step as a function of the water activity (from 0 to 1, corresponding to the partial pressure of water in the cell).

4.2.4 Reference Raman vibrational spectra

The following protocol was applied for the Raman spectroscopy and Raman micro spectroscopy measurements.

1. Instrument Setup: Ensure that the spectrometer is powered on and warmed up (30 minutes). Verify that the laser is properly aligned and focused. Calibrate the device using the calibration standards (using a slice of silicon that has a single peak around 520 cm^{-1}).
2. Sample Preparation: Select the sample of interest and prepare it in the appropriate size and place it in the holder. All the samples used for Raman were either solid (powder or one solid part) or pure liquids. The formulation of paper or plastic samples requires a previous imbibition in appropriate solutions at different concentrations (0.5, 1, 2, and 5 g/L). These samples were dried on a microscope glass slide under the airflow of a fume hood before the Raman acquisition. The liquid samples were dropped on a curved glass slide or into a plastic cuvette before acquisition. Several supports are used for this project, regarding the nature of the sample and the acquisition needed. Three different glass slides were used, a classic microscope slide for opaque solids (paper, board, or plastic), glass slides with holes to pour liquids inside, and a glass slide covered by an 8-well plastic cuvette. For environmental reasons, the slides were cleaned with a solvent (ethanol or acetone) and reused when possible.

3. Experimental Settings: Many acquisition parameters can be changed to improve the quality of the image, the intensity, and the resolution of the Raman signal. The main parameters set during the measurements of the project are listed below:
    a. Laser: two different laser sources are available (532 nm and 785 nm).
    b. Acquisition time, which corresponds to the time of illumination of the sample by the laser.
    c. Laser power, adjusted from 0.01% to 100% of the laser capacity by filters.
    d. Spectral range, from 50 cm^{-1} up to 4000 cm^{-1}.
    e. Pinhole opening, which plays a role on the focal distance.
    f. Objective lens, from 5x to 100x magnification, with different numerical apertures and working distances.
4. Data Acquisition: Position the sample under the laser beam, and ensure it is properly aligned. Move the objective until the focal plane of the desired sample is reached. The acquisition is controlled and started by the user on the LabSpec6 software.
5. Data Analysis: The acquired data (Raman spectrum/spectra, picture, map) are saved and exported to a suitable software for analysis. A baseline correction and peak indexing can be performed on the acquired Raman spectrum with the LabSpec6 software.

5 MAIN RESULTS AND DISCUSSION

Prior to delving into this section of the report, it is crucial to acknowledge that the objective was to analyze both recycled paper and plastic food packaging. However, due to the time required for the method development, the current results presented are just focused on paper and board materials. Nevertheless, it is important to note that the procedure employed for studying recycled plastic FCM will remain consistent, with some adjustments in the methods due to the intrinsic different nature of paper (porous) and plastics (dense).

5.1 Vibrational spectra of reference substances and their detection in paper and board.

As stated previously, one of the key objectives of our study was to use Raman Chemical Imaging as a tool for characterizing the presence and distribution of contaminants in recycled paper FCM. In order to accomplish this, we initially constructed a spectral database encompassing all the molecules listed in Table 7 which are potential contaminants found in recycled paper and/or plastic food packaging. However, it is important to note that the quality spectra rely on several factors, including the nature of the contaminants and their physical state. For solid samples, the Raman spectra generally yielded satisfactory results, while liquid samples consistently exhibited an unidentified peak at approximately 2500 cm^{-1}. Thus, considering these sample variations, we aimed to obtain an optimal parameter for acquiring high-quality spectra by selecting both low-quality and high-quality spectra within each molecular family and comparing them.

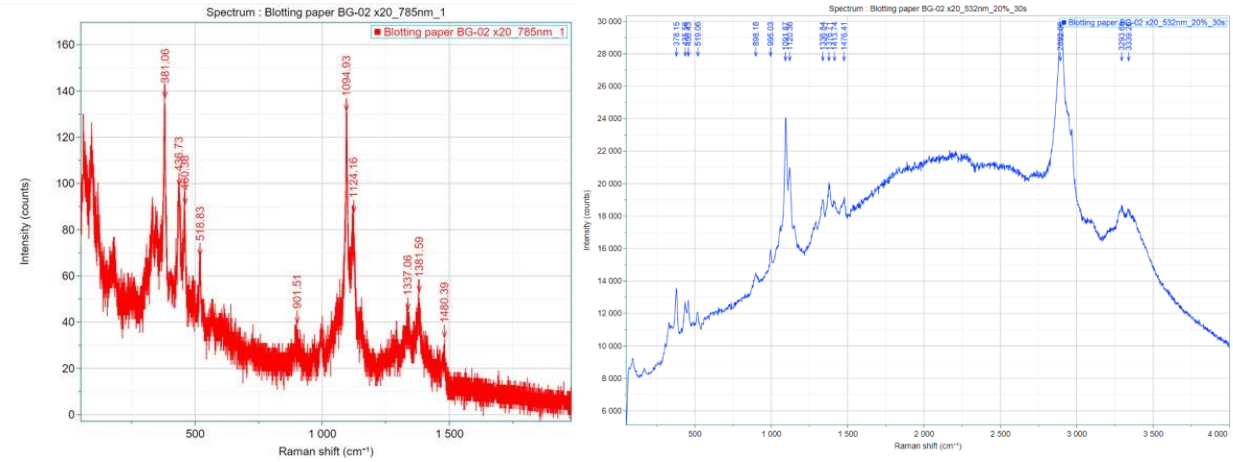


Figure 19-Raman spectra of blotting paper obtained with laser 785 nm (left) and 532 nm (right).

Once we completed the Raman spectra analysis using the best-quality spectra for all the molecules, we proceeded to generate a reference database of Raman spectra for the packaging materials. Figure 19 demonstrates measurements conducted with two different laser sources, 532 nm (green) and 785 nm (red), for each type of paper -blotting, Gerstar, and CupForma. The Raman spectra for the latter two types are provided in the Appendix 2. It is worth mentioning that the use of 785 nm laser was intended to eliminate cellulose fluorescence; however, it requires a longer acquisition time and higher laser power to achieve optimal resolution and intensity.

Table 11-Database of the peaks of reference recycled food packaging materials. The spectrums were obtained with the two lasers of 532 and 785 nm.

Blotting paper	532 nm	378,15	435,56	458,43	519,06	898,18	1091,87	1120,36	1336,84	1419,47	1476,47	2892,06	3293,69	3339,26
	785 nm	381,06	436,73	460,38	518,83	901,51	1094,93	1124,16	1337, 06	1381,59	1480,39	-	-	-
Gerstar paper	532 nm	371,71	430,34	461,65	513,84	892,48	1089,02	1123,21	1388,11	1473,56	2889,9	3208,23	3302,23	376,92
	785 nm	377,37	435,77	458,49	508,24	897,58	1095,5	1120,37	1318,02	1467,54	-	-	-	377,37
CupForma paper	532 nm	376,92	-	507,95	898,18	1089,02	1120,36	1376,71	1473,56	-	2889,21	3216,78	3302,23	-
	785 nm	379,49	434,65	510,35	896,46	1091,13	1119,25	1379,89	1379,89	1473,99	-	-	-	-

Among all the spectra obtained for various molecules, p-terphenyl was selected as the focal molecule for detecting contaminants in the packaging material. The primary reason for this choice, in addition to its high-quality Raman spectra, is that it has already been characterized in recycled food packaging (Parigoridi et al., 2014; Sturaro et al., 1995). The secondary reason is its chemical structure, p-terphenyl being a 3-ring polyaromatic hydrocarbon, close to the structure of PAH contaminants found in FCM.

Table 12-Raman peaks (in cm-1) of p-terphenyl and their corresponding functional groups.

p-terphenyl (92-94-4)	
532 nm	Functional groups
987,80	*Aromatic ring*
1032,93	*Aromatic ring*
1157,68	*Aromatic ring*
1213,42	*Aromatic ring*
1266,51	*C-C aliphatic chain*
1497,44	*C-C aliphatic chain*
1500,34	*Aromatic ring*
3058,21	*Aromatic -CH*

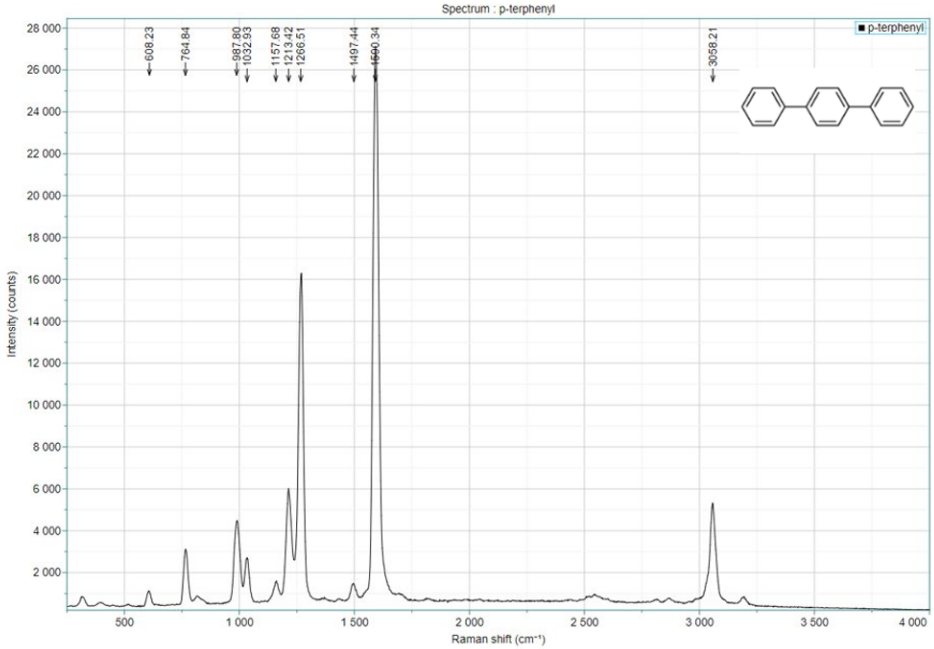


Figure 20-Raman spectra of p-terphenyl, obtained on pure solid p-terphenyl with the laser 532 nm.

Therefore, it can serve as a reference molecule to assess whether Raman spectroscopy can effectively identify contaminants in packaging materials. Moreover, our aim was to go deeper into the analysis by examining the distribution of contaminants on two levels: (a) different positions within a single cellulose fiber, and (2) their distribution among the fibrous network of the matrix. To conduct this analysis, it was crucial to determine the appropriate contamination method and parameters (Table 13). In this case, p-terphenyl was initially dissolved in ethanol 96%. Once prepared the solution, a film of blotting paper was

dipped inside the solution and left it until its evaluation with the Raman. The results of this analysis are presented in Figure 21.

Table 13-Main parameters of the Raman spectrometer selected for mapping of blotting paper contaminated in a solution of 2g/l of p-terphenyl in DCM/EtOH.

Date	14.04.2023 1...	Acq. time (s)	10	Accumulations	2	Laser	532nm_Edge
Spectrometer...	1949.25	Hole (µm)	100	Slit		Grating	600 (500nm)
ND Filter	50% (39mW)	Objective	20x	ICS correction	Off	Range (cm-¹)	

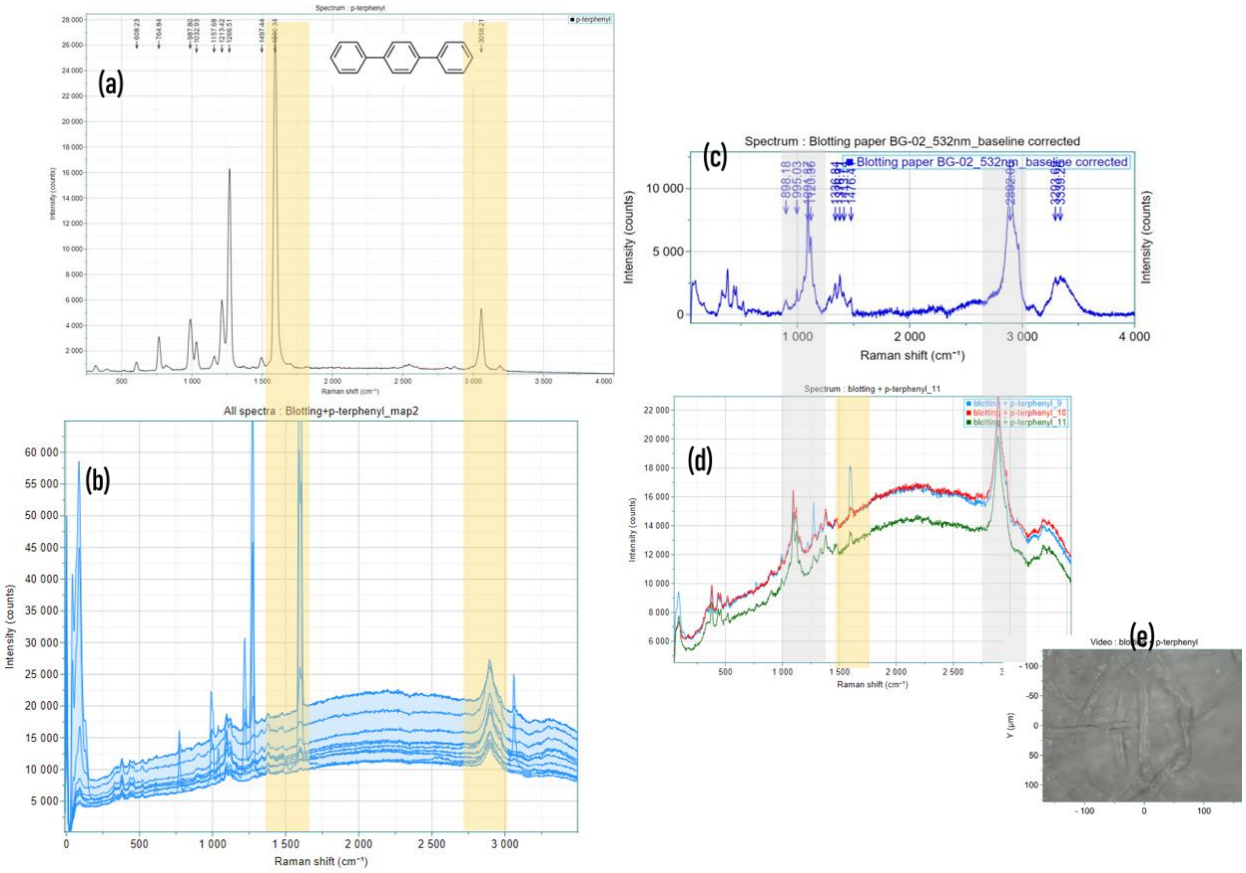


Figure 21-(a) Raman spectrum of p-terphenyl; (b) Map Raman spectra of contaminated blotting paper in a solution of 2 g/L of p-terphenyl in DCM/EtOH. (c) Raman spectrum of blotting paper; (d) Raman spectra of 3 different positions in the same cellulose fiber of the blotting paper contaminated with p-terphenyl; (e) Raman image of the targeted cellulose fiber. Molecular Raman footprint peaks are highlighted in yellow for p-terphenyl and gray for cellulose. All the spectra were obtained with the 532 nm laser.

As depicted in the previous figure, both in the map and fiber analyses, the presence of cellulose is consistently observed, while p-terphenyl is occasionally detected. This observation confirms that the distribution of the contaminant is not homogeneous in the fibrous network of the paper. This heterogeneous distribution can be attributed to two different phenomena: (1) the affinity of the solvent with cellulose,

creating menisci in cross-sections of fibers and (2) the capability of p-terphenyl (melting point MP = 212°C) to crystallize during solvent evaporation. The heterogeneous distribution of molecules in the cellulose matrix can be compared to the actual nature of the recycled material. Indeed, the recycling process manufactures a material composed of diverse fibers originating from different sources. Due to the significant variability in composition, the substances present in a contaminated paper packaging could be released unevenly into the food. This parameter is one of the most difficult to control while performing migration tests. Developing further the method of chemical imaging to detect contaminants in the FCM matrix could help understanding some migration mechanisms.

Once it has been demonstrated that the Raman spectroscopy is a promising tool for identifying the presence of contaminants in paper packaging, it would be intriguing to go further and investigate the origin or source of the contamination as well as how it diffuses through the material. As previously presented in section 2.3.3 of this report, intrinsic properties of the substance's diffusion in materials must be determined experimentally to better understand the contamination and their migration to food. While Raman spectroscopy could assess the migration of poorly volatile substances, the sorption of volatile compounds on P&B was evaluated with a microbalance. The results of water absorption and desorption on several cellulosic materials are discussed in the next paragraphs.

5.2 Water sorption properties on paper and board.

The secondary objective of understanding contamination and migration in recycled food packaging, presented in section 3.1, was addressed by conducting a Dynamic Vapor Sorption (DVS) test to acquire sorption properties and diffusion coefficient data of the paper packaging materials.

The DVS analysis involved subjecting the various paper packaging materials to water, allowing us to gather data on their sorption and desorption properties. To construct the corresponding isotherms, we used the DVS test to calculate the mass uptake of water in the air relative to the partial pressure of water in the air at a given time (t). The results of the DVS, just

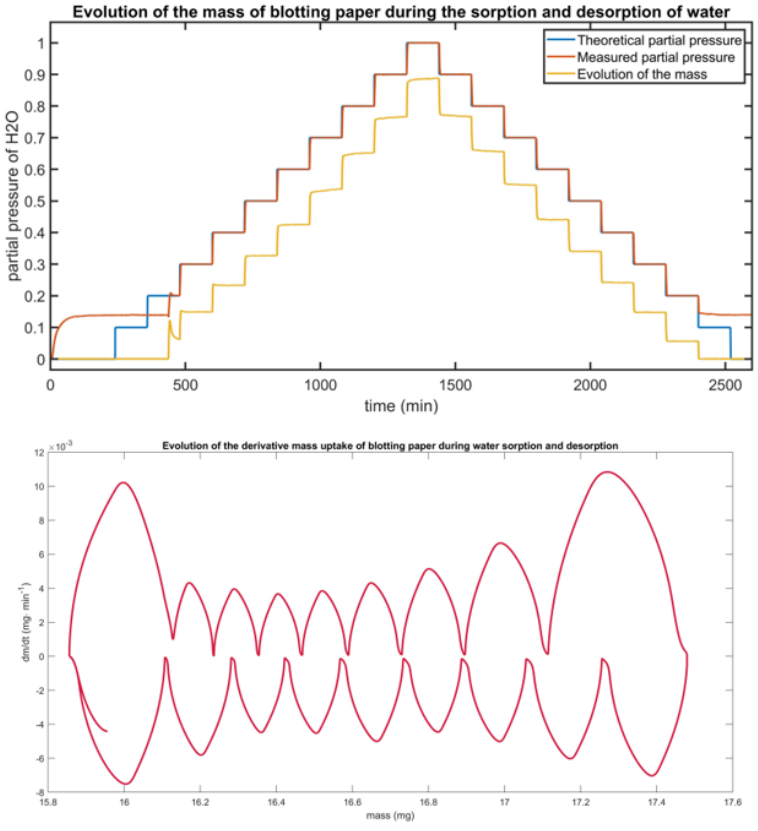


Figure 22-Evolution of the mass (above)/ derivative mass (below) uptake of the blotting paper during water sorption-desorption.

for one of the paper packaging materials (blotting paper), are shown in the following figures.

Figure 22 illustrates the isotherms of sorption (from left to right corresponding to the mass uptake) and desorption (from right to left corresponding to a mass decrease) for the different paper types with water. These isotherms provide detailed representation of the water activity of each material in relation to the mass of water in the material. Notably, for the same water activity, the mass uptake of water was the highest in CupForma paper, followed by blotting paper, and finally by Gerstar paper.

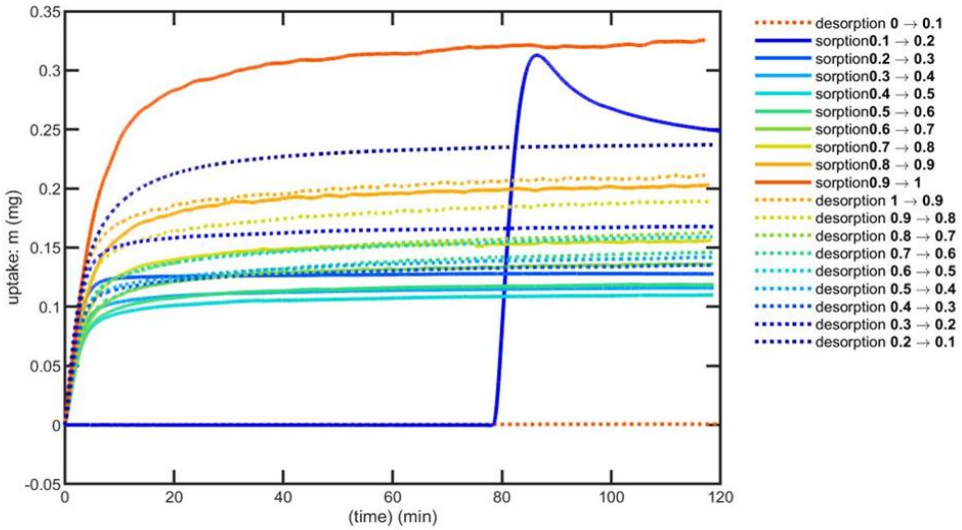


Figure 23-Mass uptake of the paper during sorption and desorption steps of the DVS.

On the other hand, when analyzing the moisture sorption isotherms of virgin blotting paper with two microfibrillated cellulose functional barrier films (Figure 24), we can see that the mass uptake of virgin blotting paper is less than the one of the MFC.

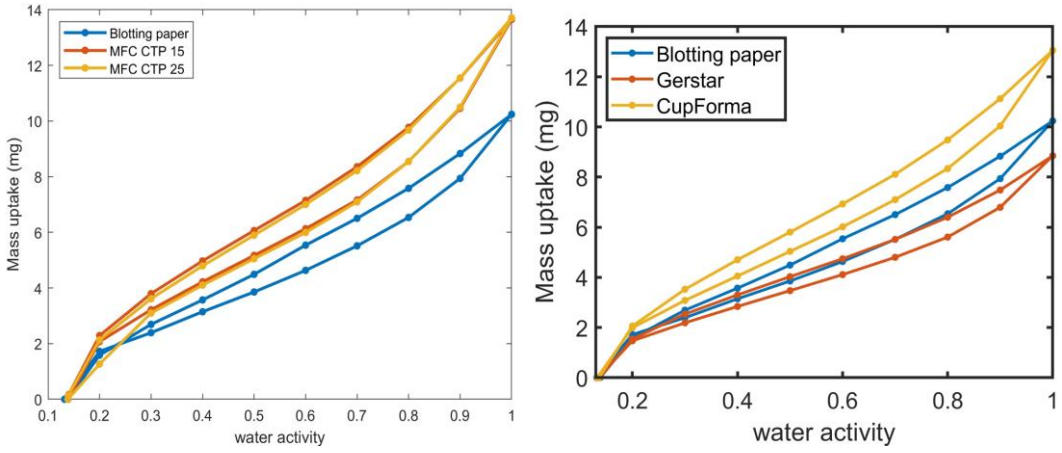


Figure 24-(Left) Sorption-desorption isotherms of blotting, Gerstar and Cup Forma paper. (Right) Sorption-desorption isotherms of virgin blotting paper and blotting paper laminated with two microfibrillated cellulose functional barriers.

As a result, from the graphs, it is evident that moisture properties exhibit variations depending on the paper type and composition. Specially, in the case of CupForma paper, it is important to note that it consists of three layers, and it is made of bleached board. Generally papers produced from bleached pulps are known for being whiter, brighter, softer, and more absorbent compared to those made from unbleached pulps (Bajpai, 2021). Furthermore, the fiber structure plays a significant role in this variation. Bleached paper typically undergoes an intensive refining process, which breaks down the fibers and increases their surface area, letting the water penetrate more easily. Additionally, bleached paper is often composed of softwood fibers, which are longer and more flexible than hardwood (used typically for blotting and Gerstar paper). This flexibility provides additional pathways for the water to flow. It is important to highlight that the bleaching process involves chemicals such as peroxide or chlorine compounds to remove impurities. These chemicals modify the surface of the fibers, making them more hydrophilic, and thereby improving water absorbency (Solomon, 1996).

On the other hand, the difference in moisture sorption between blotting paper and Gerstar can be attributed to the hardwood fibers. Gerstar paper has part of its composition with these types of fibers, meaning less flexibility and reducing the water flow pathways. Additionally, Gerstar features on side coated with $CaCO_3$ and latex. These components provide smoothness and printability. However, they are hydrophobic in nature, meaning that they repel water (Atla et al., 2017; Faille et al., 2019).

The isotherms of blotting paper, both with and without microfibrillated cellulose (MFC), reveal a notable difference in sorption-desorption rates. Specifically, the presence of MFC in the blotting paper leads to a higher rate of water absorption and desorption. This observation suggests that the inclusion of MFC creates a functional barrier that alters the water absorption characteristics of the base material. MFC consists of tiny cellulose fibers that are long and slender. When incorporated into the blotting paper, these fibers create a network that significantly increases the surface area (S. Nguyen & Lee, 2021), thereby facilitating greater water absorption. Furthermore, cellulose, the primary component of MFC, has a hydrophilic nature (Lavoine et al., 2014), meaning it has a natural affinity for water, improving the water absorbance capacity of the material.

The sorption-desorption rates of water on several cellulosic materials were determined to better understand their behavior towards mass transfer phenomena. However, not only the interactions between the matrix and the contaminant are important when it comes to evaluating the migration to food. One key parameter experimentally determined is the diffusion coefficient, specific to a material-molecule couple in specific conditions. The third results section of this report focuses on the Roe-type test implemented to estimate apparent diffusion coefficients in P&B materials.

5.3 Effective diffusivities of reference substances in paper and board.

To complete the findings obtained through DVS and acquire diffusion coefficient data, we conducted a test of contaminant migration within the paper materials. Using two pre-contaminated paper films, referred to as the sources, our objective was to observe the transfer of contaminants from the source across the other layers over time. By evaluating the results at various time intervals, we were able to calculate a dimensionless time called Fourier number (Fo) by Matlab programming. Obtaining this Fourier number is a key step for determining the diffusion coefficient of a specific contaminant at a given material. The aim of this analysis is to leverage the information on migration time, Fourier number, and spatial factors to calculate the diffusion coefficient of contaminants within a specific material (equation 2)*(Ostrogorsky & Glicksman, 2015)*.. This comprehensive approach allows us to gain a deeper understanding of contaminant behavior and the potential impact on the overall system.

Equation 2- (D) Diffusion coefficient equation: (Fo) Fourier number, (l) length, (t) time

$$D = (Fo \times l^2)/t \qquad (2)$$

In our report, we focused on the analysis of blotting paper as the selected material and DBP (Di-n-butyl phthalate) as the target contaminant. DBP was chosen due to its documented presence in recycled packaging materials and the significant health concerns associated with it (Aurela et al., 1999; Cirillo et al., 2011). As a member of the phthalate's family, DBP has been linked to adverse effects on the liver and kidney functions, making it interesting for our risk assessment. This molecule also presents an aromatic ring conjugated to an ester function, making it easily detectable by UV spectroscopy in the extraction solvent.

We initially focused on developing an effective method to obtain reliable results. To achieve this, we conducted a series of experiments using eight layers of blotting paper, where two of the layers were immersed in a contaminant solution for a duration of one day. These two layers served as the sources and were located at positions 3 and 6 within the stack. For these experiments we used the same solution for both dissolving the contaminant and extracting it from the paper films. Initially, we used a mixture of dichloromethane and ethanol in a 3:1 proportion. However, subsequent results revealed that using only 96% ethanol had better results, obtaining a concentration of 1.55 g/L of DBP.

The procedure involved immersing two paper films in the solution overnight, followed by assembling the stack of papers and placing it directly into an oven set at 40ºC. Through several trial runs, we determined that migration occurred within optimal time intervals of 30 minutes, 1 hour, and 2 hours, allowing us to observe the mass transfer through the films effectively. Subsequently, the extraction process was performed in a shaker for one day, and the concentration in the extraction solutions, (assuming that the extraction is total) was determined using UV spectroscopy. Not only did we consider the change in solvent, but we also considered the side effects of the paper films when refining the method. During the preparation of the stack, each film is overlaid on top of another. However, these films may not align perfectly, potentially leading

to the direct transfer of contaminants from non-adjacent layers. To prevent this, after the stack was prepared, all the films were reshaped by cutting the non-stacked borders into circles with a diameter of 28 mm. Additionally, following the migration process and before adding them to the extraction solvent, small circles with a diameter of 18 mm were cut from the center of each film.

Once we had developed the method, our objective was to enhance the accuracy of the results by conducting a new test using fourteen layers of blotting paper. In this test, we positioned two sources at positions 5 and 10 within the stacks. The procedure for this test remained the same as described before. The results of the two types of experiments can be seen in Figures 25 and 26.

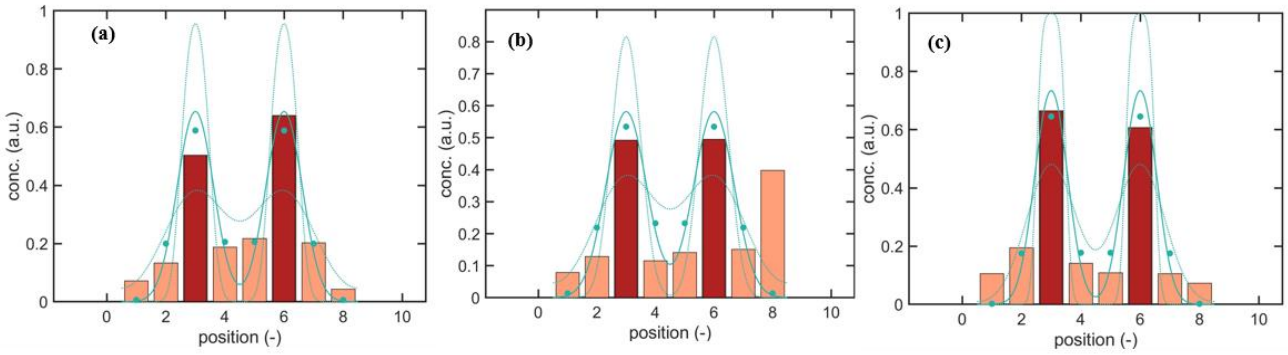


Figure 25-Concentration profiles of DBP in blotting paper, after several times of Roe test at 40°C with 8 layers and 2 sources. (a) 30 minutes, (b) 1h, (c) 2h.

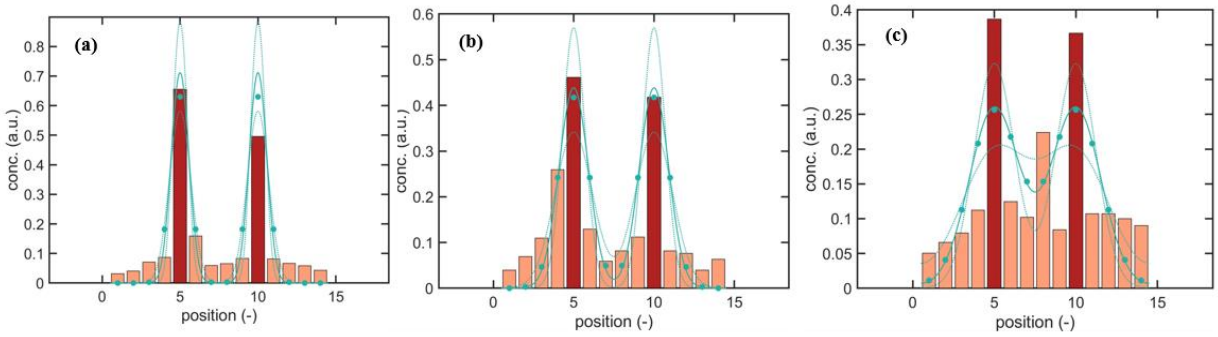


Figure 26- Concentration profiles of DBP in blotting paper, after several times of Roe test at 40°C with 14 layers and 2 sources. (a) 30 minutes, (b) 1h, (c) 2h.

Based on the findings depicted in Figures 25 and 26, it is evident that there is a noticeable trend of contaminant migration across different layers over the time. Following a 30-minute duration in the oven, an apparent migration of contaminants from the sources to the adjacent layers is observed, with higher concentrations found in the layers closest to the sources. Additionally, at this time, layers in positions 4 and 5 (among the eight layers) as well as 6 and 8 (among the fourteen layers) exhibit higher concentrations compared to the layers not situated between the sources. This can be explained by the fact that the intermediate layers receive continuous mass transfer from both sources (assuming similar values for the diffusion coefficients).

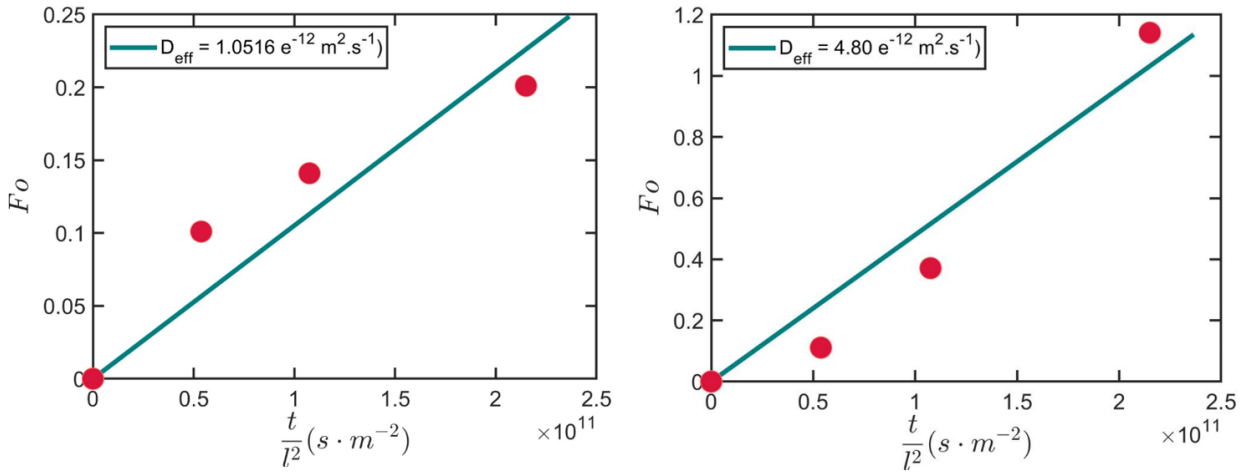


Figure 27-Fourier number obtained for several times of Roe test; (left) data obtained for the eight layers Roe test, and (right) data of the fourteen layers Roe test.

In both graphs, the slope of the green line represents the diffusion coefficient value obtained by the equation represented in Figure 25. This value indicates the transfer rate of molecules through the porous material over time. The effective diffusion coefficient for the eight and the fourteen layers test was 1.05×10^{-12} $m^2 \cdot s^{-1}$ and 4.80×10^{-12} $m^2 \cdot s$ respectively. These values are in the same order of magnitude for the same molecule, which means that the method can be applied either with eight or fourteen layers to obtain apparent diffusion coefficients. Few values of diffusion coefficient of molecules in cellulosic materials have been published, but we can compare to the order of magnitude in plastics. Diffusion coefficients range from 10^{-18} m^2/s to 10^{-8} m^2/s regarding the nature of the polymer (rubbery or glassy) (Kruczek, 2015). The experimental values presented here are comparable to the lower values of diffusion in rubbery polymers, which generally have portions of chains that can freely move but fewer free volumes than glassy polymers (Kruczek, 2015). Within the porous structure of paper and board, we expect values between 10^{-10} and 10^{-14} $m^2.s^{-1}$, as determined by the Piringer model and presented in the study of Nguyen et al. (2017). In the case of cellulosic materials, the diffusion is controlled by the affinity of the substances for the cellulose and by the structure (porosity, pore size, tortuosity) of the fibrous material. Further experiments using the Roe-type method with other molecules could lead to a conclusion regarding the link between diffusion and volatility of the molecule.

5.4 General discussion

From all the results presented and detailed above, we can certainly agree that the behavior of contaminants in each packaging material depends on the interactions with the solvent and the polymer, as well as depends on the proper nature of the molecule. Moreover, we have proven that Raman spectroscopy has the potential to be used for future chemical imaging.

Based on the obtained results, it is evident that Raman spectroscopy holds potential for effectively localizing the distribution of various contaminants within packaging materials. However, it should be noted that we did not have sufficient time to employ this technique for quantifying the concentration of contaminants within the cellulose matrix. To accomplish this, further analyses are required, involving repeated measurements of each contaminant at different concentrations. By generating calibration Raman spectra, it would be possible to establish a quantitative framework for future commercial packaging, enabling accurate quantification of contaminants.

From the water sorption isotherms acquired with the DVS microbalance, we can easily highlight that the moisture properties exhibit variations depending on the paper type and manufacturing parameters. Therefore, it is crucial to measure isotherms specifically for the food contact material (FCM) of interest. This information holds significant industrial importance as it helps the production process in selecting the most suitable paper and paperboard materials and facilitates the development of recycled packaging materials that exhibit minimal migration of molecules, thus ensuring the protection of human health.

The Roe-type test, whose methodology was adapted from a test conducted on plastics, appeared to be an efficient method to calculate the diffusion coefficient of contaminants in a reference blotting paper. However further studies are required to improve the accuracy of the technique as well as analyze a wider range of samples, including in this case plastic packaging material.

In general, the experimental methods developed during the internship appeared to be complementary to assess the distribution and migration of contaminants in food contact materials. While Raman chemical imaging provided information about the heterogeneous distribution of contaminants in cellulosic materials, DVS and diffusion data are of interest to better understand the mechanisms involved during migration to food. Further investigation of these methods with MFC films will give more information on the barrier properties required to protect food from the contamination. The low water resistance of MFC films, measured by DVS, could be considered a critical limitation to their use as a barrier, and should be improved for further applications in food packaging. However, further investigation is needed to analyze the moisture sorption isotherms with the contaminant of interest and not only with water. This will let us evaluate the ability of MFC to act as a functional barrier and a greener and real solution for cross-contamination in food packaging.

6 CONCLUSIONS AND PERSPECTIVES

6.1 Main findings

As mentioned earlier, the Circular Economy is no longer an option but a necessity. Therefore, it is crucial to develop feasible solutions without delay. Recycling has already proven to be an effective approach for reducing carbon footprint. Addressing our concerns about health hazards associated with recycled materials, the results presented here contribute to the broader body of research focused on minimizing human exposure to contaminants and developing safer and greener Food Contact Materials (FCM).

This report highlights three techniques that can be employed to analyze the migration of contaminants from recycled packaging to food. By utilizing these techniques, we can evaluate the effectiveness of recycling processes and assess the safety of each recycled packaging prior to its use, thereby assisting the packaging industry in transitioning entirely towards sustainable recycled packaging. These efforts align the European Directives (EC) 2019/ 904, (EC) 2022/1616, and (EC) 2023/2006, and help achieve their objectives.

The experimental work done in the Joint SayFood Mixed Research Unit over the past six months have led to many conclusions regarding the evaluation of contaminated FCM. The main findings of this work, obtained with three complementary techniques, will help the future development of safer food packaging using recycled materials.

6.2 Perspectives

Further perspectives are divided into the two types of materials that I intend to analyze since the beginning, paper, and plastic food packaging materials.

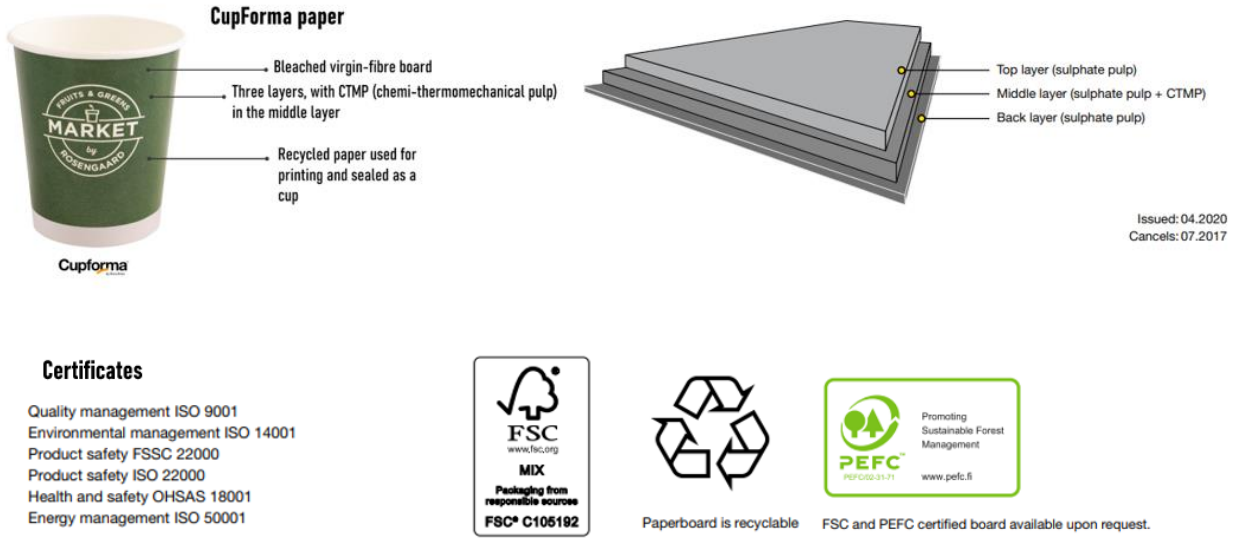
On one hand, we will focus on carrying a deeper and more accurate analysis of the Roe-type test on the different types of paper, including Gerstar and CupForma. Moreover, for the interest of a more complete risk assessment approach, we will perform a Roe-type test not only varying the type of papers but also changing the contaminant to p-terphenyl since it is the one already detected by the Raman spectra. Finally, following the line of analyzing paper materials with Raman spectroscopy, it would be interesting to be able to identify proper peaks of the molecule of interest (p-terphenyl) in the already proposed commercial packaging, and be able to quantify its concentration. For this, previously it will be needed to do a calibration Raman spectrum.

On the other hand, referring to plastic packaging materials, the perspective would be to carry out the same experiments to study the possibility of detecting the molecule of interest with Raman spectroscopy as well as obtain effective diffusivities to in the future be able to develop a mass transfer model.

7 APPENDICES

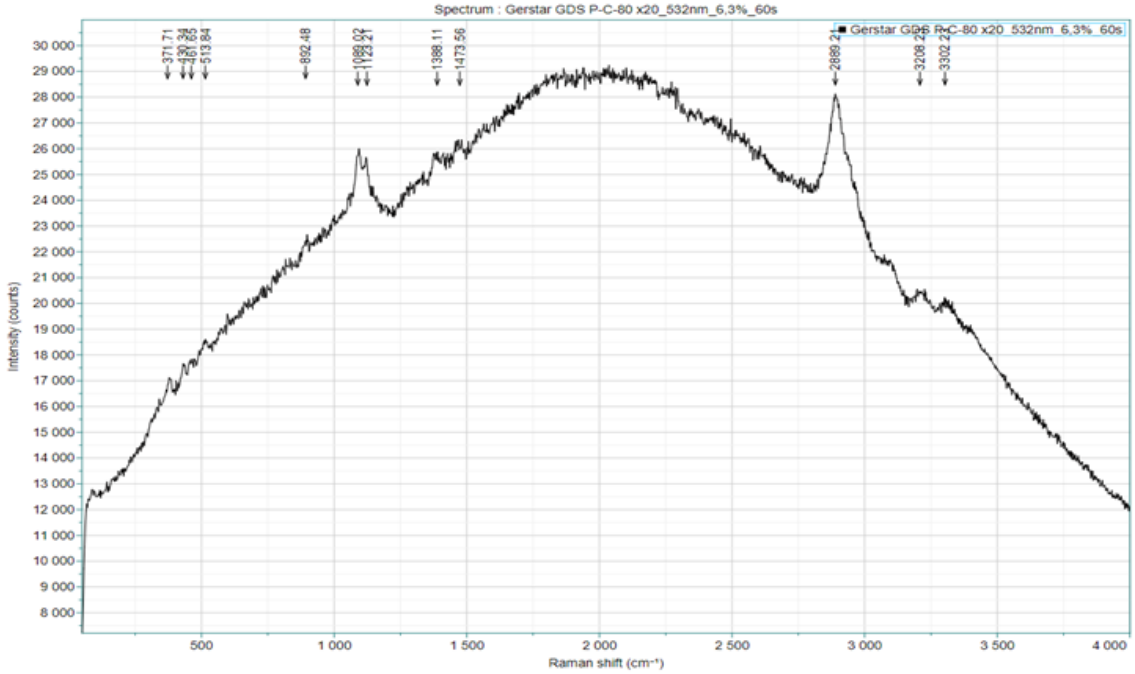
Appendix 1. CupForma packaging material's commercial information.

All the information of paper packaging samples comes from private companies, so it is not accessible to public.

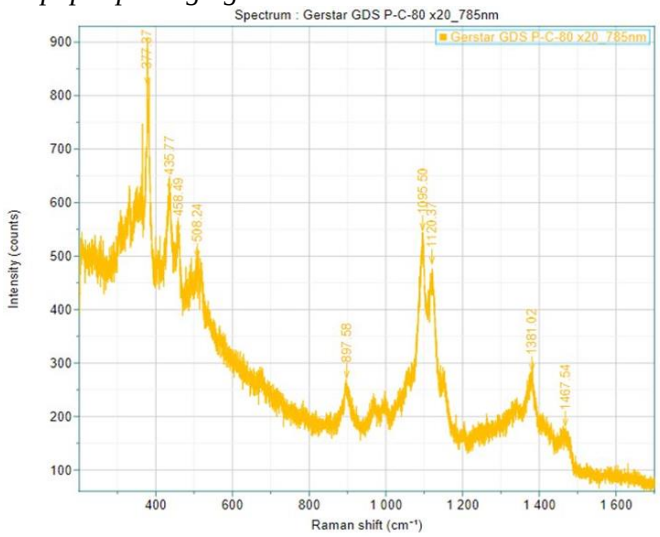


Appendix 2. All the following spectra of Gerstar and CupForma paper packaging material with different lasers

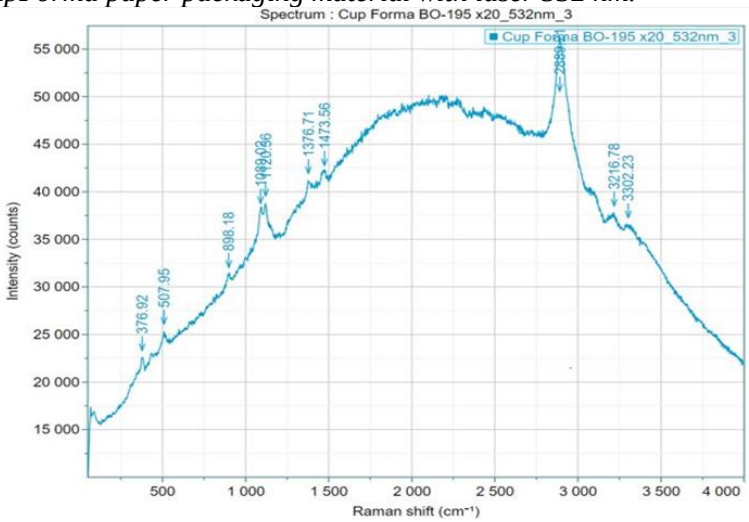
(1) Raman spectra of Gerstar paper packaging material with laser 532 nm.



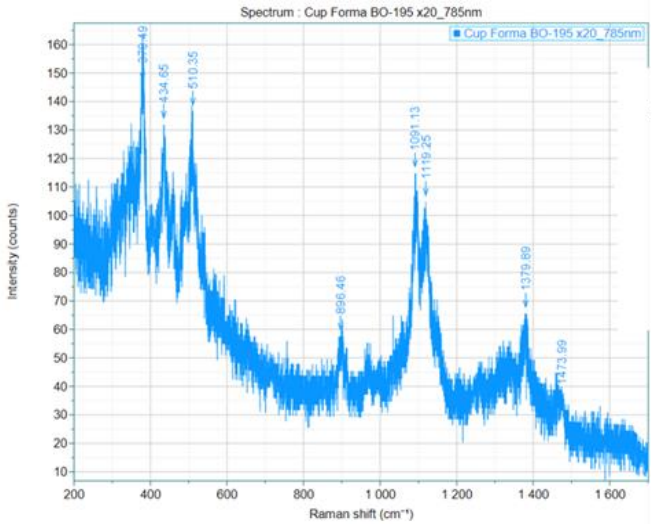
(2) Raman spectra of Gerstar paper packaging material with laser 785 nm.



(3) Raman spectra of CupForma paper packaging material with laser 532 nm.



4) *Raman spectra of CupForma paper packaging material with laser 785 nm.*



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